Removal of Bisphenol A from Water Using Iron Oxide Adsorbents

BY

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THESIS

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DB

TABLE OF CONTENTS

CI	LAPTER
•	RESEARCH BACKGROUND
	1.1 INTRODUCTION
	1.2 REMOVAL TECHNOLOGIES.
	1.2.1 Oxidation of Bisphenol A using ozonation
	1.2.2Chlorination of Bisphenol A.
	1.2.3 Electrochemical oxidation of Bisphenol A
	1.2.4 Photooxidation of Bisphenol A.
	1.2.5 Biodegradation of Bisphenol A
	1.2.6 Ultrasonic degradation of Bisphenol A
	1.2.7 Degradation of Bisphenol Ausing Ferrate (VI) and zero-valent Aluminum oxidation
	1.2.8Adsorption of Bisphenol A
	1.2.8.1 Adsorption of Bisphenol A onto carbonaceous materials
	1.2.8.2 Adsorption Bisphenol A onto soils and sediments
	1.2.8.3 Adsorption Bisphenol A onto minerals
	1.3 SUMMARY OF TECHNOLOGIES FOR REMOVAL OF BPA FROM
	WATER
	1.4 PROPOSEDRESEARCH
	1.4.1 The effect of adsorbent dosage on the adsorption of BPA
	1.4.2 Adsorption equilibrium isotherms and adsorption kinetics
	1.4.3 Effect of pH and ionic strength on the adsorption of BPA
	1.4.4 BPA byproducts degradation
	1.4.5 Statistical analysis and multivariate linear regression
	1.4.6 Removal of hydroquinone from water using iron oxides adsorbents
	1.4.7 Risk assessment of BPA exposure
	1.5 REFERENCES.
•	KINETIC STUDYAND SEQUENTIAL BATCH EXTRACTION
	2.1 INTRODUCTION.
	2.1.1 Kinetics studies done on carbonaceous adsorbent materials
	2.1.2Kinetics studies done on minerals
	2.1.3 Kinetics studies done on polymers
	2.2 KESERCH UBJECTIVE
	2.3 MATERIALS AND METHODS
	2.3.2Kinetic Experiments
	2.3.2.1 Routine analysis
	2.3.2.2 TDS and pH analysis
	2.3.2.3 Liquid-liquid extraction (LLE)
	2.3.2.4 BPA analysis.
	2.3.3Effect of pH and batch extractions.
	2.4 RESULTS AND DISCUSSION
	2.5 CONCLUSIONS

CH	<u>IAPTER</u>	PAGE
	2 6 REFERENCES	163
		105
III.	ADSORPTION OF BISPHENOL A ONTO MINERAL OXIDES	169
	3.1 INTRODUCTION.	169
	3.2 ADSORPTION OF BISPHENOL A ONTO CARBONACEOUS MATERIALS	184
	3.2.1Adsorption of BPA onto carbon and porous carbon	184
	3.2.2Adsorption of BPA onto activated carbon	186
	3.2.3Adsorption of BPA onto carbon nanomaterials	189
	3.2.4Adsorption of BPA onto polymeric adsorbents	191
	3.2.5Adsorption of BPA onto soils	193
	3.2.6Adsorption of BPA onto sediments	195
	3.2.7Adsorption of BPA onto minerals	198
	3.3 RESEARCH OBJECTIVE	203
	3.4 MATERIALS AND METHODS	204
	3.4.1Chemicals	204
	3.4.2 Adsorption Capacity	204
	3.4.2.1 Routine analysis	205
	3.4.2.2 TDS and pH analysis	205
	3.4.2.3 Liquid-liquid extraction (LLE)	206
	3.4.2.4 BPA analysis	206
	3.4.3Time Study	207
	3.5 RESULTS AND DISCUSSION	208
	3.6 CONCLUSIONS	227
	3.7 REFERENCES	231
		• 10
IV.	THE EFFECT OF pH AND IONIC STRENGTH VARIATION.	249
	4.1 INTRODUCTION.	249
	4.2 THEINFLUENCE OF PH ON THE REMOVALOF BPA USING DIFFERENT	051
	REMOVAL PROCESSES	251
	4.2.1 The influence of pH on adsorption.	253
	4.3 THE INFLUENCE OF IONIC STRENGTH ON THE REMOVAL OF BPA	256
	4.4 MATERIALS AND METHODS	258
	4.4.1 Chemicals.	238 259
	4.4.2 The pH effect study	258
	4.4.2.1 Routine analysis	259
	4.4.2.2 TDS and pH analysis.	259
	4.4.2.3 Soluble calcium and iron analysis	259
	4.4.2.4 Liquid-liquid extraction (LLE).	260
	4.4.2.5 Zeta potential measurements.	260
	4.4.2.0 BPA analysis.	200
	4.4.510HIC Strength Study	201
	4.5 KEDULID AND DIDUUDDIUN	203
		307

CI	<u>CHAPTER</u> P	
	4.7 REFERENCES	309
V.	BPA BYPRODUCTS DEGRADATION	316
	5.1 INTRODUCTION.	316
	5.2 ENVIRONMNETAL FATE OF BISPHENOL A	318
	5.2.1 Level I assessment of BPA using equilibrium conditions	319
	5.2.2 Level II assessment of BPA using environmental loss processes	321
	5.2.3 Level III assessment of BPA using nonequilibrium steady state	322
	5.3 BPA BYPRODUCTS FORMATION UNDER ULTRASOUND	327
	5.4 BPA BYPRODUCTS FORMATION UNDER ELECTROCHEMICAL TREATMENT	341
	5.5 BPA BYPRODUCTS FORMATION UNDER PHOTOOXIDATION	355
	5.6 BPA BYPRODUCTS FORMATION UNDER BIOLOGICAL DEGRADATION	361
	5.6.1 BPA byproducts formation under bacterial degradation	361
	5.6.2 BPA byproducts formation under enzyme degradation	368
	5.7 BPA BYPRODUCTS FORMATION UNDER OZONE OXIDATION	370
	5.8 BPA BYPRODUCTS FORMATION UNDER CHLORINATION	372
	5.9 CONCLUSIONS AND DISCUSSION	377
	5.10 REFERENCES	380
	 6.2 STATISTICAL ANALYSIS FOR CHAPTER 2 6.3 STATISTICAL ANALYSIS FOR CHAPTER 3 6.4 STATISTICAL ANALYSIS FOR CHAPTER 4 6.5 RESULTS AND DISCUSSION 	390 391 392 395
	6.5.1Statistical Analysis for Chapter 2	395
	6.5.1.1 Statistical analysis for the 30 days time study for hematite H	395
	6.5.1.2 Statistical analysis for the 30 days time study for magnetite M1	397
	6.5.1.3 Statistical analysis for the 30 days time study for magnetite M2	398
	6.5.1.4 Statistical analysis for the 30 days time study for hematite H and magnetite M1 and M2	400
	6.5.1.5 Statistical analysis for the 30 days time study for hematite H and magnetite M1,	
	M2 with independent variable interactions	403
	6.5.2Statistical Analysis for Chapter 3	410
	6.5.2.1 Statistical analysis for the 1 dayisotherm study for hematite H	410
	6.5.2.2 Statistical analysis for the 7 days isotherm study for hematite H	412
	6.5.2.3 Statistical analysis for the 1 and 7 daysisotherm for hematite H	414
	6.5.2.4 Statistical analysis for the 1and 7 days isotherm study for hematite H with	
	independent variable interactions	417
	6.5.3Statistical Analysis for Chapter 36.5.3.1 Statistical analysis for 1g, 2g, and 5g of hematite H adsorbent at different	422
	pHs	422

CHAPTER	PAGE
6.5.3.2 Statistical analysis for 1g, 2g, and 5g of hematite H adsorbent at different pH	
with independent variable interactions	425
6.5.3.3 Statistical analysis for hematite H adsorbent in the presence of calcium ions	431
6.5.3.4 Statistical analysis for hematite H adsorbent in the presence of calcium ions	
with independent variable interactions	434
6.5.3.5 Statistical analysis for hematite H adsorbent in the presence of potassium ions	441
6.5.3.6 Statistical analysis for hematite H adsorbent in the presence of potassium	
ions with independent variable interactions	444
6.6 REFERENCES	450
VII. REMOVAL OF HYDROQUINONE FROM WATER USING IRON OXIDES	
ADSORBENTS	451
7.1 INTRODUCTION	451
7.2 ADSORPTION OF HYDROQUINONE	458
7.3 RESEARCH OBJECTIVE	462
7.4 MATERIALS AND METHODS	463
7.4.1Chemicals	463
7.4.2 Time Study	463
7.4.3 Extraction Study	465
7.4.4 Adsorbent dosage Study	465
7.4.5 Control atmosphere chamber	466
7.4.5.1 Routine analysis	466
7.4.5.2 TDS, pH,and alkalinity analysis	467
7.4.5.3 Soluble iron analysis	467
7.4.5.4 Liquid-liquid extraction (LLE)	467
7.4.5.5 HQ and BQ analysis	468
7.5 RESULTS AND DISCUSSION	470
7.6 CONCLUSIONS	509
7.7 REFERENCES	512
	- 1 -
VIII. RISK ASSESSMENT OF BISPHENOL A (BPA) EXPOSURE.	516
	516
8.2 STUDY OBJECTVES.	518
8.3 METHODS.	519
8.3.1 Hazard Identification	519
8.3.2 I OXICITY assessment	523
8.3.3 Exposure assessment	526
8.3.3.1 Model Setup	529
8.4 KESULIS AND DISCUSSION	533
8.5 CUNCLUSIUNS	5/6
8.6 KEFEKENCES	579

<u>CHAPTER</u>	PAGE
IX. CONCLUSIONS AND RECOMMENDATIONS.	594
9.1 CONCLUSIONS.	594
9.2 RECOMMMENDATIONS.	596
CITED LITERATURE	598
CURRICULUM VITAE	647

LIST OF TABLES

TAB	<u>LE</u> <u>PA</u>	GE
1.1	Physicochemical properties of bisphenol A	2
1.2	Global BPA production capacity	4
1.3	Environmental relevant concentrations of BPA and their locations in aquatic systems	6
1.4	Redox potential for some oxidizers	12
1.5	Removal of BPA using ozonation	13
1.6	Levels of BPA and chlorination products from various chlorination conditions	20
1.7	Identified BPA Conversion and Degradation Products	32
1.8	The rate of photocatalytic degradation of BPA under different conditions	36
1.9	Summary of potential biological organisms capable of biodegrading BPA	46
1.10	Parameters studied for adsorption of Bisphenol A on different adsorbents	55
2.1	Nanoparticles and composites summary of iron oxides: synthesis, characterization and applications	109
2.2	Nano-magnetite particles or composites binding onto carbon nanotubes (CNTs)	110
2.3	Chemicals	124
2.4	Total BPA concentration linear regression parameters for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution	139
2.5	Water BPA concentration linear regression parameters for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution	139
2.6	Solution pH values for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution	140
2.7	Solution TDS values for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution	140
2.8	Total BPA concentration linear regression parameters for the 30 days time study, $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution	150
2.9	Water BPA concentration linear regression parameters for the 30 days time study, $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution	150
2.10	Solution pH values for the 30 days time study, $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution	151
2.11	Solution TDS values for the 30 days time study, $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution	151
2.12	BPA concentration (mg/L) as function of pH for Magnetite (M1)	157
2.13	pH for Magnetite (M1) and Deionized Water (DI) extracts	157

TABLE

PAGE

2.14	TDS for Magnetite (M1) and Dionized Water (DI) extracts	157
2.15	BPA concetration (mg/L) as function of pH for Magnetite (M2)	158
2.16	pH for Magnetite (M2)	158
2.17	TDS for Magnetite (M2) and Dionized Water (DI) extracts	159
2.18	BPA concentration (mg/L) as function of pH for Hematite (H)	159
2.19	pH for Hematite (H) and Dionized Water (DI) extracts	160
2.20	TDS for Hematite (H) and Dionized Water (DI) extracts	160
3.1	Parameters studied for adsorption of Bisphenol A on different adsorbents	178
3.2	BET Surface Area, Langmuir, and Freundlich parameters for activated carbon	187
3.3	Chemicals	204
3.4	Langmuir and Freundlich constants for Hematite (H) as a function of time with pH 2 and 50 mL solution	213
3.5	Freundlich constants for Magnetite (M1) as a function of time with DI, and $C_0 = 1.2 \text{ mg/L}$	218
3.6	pH Variation for Magnetite (M1)	218
3.7	TDS Variation for Magnetite (M1)	218
3.8	Freundlich constants for Magnetite (M2) as a function of time with DI, and $C_0 = 1.2 \text{ mg/L}$.	222
3.9	pH Variation for Magnetite (M2)	222
3.10	TDS Variation for Magnetite (M2)	222
3.11	Freundlich constants for Hematite (H) as a function of time with DI, and $C_0 = 1.2 \text{ mg/L}$	226
3.12	pH Variation for Hematite (H)	226
3.13	TDS Variation for Hematite (H)	226
4.1	Chemicals	258
4.2	Power function constants for Hematite (H) as a function of pH, and 1g sorbent: 50 mL solution	266
4.3	pH for Hematite 1g:50 mL	266
4.4	TDS for Hematite 1g:50 mL	266
4.5	Soluble Iron (Fe) for Hematite 1g:50 mL	267
4.6	Power function constants for Hematite (H) as a function of pH, and 2g sorbent: 50 mL solution.	270

TABLE

PAGE

4.7	pH for Hematite 2g:50 mL	270
4.8	TDS for Hematite 2g:50 mL	270
4.9	Soluble Iron (Fe) for Hematite 2g:50 mL	271
4.10	Power function constants for Hematite (H) as a function of pH, and 2g sorbent:50 mL solution	274
4.11	pH for Hematite 5g:50 mL	275
4.12	TDS for Hematite 5g:50 mL	275
4.13	Soluble Iron (Fe) for Hematite 5g:50 mL	276
4.14	Total Bisphenol A (BPA) removal with Hematite (1g:50 mL) as function of pH	280
4.15	Total Bisphenol A (BPA) removal with Hematite (2g:50 mL) as function of pH	284
4.16	Total Bisphenol A (BPA) removal with Hematite (5g:50 mL) as function of pH	288
4.17	Removal of BPA with Hematite, C ₀ =1.2 mg/L	292
4.18	pH for Hematite 5g:50 mL as a function of CaCl ₂	300
4.19	pH for Hematite 5g:50 mL as a function of $CaCl_2 + 1mM NaHCO_3$	300
4.20	pH for Hematite 5g:50 mL as a function of CaCl ₂ at pH2	300
4.21	Soluble iron (Fe) for Hematite 5g:50 mL as a function of CaCl ₂	301
4.22	Soluble iron (Fe) for Hematite 5g:50 mL as a function of $CaCl_2 + 1mM$ NaHCO ₃ .	301
4.23	Soluble iron (Fe) for Hematite 5g:50 mL as a function of CaCl ₂ at pH 2	301
4.24	Calcium (mg/L) concentration for Hematite 5g:50 mL as a function of ionic strength	302
4.25	pH for Hematite 5g:50 mL as a function of KCl	306
4.26	Soluble iron (Fe) for Hematite 5g:50 mL as a function of KCl	306
5.1	EQC Level III results: BPA distribution in each medium comportment based on single and multiple emissions	323
5.2	Main intermediates formed by ultrasound and identified by HPLC/MC electrospray	328
5.3	The Main intermediates during the BPA ultrasonic irradiation alone	336
5.4	Identified BPA Conversion and Degradation Products	345
5.5	Identification of Intermediates	348
5.6	Identification of Intermediates based on oxidative coupling reaction leading to products greater than that of BPA	351

6.0	Analysis of Variance (ANOVA) for Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	396
6.1	Pearson correlation between independent variables for Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	396
6.2	Final Model Statistical Information for Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	396
6.3	Analysis of Variance (ANOVA) for Magnetite M1 with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	397
6.4	Pearson correlation between independent variables for Magnetite M1 with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	398
6.5	Final Model Statistical Information for Magnetite M1 with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	398
6.6	Analysis of Variance (ANOVA) for Magnetite M2 with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	399
6.7	Pearson correlation between independent variables for Magnetite M2 with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	400
6.8	Final Model Statistical Information for Magnetite M2 with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	400
6.9	Analysis of Variance (ANOVA) for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	402
6.10	Pearson correlation between independent variables for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	402
6.11	Final Model Statistical Information for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days	402
6.12	Analysis of Variance (ANOVA) for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions	405
6.13	Final Model Statistical Information for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions	406
6.14	Pearson correlation between independent variables for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions	407
6.15	Analysis of Variance (ANOVA) for Hematite H for 1 day isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	411

6.16	Pearson correlation between independent variables for Hematite H for 1 day isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	411
6.17	Final Model Statistical Information for Hematite H for 1 day isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	411
6.18	Analysis of Variance (ANOVA) for Hematite H for 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	413
6.19	Pearson correlation between independent variables for Hematite H for 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	413
6.20	Final Model Statistical Information for Hematite H for 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	414
6.21	Analysis of Variance (ANOVA) for Hematite H for 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	415
6.22	Pearson correlation between independent variables for Hematite H for1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0.	416
6.23	Final Model Statistical Information for Hematite H 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0	416
6.24	Analysis of Variance (ANOVA) for Hematite H for 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0 with the independent variables interactions	419
6.25	Final Model Statistical Information for Hematite H 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0 with the independent variables interactions.	420
6.26	Final Model Statistical Information for Hematite H 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0 with the independent variables interactions.	421
6.27	Analysis of Variance (ANOVA) for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L	423
6.28	Pearson correlation between independent variables for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L.	423
6.29	Final Model Statistical Information for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L	424

6.30	Analysis of Variance (ANOVA) for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions	426
6.31	Final Model Statistical Information for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions	427
6.32	Pearson correlation between independent variables for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions	428
6.33	Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions	432
6.34	Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions	432
6.35	Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions	433
6.36	Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interactions	436
6.37	Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interactions	437
6.38	Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interactions	438
6.39	Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions.	442
6.40	Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions	442
6.41	Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions	443

6.42	Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction	445
6.43	Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction.	446
6.44	Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction	447
7.0	Physicochemical properties of Hydroquinone (HQ)	452
7.1	Physicochemical properties of Benzoquinone (BQ)	453
7.2	Chemicals	463
7.3	Total HQ+BQ concentration (μ mol/L) as function of time for oxic system for magnetite (M1)	475
7.4	Total HQ+BQ concentration (μ mol/L) as function of time for oxic system for magnetite (M2)	475
7.5	Total BPA concentration linear regression parameters for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	475
7.6	Solution pH values for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	476
7.7	Solution TDS (mg/L) values for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent: 50mL solution	476
7.8	Alkalinity for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent: 50mL solution	476
7.9	Solution soluble iron (Fe mg/L) for the oxic 7 days time study, $C_{0(HQ)} = 110.11$ µmol/L, 5g sorbent : 50mL solution	476
7.10	Total BPA concentration linear regression parameters for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	483
7.11	Total HQ+BQ concentration (µmol/L) as function of time for anoxic system for magnetite (M1)	485
7.12	Total HQ+BQ concentration (µmol/L) as function of time for anoxic system for magnetite (M2)	485
7.13	Solution pH values for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	485
7.14	Solution TDS values for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	486

7.15	Solution soluble iron (Fe) for the anoxic 7 days time study, $C_{0(HQ)} = 110.11$ µmol/L, 5g sorbent : 50mL solution	486
7.16	Alkalinity (mg/L as CaCO ₃) for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution	486
7.17	Solution ORP (mV) values for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution	486
7.18	Total BPA concentration linear regression parameters for the anoxic 30 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	497
7.19	Total HQ+BQ concentration (μ mol/L) as function of time for anoxic system for magnetite (M1).	497
7.20	Total HQ+BQ concentration (μ mol/L) as function of time for anoxic system for magnetite (M2).	498
7.21	Solution pH values for the 30 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution.	498
7.22	Solution TDS values for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution.	499
7.23	Solution soluble iron (Fe) for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	499
7.24	Alkalinity for the anoxic 30 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent: 50mL solution.	500
7.25	Solution ORP values for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	500
7.26	Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic system with C _{0(HQ)} = 110.11 μ mol/L and 50mL solution	501
7.27	Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic systems (Case A-C) with C _{0(HQ)} = 110.11 μ mol/L and 50mL solution for Magnetite (M2)	502
7.28	Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic systems (Case D-G) with $C_{0(HQ)} = 110.11 \mu$ mol/L and 50mL solution for Magnetite (M2)	503
7.29	Total pH and TDS for anoxic systems (Case 1-4) with $C_{0(HQ)} = 110.11 \ \mu mol/L$ and 50mL solution for Magnetite (M2)	504
7.30	Total pH and TDS for oxic system with $C_{0(HQ)}$ = 110.11 $\mu mol/L$ and 50mL solution)	507
7.31	Total pH and TDS for anoxic system with $C_{0(HQ)}$ = 110.11 $\mu mol/L$ and 150mL solution.	508
7.32	Total pH and TDS for oxic system with $C_{0(HQ)} = 11.1 \ \mu mol/L$ and 150mL solution	509

7.33	Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic system with C _{0(HQ)} = 110.11 μ mol/L and 150mL solution	509
8.1	Concentrations used for both CTE and RME calculations for the EDI	522
8.2	Adverse Health effects in rats and mouse laboratory studies in the presence of BPA under recommended EPA safe dose limit of 50,000 μ g/Kg-BW/day	524
8.3	CTE estimated daily intake (μ g/kg-bw-day) calculations for Case 1	534
8.4	RME estimated daily intake (µg/kg-bw-day) calculations for Case 1	534
8.5	CTE exposure risk calculations for Case 1 using Subchronic RfD of 50 μ g/kg-day	535
8.6	CTE exposure risk calculations for Case 1 using Subchronic RfD of 10μ g/kg-day	535
8.7	CTE exposure risk calculations for Case 1 using Subchronic RfD of 2 μ g/kg-day	535
8.8	RME exposure risk calculations for Case 1 using Subchronic RfD of 50 μ g/kg-day	536
8.9	RME exposure risk calculations for Case 1 using Subchronic RfD of 10 µg/kg- day	536
8.10	RME exposure risk calculations for Case 1 using Subchronic RfD of 2 µg/kg-day	536
8.11	CTE and RME exposure risk calculations for Case 1 and the percentage contribution of each pathway using Subchronic RfD of $50 \mu g/kg$ -day	538
8.12	CTE estimated daily intake (µg/kg-day) calculations for Case 2	539
8.13	RME estimated daily intake (µg/kg-day) calculations for Case 2	539
8.14	CTE exposure risk calculations for Case 2 using Subchronic RfD of 50 μ g/kg-day	540
8.15	RME exposure risk calculations for Case 2 using Subchronic RfD of 50 μ g/kg-day	540
8.16	CTE and RME exposure risk calculations for Case 2 and the percentage contribution of each pathway using Subchronic RfD of 50 μ g/kg-day	541
8.17	CTE estimated intake (µg/kg-day) calculations for Case 3	542
8.18	RME estimated intake (µg/kg-day) calculations for Case 3	542
8.19	CTE exposure risk for Case 3 using Subchronic RfD of 50 μ g/kg-day	542
8.20	CTE exposure risk for Case 3 using Subchronic RfD of 10 μ g/kg-day	543
8.21	CTE exposure risk for Case 3 using Subchronic RfD of 2 μ g/kg-day	543
8.22	RME exposure risk for Case 3 using Subchronic RfD of 50 µg/kg-day	543
8.23	RME exposure risk for Case 3 using Subchronic RfD of 10 µg/kg-day	543
8.24	RME exposure risk for Case 3 using Subchronic RfD of 2 µg/kg-day	544

8.25	CTE and RME exposure risk calculations for Case 3 and the percentage contribution of each pathway using Subchronic R_fD of 50 $\mu g/kg$ -day	544
8.26	CTE and RME exposure risk calculations using Subchronic RfD of 50 μ g/kg-day and estimated daily intake for Case 1, 2, and 3	544
8.27	CTE estimated daily intake (µg/kg-day) calculations for Case 4	546
8.28	RME estimated daily intake (µg/kg-day) calculations for Case 4	547
8.29	CTE exposure risk for Case 4 using Subchronic R_fD of 50 $\mu g/kg$ -day	547
8.30	RME exposure risk for Case 4 using Subchronic $R_f D$ of 50 μ g/kg-day	548
8.31	CTE exposure risk for Case 4 and the percentage contribution of each pathway using Subchronic R_fD of 50 $\mu g/kg$ -day	548
8.32	RME exposure risk calculations for Case 4 and the percentage contribution of each pathway using Subchronic R_fD of 50 $\mu g/kg$ -day	549
8.33	CTE exposure risk calculations using Subchronic R_fD of 50, 10, and 2 µg/kg-day for Case A,B,C, and D with the percentage contribution of each pathway for 1 year.	551
8.34	RME exposure risk calculations using Subchronic R_fD of 50, 10, and 2 µg/kg-day for Case A,B,C, and D with the percentage contribution of each pathway for 1 year	552
8.35	CTE and RME estimated daily intake (µg/kg-day) calculations for Case E	556
8.36	CTE and RME exposure risk calculations for Case E using Subchronic $R_{\rm f}D$ of 50 $\mu g/kg$ -day	558
8.37	CTE and RME exposure risk calculations for Case E using Subchronic R_fD of 10 $\mu g/kg$ -day	559
8.38	CTE and RME exposure risk calculations for Case E using Subchronic R_fD of 2 $\mu g/kg\text{-}day$	560
8.39	Case E CTE and RME exposure risk calculations and the percentage contribution of each pathway using Subchronic $R_f D$ of 50 μ g/kg-day	563
8.40	CTE and RME estimated daily intake (µg/kg-day) calculations for Case F	567
8.41	CTE and RME exposure risk calculations for Case F using Subchronic $R_{\rm f}D$ of 50 $\mu g/kg$ -day	569
8.42	CTE and RME exposure risk calculations for Case F using Subchronic R_fD of 10 $\mu g/kg$ -day	570
8.43	CTE and RME exposure risk calculations for Case F using Subchronic $R_{\rm f}D$ of 2 $\mu g/kg\text{-}day$	571

<u>TAB</u>	<u>LE</u> <u>P</u>	<u>AGE</u>
8.44	Case F CTE and RME exposure risk calculations and the percentage contribution	
	of each pathway using Subchronic R _f D of 50 µg/kg-day	574

LIST OF FIGURES

<u>FIGU</u>	JRE	PAGE
1.1	Bisphenol A	2
1.2	Species distribution diagram of bisphenol A	3
1.3	Bisphenol A removal (initial[BPA] = 100 +/- 1.4 μ M) as a function of the applied ozone dose at 20+/-2 ^o C, in Milli-Q purified solution (initial pH = 6.5)	15
1.4	Transformation products variation according to the ozone dose applied	16
1.5	Proposed reaction pathways for the formation of products B ₁ -B ₅	16
1.6	Half-lives profiles for the reaction of bisphenol A with chlorine for concentrations of chlorine of 0.2, 1.0 and 2.0 mg/L	19
1.7	Chlorination of bisphenol A in ultra-pure water ([BPA] ₀ = 5 μ M; [Cl ₂] ₀ = 38 μ M (2.7 mg/L); pH = 8.0	19
1.8	Presumed chlorination reaction scheme of BPA	21
1.9	Pathways of chloro-substitution reaction between bisphenol A and HOC1	22
1.10	Formation of polychlorinated phenoxyphenols	22
1.11	Liner sweep voltammograms for the oxidation of the 0.1mM BPA in a 0.1 M Na_2SO_4 buffer solution at the GC electrode at different solution pH values. Scan rate 0.01 V/s.	24
1.12	a) Liner sweep voltammograms for the oxidation of 0.1, 0.2, 1.0 mM BPA in a 0.1 M Na_2SO_4 buffer solution (pH 5.8) at a scan rate 0.015 V/s. b) The relationship between the concentration of bisphenol A and the oxidation peakcurrent.	25
1.13	Relationships between the efficiency of removal of bisphenol A and treatment time with application of a potential 0.75 V in 1×10^{-6} M (\bullet), 1×10^{-5} M (\blacktriangle), 1×10^{-6} M (\bullet), 1×10^{-6}	25
1.14	(a) Effect of I_{appl} on anodic oxidation of BPA with BDD (BPA, 20 mg dm ⁻³ ; electrolyte, 0.1M Na ₂ SO ₄ ; pH 6; <i>T</i> , 25°C) (•) 14.28mAcm ⁻² , (▲) 25mAcm ⁻² and (■) 35.7mAcm ⁻² . (Inset) Corresponding kinetic analysis assuming a pseudo-first order reaction for BPA decay. (b) Decay of different initial concentration of BPA by anodic oxidation with BDD at 35.7mAcm ⁻² (electrolyte,0.1M Na ₂ SO ₄ ; pH 6; <i>T</i> , 25°C) (•) 10mgdm ⁻³ , (▲) 20mgdm ⁻³ and (■) 30mgdm ⁻³	27
1.15	a) TOC abatement with reference to electrolysis time at three different I_{appl} for the mineralization of BPA with BDD anode (BPA, 20 mg dm ⁻³ ; electrolyte, 0.1M Na ₂ SO ₄ ; pH 6; <i>T</i> , 25°C) (•) 14.28mAcm ⁻² , (\blacktriangle) 25mAcm ⁻² and (\blacksquare) 35.7mAcm ⁻² . b) TOC removal for three different initial concentration of BPA at constant I_{appl} 35.7mAcm ⁻² (electrolyte, 0.1M Na ₂ SO ₄ ; pH 6; <i>T</i> , 25°C) (•) 10mgdm ⁻³ , (\blacksquare) 20mgdm ⁻³ and (\bigstar) 30 mgdm ⁻³ .	28

P	A	G	E
			_

1.16	Electrochemical destruction of BPA as a function of the charge consumed on the four different anodes at the current densities of (a) $10mA/cm^2$ and(b) $50mA/cm^2$	29
1.17	Concentrations of the intermediate products of EC degradation of BPA at a current density of 10 mA/cm ² on the (a) Pt, (b) Ti/RuO_2 , (c) $Ti/Sb-SnO_2$ and (d) Ti/BDD anodes.	30
1.18	Reaction pathway of electrochemical BPA degradation	31
1.19	Main steps during BPA degradation by photocatalysis	35
1.20	(a) Effect of excitation wavelengths on the photocatalytic degradation efficiency for BPA (Note: C_0 denotes the equilibrium concentration of BPA after adsorption in the dark) and (b) comparison of BPA removal performance under various excitation wavelengths for N-TiO ₂ /AC, TiO ₂ , N-TiO ₂ and P25	37
1.21	BPA photolysis and photo degradation by CN-TiO2(120/300) under different Vis- LED irradiation for 5 h at neutral pH	38
1.22	Photodegradation of BPA by TiO ₂ immobilized with every binder (at the initial concentration of 10mg BPA/l, 3-coating times, pH 4.5, and 30 0 C): \circ , 1 wt% PVA; \Box , 1 wt% PVdC; \diamond , 1 wt% PVdF; Δ , 1wt% Teflon; and \blacksquare , 1 wt% titanium sol-solution.	39
1.23	Proposed stepwise photodegradation of BPA with a TiO_2 film of about 5.29 μ m thickness	40
1.24	BPA degradation under different ultrasonic intensities. BPA concentration: 100 μ g/L; ultrasonic frequency: 20 kHz; pH: 6.5; temperature: 25±0.5 ⁰ C; (\Rightarrow)20W/cm ² ; (\Diamond) 40W/cm ² ; (\blacksquare) 60W/cm ² ; (\Box) 80W/cm ²	50
1.25	Main degradation pathways of low-concentration BPA during ultrasonic treatment	51
1.26	Main reactions leading to BPA mineralization by the combined ultrasound/solar light/Fe(II) system	53
1.27	BPA (118 μ mol/L) elimination by ultrasound, TiO ₂ photocatalysis (PC), photo- Fenton and combined ultrasound/Fe ²⁺ /TiO ₂ photo assisted processes applied to solutions saturated with oxygen. Fe ²⁺ 100 μ mol/L; Volume: 300 mL; pH: 3; temperature: 22 ± 2 ^o C. Ultrasound: 300 kHz/80W; solar simulator irradiation	53
1.28	Adsorption of bisphenol A onto various activated carbons at 298 K and pH 7.0; $C_0 = 60 \text{ mg/L}$	59
2.1	Total BPA concentration as a function of time: $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	132
2.2	Total BPA concentration as a function of time for Magnetite (M1): $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	133

2.3	Total BPA concentration as a function of time for Hematite (H): $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	134
2.4	Water BPA concentration as a function of time: $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	135
2.5	Water BPA concentration function for Magnetite (M1): $C_0 = 1.2 \text{ mg/L}, 5g$ sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	136
2.6	Water BPA concentration function for Hematite (H): $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	137
2.7	pH variation as a function of time: $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	138
2.8	Total BPA concentration as a function of time: $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	143
2.9	Total BPA concentration function for Magnetite (M1): $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution a) Zero order, b) First order, and c) Second order	144
2.10	Total BPA concentration function for Hematite (H): $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution a) Zero order, b) First order, and c) Second order	145
2.11	Water BPA concentration as a function of time: $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	146
2.12	Water BPA concentration function for Magnetite (M1): $C_0 = 10 \text{ mg/L}$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	147
2.13	Water BPA concentration function for Hematite (H): $C_0 = 10 \text{ mg/L}$, 5g sorbent: 50mL solution a) Zero order, b) First order, and c) Second order	148
2.14	pH variation as a function of time: $C_0 = 10 \text{ mg/L}$, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	149
2.15	Total BPA concentration as a function of pH: $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	154
2.16	Water BPA concentration as a function of pH: $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	155
2.17	Total BPA concentration distribution as a function of pH: $C_0 = 1.2 \text{ mg/L}$, 5g sorbent :50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)	156
3.1	Langmuir isotherms for 1 day pH 2: a) 1g sorbent: 50mL solution, b) 2g sorbent: 50mL solution and c) 5g sorbent : 50mL solution	209
3.2	Langmuir isotherms for 7 days pH 2: a) 1g sorbent: 50mL solution, b)2g sorbent : 50mL solution and c) 5g sorbent : 50mL solution	210

3.3	Freundlich isotherms for 1 day pH 2: a) 1g sorbent : 50mL solution, b) 2g sorbent : 50mL solution and c) 5g sorbent : 50mL solution	211
3.4	Freundlich isotherms for 7 days pH 2: a) 1g sorbent : 50mL solution, b) 2g sorbent : 50mL solution and c) 5g sorbent : 50mL solution	212
3.5	Freundlich isotherms as a function of time with $C_0=1.2$ mg/L a) 1 day, b) 3 days and c) 7days d) 10days, e) 14days and f) 21days g) 30day	215
3.6	Freundlich isotherms as a function of time with $C_0=1.2$ mg/L a) 1 day, b) 3 days and c) 7 days d) 10 days and e) 14 days	220
3.7	Freundlich isotherms as a function of time with $C_0=1.2$ mg/L a) 1 day, b) 3 days and c) 7 days d) 10 days, e) 14 days and f) 21 days	224
4.1	Zeta potential for hematite H as a function of pH	264
4.2	Power function as a function of pH: 1g sorbent : $50mL$ solution a) $C_0 = 1.2 mg/L$, b) $C_0 = 20 mg/L$, and c) $C_0 = 50 mg/L$	265
4.3	Power function as a function of pH: 2g sorbent : 50mL solution a) $C_0 = 1.2 \text{ mg/L}$, b) $C_0 = 13 \text{ mg/L}$, and c) $C_0 = 80 \text{ mg/L}$	269
4.4	Power function as a function of pH: 5g sorbent : 50mL solution a) $C_0 = 1.2 \text{ mg/L}$, b) $C_0 = 13 \text{ mg/L}$, and c) $C_0 = 130 \text{ mg/L}$ d) $C_0 = 200 \text{ mg/L}$	273
4.5	BPA percentage removal as a function of pH: 1g sorbent : $50mL$ solution a) pH = 2, b) pH = 2.5, and c) pH = 3 d) pH = 3.5, e) pH = 4, and f) pH = 5 g) pH = 7, and h) pH = 10	277
4.6	BPA percentage removal as a function of pH: $2g$ sorbent : $50mL$ solution a) pH = 2, b) pH = 2.5, and c) pH = 3 d) pH = 3.5, e) pH = 4, and f) pH = 5 g) pH = 7, and h) pH = 10	281
4.7	BPA percentage removal as a function of pH: 5g sorbent : $50mL$ solution a) pH = 2, b) pH = 2.5, and c) pH = 3 d) pH = 3.5, e) pH = 4, and f) pH = 5 g) pH = 7, and h) pH = 10	285
4.8	BPA fraction removal as a function of pH: $C_0 = 1.2 \text{ mg/L}$ a) pH = 2, b) pH = 2.5, and c) pH = 3 d) pH = 3.5, e) pH = 4, and f) pH = 5 g) pH = 7, and h) pH = 10	289
4.9	BPA percentage removal as a function of $CaCl_2$ ionic strength: 5g sorbent : 50mL solution a) $C_0 = 1.3 \text{ mg/L}$, b) $C_0 = 13 \text{ mg/L}$, and c) $C_0 = 130 \text{ mg/L}$ d) $C_0 = 1.3 \text{ mg/L}$, e) $C_0 = 13 \text{ mg/L}$, and f) $C_0 = 130 \text{ mg/L}$	295
4.10	pH variation as a function of ionic strength: 5g sorbent : $50mL$ solution a)CaCl ₂ , b) CaCl ₂ + 1mM NaHCO ₃ , and c) CaCl ₂ at pH 2	298
4.11	Soluble iron (Fe) variation as a function of ionic strength: 5g sorbent : $50mL$ solution a) CaCl ₂ , b) CaCl ₂ + 1mM NaHCO ₃ , and c) CaCl ₂ at pH 2	299

4.12	BPA percentage removal as a function of ionic strength: 5g sorbent:50mL solution a) $C_0 = 1.3 \text{ mg/L}$, b) $C_0 = 13 \text{ mg/L}$, and c) $C_0 = 130 \text{ mg/L}$	304
4.13	pH variation as a function of ionic strength: 5g sorbent : 50mL solution	305
4.14	Soluble iron (Fe) variation as a function of ionic strength: 5g sorbent : 50mL solution.	305
5.1	Level I EQC modeling diagram	320
5.2	Level II EQC modeling diagram	321
5.3	Level III EQC modeling diagram (100kg/h released simultaneously to air, water and soil	323
5.4	Monohydroxylated BPA formation and perhydroxyl generation from BPA reaction with •OH radical in oxygenated medium	327
5.5	Main sonochemical degradation pathways of Bisphenol A. 300 kHz, 80W and oxygen saturating gas	329
5.6.	Change in BPA by-products during ultrasonic treatment of a solution saturated with oxygen. Frequency: 300 kHz; power: 80W; volume: 300mL; temperature: 20 ± 1^{0} C. Monohydroxylated-4-isopropenylphenol (A), 4-isopropenylphenol(B), 4-hydroxya- cetophen-one(C), dihydroxylatedbisphenolA(D), quinone of dihydroxylated bisphenolA (E), monohydroxylated bisphenol A (F) and quinone of monohydroxylated bisphenol A (G)	330
5.7	BPA degradation during ultrasonic, Fenton's oxidation and ferro sonication pre- treatment of WWS: a) Proposed region of attack (a - the site of intraenol ring cleavan- ge) and b) proposed pathway of degradation based on m/z ratios obtained furing LC-MS/MS analysis	331
5.8	The effect of inorganic ions on the rate of BPA sonochemical degradation. (initial BPA concentration 0.12 μ M; 300 kHz; 300 ml; 80 W; pH 8.3; T = 21 0 C in absence or presence of 6 mM inorganic salts NaCl, Na ₂ SO ₄ , Na ₂ HPO ₄ , or NaHCO ₃)	333
5.9	Reaction pathway proposed for the first intermediates formation in the case of the reaction of CO_3^{-1} with BP	334
5.10	Main degradation pathways of low-concentration BPA during US treatment	335
5.11	Concentrations of the intermediates during BPA ultrasonic irradiation. BPAconcentration:100 μ g/L; ultrasonicfrequency:20kHz; ultrasonic intensity: 60W/cm2; pH:6.5; temperature: 25 \pm 0.5 ^o C. (\circ)Monohydroxylated BPA; (\blacktriangle) phenol; (\triangle)4-isropenylphenol; (\blacksquare)hydroquinone; (\square)4-hydroxyacetophenone; (\blacklozenge)2-hydroxypropionic acid; (\Diamond) glycerol	337

5.12	BPA (118 μ mol/L) elimination by ultrasound, TiO ₂ photocatalysis (PC), photo- Fenton and combined ultrasound/Fe ²⁺ /TiO ₂ photoassisted processes applied to solutions saturated with oxygen	339
5.13	Changes in levels of BPA, total organic carbon (TOC), monohydroxylated BPA, and aliphatic acids during BPA (118 μ mol/L) degradation by photo-Fenton	340
5.14	Main reactions leading to BPA mineralization by the combined ultrasound/solar light/ Fe(II) system	340
5.15	Concentration of the intermediates products of EC degradation of BPA at current density of 10 mA/Cm ² on the a) Pt, b) Ti/RuO ₂ , c)Ti/Sb-SnO ₂ and d) Ti/BDD	342
5.16	Reaction pathway of electrochemical BPA degradation	343
5.17	Expected BPA degradation pathway	344
5.18	The central role of the hydroxycyclohexadienyl radical of BPA in the degradation pathway of the BPA substrate. "R" denotes the C_6H_5OH moiety	352
5.19	Intermediate formation proceeding from resonance-stabilized radicals (see Figure 5.18) along with the assignment of the identified analytes	354
5.20	Main steps during BPA degradation by photocatalysis	356
5.21	Pathway of BPA photodegradation in the solution containing only algae	358
5.22	The scheme of proposed mechanism of photosensitized degradation of BPA involved oxygen in HS solution	359
5.23	Proposed photodegradation pathway of BPA in SRFA solution under simulated solar irradiation	360
5.24	Possible metabolic pathway of BPA	363
5.25	Bisphenol A degradation and metabolite formation during resting-cell assay with strain MV1 cells grown on bisphenol A. Symbols: •, BPA; \Box , 4-HBA; \circ , 4-HAP; \land BHPP: • BHPPD	364
5.26	Metabolic pathway for BPA biodegradation by strain MV1	366
5.27	Metabolic pathway for BPA by bacterium strain MV1	366
5.28	Proposed pathway for BPA degradation by MnP	369
5.29	The oxidation of BPA by crude enzyme prepared from potato	369
5.30	Proposed reaction pathways for the formation of products B1-B5	371
5.31	Proposed reaction pathways for the formation of products b2 and b3	372
5.32	Presumed chlorination reaction scheme of BPA	373
5.33	Pathways of chloro-substitution reaction between bisphenol A and HOC1	374

5.34	Formation of polychlorinated phenoxyphenols	375
5.35	Chlorination of BPA in synthetic water. Insert in figure 5.34a shows the consumption of chlorine vs. time	376
6.1	Predicted and experimental equilibrium BPA concentrations (C_e) for magnetite M1, M2 and hematite H for the 30 days time study	403
6.2	Predicted and experimental equilibrium BPA concentrations (C_e) for magnetite M1,M2 and hematite H for the 30 days time study with independent variables interactions	406
6.3	Predicted and experimental equilibrium BPA concentrations (C_e) using hematite H for the 1 and 7 days isotherm study	417
6.4	Predicted and experimental equilibrium BPA concentrations (C_e) using hematite H for the 1 and 7 days isotherm study with independent variables interactions	420
6.5	Predicted and experimental equilibrium BPA concentrations (C_e) using 1g, 2g, and 5g of hematite H for at different pHs	424
6.6	Predicted and experimental equilibrium BPA concentrations (C_e) using 1g, 2g, and 5g of hematite H for at different pHs with independent variables interactions.	427
6.7	Predicted and experimental equilibrium BPA concentrations (C _e) for hematite H in the presence of Calcium ions	433
6.8	Predicted and experimental equilibrium BPA concentrations (C_e) for hematite H in the presence of Calcium ions with independent variables interactions	436
6.9	Predicted and experimental equilibrium BPA concentrations (C _e) for hematite H in the presence of Potassium ions	443
6.10	Predicted and experimental equilibrium BPA concentrations (C_e) for hematite H in the presence of Potassium ions with independent variables interactions	446
7.0	Hydroquinone (HQ)	453
7.1	Benzoquinone (BQ)	453
7.2	Conversion of HQ to BQ with Cu(II) mediation	455
7.3	Proposed mechanism for conversion of HQ into SQ and BQ	456
7.4	Degradation of HQ in the presence of iron oxides	457
7.5	Pathways for oxidation of HQ through SQ to BQ. Oxidation proceeds via the top pathway for pHs < 5 , and the bottom pathway for pH > 5	458
7.6	Adsorption isotherms of hydroquinone on the carbonized product (CZ) and sulfuric acid-activated carbons at 298 K	459

PAGE

7.7	Sorption of hydroquinone by ODTMA-B and HDTMA-B at various pH (dotted: ODTMA-B, line: HDTMA-B)	460
7.8	Illustration o conceivable adsorption behaviors on hematite. Iron atoms are dark grey, oxygen is white, carbon is black, and protons are light gray. a) Chemisorption via a bridging oxygen. b) Chemisorption via a π -backbonding complex	461
7.9	Total concentration as a function of time for the oxic study: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Hydroquinone (HQ), b) Benzoquinone	471
7.10	Total concentration partition for the oxic study as a function of time: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) 1Day, b) 3Days, and c) 7Days	472
7.11	Total HQ+BQ as a function of time for the oxic study for Magnetite M1: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	473
7.12	Total HQ+BQ as a function of time for the oxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	474
7.13	Total concentration as a function of time for the anoxic study: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Hydroquinone (HQ), b) Benzoquinone (BQ), and c) HQ+BQ	479
7.14	Total concentration partition for the anoxic study as a function of time: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) 1 Day, b) 3Days, and c) 7Days	480
7.15	Total HQ+BQ as a function of time for the anoxic study for Magnetite M1: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	481
7.16	Total HQ+BQ as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	482
7.17	Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	483
7.18	Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	484
7.19	Total concentration as a function of time for the anoxic study: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Hydroquinone (HQ), b) Benzoquinone (BQ), and c) HQ+BQ	489

7.20	Total concentration partition for the anoxic study as a function of time: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) 1 Day, b) 3 Days, and c) 5 Days d) 7 Days, e) 10 Days, and f) 14 Days g) 19 Days, h) 22 Days, and i) 26 Days j) 30 Days	490
7.21	Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution	493
7.22	Total HQ+BQ as a function of time for the anoxic study for Magnetite M1: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	494
7.23	Total HQ+BQ as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order	495
7.24	Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order.	496
7.25	Total HQ+BQ % removal as a function of adsorbent for oxic study for: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 50mL solution a) Magnetite (M1), and b) Magnetite (M2)	506
7.26	Total HQ+BQ % removal as a function of adsorbent for anoxic study for: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 150mL solution a) Magnetite (M1), and b) Magnetite (M2)	507
7.27	Total HQ+BQ % removal as a function of adsorbent for oxic study for: $C_{0(HQ)} = 11.01 \ \mu mol/L$, 150mL solution a) Magnetite (M1), and b) Magnetite (M2)	508
8.1	CTE and RME exposure risk calculations for Case 1 using Subchronic R_fD of 50,10, and 2 $\mu g/kg$ -day	537
8.2	CTE and RME exposure risk calculations for Case 2 using Subchronic R_fD of 50 $\mu g/kg$ -day	540
8.3	CTE and RME exposure risk calculations for Case 3 using Subchronic R_fD of 50,10, and 2 $\mu g/kg$ -day	545
8.4	CTE and RME exposure risk calculations for Case B using Subchronic R_fD of 50,10, and 2 $\mu g/kg$ -day	553
8.5	CTE and RME exposure risk calculations for Case D using Subchronic R_fD of 50,10, and 2 μ g/kg-day	554
8.6	CTE and RME estimated daily intake for Case E for different age groups	557
8.7	CTE and RME EDI percentage for different age groups for Case E	557
8.8	Case E CTE and RME exposure risk calculations for each pathway of exposure using Subchronic R _f D of 50,10, and 2 μ g/kg-day	561

FIGURE

PAGE

8.9	Case E CTE and RME exposure risk calculations for each age group using Subchronic $R_f D$ of 50,10, and 2 μ g/kgday	562
8.10	Case E CTE and RME exposure risk percentage for each exposure pathway	564
8.11	CTE and RME estimated daily intake for Case F for different age groups	568
8.12	Case F CTE and RME EDI percentage for different age groups for Case F	568
8.13	Case F CTE and RME exposure risk calculations for each pathway of exposure using Subchronic RfD of 50,10, and 2 $\mu g/kg$ -day	572
8.14	Case F CTE and RME exposure risk calculations for each age group using Subchronic RfD of 50,10, and 2 $\mu g/kg$ -day	573
8.15	Case F CTE and RME exposure risk percentage for each exposure pathway	575

SUMMARY

Bisphenol A (BPA) is a building block for several polymer additives. It is a compound that has been recently designated as an endocrine disrupting compound (EDC). The aqueous medium is the major route of pollution through industrial wastewater discharge, landfill leachate infiltration, and wastewater treatment plant effluents. A risk assessment of BPA indicates adverse health effects using different ingestion scenarios, where the exposure to BPA through ingestion of drinking water could alone pose a hazardous health effect at environmentally relevant concentrations for an oral subchronic reference dose (RfD) of 2 μ g/kg-day. Therefore, the removal of BPA from water is necessary to decrease the risk of human exposure to water contaminated with BPA.

Adsorption is a technology that has been used in water treatment for many years and is relatively easy to operate than other technologies capable of removing BPA. Adsorption has been used for a long time for the removal of organic and inorganic pollutants from water. Other technologies employed for the removal of BPA typically produce a large number of different degradation byproducts of BPA with an estrogenic activity greater than BPA itself. Even though other organic adsorbents such as activated carbon are capable of removing BPA at higher rates or capacities, they are still relatively expensive.

The removal of BPA from water was investigated using adsorption of BPA onto several iron oxide adsorbents: two magnetites (Fe_3O_4) and one hematite (Fe_2O_3). Iron oxides may serve as sustainable adsorbents due to lower cost and ease of regeneration using a blast furnace, when compared to organic adsorbents such as activated carbon. The adsorption of BPA from water onto iron oxide adsorbents was investigated as a function of pH, ionic strength, time, initial BPA concentration, adsorbent dosage, and type of adsorbent.

SUMMARY (continued)

The effect of pH on adsorption was investigated, showing that hematite H was able to remove more BPA at lower pH values. The removal of BPA at an initial concentration of 1.2 mg/L was about 95 percent at an acidic pH of 2.0. The maximum adsorption capacities on hematite at pH 2 were found to range from 253 to 302 mg/kg and from 337 to 396 mg/kg after 2 and 7 days, respectively. The effect of solution ionic strength on adsorption was investigated. There was a positive effect on adsorption due to calcium with and without bicarbonate with an increase in the adsorption with increasing ionic strength. The effect of potassium was not as strong as the effect of calcium, due to the lower positive valence of potassium ions as compared to calcium ions. The effect of calcium (Ca^{2+}) and potassium (K^{+}) ions were evaluated at ionic strengths of 1, 5, 50, 100 and 500 mM. The effect of Ca^{2+} ions was also evaluated in the presence of 1 mM sodium bicarbonate (NaHCO₃). From the experiments performed with calcium at different initial BPA concentrations of 1.3, 13 and 130 mg/L, it was found that there no effect on the adsorption of BPA at acidic conditions at concentration of 1.3 and 13 mg/L with a slight increase in the adsorption at 100 and 500 mM concentrations of calcium. There was a positive effect on adsorption due to calcium with and without bicarbonate with an increase in the adsorption with increasing ionic strength. The effect of potassium was not as strong as the effect of calcium.

Hydroquinone (HQ) and benzoquinone (BQ) are two intermediates of BPA degradation which occur either naturally in the environment or in engineered systems, where BQ is a product of HQ oxidation. At an initial concentration of 110 µmol/L, HQ was completely removed along with BQ (produced from HQ) after 30 days and 19 days by magnetite M1 and magnetite M2, respectively. The removal of BPA from water using the three iron oxides was statistically

SUMMARY (continued)

using multivariate linear regression (MLR) models. The MLR models were obtained using up to three interactions between the different independent variables that affected the adsorption. The MLR models could be used to understand the independent variables which had the strongest effect on adsorption, and to engineer a better treatment system for removal of BPA from water.

CHAPTER I

RESEARCH BACKGROUND

1.1 INTRODUCTION

Bisphenol A (BPA), is an organic compound that has two phenol functional groups. It is a building block for several important polymers and polymer additives. It is an important monomer that had been used for the production of polycarbonate in 1995 at a rate of 2-3 million tons annual production, and it is also used as stabilizer or antioxidant for many types of plastics such as polyvinyl chloride (PVC) (Ash and Ash, 1995). BPA is also used in the production of other plastics throughout the world, and is also known as 2,2-bis(4'-hydroxyphenoyl) propane, 4,4' -isopropyllidenediphenol, and 2,2'-bis(4-hydroxyphenyl) propane (Huang et al., 2012). It is also used in unsaturated polyester-styrene resins, flame retardants, food and drink packaging, and as antioxidants in plastics (Barnabe et al., 2009). Even though BPA is not a strong estrogenic compound, having a estrogenic activity with a potential of four orders of magnitude lower than that of 17β -estridol (Barnabe et al., 2009), has still manage to do harm in the environment and is a potential health risk for humans even at low concentrations (Crain et al., 2007). In fact, when a proposed ranking system was done for pharmaceuticals, personal care products and endocrinedisrupting chemicals or EOCs, out of 100 chemicals, the overall priority for BPA was second place and 17β-estridol came only in place seventeen for the overall score (Kumar and Xagoraraki, 2010). It was also reported that BPA has some anti-androgenetic activity (Birkett and Lester, 2003). Different formulations of solid bisphenol A bis(diphenyl phosphate) (S-BDP) and organo-montmorillonite (OMMT) were build based on polycarbonate (PC) and through different process help to create flame retardancy (Feng et al., 2010). Some physicochemical properties of BPA are listed in Table 1. BPA at room temperature has a solid state (Tsai, 2006a).

Figure 1.1 presents the formula developed for the BPA and Figure 1.2 the specific distribution of BPA. BPA may absorb to sediments having a K_{oc} of 314 to 1524, low volatility, and a low bioaccumulation potential in aquatic organisms with BCF_s in the range of 5 to 68 (Staples et al., 1998).

Physicochemical properties of bisphenol A		Reference
Case Number	80-05-7	Lide, 2007
Formula	$C_{15}H_{16}O_2$	Lide, 2007
Molecular Weight g mol ⁻¹	228.287	Lide, 2007
Density	1.195 g/cm^3	Staples et al., 1998
Melting point (⁰ C)	153	Lide, 2007
Boiling point (4 mm Hg) (⁰ C)	220 ⁰ C	Lide, 2007
Aqueous solubility	120-300 mg/L	Verschueren, 2009
Henry's Law Constant (25 [°] C)	1x 10 ⁻¹⁰	Staples et al., 1998
Vapor pressure	5.3 x 10 ⁻⁶ Pa	Cousins et al., 2002
Vapor pressure @ $170 {}^{0}$ C	0.2 mm Hg	Verschueren, 2009
$\log K_{\rm OW}$	2.20-3.82	Staples et al., 1998
	3.40	Cousins et al., 2002
Log K _{OC}	314	Staples et al., 1998
pK _a	9.59 and 10.2	Staples et al., 1998

Table 1.1 Physicochemical properties of bisphenol A



Figure 1.1 – Bisphenol A



Figure 1.2 – Species distribution diagram of bisphenol A (Toledo et al., 2005)

Since 1930, BPA has been suspected to be hazardous to humans via estrogenic activity, and has recently been designated as an endocrine disrupter compound (EDC). Like natural estrogens, these estrogenic chemicals can bind to the estrogen receptor and regulate the activity of estrogen responsive genes. Therefore, such effects have raised concern that prolonged exposure to environmentally relevant concentrations of these chemicals could result in reproductive toxicity. Endocrine disruptors include (a) natural compounds such as steroid hormones naturally secreted by humans and animals and (b) anthropogenic compounds such as synthetic hormones or agricultural and industrial chemicals (pesticides, bisphenol A, phthalates plasticizers, etc.). The presence of these EDCs is supposed to cause the feminization of male fish observed in several countries over the past 20 years (Jobling et al., 1998; Larsson et al., 1999). Also the blood levels of bisphenol A in humans had been statistically associated with the cause of different human diseases such as ovarian dysfunction, recurrent miscarriage, and endometrial hyperplasia.

BPA and its derivatives are still commonly used as monomers in the production of polycarbonate and epoxy resins, and as an antioxidant or stabilizing agent for plastics. Even

though the use of BPA and its derivates had been used in other processes (Iwase et al., 2010), the industry of plastics is the main BPA consumer. It was estimated that over 200,000 tons of BPA are produced every year by Japan (Kamiura et al., 1997). BPA is widely produced and found in the environment all over the world from Europe to Japan (Yamamoto et al., 2001). The capacity production of BPA had increased over the years, with US being the highest producer (Jiao et al., 2008). We can see in Table 1.2 a global perspective about the total production of BPA. In 2007 the production capacity of BPA was estimated to be about 4.7×10^6 tonnes annually. For 2007 the total production of BPA in the Asia-Pacific region was 43.5 % of the global total output. Thus, the demand of the Asian countries in the future, especially China, will depend greatly the total global production (Jiao et al., 2008). The supply and demand had been increasing drastically for China since 2001 from on output of 12,000 tonnes and import of 94,000 tonnes, totaling a volume consumption of 106,000 tonnes to 2008 with a import of 460,000 tonnes and output of 110,000 tonnes totaling a volume consumption of 570,000 tonnes (Yu and Jia, 2008). The use of Bisphenol A to manufacture different products it had been speculated that human exposure could reach high levels.

Country/ Region	Production Capacity (10 ³ tonnes /year)	Percentage (%)
United States	1075	22.9
Taiwan	615	13.1
Japan	611	13.0
Germany	456	9.7
The Netherlands	410	8.7
Spain	280	6.0
Korea	260	5.5

 Table 1.2 Global BPA production capacity (Jiao et al., 2008)
Singapore	230	4.9
Belgium	220	4.7
China (Mainland)	167	3.6
Russia	165	3.5
Thailand	160	3.4
Brazil	27	0.6
Poland	12	0.3
Czechoslovakia	8.5	0.2
Total	4696.5	100

The spread of BPA contamination in the environment had been seen all over the world in places such as: surface fresh water, waste water, landfill leachate, air, and dust particles. Table 1.3 presents some locations and BPA levels in the environment across the world. Based on the concentrations that we have from fresh water, marine water, landfill leachate, underground water, sediments, soils, particular matter, atmosphere, and dust we can see that the greatest concentrations are in the body of waters and especially in landfill leachate. The leaching of BPA from landfill could pose a real health risk for the humans, because of the drinking water use from underground aquifers. The municipal landfill had become a source of emerging pollutants such as: aliphatic alcohols and ethers, aldehydes and ketones, aliphatic acids and esters, aromatic carboxylic acids and esters, polyaromatic hydrocarbons + substituted PAHs, terpenoids, phthalic acid esters, phosphoric acid derivatives, phenolic compounds, benzene derivatives, alkenes and cycloalkanes, steroids, vitamin, benzthiazoles, pesticidecides, N-containing compounds, Scontaining compounds, sulfonamides, drugs and metabolites, non-steroidal inflammatory drug, metabolite of analgetic drug, and anti-infective agent (Eggen et al., 2010). The BPA can concentrate in the landfill leachate from the decomposition of plastic bottles or epoxy resins (Bae

et al., 2002). When the leachate reaches the underground water wells or aquifer even after dilution can be at levels that could have an adverse health effect on humans. Thus, the removal of BPA before the water is consumed during the water treatment process or even the treatment of leachate is very important. Drinking water contaminated with bisphenol A has a major effect on human health. Thus the treatment of drinking water is crucial in preventing and stopping the infection of human and animal populations. Various technologies have been evaluated for the removal of bisphenol A from water. Each technique has advantages and disadvantages. It is very important that the removal to be not just economical and efficient, but also to be done using a conventional water treatment process that is practical and easy to manage.

Surface waters					
Location	Measured concentration	Comments	Reference		
The Netherlands	21 (µg/L)	River water	Belfroid et al., 2002		
Japan	19 (µg/L)	River water	Crain et al., 2007		
Japan	500 - 900 (ng/L)	River water	Huang et al., 2012		
Japan	0.23 (µg/L)	River water	Crain et al., 2007		
Japan	0.058 (µg/L)	River water	Crain et al., 2007		
China	0.33 - 3,920 (ng/L)	River water (different sources)	Huang et al., 2012		
Switzerland	9 - 76 (ng/L)	River water	Voutsa et al., 2006		
Italy	0.494 (µg/L)	River water	Vigano et al., 2006		
Korea	39.4 (µg/L)	River water	Ko et al., 2007		
Korea	6.9 - 59 (ng/L)	River water	Yoon et al., 2010		
Portugal	10.7 (µg/L)	River water	Ribeiro et al., 2009		
Portugal	1.1 - 683 (ng/L)	River water	Jonkers et al., 2010		
Spain	52 - 219 (ng/L)	River water	Huang et al., 2012		
Spain	0.120 - 2.572 (µg/L)	River water	Rodriguez-Mozaz et al., 2005		
United States	0.147 (µg/L)	River water	Crain et al., 2007		
United States	0 - 147.2 (ng/L)	River water	Zhang et al., 2007		
Germany	0.016 (µg/L)	River water	Crain et al., 2007		
Germany	8.9 - 776 (ng/L)	River water	Huang et al., 2012		
Germany	0.5 - 14 (ng/L)	River water	Kuch and Ballschmiter, 2001		
United Kingdom	5.3 - 24 (ng/L)	River water	Huang et al., 2012		
Nigeria	0.03 - 0.23 (µg /L)	River water (18 observations)	Ignatius et al., 2010		
Europe	Max. = $68 (ng/L)$	Danube River	Loos et al., 2010		

 Table 1.3 Environmental relevant concentrations of BPA and their locations in aquatic systems

Europe	Max. = 490 (ng/L)	Danube Tributary River	Loos et al., 2010
Nigeria	0.03 - 0.92 (µg /L)	Rain water (24 observations)	Ignatius et al., 2010
United States	12 (µg/L)	Stream water	Crain et al., 2007
United States	0.09 - 12 (µg /L)	Stream water	Kolpin et al., 2002
United States	Max 420 (ng/L)	Drinking water treatment plant	Huang et al., 2012
China	15 - 63 (ng/L)	Tap water (different sources)	Huang et al., 2012
Germany	0.002 (µg/L)	Drinking water	Crain et al., 2007
Germany	0.5 - 2.0 (ng/L)	Drinking water	Kuch and Ballschmiter, 2001
Nigeria	0.01 - 0.52 (µg /L)	Tap water (38 observations)	Ignatius et al., 2010
Nigeria	0.01 - 0.58 (µg /L)	Well water (36 observations)	Ignatius et al., 2010
Spain	0.007 - 0.014 (ng/L)	Drinking water	Rodriguez-Mozaz et al., 2005
Japan	8,000 - 370,000 (ng/L)	Effluents 8 paper recycling plants	Huang et al., 2012
South Taiwan	623 - 16,200 (ng/L)	Industrial wastewaters	Huang et al., 2012
Canada	230 - 149,200 (ng/L)	Industrial effluents	Huang et al., 2012
United States	Ave. = 4 upstream Ave. = 8 downstream (μ g/L)	Industrial effluents	Staples et al., 2000
Germany	0.41 (µg/L)	Surface water	Crain et al., 2007
Germany	0.005 - 0.4 (µg/L)	Surface water	Fromme et al., 2002
Germany	4.8 - 47 (ng/L)	Surface water	Kuch and Ballschmiter et al., 2001
Japan	20.2 - 30.1 (ng/L)	Surface water	Huang et al., 2012
Japan	0.90 (µg/L)	Surface water	Kang and Kondo, 2006 Crain et al., 2007
Austria	0.60 (µg/L)	Surface water	Crain et al., 2007
The Netherlands	11 - 170 (ng/L)	Surface water	Belfroid et al., 2002
North America	95 th percentile 0.47 (µg/L)	Surface water (1068 observations)	Klecka et al., 2009
Europe	95 th percentile 0.35 (µg/L)	Surface water (848 observations)	Klecka et al., 2009
Brazil	25 - 84 (µg/L)	Surface water (6 observations)	Sodre et al., 2010
The Netherlands	10 - 330 (ng/L)	Fetuary	Belfroid et al. 2002
The Netherlands	Max 21 (µg/L)	Estuary	Demoid et al., 2002
The Netherlands	0.330 (µg/L)	Estuary	Crain et al., 2007
Korea	46 (ng/L)	Coastal Seawaters	Huang et al., 2012
Japan	5 - 58 (ng/L)	Seawaters	Huang et al., 2012
Italy	0.030 (µg/L)	Lagoon water	Crain et al., 2007
Singapore	40 - 190 (ng/L)	Seawaters	Huang et al., 2012
Germany	0.05 - 249 (ng/L)	Seawaters	Huang et al., 2012
Spain	49.1 - 196 (ng/L)	Seawaters	Huang et al., 2012
The Netherlands	10 - 330 (ng/L)	Seawaters	Huang et al., 2012
Europe	95^{th} percentile 0.088 (µg /L)	Seawaters (115 observations)	Klecka et al., 2009
Portugal	1.1 - 17 (ng/L)	Seawaters	Jonkers et al., 2010
United States	0.158 (µg/L)	Canal water	Crain et al., 2007
	Non-S	Surface waters	
Japan	1.3 - 17,200 (µg/L)	Landfill leachate	Yamamoto et al., 2001
Japan	5,400 (µg/L)	Landfill leachate	Crain et al., 2007
Japan	5.1 (µg/L)	Treated landfill leachate	Crain et al., 2007

Japan	8,000 - 370,000 (ng/L)	Landfill leachate	Huang et al., 2012
China	13 - 2,923 (µg/L)	Landfill leachate (8 observations)	Xiangli et al., 2006
Japan	7.53 - 2,980 (µg/L)	Landfill leachate (7 observations)	Yasuhara et al., 1999
China	5 - 100 (µg/L)	Landfill leachate	He et al., 2009
Japan	0.009 - 3,600 (µg/L)	Landfill leachate	Kurata et al., 2008
China	15.2 - 8,540 (ng/L)	Wastewater effluent	Wang et al., 2010
China	145.2 - 6,993 (ng/L)	Wastewater influent	Wang et al., 2010
China	3.7 - 994.5 (ng/L)	Wastewater	Nie et al., 2012
Austria	5.8 (µg/L)	Wastewater	Furhacker et al., 2000
Mexico	0.712 - 2.86 (µg/L)	Wastewater	Gibson et al., 2007
Canada	1.28 (µg/L)	Wastewater treatment plant influent	Lee et al., 2005b
Canada	31 - 223 (ng/L)	Wastewater treatment plant effluents	Huang et al., 2012
Canada	193 - 2,440 (ng/L)	Wastewater treatment plant influents	Huang et al., 2012
Canada	33 - 36,700 (ng/g)	Sewage sludge	Lee and Peart, 2000
United States	6, 50 (ng/I)	Secondary effluent	Huang et al. 2012
Office States	0 - 50 (lig/L)	wastewater treatment plant	fluang et al., 2012
United States	281 - 3 642 (ng/L)	Primary effluent wastewater	Huang et al 2012
Onice States	201 3,012 (lig/L)	treatment plant	fitung et un, 2012
United States	20 - 55 (ng/L)	Treated septages/wastewaters	Huang et al., 2012
United States	94 - 150 (ng/L)	Untreated wastewaters	Huang et al., 2012
United States	110 - 1700 (ng/L)	Untreated septages	Huang et al., 2012
United States	1.7 (µg/L)	Untreated sewage	Crain et al., 2007
United States	0.094 - 0.15 (µg/L)	Untreated wastewater	Rudel et al., 1998
Spain	1.5 (µg/L)	Sewage treatment influent	Crain et al., 2007
Spain	$0.27 (\mu g/L)$	Sewage treatment effluent	Crain et al., 2007
Spain	10 - 2,500 (ng/L)	Wastewater	Huang et al., 2012
Spain	1,270 and 1,105(ng/L)	Wastewater	Hernando et al., 2004
Spain	13.4 (ng/L)	Wastewater	Vega-Morales et al., 2010
Portugal	0.15 - 1.55 (μg/L)	Wastewater	Mauricio et al., 2006
Portugal	120 - 683 (ng/L)	Wastewater	Jonkers et al., 2010
United States	1.4 (μg/L)	Landfill plume	Crain et al., 2007
United Kingdom	1.2 (µg/L)	Crude wastewater	Crain et al., 2007
United Kingdom	0.046 (µg/L)	Treated waste water	Crain et al., 2007
United Kingdom	1105 (ng/L)	Wastewater treatment plant influents	Huang et al., 2012
United Kingdom	19.2 (ng/L)	Wastewater treatment plant effluents	Huang et al., 2012
Germany	0.70 (µg/L)	Sewage treatment effluent	Crain et al., 2007
Sweden	0.49 (µg/L)	Sewage treatment effluent	Larsson et al., 1999
Germany	12,205 (ng/L)	Wastewater	Hohne and Puttmann et al., 2008
Greece	0.15 (µg/L)	Wastewater	Stasinakis et al., 2008
France	450 (ng/L)	Wastewater	Jeannot et al., 2002
Singapore	0.01 - 2.05 (µg /L)	Sludge	Hu et al., 2007
Japan	300 (ng/L)	Wastewater	Zhang et al., 2008a
Korea	1 (ng/L)	Wastewater	Kim et al., 2007a,b
Brazil	2.5 (µg/L)	Wastewater	Sodre et al., 2010
Spain	51.6 - 207 (ng/L)	Ground water	Huang et al., 2012
Austria	0.93 (µg/L)	Ground water	Crain et al., 2007

United States	0.003 - 1.41 (µg/L)	Ground water	Rudel et al., 1998
	Soi	ils / Sediments	
North America	$34 (n\sigma/\sigma dw)$	Sediments fresh water (71	Klecka et al 2009
North America	5.4 (lig/g-uw)	observations 90^{th} percentile)	Riceka et al., 2009
Europe	256 (ng/g-dw)	Sediments fresh water (249 observations 95 th percentile)	Klecka et al., 2009
Germany	0.01 - 0.2 (mg/Kg-dw)	Sediments fresh water	Fromme et al., 2002
Germany	0.5 - 15 (ng/g)	River sediments	Bolz et al., 2001
Germany	70 - 770 (ng/g)	Municipal treatment plant sediments	Bolz et al., 2001
Germany	10 - 380 (ng/g)	Fresh deposited sediments	Stachel et al., 2003
Germany	7 - 1,630 (ng/g)	River sediments	Stachel et al., 2005
Germany	10 - 190 (ng/g)	River sediments	Fromme et al., 2002
China	0.7 - 5.4 (ng/g)	River sediments	Huang et al., 2012
China	0.6 - 59.6 (ng/g)	River sediments	Lei et al., 2008
China	0.6 - 4.0 (ng/g)	River sediments	Peng et al., 2006
China	0.58 - 2.16 (ng/g)	River sediments	Huang et al., 2012
Taiwan	329 - 10,500 (ng/g)	River sediments	Lin, 2001
Korea	2.70 - 50.3 (ng/g)	Sediments	Khim et al., 1999
Korea	1.0 - 53.5 (ng/g)	Sediments	Khim et al., 2001
United Kingdom	3.4 - 9 (ng/g)	River sediments	Liu et al, 2004
Italy	Maximum 600 (ng/g)	Suspendent matter (river)	Patrolecco et al., 2004
The Netherlands	5.6 - 56 (ng/g)	Suspendent matter (surface waters)	Vethaak et al., 2005
The Netherlands	1.1 - 43 (ng/g)	Suspendent matter (surface waters)	Vethaak et al., 2005
Japan	0.11 - 48.0 (ng/g)	Surface water sediments	Hashimoto et al., 2005
United States	40 - 800 (ng/g)	Soil / sediments	Burkhardt et al., 2005
North America	3.5 (ng/g-dw)	Sediments marine water (14 observations median conc.)	Klecka et al., 2009
United States	1.5 - 5.0 (ng/g)	Marine sediments	Stuart et al., 2005
Europe	566 (ng/g-dw)	Sediments marine water (67 observations median conc.)	Klecka et al., 2009
Japan	0.5 - 11	Sea sediments	Kawahata et al., 2004
		Dust	
United States	820 (ng/g)	Private houses (118	Rudel et al., 2003
		observations -median conc.)	<i>,</i>
United States	30 (ng/g)	Day-care centers (19 observations -median conc.)	Wilson et al., 2007
United States	30 (ng/g)	Day-care centers (23	Wilson et al., 2007
		observations -median conc.)	
Germany	555 (ng/g)	Private houses (12 observations -median conc.)	Volkel et al., 2008
Belgium	4,685 - 8,380 (ng/g)	Offices	Geens et al., 2009
Belgium	535 - 9,730 (ng/g)	Private houses (18	Geens et al., 2009
	Atm	osnhere (ng/m ³)	
United States	100 - 2 500	Urban Site (1997)	Wilson et al 2001
China	380 - 1 260	Urban Site (2007)	Fu and Kawamura 2010
China	230 - 860	Urban Site (2007)	Fu and Kawamura 2010
China	70 - 2.340	Urban Site (2007)	Fu and Kawamura 2010
China	20 - 1.980	Urban Site (2007)	Fu and Kawamura. 2010
Hong Kong	30 - 690	Urban Site (2007)	Fu and Kawamura, 2010

Japan	10 - 1,920	Urban Site (2000/2001)	Matsumoto et al., 2005
Japan	70 - 930	Urban Site (2008/2009)	Fu and Kawamura, 2010
New Zealand	4 - 1,340	Urban Site (2004)	Fu and Kawamura, 2010
New Zealand	95 - 1,480	Urban Site (2004)	Fu and Kawamura, 2010
India	200 - 17,400	Urban Site (2007)	Fu and Kawamura, 2010
India	100 - 9,820	Urban Site (2008)	Fu and Kawamura, 2010
China	30 - 240	Rural Site (2006)	Fu and Kawamura, 2010
Germany	5 - 15	Rural Site (2001)	Berkner et al., 2004
California Coast	8 - 16	Marine Region (1989)	Fu and Kawamura, 2010
North Pacific	1-2	Marine Region (1989)	Fu and Kawamura, 2010
North Atlantic	4 - 6	Marine Region (1989)	Fu and Kawamura, 2010
Indian Ocean	6	Marine Region (1990)	Fu and Kawamura, 2010
South China Sea	6	Marine Region (1990)	Fu and Kawamura, 2010
East China Sea	7 - 27	Marine Region (1990)	Fu and Kawamura, 2010
ChichieJima			
Island, Western	2 - 23	Marine Region (1990)	Fu and Kawamura, 2010
North Pacific			
Rishiri Island,	4 22	Marina Pagion (2002)	Eu and Kawamura 2010
North Japan Sea	4 - 32	Wallie Region (2003)	Fu and Kawamura, 2010
Alert, Canadian	1 11	Polar Pagion (1001)	Fu and Kawamura 2010
High Arctic	1 - 11	Folai Region (1991)	Fu and Kawamura, 2010
Alert, Canadian	2 17	Polar Region (2000)	Fu and Kawamura 2010
High Arctic	2 - 17	Total Region (2000)	Tu allu Kawallura, 2010
Syowa Station,	1 - 11	Polar Region (1991)	Fu and Kawamura 2010
Antartica	1 - 11	i olai Regioli (1991)	i u anu ixawamura, 2010

The development of treatment techniques for the decomposition, detoxification and removal of BPA in water has been investigated and different methods of removal had been examined. Several treatment processes used for the removal of BPA in water or wastewater had used chemical (Sajiki and Yonekubo, 2002), biological (Staples et al., 1998), photochemical (Ohko et al., 2001), and as well as electrochemical processes (Boscoletto et al., 1994; Tanaka et al., 1999; Tanaka et al., 2002; Zorpas et al., 2011).

1.2 REMOVAL TECHNOLOGIES

Recently the increase use of personal care products (PPCPs), pharmaceuticals, and endocrine-disrupting compounds (EDCs) lead to an increase in drinking water supplies concentrations. These compounds in many cases had been able to pass the traditional water treatment processes (Westerhoff et al., 2005). The BPA, which is an EDC, had started to become a priority not only in the drinking water industry but also in food and wastewater sludge also (Barnabe et al., 2009). As mentioned earlier Kumar and Xagoraraki, 2010 reported that out of 100 chemicals as pharmaceuticals, personal care products and endocrine-disrupting chemicals or EOCs, overall priority for BPA was second place for the overall score. For the occurrence BPA was third place, for ecological effect was 35, for the health effect was 29, and when compare to the surface/source water BPA was second in highest priority of concern out of the EDCs.

In the last few years the removal of EDCs through different chemical oxidants had been studied and reported. The processes are known as chemical advanced oxidation (CAO) or advance oxidation processes (AOPs). Under the CAO the pollutant is mineralized in wastewater to CO₂ or is changed to a different metabolite product by strong oxidation-reduction reactions (Liu et al., 2009). The AOPs can be divided into two categories: 1) Photochemical processes and 2) Non-photochemical processes. The photochemical processes are ultra violet (UV) oxidation processes, UV/H₂O₂, UV/O₃, UV/H₂O₂/O₃, UV/Ultrasound, pthoto-fenton, photocatalysis, vacuum UV (VUV), and microwave (Gultekin and Ince, 2007). For the non-photochemical processes there is the ozonation, Fenton, ultrasound (US), US/H₂O₂, US/O₃, US/Fenton, electrochemical oxidation, supercritical water oxidation, ionizing radiation, electron-beam irradiation, wet-air oxidation, and pulsed plasma (Gultekin and Ince, 2007).

The CAO processes efficiency depends on the redox potential and follows the following order $FeO_4^{2-} > O_3 > S_2O_4^{2-} > H_2O_2 > Cl_2 > ClO_2$ (Jiang and Lloyd, 2002). We can see the redox potentials for some oxidizers that are used as oxidants/disinfectants in water and wastewater treatment listed in Table 1.4. For a better removal sometimes different processes are combined such as UV/O₃, UV/H₂O₂, and UV/Fenton (Klavarioti et al., 2009). These methods are based on

Wang, 2001).

Oxidant / Disinfectant	Reaction	E ⁰ /V	Oxidizer	Reference
Ferrate (VI)	$FeO_4^{2-} + 8H^+ + 3e \leftrightarrow Fe^{3+} + 4H_2O$	2.20	FeO ₄ ²⁻	Jiang and Lloyd, 2002
Ozone	$O_3 + 2H^+ + 2e \leftrightarrow O_2 + 2H_2O$	2.076	O_3	Jiang and Lloyd, 2002
Peroxydisulfate	$S_2O_4^{2-}(aq) + 2e \leftrightarrow 2SO_4^{2-}$	2.01	$S_2 O_4^{2-}$	Liang et al., 2004
Hydrogen Peroxide	$H_2O_2 + 2H^+ + 2e \leftrightarrow 2H_2O$	1.780	H_2O_2	Crittenden, 2005
Permanganate	$MnO_4^{2-} + 4H^+ + 3e \leftrightarrow MnO_2 + 2H_2O$	1.679	MnO_{4}^{2-}	Jiang and Lloyd, 2002
Aluminum	Al (s) \leftrightarrow Al ²⁺ + 3e	1.66	Al	Crittenden, 2005
Permanganate	$MnO_4^{2-} + 8H^+ + 5e \leftrightarrow Mn^{2+} + 4H_2O$	1.507	MnO_{4}^{2-}	Jiang and Lloyd, 2002
Hypochlorous acid	$HClO + H^+ + 2e \leftrightarrow Cl^- + H_2O$	1.482	HC1O	Jiang and Lloyd, 2002
Perchlorate	$ClO_4^- + 8H^+ + 8e \leftrightarrow Cl^- + 4H_2O$	1.389	ClO_4^-	Jiang and Lloyd, 2002
Chlorine	$Cl_2(g) + 2e \leftrightarrow 2Cl^-$	1.358	Cl_2	Jiang and Lloyd, 2002
Dissolved Oxygen	$O_2 + 4H^+ + 4e \leftrightarrow 2H_2O$	1.229	O_2	Jiang and Lloyd, 2002
Chlorine dioxide	$ClO_2(aq) + e \leftrightarrow ClO_2^-$	0.954	ClO ₂	Jiang and Lloyd, 2002
Hypochlorite	$ClO^- + H_2O + 2e \leftrightarrow Cl^- + 2OH^-$	0.841	Cl0-	Jiang and Lloyd, 2002
Chlorine dioxide	$ClO_2(g) + 2H_2O + 5e \leftrightarrow Cl^- + 4OH^-$	0.799	ClO ₂	Crittenden, 2005
Iron	Fe (s) \leftrightarrow Fe ²⁺ + 2e	0.44	Fe	Crittenden, 2005

Table 1.4 Redox potential for some oxidizers

1.2.1 OXIDATION OF BISPHENOL A USING OZONATION

Ozonation had been used in drinking water treatment for taste, odor and disinfection, also for wastewater disinfection in the past (Klavarioti et al., 2009). Studies had been done even on site for drinking water plants (Ternes et al., 2002; Hua et al., 2006; Jasmin et al., 2006; Vieno et al., 2007) and wastewater treatment plants (WWTPs) (Ternes et al., 2003; Huber et al., 2005; Nakada et al., 2007). During the ozonation two strong oxidants can oxidize EDCs and other organic pollutants, which are the molecular ozone O_3 and the HO• radicals (Hoigne and Bader, 1983a, 1983b). The HO• radicals are formed by the decomposition of aqueous ozone in water as it reacts with the hydroxide ion (OH^-) (Staehelin and Hoigne, 1982). Ozonation had been proven to be effective for the oxidation of phthalate (Wu et al., 2000), p-chlorophenol (Andreozzi and Marotta, 1999), phenol (Legube et al., 1983), cofibric acid, ibuprofen, diclofenac (Zwiener and Frimmel, 2000), amoxiline, antrazine (Esplugas et al., 2007) and other organic compounds.

It is important to state that under acidic conditions the presence of radical scavengers inhibit the chain reaction that accelerates the decomposition of O_3 , under this circumstances the direct reaction of aqueous ozone with BPA dominates. In the presence of solutes the radical chain reaction is improved and the transformation of the ozone to HO• radicals is accelerated and the reaction between the BPA and HO• radicals dominates (Hoigne and Bader, 1983a; Staehelin and Hoigne, 1985). In Table 1.5 we can see different experiments done for the removal of BPA using ozonation.

Solution	Oxidant	Operational conditions	Main Conclusions	Reference
Aqueous Solution	O ₃ , O ₃ /UV	$\begin{array}{l} C_{0} = 0.5 \ \mbox{or} \ 1 \mu g/L \\ C_{O3} = 7.56\text{-}15.89 \\ \mu \mbox{mol/min} \end{array}$	1) The degradation of BPA was more efficient with O_3/UV than O_3 alone.	Irmak et al., 2005
Purified water	O ₃	pH 2.5 - 10.5 T = $20 \ {}^{0}C$	1) The removal of BPA with ozone when compare the apparent second order rate constant to that of chlorine was greater. 2) The apparent second order rate constant increased with the increase of pH.	Deborde et al., 2005
Purified water	O ₃	$T = 20 \ ^{0}C$ pH = 6.5 $C_{0} = 100 \ \mu M$ $C_{O3} = 15 - 400$ μM	1) The removal of BPA with ozone can lead to formation of byproducts that will require additional ozone to remove. Also further transformation of these by- products will lead to smaller and more polar compounds such as acids or aldehydes.	Deborde et al., 2008
Effluent of primary	O_3	$TOC_0 = 27.2 - 48.6 \text{ mg/L}$	1) The BPA was degraded to lower than 10 ng/L from 326 at 0.4 mg $O_3/mg C$ of	Zhang et al., 2008

 Table 1.5 Removal of BPA using ozonation

settling tank		$C_{O3} = 40 \text{ and } 85$ mg/L $C_{O3} = 0.4 \text{ mg}$ O_3/TOC_0	consumed ozone. 2) The presence of suspended solids (SS) in the experiment 38-67 mg/L had no influence for the removal.	
Aqueous Solution	O ₃	$C_{HCO3}^{} = 1.0 - 8.0$ mM $C_{O3} = 1.4, 2.2 \text{ and}$ 5.1 mg/L $C_0 = 23.0 - 57.0$ μ M pH = 2 - 10	aqueous solution was found to be linear related to the ozone concentration. 2) The removal increased with an increase in pH from 2 to 7, but further increase to 10 decreased the removal. 3) The concentration of bicarbonate showed no significant effect on the removal of BPA at 35 μ M.	Garoma and Matumoto, 2009
Distill Water	O ₃	$T = 20 \ ^{0}C$ $C_{O3} = 1.5 \ mg/L$ $C_{0} = 100 \ nM$ pH = 7.5	1) The removal of BPA was greater than 99 %. 2) After the removal due to the formation of byproducts a residual estrogenic response could be still present.	Alum et al., 2004

During the ozonation, byproducts formation had been reported in the aqueous solution after the removal of BPA (Deborde et al., 2008). Deborde et al., 2008 performed ozonation experiments with Milli-Q purified water, in Pyrex batch reactors of 125 mL, at 20 ^oC and with an initial pH of 6.5. One set of experiments were done in excess presence of BPA with low ozone doses in order to study the chemical structure of the primary transformation products. Aqueous ozone solution of 15 to 400 mM was added with a glass syringe in a 100mL solution that contained a 100mM BPA concentration. The second tests were done with ozone aqueous solution greater than 400mM, which was added to different solutions that contained different concentrations of BPA.

The dissolved ozone concentration was determined according to the indigo method that was previously used by Bader and Hoigne, 1981. The pH in the preliminary experiments decreased from 6.5 to about 4.5 at the end of the experiments, which was believe to be due to the formation of carboxylic acids. For the complete BPA removal seen in Figure 1.3, the ozone doses had to be about 4 to 4.5 times higher than the initial BPA concentrations.



Figure 1.3 – Bisphenol A removal (initial[BPA] = 100 +/- 1.4 μ M) as a function of the applied ozone dose at 20 +/- 2⁰C, in Milli-Q purified solution (initial pH = 6.5) (Deborde et al., 2008)

As a result of the transformation, the byproducts in ozonated BPA solution were characterized by LC–UV and mass spectrometry analyses LC–MS and MS/MS. The byproducts were named B1 to B5 and after different investigations the chemical structures were determined to be that of muconic acid derivates of BPA, benzoquinone, 2-(4-hydroxyphenyl)-propanol-2-ol, orthoquinone, and catechol. In Figure 1.4 we can see the transformation of BPA and byproduct formation to the different ozone doses that were applied.

In Figure 1.5 we can see a proposed reaction pathway for the formation of all five byproducts. It is true that the formation of these byproducts under water treatment could be negligible due to low BPA initial concentrations, however using today's technology the cost of ozone production is still high, which is the reason that is not widely used in water treatment in United States today.



Figure 1.4 - Transformation products variation according to the ozone dose applied. (Deborde et al., 2008)



Figure 1.5 - Proposed reaction pathways for the formation of products B_1 - B_5 . (Deborde et al., 2008)

1.2.2 CHLORINATION OF BISPHENOL A

Chlorination had been used in the United States (US) for more than 100 years to disinfect water and contributed to the improvement of public health. Chlorination has been used for both drinking and wastewater treatment in US to react with organic and inorganic chemicals. For example, in the US the use of free chlorine (HOCl and OCl⁻) had been used to oxidize inorganic species such as Fe(II), Mn(II), and S(II), and phenolic compounds (Gallard and Von Gunten, 2002). The free chlorine can react rapidly with phenolic compounds because of the interaction of the hypochlorous acid and the deprotonated phenolate anion (Faust and Hunter, 1967). However, in the presence of ammonia the free chlorines will produce chloramines that are usually less active than free chlorines. This could be very important in the removal of BPA from wastewater due to high levels of ammonia that could be present, which will convert the free chlorine into monochloramine in a wastewater effluent that has not pass to the nitrification step yet.

Few studies on the fate of BPA had been done using chlorine reagent. A apparent secondorder rate constant of 61.8 M⁻¹s⁻¹ at pH 7 and 20 ⁰C had been reported for the reaction of chlorine and BPA (Gallard et al., 2004). The half-life of BPA had been found to be 13 minutes for a concentration of total chlorine of 1 mg/L. Just as in case of ozonation the reaction of BPA with chlorine can lead to the formation of numerous byproducts (Hu et al., 2002, Yamamoto and Yasuhuru, 2002), mainly because of the polychlorination of the aromatic rings. Some of the halogenated derivates of BPA had been characterized in detail by ion trap mass spectrometry and NMR spectrometry (Gallart-Ayala et al., 2007). Toxicity studies of the chlorinated derivates of BPA had suggested that their estrogenic activity is stronger than that of BPA alone (Takemura et al., 2005). The chlorination of BPA can occur during water disinfection and bleached paper recycling. The derivates of BPA are monochloro-, dichloro-, trichloro-, and tetrachlorobisphenol A, which can be released into the environment. Some of these compounds have been found in concentrations of $0.2 - 2.0 \ \mu g/L$ in the final effluents from paper recycling plants (Fukazawa et al., 2001). Hu et al., 2002 showed that most of the chlorinated BPA byproducts are reacting less efficiently than BPA. After one hour of the BPA chlorination, estrogenic activity had been still observed (Hu et al., 2002, Lee et al., 2004). Korshin et al., 2006 reported that the chlorination of BPA with chlorine gas produces 80% of some chlorinated BPA byproducts, with the remaining byproducts being chloroacetic acids (HAAs) dominated by dichloroacetic acids and trhichloroacetic acids and small traces of monochloroacetic acids. BPA and its chlorinated the humans (Fernandez et al., 2007).

To better understand the behavior of BPA degradation with chlorine as a function of pH and chlorine concentration, we can see the profile of half-lifes in Figure 1.6. The chlorination was done diluting sodium hypochlorite NaOCl. We can see that the half-lives of BPA deceases substantially with an increase of pH. Also in Figure 1.7 we can see the degradation of BPA using chlorine concentration of 2.7 mg/L and the formation of chlorinated byproducts. When other sets of experiments were performed with chlorine concentration of 1 mg/L and pH = 7.0 at a lower BPA concentration of 500 nM (114 μ g/L) in the presence of isolated humic substances from treated water, the disappearance of the chlorinated byproducts took more than 22 hours (Gallard et al., 2004). Yamamoto and Yasuhara, 2002 performed chlorination of BPA solutions at a concentration of 1 mg/L with sodium hypochlorite solution at temperature of 20 - 25 ^oC and pH between 8.0 to 9.0.



Figure 1.6 - Half-lives profiles for the reaction of bisphenol A with chlorine for concentrations of chlorine of 0.2, 1.0 and 2.0 mg/L. (Gallard et al., 2004)



Figure 1.7 - Chlorination of bisphenol A in ultra-pure water ($[BPA]_0 = 5 \mu M$; $[Cl_2]_0 = 38 \mu M$ (2.7 mg/L); pH = 8.0). (Gallard et al., 2004)

We can see in Table 1.6 the chlorination of BPA at different chlorine concentrations and

the formation of byproducts after a reaction time of 60 minutes.

Table 1.6	Levels of BPA	and chlo	orination	products	from	various	chlorination	conditions
(Yamamot	o and Yasuha	a, 2002)						

Initial Cla	Reaction time	Residua	1 Cl	BPA	T ₄ CBPA	T ₃ CP	2-M ^b	$2, 6-D_2{}^b$	$2, 2'-D_2{}^b$	$2, 2', 6-T_3{}^b$
(mg/l)	(min)	(mg/l)	(µmol/l)	(µmol/l)	(µmol/l)	(µmol/l)	(µmol/l)	(µmol/l)	(µmol/l)	(µmol/l)
1.03 (29.2)	0	-		4.45	N.D.°	N.D.	N.D.	N.D.	N.D.	N.D.
	5	0.61	17.2	2.97	0.01	0.005	0.94	0.19	0.22	0.10
	15	0.43	12.1	1.26	0.11	0.008	0.98	0.39	0.31	0.36
	30	0.31	8.74	1.28	0.20	0.014	1.02	0.44	0.33	0.70
	60	0.13	3.77	0.41	0.31	0.021	0.56	0.27	0.18	0.62
2.07 (58.3)	0	_		4.45	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	1.18	33.3	0.62	0.25	0.008	0.83	0.41	0.65	0.53
	15	0.80	22.6	0.070	1.38	0.015	0.16	0.12	1.02	1.16
	30	0.58	16.4	0.009	1.70	0.024	0.03	0.02	0.61	0.82
	60	0.22	6.21	N.D.	0.74	0.062	N.D.	N.D.	0.08	0.07
5.12 (144)	0	-		4.91	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	5	2.93	82.7	0.064	0.98	0.014	0.17	0.11	0.39	0.54
	15	2.60	73.3	0.005	1.67	0.039	0.06	0.07	0.05	0.13
	30	2.04	57.5	N.D.	1.04	0.11	0.03	0.04	0.06	0.10
	60	1.61	45.5	N.D.	0.60	0.093	0.02	0.02	0.02	0.04
10.24	0	_		4.91	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
(289)	5	7.90	223	N.D.	0.73	0.022	N.D.	N.D.	0.04	0.13
	15	7.38	208	N.D.	0.70	0.029	N.D.	N.D.	N.D.	0.02
	30	7.23	204	N.D.	0.47	0.037	N.D.	N.D.	N.D.	N.D.
	60	5.99	169	N.D.	0.25	0.040	N.D.	N.D.	N.D.	N.D.

 $T_4CBPA = 2, 2', 6, 6'$ -tetrachlorobisphenol A; $T_3CP = 2, 4, 6$ -trichlorophenol; 2-M = 2-chlorobisphenol A; 2, 6- $D_2 = 2, 6$ -dichlorobisphenol A; 2, 2' - $D_2 = 2, 2'$ -dichlorobisphenol A; 2, 2', 6- $T_3 = 2, 2', 6$ -trichlorobisphenol A. ^aMolar concentrations (µmol/L) are shown in parentheses.

^bThese congeners are tentatively determined using calibration curves for BPA and T₄CBPA.

°N.D.: non detectable; detection limits were 0.002 μ mol/L for BPA, 0.005 μ mol/l for T₄CBPA, 0.002 μ mol/l for T₃CP.

In Figure 1.8 we can see a presumed transformation of BPA to chlorinated byproducts. Hu et al., 2002 reported also a proposed chloro-substitution reaction between bisphenol A and hypochlorous acid (HOCl) and formation of polychlorinated phenoxyphenols in purified water. The experiments were carried for a $500\mu g/L$ BPA concentration and 1.46 mg/L sodium hypochlorite at on adjusted pH of 7.5 with phosphoric acid at 25 ^oC. The pathways can been seen in Figure 1.9 and 1.10 for chloro-substitution reaction and formation of polychlorinated phenoxyphenols.



Figure 1.8 - Presumed chlorination reaction scheme of BPA. (Yamamoto and Yasuhara, 2002)



Figure 1.9 - Pathways of chloro-substitution reaction between bisphenol A and HOCl. (Hu et al., 2002)



Figure 1.10 - Formation of polychlorinated phenoxyphenols. (Hu et al., 2002)

1.2.3 ELECTROCHEMICAL OXIDATION OF BISPHENOL A

Another potential process of removing BPA is electrochemical oxidation. Electrochemical oxidation had been used to treat different organic pollutants from water and wastewater treatment (Chen, 2004; Zorpas, 2011). During the electrochemical (EC) oxidation BPA can be oxidized directly with the carbon or metal anodes (Andreescu et al., 2003; Ngundi et al., 2003; Kuramitz et al., 2004), or indirectly by O₃ and HO• radicals, which can be produced with the boron-doped diamond or metal oxides electrodes (Boscoletto et al., 1994; Tanaka et al., 2002; Gozmen et al., 2003; Murugananthan et al., 2008). There are few studies done using electrochemical oxidation on BPA. In two studies the electrochemical oxidation of BPA was done using voltammetric technique with a glassy carbon electrode (Kuramitz et al., 2001; Kuramitz et al., 2004). Also there was another study done using anodic oxidation of BPA using a boron-doped diamond (BDD) electrode at galvanostatic mode (Murugananthan et al., 2008). Other studies were done using a undivided flow-through EC cell with cobalt-promoted PbO₂ as anode and stainless steel as cathode (Korshin et al, 2006), platinum (Pt) electrodes (Andreescu et al., 2003), platinum coated titanium (Pt/Ti) and tin dioxide coated (SnO₂/Ti) electrode (Tanaka et al., 2002), Pt, Ti/RuO₂, Ti/Sb-SnO₂ and Ti/BDD anodes were also used (Cui et al., 2009). Finally in one study the use of indirect EC using Fenton reaction was used as a source of HO• radicals production (Gozmen et al., 2003, Poerschmann et al., 2010).

The electrochemical oxidation of BPA could happen by the polymerization as the electrode responses to the ferrocyanide ions. EC removal of BPA was done using a potentiostatgalvanostat HA-301 and carbon fiber (CF) was used in a 0.1 M Na₂SO₄ buffer solution treated at potentiostatically of 0.75 V vs. the Ag/AgCl electrode in the solutions (Kuramitz et al., 2001). For the determination of the potential current needed to be applied at different pHs a sweep voltammograms for the oxidation of the 0.1mM BPA in a 0.1M Na₂SO₄ buffer solution was done and is presented in Figure 1.11. We can see from Figure 1.11 that at pH 10.0 we need about 0.86V for the BPA to be oxidized, and most of the potentials decreased with an increased in pH.



Figure 1.11 - Liner sweep voltammograms for the oxidation of the 0.1mM BPA in a 0.1 M Na_2SO_4 buffer solution at the GC electrode at different solution pH values. Scan rate 0.01 V/s. (Kuramitz et al., 2001)

To study the behavior of the EC oxidation at constant pH another sweep voltammograms for several concentrations of BPA in a 0.1 M Na₂SO₄ buffer solution with a pH of 5.8 at a fixed scan rate of 0.015 V/s was done and we can see the results in Figure 1.12a. Also we can see the relationship between different BPA concentrations at different pHs and the peak current need to oxidize the BPA in Figure 1.12b. Finally for this study we can see the removal percentage of BPA at different concentrations at constant pH of 5.8 with and without current in Figure 1.13. From this we can conclude that the high removal of BPA was due to the formation of electropolymerization of BPA film on the CF electrode surface, and not to the hydrophobic adsorption of the BPA to the CF electrode. In 10 minutes a complete removal from a 50mL solution with BPA concentration of 1 x 10^{-6} M was achieved. The treatment of large volumes of water and the process effectiveness has to be investigated. Also the regeneration of the electrode could be costly and time consuming. When the concentration of BPA increased from 1×10^{-6} M to 1×10^{-5} M it had to reach the time of 60 minutes from 10 minutes for the same removal efficiency. Also when the concentration was raised one more order of magnitude to 1×10^{-4} the percentage removed dropped from 100 to 20 percent even after 60 minutes and seemed to remain constant.



Figure 1.12 - a) Liner sweep voltammograms for the oxidation of 0.1, 0.2, 1.0 mM BPA in a 0.1 M Na₂SO₄ buffer solution (pH 5.8) at a scan rate 0.015 V/s. b) The relationship between the concentration of bisphenol A and the oxidation peakcurrent. (Kuramitz et al., 2001)



Figure 1.13 – Relationships between the efficiency of removal of bisphenol A and treatment time with application of a potential 0.75 V in 1 x 10⁻⁶ M (•), 1 x 10⁻⁵ M (\blacktriangle), 1 x 10⁻⁴ M (\blacksquare), bisphenol A solution (pH 5.8) and without a potential in 1 x 10⁻⁶M (\circ), 1 x 10⁻⁵ M (Δ), 1 x 10⁻⁴ M (\blacksquare), bisphenol A solution (pH 5.8). (Kuramitz et al., 2001)

Murugananthan et al., 2008 conducted an anode oxidation of BPA using boron-doped diamond (BDD) after similar electrode Si/BDD had been reported to be able to removed chloromethyphenoxty (Boye et al., 2006), 4 chlorophenol (Rodrigo et al., 2001), and phenol (Iniesta et al., 2004). BDD electrode could generate absorbed hydroxyl radicals because of water decomposition according to the following equation 1:

$$BDD + H_2O \rightarrow BDD(HO\bullet)_{ads} + H^+ + e^-$$
(1)

We can see the BPA (20mg/L) oxidation as a function of electrolysis with BDD electrode at three different applied current densities (I_{appl}) ranging from 14.28 to 35.7 mA/cm² in Figure 14a. Here we can see that the oxidation of BPA is very dependable on the current intensity applied. It takes 4 hours for the BPA to be fully removed at a high I_{appl} of 35.7 mA/cm² and it takes more than twice, actually 10 hours, to do the same at a lower $I_{appl of}$ 14.28 mA/cm². This is due to the constant formation of HO• radicals at a constant I_{appl} , and that the formation of HO• radicals increase with an increase of I_{appl} . From Figure 1.14b we can see that the rate of decay decreased as the concentration of BPA increased due to the creation of intermediates that competed with BPA for the HO• radicals. Following the same pattern as the oxidation of BPA from Figure 1.14a, we can see that the mineralization of BPA which was faster with an increase in the I_{appl} . This was due to an increase of HO• radicals, with an increase in I_{appl} as earlier found (Brillas et al., 2004). We can see that it took 14 h at 35.7 mA/cm² for the complete combustion of BPA and 24h at lower I_{appl} of 14.28 mA mA/cm².

From Figure 1.15 we can see the specific electrical charge that is needed for an equal amount of total organic carbon (TOC) removal is increased with an increased in I_{appl} . There was a waste of HO• radicals at a higher I_{app} , because of other parallel reactions such as O₂, peroxodisulfate $(S_2O_8^{2-})$, and hH_2O_2 which is given in the following equations 2, 3, and 4. Finally the

mineralization of BPA with BDD anode leads to the formation of CO_2 as a final product according to equation 5.

$$BDD(HO\bullet) \rightarrow BDD + 1/2O_2 + H^+ + e^-$$
(2)

$$2SO_4^{2-} \to S_2 O_8^{2-} + 2e^-$$
(3)

$$2 \operatorname{HO} \bullet \to \operatorname{H}_2 \operatorname{O}_2^- \tag{4}$$



Figure 1.14 - (a) Effect of I_{appl} on anodic oxidation of BPA with BDD (BPA, 20 mg dm⁻³; electrolyte, 0.1M Na₂SO₄; pH 6; *T*, 25°C) (•) 14.28mAcm⁻², (\blacktriangle) 25mAcm⁻² and (\blacksquare) 35.7mAcm⁻². (Inset) Corresponding kinetic analysis assuming a pseudo-first order reaction for BPA decay. (b) Decay of different initial concentration of BPA by anodic oxidation with BDD at 35.7mAcm⁻² (electrolyte, 0.1M Na2SO4; pH 6; *T*, 25°C) (•) 10mgdm⁻³, (\bigstar) 20mgdm⁻³ and (\blacksquare) 30mgdm⁻³. (Murugananthan et al., 2008)



Figure 1.15 - (a) TOC abatement with reference to electrolysis time at three different I_{appl} for the mineralization of BPA with BDD anode (BPA, 20 mg dm⁻³; electrolyte, 0.1M Na₂SO₄; pH 6; *T*, 25°C) (•) 14.28mAcm⁻², (\blacktriangle) 25mAcm⁻² and (\blacksquare) 35.7mAcm⁻². (b) TOC removal for three different initial concentration of BPA at constant I_{appl} 35.7mAcm⁻² (electrolyte, 0.1M Na₂SO₄; pH 6; *T*, 25°C) (•) 10mgdm⁻³, (\blacksquare) 20mgdm⁻³ and (\bigstar) 30 mgdm⁻³. (Murugananthan et al., 2008)

Cui et al., 2009 conducted a study of EC with four different anodes as Pt, Ti/RuO2, Ti/Sb-SnO₂, and Ti/BDD. From Figure 1.16 we can see that only three anodes were able to totally removed BPA at both 10 mA/cm² and 50 mA/cm². Just like in the previous studies presented earlier EC process had the problem of byproducts formation. In Figure 1.17 we can see the byproducts formation during EC process at 10 mA/cm². Some of these intermediates came in accordance with those found in other studies.



Figure 1.16 – Electrochemical destruction of BPA as a function of the charge consumed on the four different anodes at the current densities of (a) 10 mA/cm^2 and (b) 50 mA/cm^2 . (Cui et al., 2009)



Figure 1.17 – Concentrations of the intermediate products of EC degradation of BPA at a current density of 10 mA/cm² on the (a) Pt, (b) Ti/RuO₂, (c) Ti/Sb–SnO₂ and (d) Ti/BDD anodes. (Cui et al., 2009)

Through EC oxidation there had been intermediates derivates found such as hydroxylated BPA and phenol derivatives such as hydroquinone, benzoquinone, catechol, resorcinol, hydroxy benzoic acid, isopropenylphenol, and isopropylphenol (Boscoletto et al., 1994; Gozmen et al., 2003). We can see the pathway reaction and byproducts formation during EC BPA degradation until complete mineralization proposed by Cui et al., 2009 in Figure 1.18.



Figure 1.18 – Reaction pathway of electrochemical BPA degradation (Cui et al., 2009)

In Table 1.7 we can see the list of BPA byproducts as a result of electrochemical generated Fenton reagent using ferric and copper ions.

compound	chemical structure	methods
m-monohydroxylated BPA	HO-CH ₃ OH-OH	LC-MS
o-monohydroxylated BPA	HO-C-C-C-OH CH ₃ OH	LC-MS
dihydroxylated BPA	HO CH ₃ OH CH ₃ OH CH ₃ OH OH	LC-MS
phenol	он	GC-MS
catechol	OH OH	HPLC and GC-MS
hydroquinone	но-Он	HPLC and GC-MS
benzoquinone	0=0	HPLC and GC-MS
resorcinol	он — он	HPLC and GC-MS
4-isopropenylphenol	CH_2 CH_2 CH_3 OH	GC-MS
4-hydroxy mandelic acid	НОТОН	GC-MS
4-hydroxy benzoic acid	но он	GC-MS
butendionic acid	HOOC-CH=CH-COOH	GC-MS
4-oxobutenoic acid	0 HOOC-CH=CH-C-H	GC-MS
acetic acid	CH ₃ COOH	HPLC and GC-MS
	ncom	

Table 1.7 - Identified BPA Conversion and Degradation Products (Gozmen et al., 2003)

1.2.4 PHOTOXIDATION OF BISPHENOL

Another approach of degrading BPA is photodegradation, which could be done in water or in atmosphere and occurs by either direct photolysis or photooxidation. The process of photolysis occurs when a chemical that is dissolved in water absorbs sunlight that has a wavelength higher than 290 nm which in turn will produce a photochemical alteration (Staples et al., 1998). These two processes can both take place in water and in the atmosphere. According to Staples et al., 1998 BPA is easier to photooxidise in atmosphere than in water with half-lives of 0.74 to 7.4 and 66 to 160h, respectively. The H₂O₂ formed by the photolysis of Fe(III)–oxalate complexes can react with Fe²⁺ according to Fenton mechanism (Zuo et al., 1992). The Fe(III)– oxalate complexes were used as a catalyst in the photodegradation of dyes (Zepp et al., 1992), and BPA (Zhou et al., 2004). BPA in water has no absorption to the light with wavelength above 365 nm.

Multiple studies had been done using AOP photo-Fenton process to oxidize and degrade different organic substances (Neyens and Baeyens, 2003; Katsumata et al., 2004; Chiou et al., 2006). For example HO• radicals are formed using UV light, hydrogen peroxide and Fe^{2+} or Fe^{3+} ions following the reactions presented in equations 6 to 8:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$$
(6)

$$\operatorname{Fe}^{3+} + \operatorname{OH}^{-} \to \operatorname{Fe}(\operatorname{OH})^{2+}$$
 (7)

$$\operatorname{Fe}(\operatorname{OH})^{2+} + h\nu \rightarrow \operatorname{HO} + \operatorname{Fe}^{2+}$$
 (8)

Another recently used chemical compound for the photocatalysis is titanium dioxide TiO₂ that was used for oxidation in water treatment (Devipriya and Yesodharan, 2005; Malato et al., 2007). A UV light with the wavelength $\lambda \leq 387$ nm is used to excite an electron, producing an electron-hole pair according to the following equation 9:

$$TiO_2 + hv \rightarrow TiO_2 (e^- + h^+)$$
(9)

In combination with photocatalysis oxygen and hydrogen peroxide that was dissolved in the solution can continue to excite electrons, thus limiting the recombination of the electron-hole.

$$\mathrm{TiO}_{2}(\mathrm{e}^{-}) + \mathrm{O}_{2} \rightarrow \mathrm{TiO}_{2} + \mathrm{O}_{2}^{-} \tag{10}$$

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + HO^{\bullet} + OH^-$$
(11)

After all these transformations the organic pollutants, such as BPA, may undergo oxidation directly at the electron-hole. The water molecules and hydroxide surface-bound species may also make charge transfer with the electron-hole and creating HO• radicals following the equations 12 through 15:

$$TiO_2(h^+) + R \rightarrow Oxidation Products$$
 (12)

$$HO\bullet + R \rightarrow Oxidation \ Products \tag{13}$$

$$TiO_2(h^+) + H_2O \rightarrow TiO_2 + HO^{\bullet} + H^+$$
(14)

$$\operatorname{TiO}_2(h^+) + OH^- \rightarrow \operatorname{TiO}_2 + HO\bullet$$
 (15)

Torres et al., 2010 had conducted different experiments for the mineralization of BPA using ultrasound and photoassisted processes. One such experiment was the mineralization of BPA in saturated oxygen conditions through photooxidation with 10 mg and 50 mg/L TiO₂. It was found that at 10 mg/L TiO₂ concentration after 4 hours 60% of the initial concentration of BPA (118 μ mol/L) was removed, and at 50 mg/L TiO₂ there was 92 % removal. Also the removal of total dissolved organic carbon after 4 hours was 5 % for the 10 mg/L of TiO₂ and 12 % for 50 mg/L TiO₂. This process plus other two AOPs studied by Torres et al., 2010 had the same byproducts formation as mono- and di-hydroxylated BPA that has been reported by other studies (Torres et al., 2007b; 2008a; 2008b). It was concluded that the degradation of BPA was

due to the HO• radicals interaction with the BPA molecules. We can see the proposed pathway degradation of BPA by photocatalysis in Figure 1.19.



Figure 1.19 – Main steps during BPA degradation by photocatalysis (Torres et al., 2010)

Chiang et al., 2004 had studied the photocatalytic degradation and mineralization of BPA by TiO₂ and platinized TiO₂. The experiments were done at pH 3.0 and 10.0 and the platinum percentage by weight was 0.2, 1.0, and 2.0. For this study three different samples of TiO₂ were used as Millennium PC 50, Degussa P25, and Hombikat UV100. The experiments were done in the presence of oxygen, by pumping air at a rate of 50 ml/min, with a solution of BPA of 20 mg/L and a photocatalyst concentration of 0.1g/L. It was found that at pH 3.0 the BPA was completely mineralized to CO₂ after 120 minutes. At pH 10.0 only 20-30 % was mineralized to CO₂ and the rest were transformed into byproducts. It was reported that the byproducts created at pH 10.0 were less toxic compared to that of BPA. The byproducts created at pH 3.0 were more

toxic than BPA alone. The byproducts that were formed at pH 10.0 were different than those at pH 3.0 and also less degradable than BPA. The platinization helped the mineralization when the platinum load was between 0.2 to 1.0 % by weight becoming 3 to 6 times better. The TiO_2 P25 also degraded and mineralized twice as fast as the other two sources of TiO_2 . The results of the BPA degradation under different conditions can been seen in Table 1.8.

 Table 1.8 - The rate of photocatalytic degradation of BPA under different conditions

 (Chiang et al., 2004)

TiO ₂ sample	Pt loading (wt.%)	BPA degradation rate ^a $(M/min \times 10^6)$		Percent of carbon mineralized (%)				Maximum intermediate concentration ^b (ppm C)	
		рН 3	рН 10	рН 3		pH 10		рН 3	pH 10
				60 min	120 min	60 min	120 min		
P25	_	8.16 (-)	6.63 (-)	62	100	11	20	8.0	14.4
	0.2	11.7 (1.4×)	13.3 (2.0×)	84	100	25	25	9.5	13.4
	1.0	26.2 (3.2×)	$14.7 (2.2 \times)$	99	99	12	15	8.1	14.0
	2.0	19.7 (2.4×)	14.4 (2.2×)	97	97	18	19	9.2	13.0
UV100	_	1.95 (-)	3.32 (-)	35	65	12	25	5.0	13.7
	0.2	7.28 (3.7×)	6.42 (1.9×)	89	99	16	17	2.9	13.6
	1.0	11.4 (5.9×)	5.81 (1.7×)	87	94	19	25	3.7	12.5
	2.0	3.95 (2.0×)	5.38 (1.6×)	23	46	17	26	7.1	12.5
PC50	_	3.66 (-)	3.04 (-)	25	57	18	24	7.6	11.6
	0.2	7.97 (2.2×)	11.3 (3.7×)	73	99	19	33	5.8	12.7
	1.0	6.60 (1.8×)	9.65 (3.2×)	54	99	13	30	7.0	14.0
	2.0	3.64 (1.0×)	9.53 (3.1×)	30	61	16	30	7.9	13.1

^a Number in parentheses represents the factor of enhancement of the Pt-TiO₂ sample compared to un-platinized TiO₂ blank material.

^b The total amount of intermediates generated at a particular time during reaction was calculated from the formula (TOC - [carbon in BPA]) and the unit is in ppm carbon.

The photocatalytic degradation of BPA using TiO₂ powder and TiO₂-zeolite sheets that were prepared by a paper-like composite was analyzed under UV irradiation. The TiO₂ powder was able to remove more the 90 % of a BPA solution of 100 μ M after 24 hours, and the TiO₂ sheet was able to do the same after 72 hours. TiO₂-zeolite sheets were than prepared using Ytype zeolite, which were the only effective ones for the BPA adsorption. Using the UV irradiation after 148h most of the BPA was removed from 100 μ M BPA solution, which was similar to that of TiO₂ powder removal. Ohko et al., 2001 performed degradation of BPA at 170 μ M (40 mg/L) using TiO₂ under UV irradiation. After 6 hours of UV radiation the estrogenic activity for BPA reduced with only 10%, even though the remaining concentration of BPA in the solution was only 35%. Yap et al., 2010 has synthesized using a sol-gel method with a nitrogendoped titanium dioxide that was attached to activated carbon (N-TiO₂/AC). This combination of chemicals was found to be able to photodegrade the BPA under visible light 420-630 nm illumination. The dosage used for the photocatalytic degradation (PCD) of N-TiO₂/AC was 0.25g/L. There were three wavelength spectrum used: the solar spectrum, 280-400nm, and 420-630 nm. We can see the degradation of BPA with 4 different chemicals N-TiO₂/AC, TiO₂, N-TiO₂, and P25 after a irradiation of 3 hours in Figure 1.20.



Figure 1.20 - (a) Effect of excitation wavelengths on the photocatalytic degradation efficiency for BPA (Note: C_0 denotes the equilibrium concentration of BPA after adsorption in the dark) and (b) comparison of BPA removal performance under various excitation wavelengths for N-TiO₂/AC, TiO₂, N-TiO₂ and P25. (Yap et al., 2010)

Wang and Lim, 2010 synthesized a carbon and nitrogen doped TiO₂ (CN-TiO₂) using solvothermal method. There were different formation of CN-TiO₂ depending on the temperature of solvothermal treatment and the calcination temperature. For example, a compound that was made at a temperature of 120 °C for solvothermal treatment and 300 °C for calcination was denoted as CN-TiO₂(120/300), which was also found to be the most effective in removing BPA. For the photodegradation using four different LED strips with the main emission for blue light with a wavelength of λ = 465nm, green light λ = 523nm, yellow light λ = 589nm, and white light emitting at around 500-600nm. The photocatalyst dosage was 0.5 g/L with a BPA concentration of 5 ppm. We can see the results of the BPA removal, TOC removal, and BPA photolysis with the UV irradiation for 5 hours at neutral pH in Figure 1.21. In a study done with different solar advanced oxidation process with one of them being the TiO₂ photocatalysis used for the degradation of BPA was found that the presence of hematite (α – Fe₂O₃) increased the efficiency on the degradation.



Figure 1.21 - BPA photolysis and photodegradation by CN-TiO2(120/300) under different Vis-LED irradiation for 5 h at neutral pH. (Wang and Lim, 2010)

Lee et al., 2004 used a sol-gel method to immobilize TiO_2 on to Teflon resin, polyvinylalcohol (PVA), polyvinylidenechloride (PVdC), polyvinylidenefluoride (PVdF), and glass tube. The bidding of TiO_2 to the glass tube was the most efficient since the Teflon, PVA, PVdC, and PVdF are long polymeric chains that are photodegradable themselves, thus with time the immobilized TiO_2 particles will decrease. We can see the photodegradation of BPA in Figure 1.22, and the proposed byproducts formation of intermediates in Figure 1.23.



Figure 1.22 - Photodegradation of BPA by TiO₂ immobilized with every binder (at the initial concentration of 10mg BPA/l, 3-coating times, pH 4.5, and 30 0 C): \circ , 1 wt% PVA; \Box , 1 wt% PVdC; \diamond , 1 wt% PVdF; Δ , 1wt% Teflon; and \blacksquare , 1 wt% titanium sol-solution. (Lee et al., 2004)

Other studies tried to simulate lake water that is more realistic environment than a distilled water or purified water solution. Peng et al., 2006 studied the degradation of BPA containing algae, humic acid, and Fe^{3+} ions. After 4 hours of irradiation with raw Chlorella vulgaris 6.5 x 10⁹ cells/L , 20 µmol/L Fe³⁺, 4 mg/L humic acid, and BPA concentration of 2 mg/L there was only 36 % removal.



Figure 1.23 - Proposed stepwise photodegradation of BPA with a $\rm TiO_2$ film of about 5.29 μm thickness. (Lee et al., 2004)
Photodegradation of BPA in the presence of humic substances (HS) such as Fluka humic acid (FLHA), surwannee river fulvic acid (SRFA), Nordic lake humic acid (NOHA), and nordic lake fulvic acid (NOFA) was done. It was found that the humic substances can induce indirect photolysis of BPA under solar irradiation. Out of all the four substances, SRFA was able to remove the most BPA. It was determined that through the excitement of HS there was production of HO• radicals, O_2 , and H_2O_2 which degraded the BPA.

The photooxidation of BPA in the presence of ferric and carboxylate salts induced by photolysis induced by a 125W high-pressure mercury lamp with $\lambda \ge 365$ nm was studied (Zhou et al., 2004). The Fe (III)-oxalate complexes are common chemicals in natural water. The rate of photooxidation increased with the increase of BPA concentration from 2 to 5 mg/L, but remained the same when was increased to 10mg/L. The mechanisms of degradation under the photooxidation was believe to be due to the formation of HO• radicals and O₂ peroxidation. Chen et al., 2006b and 2007 was able to photodegrade BPA using UV in combination with H₂O₂. He found that the UV alone was not able to degrade BPA effectively.

The photodegradation of BPA presented in equations 6 to 8, which are based on the presence of Fenton reagents, had been studied by Katsumata et al., 2004. Different concentrations of H_2O_2 and Fe(II) were used to see the effect on the BPA removal. It was observed that a higher concentrations of H_2O_2 and Fe(II) resulted in a faster and higher removal of BPA. After pH 4.0 was found to be the optimal pH for the reaction, different concentration of H_2O_2 and Fe(II) were used with the highest one being 4 x 10^{-4} mol/L for both H_2O_2 and Fe(II). The complete removal of BPA at these conditions was achieved in 9 minutes.

1.2.5 BIODEGRADATION OF BISPHENOL A

Few microorganisms had been found to be able to biodegrade BPA. Bacteria, fungi, and planktons. Also many enzymes from different sources had been used to biodegrade BPA. BPA can also be biodegraded by plants, animals such as fish, birds, and mammals (Kang et al., 2006). Bacteria from different sources had been found to be able to biodegrade BPA, which include soils (Sasaki et al., 2005), wastewater treatment plants (Lobos et al., 1992; Spivack et al., 1994), and river waters (Ike et al., 2000; Kang and Kondo, 2002a, 2002b; Kang et al., 2004). In two different studies was found that the BPA was removed above 90 % between the influent and effluent from a wastewater treatment plant (Staples et al., 1998; Furhacker et al., 2000). The BPA was degraded in river by microbial populations from Houston canal having half-life of 4 days, with an overall removal greater than 96% for 3 to 5 days (Dorn et al., 1987). In an activated sludge treatment the removal of BPA was greater than 99 % with acclimated populations of bacteria after 14 days. Bacteria that could biodegrade BPA were found in rivers with half-lives an average of 5 days for the degradation of BPA (Dorn et al., 1987; Ike et al., 2000; Klecka et al., 2001; West et al., 2001; Kang and Kondo, 2002a; 2002b; Kang et al., 2004; Suzuki et al., 2004; Kang and Kondo, 2005). Even thought a lot of strains of bacteria could biodegrade BPA, not all of them are capable of doing it at high efficiency. Kang and Kondo, 2002a studied 11 strains of bacteria, from which 10 were able to biodegrade BPA at rates from 18 to 91%, and only two the Pseudomonas sp. and Pseudomonas putida strain was able to biodegrade at more the 90%. Jin et al., 1996 found that 40 out of 44 strains were able to biodegrade BPA, but only six strains were able to biodegrade BPA completely.

Lobos et al., 1992 and Spivack et al., 1994 were able to isolate gram-negative bacteria called MV1 from wastewater treatment plant that was able to biodegrade BPA. Voordeckers et

al., 2002 studied the biodegradation of tetrabromobisphenol A (TBBPA), tetrachlorobisphenol A (TCBPA), and BPA in estuaries sediments. The TBBPA and TCBPA would easily get transported to the sediments because of their hydrophobicity. It was found that under methanogenic and sulfidogenic conditions there could be a complete dehalogination of TBBPA to BPA, but BPA could not be further reduced. Also was found that the TCBPA could be biodegradable to DCBPA. It was also found that BPA in seawater could stay without being biodegraded for longer periods of time such as 30 days (Ying and Kookana, 2003; Kang and Kondo, 2005).

The biodegradation of BPA by fungi is also limited just like the bacteria degradation (Yim et al., 2003; Chai et al., 2005). In the study done by Chai et al., 2005 found that out of 26 different fungi only11 strains were able to biodegrade BPA more than 50 %. The degradation of BPA is done by enzymes such as manganese peroxide (MnP) and laccase. These two enzymes are produced by *basidiomycetes* fungi (Hirano et al, 2000; Fukuda et al., 2001; Tsutsumi et al., 2001; Uchida et al., 2001; Suzuki et al., 2003). MnP can oxidize some phenolic compounds in the presence of H_2O_2 or Mn(II) being a heme peroxidase. Laccase on the other hand is a multicopper oxidase and could catalyze the oxidation of phenolic compounds with one-electron by reducing oxygen to water (Reinhammar, 1984). Few studies had reported that the BPA could be biodegraded by MnP and laccase (Hirano et al., 2000; Fukuda et al., 2001; Tsutsumi et al., 2001; Uchida et al., 2001; Suzuki et al., 2003; Saito et al., 2004; Lee et al., 2005a). The BPA polymerization forming oligomers could be included in the step of metabolism of BPA by laccase (Uchida et el., 2001). Other sources of enzyme capable of biodegrading the BPA were obtained from white rod fungus (Cabana et al., 2007), gills of digestive glands from the

freshwater snail, (Li et al., 2010), potato (Xuan et al., 2002), fungi cunninghamella elegans

(Keum et al., 2010), and white rot fungus *irpex lacteus* (Shin et al., 2007)

The biodegradation of BPA by *Chlorella fusca* var. *vacuolata* a green alga has been found by Hirooka et al., 2003 and 2005. The removal of BPA at 40 μ M was 85 % after 120 h in light conditions, and was only 22% in dark conditions (Hirooka et al., 2003). One of the intermediates of BPA biodegradation by *C. fusca* was monohydroxybisphenol A (Hirooka et al., 2005). When marine phytoplankton *Nannochloropsis* sp. and *C. gracilis* used as a medium for BPA, with a concentration of 40 μ M, which was placed under light for 6 days the amount recovered was 13-34 % and 25-53 %, respectively (Ishihara and Nakajima, 2003). During the study it was concluded that the BPA was accumulating in the zooplankton through phytoplankton cells. Two strains KA4 and KA5 with high BPA biodegradability about 90% were identified as a *Pseudomonas* sp. and a *P. putida* strain. The *P.putida* it was shown in previous studies that have the biodegradability of nonylphenol, and polyethoxylates (John et al., 1998; Tanghe et al., 1999).

Plants had been used for bioremediation of different pollutants by direct adsorption into their roots. Studies were one for BPA biodegradation by adsorbing it into the plants (Hamada et al., 2002; Nakajima et al., 2002; Noureddin et al., 2004; Loffredo et al., 2010), plant enzymes (Sakurai et al., 2001; Xuan et al., 2002; Yoshida et al., 2002), and cell suspension cultures (Nakajima et al., 2002; Schmidt and Schuphan, 2002; Chai et al., 2003; Nakajima et al., 2004). Noureddin et al., 2004 had found that the BPA adsorbed inside the plant vary depending on the part of the plant. He found that only 10 % was in the roots, some in the stems, and nothing in the leaves. This is a indication that the adsorption by the plant will depend on the plant species. The peroxidase and polyphenol oxidase are two oxidative enzymes that are associated with BPA metabolism (Caza et al., 1999; Yoshida et al., 2001, 2002; Sakuyama et al., 2003). Enzymes that were prepared from vegetables and fruits were able under incubation to biodegrade BPA (Xuan et al., 2002). Endo et al., 2000 found that polyphenol oxidase from mushroom could not oxidize the BPA. However, Yoshida et al., 2001 and 2002 reported degradation of BPA with polyphenol oxidase from mushroom.

The biodegradation could be accomplished by animals and humans only to some degree. For example freshwater clam *Pisidium amnicum*, which is a invertebrate, showed to have a halflive for BPA of 221 hours at 1.8° C and 43 hours at 11.6° C (Heinonen et al., 2002). Lindholst et al., 2003 examined the BPA degradation from zebra fish (Danio rerio) and identified two BPA byproducts as BPA sulfate and BPA glucuronic acid. The tests were done at 100 µg/L for a period of 7 days, than the fish were transferred to clean ground water. After 2 h the BPA and BPA sulfate started to be eliminated and the decrease was from 100 to 29.3% and 29.4%, respectively. At end after a period of 168h the BPA was down to 10.4% and BPA sulfate to a 4.6%. The BPA glucuronic acid was down to 67% in the first 2h and 7.5% after 7days (Lindholst et al., 2003). Yokota et al., 2002 reported that the BPA was mainly metabolized in the carp (*Cyprinus carpino*) intestine to BPA glucuronide. ¹⁴C-BPA that was administered orally and intravenously was easily removed via bile and through feces by chicken (Halldin et al., 2001).

The biodegradation of BPA by mammals had also been studied and regardless of the route of administration, the dose, and the animal in the experiment the free BPA was usually excreted in the feces for about 56-82 % and the metabolites in urine for about 13-28 % (Yokota et al., 1999; Pottenger et al., 2000; Snyder et al., 2000). The BPA metabolism in mammals usually is glucuronided by the liver microsomes (Yokota et al., 1999) or sulfated by the sulfotransferases from the liver (Suiko et al., 2000; Nishiyama et al., 2002). It is important to

note that the UDP-blucuronosyltransferase (UGT) levels from the human liver, which helps with the glucuronidation, is lower than that in the adult rat liver (Cappiello et al., 2000; Matsumoto et al., 2002; Strassburg et al., 2002). In the rat liver the microsomal cytochrome P450 enzyme helped the metabolism of BPA into bisphenol-o-quinone from 5-hydroxy BPA and a bisphenol semiquinone (Atkinson and Roy, 1995a; 1995b). In humans the hepatic cytochrome P450s activities could be inhibit by the BPA (Hanioka et al., 1998; Niwa et al., 2000; Pfeiffer and Metzler, 2004), and the metabolites produces by the P450s increased the estrogenicity (Yoshihara et al., 2001). In humans the sulfation of BPA could be done by two sulfotransferases, the thermostable phenol sulfotransferase ST1A3 (Shimizu et al., 2002), and the simple phenol (P)-form phenol sulfotransferase SULT1A1 (Suiko et al., 2000, Nishiyama et al., 2002). The gender could also play a role in the BPA biodegradation, out of 344 rats both male and females, the male rats had lower concentration of BPA sulfate and BPA glucuronide than female rats (Pottenger et al., 2000). Even though the BPA glucuronide was found to be the major metabolite of BPA via liver microsome, other metabolies such as 5-hydroxy BPA, BPA sulfate conjugate, BPA diglucuronide were also found (Atkinson and Roy, 1995a, 1995b; Elsby et al., 2001, Nakagawa and Suzuki, 2001; Shimizu et al., 2002). We can see a summary of all the potential biodegradation of BPA from different sources in Table 1.9.

Microorganisms/ Enzymes	Strains/Source	Reference		
	Novel bacterium MV1	Lobos et al., 1992, Spivack et al., 1993, Ying et al., 2003a		
	Psudomonas paucimobilis FJ-4	Ike et al., 2000		
Bacteria	Pseudomonas sp.	Kang and Kondo, 2002a		
	Pseudomonas putida	Kang and Kondo, 2002a		
	Arthur Kill sediment (methanogenic, sulfate-, iron(III), nitrate reducing)	Voordeckers et al., 2002		

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	Streptomyces sp.	Kang et al., 2004 Sasaki et al., 2005		
	Sphingomonas sp. strain AO1			
	Pleurotus ostreatus O-48	Hirano et al. 2000		
	Phanerochaete chrysosporium ME-446	Tsutsumi et al., 2001		
	Trametes versicolor IFO-7043	Tsutsumi et al., 2001		
	Trametes villosa	Fukuda et al., 2001; Uchida et al., 2001		
	Phanerochaete chrysosporum ME-446	Suzuki et al., 2003		
	Trametes versicolor IFO-6482	Suzuki et al., 2003		
	Aspergillus fumigatus 6145	Yim et al., 2003		
	Aspergillus terreus MT-13	Chai et al., 2005		
	Aspergillus sp. MT-41	Chai et al., 2005		
	Fusarium graminearum NFRI-1280	Chai et al., 2005		
	Fusarium moniliforme 2-2	Chai et al., 2005		
	Fusarium sporotrichioides NFRI-1012	Chai et al., 2005		
	Fusarium sp. KOM-191	Chai et al., 2005		
	Penicillium expansum NFRI-1021	Chai et al., 2005		
Fungi	Paecilomyces lilacinus IFO-31847	Chai et al., 2005		
	Trichoderma viride MT-40	Chai et al., 2005		
	Byssochlamys fuluva NFRI-1226	Chai et al., 2005		
	Emericella nidulans MT-78	Chai et al., 2005		
	Stereum hirsutum	Lee et al., 2005a		
	Heterobasidium insulare	Lee et al., 2005a		
	Irpex lacteus	Shin et al., 2010		
	Trametes versicolor	Shin et al., 2010		
	Chlorella fusca var. vacuolata	Hirooka et al., 2003		
Planktons	Nannochloropsis sp.	Ishihara and Nakajima, 2003		
	Chlorella gracilis	Ishihara and Nakajima, 2003		
Manganese peroxide (MnP)	Fungi (Pleurotus ostreatus O-48, Phanerochaete chrysosporium ME- 446, Trametes versicolor IFO-7043, Phanerochaete chrysosporum ME-446 and Trametes versicolor IFO-	Hirano et al., 2000; Tsutsumi et al., 2001; Suzuki et al., 2003		

	6482)	
Laccase	Fungi (Phanerochaete chrysosporium ME-446, Trametes versicolor IFO- 7043, Trametes villosa, Phanerochaete chrysosporum ME-446, Trametes versicolor IFO-6482, Chaetomiaceae, Coriolopsis polyzona MUCL-38443	Tsutsumi et al., 2001; Fukuda et al., 2001; Uchida et al., 2001; Suzuki et al., 2003; Saito et al., 2004; Cabana et al., 2007
Peroxidase	PeroxidaseFungi (Coprinus cinereus IFO 30628), Plant (soybean and horseradish (Armoracia rusticana)), Trametes versicolor MrP1, Trametes versicolor MrP13,Sakurai et al., 200 1999; Sakuyama Watanabe et Matanabe et MrP13,	
Polyphenol oxidase	Plant (mushroom)	Yoshida et al. (2002)
Cytochrome P450	Bacteria (<i>Sphingomonas</i> sp. strain AO1), mammals (mouse and rat), Fungi - <i>Cunninghamella elegans</i> ATCC36112	Atkinson and Roy, 1995a; 1995b; Yoshihara et al., 2001; Keum et al., 2010
UDP- glucuronosyltransferase (UGT)	Fish (carp (<i>Cyprinus carpino</i>)), mammals (mouse, rat) Human	Yokota et al., 1999, 2002; Cappiello et al., 2000; Matsumoto et al., 2002; Strassburg et al., 2002
Sulfotransferase	Human	Suiko et al., 2000; Nishiyama et al., 2002

1.2.6 ULTRASONIC DEGRADATION OF BISPHENOL A

One of the AOPs is the ultrasonic treatment, which is able to generate HO• radicals through acoustic cavitations. The used of HO• radicals to oxidize the pollutants that are not biodegradable in the water had been studied and been used in water treatment (Gogate et al., 2004; Parsons et al., 2004). The ultrasound had been studied and applied to the treatment of wastewater also (Sivakumar et al., 2002; Adewuyi, 2005; Guo et al., 2006; Guo et al., 2007). The cavitations bubbles acts as a cycle of formation as growth and collapse depending on the ultrasonic wave. One of the first studies to degrade BPA with ultrasound has been done as early as 2006. Torres et al., 2007a, b, 2008 had successfully study this. Using ultrasound the complete mineralization of BPA was also possible (Kitajima et al., 2006; Torres et al., 2007b). In the absence of organic compounds the combination of HO• radicals could react together and form

 H_2O_2 . The production of HO• radicals through sonication of the water and the dissociation of oxygen happen according to the reactions found in equations 16 to 19 (Torres et al., 2007b):

$$H_2O \rightarrow HO^{\bullet} + H$$
(16)

$$O_2 \rightarrow 2O$$
(17)

$$O + H_2O \rightarrow 2 HO^{\bullet}$$
(18)

$$H + O_2 \rightarrow HO^{\bullet} + O$$
(19)

Another process used by AOP is the Fenton's process which could oxidize organic substances (Parsons et al., 2004; Neyens and Baeyens, 2003). During this process the H_2O_2 reacts with Fe²⁺ and forms HO• radicals according to the following equations 20 to 23 (Torres et al., 2007a; 2007b):

$$\mathrm{Fe}^{2+} + \mathrm{H}_2\mathrm{O}_2 \to \mathrm{Fe}^{3+} + \mathrm{HO}\bullet + \mathrm{OH}^-$$
(20)

$$\operatorname{Fe}^{3+} + \operatorname{H}_2\operatorname{O}_2 \leftrightarrow \operatorname{Fe-OOH}^{2+} + \operatorname{H}^+$$
 (21)

$$\text{Fe-OOH}^{2+} \rightarrow \text{Fe}^{2+} + \text{HOO} \bullet$$
 (22)

$$\operatorname{Fe}^{3+} + \operatorname{HOO}_{\bullet} \rightarrow \operatorname{Fe}^{2+} + \operatorname{O}_2 + \operatorname{H}^+$$
 (23)

The degradation of pollutants using HO• radicals can be efficient, but when the process is applied for treatment of wastewaters or natural waters, the reaction can be inhibited by the inorganic specie that would react with the HO• radicals, thus competing with the targeted organic compound (Kochany et al., 1995). The removal of BPA from water using conventional treatment process for drinking water could lead to the formation of byproducts that could have higher estrogenity than BPA (Niwa et al., 2002; Stackelberg et al., 2004; Korshin et al., 2006).

As many of the AOPs process, the ultrasound (US) can sometime be used alone as a process for removal or in combination with other process for a better efficiency. Very few

studies had been done for the removal of BPA using only US. Guo and Feng, 2009 reported that the BPA ($100\mu g/L$) degradation with US with calometric intensities of 20, 40, 60 and 80 W/cm² had degraded the BPA at 33.2, 44.9, 51.1, and 55%, respectively. We can see the results in Figure 1.24, from which also we can observed that the removal of BPA increased with the increased in intensity, which was agreeable with other study done with 2,4-dinitrophenol (Guo et al., 2005). Also we can observe from Figure 1.24 that the increase in efficiency goes down as we increase the intensity. The degradation of BPA using US was following a pseudo first-order kinetics model. Torres et al., 2008 also reported a degradation of BPA (118 µmol/L) after 60 minutes using US to be 85%. As previous AOP processes, the degradation of BPA by US leads to byproducts formation. Because the concentrations of BPA during these tests were low, the byproducts were finally oxidized by US. In a natural water environment or wastewater it will be important to see the pathway of degradation. We can see the pathway degradation of BPA under US reported by Guo and Feng, 2009 in Figure 1.25.



Figure 1.24 - BPA degradation under different ultrasonic intensities. BPA concentration: 100 μg/L; ultrasonic frequency: 20 kHz; pH: 6.5; temperature: 25±0.5 ⁰C; (♦)20W/cm²; (◊) 40W/cm²; (■) 60W/cm²; (□) 80W/cm². (Guo and Feng, 2009)



Figure 1.25 - Main degradation pathways of low-concentration BPA during ultrasonic treatment. (Guo and Feng, 2009)

The degradation of BPA using US alone did not prove to be very efficient, thus the combination of other process with US had been evaluated in various studies. Guo and Feng, 2009 used the addition of ozone with US to be able to degrade the BPA to zero in 60 minutes using 10 and 20 ml/min O_3 flow rate. Torres et al., 2007a, b improved the efficiency of US process by adding continuous flow of H_2O_2 and saturated the DI water with oxygen. Mohapatra et al., 2010 also found that the BPA degradation by US is less efficient and the most efficient is a combination between US and Fenton oxidation. Torres et al., 2008 also studied the BPA degradation using US in the presence of H_2O_2 found that the US frequency, power, and gas saturation has a major role in the transformation of BPA into aliphatic acids.

The main addition process to the US is the Fenton process, which favors the formation of HO• radicals. Using Fenton process multiple organic pollutants had been treated (Pulgarin and

Kiwi, 1996; Bandara et al., 1997). The process creates the ferrous ions which interacts with H_2O_2 to produce a second round of HO• radicals. Torres et al, 2008 conducted different experiments in which US in combination with solar irradiation and Fenton process had been studied to determine the best combination for the removal of BPA. The best removal was accomplished by the combination of all three processes US, Fenton, and solar irradiation (Torres et al., 2007b, 2008). For the US/Fenton/solar irradiation there was 92% removal of BPA (118µmol/L) after 60 minutes (Torres et al., 2008). For the same conditions the US with Fenton process only had 89% removal, and US alone had 85% removal. We can see the BPA mineralization by combined US/solar irradiation/Fe(II) system in Figure 1.26. Torres et al., 2010 also reported a better removal efficiency using a combination of US and Fenton processes. In addition to the Fe²⁺ ions there was also the titanium dioxide photocatalysis (PC) added to the solution for a better removal of BPA. We can see in the Figure 1.27 the differences in removing the BPA from water solution using the combination of different AOPs process and their efficiency in removing BPA.

Torres et al., 2007a performed tests for the removal of BPA (118 μ mol/L) in deionised water at pH 3.0 and natural water at pH 7.6. The natural water simulation had Ca²⁺ = 486 mg/L, Na⁺ = 9.1 mg/L, Cl⁻ = 10mg/L, SO₄²⁻ = 1187 mg/L, and HCO₃⁻ = 402 mg/L. For the Fenton process ferrous sulfate 100 μ mol/L was used in combination with continuous addition of H₂O₂.

It was found that the US (300kHz, 80W) and Fenton process had similar removal efficiencies for BPA in DI water. For the removal of total organic carbon (TOC) and chemical oxygen demand (COD) the Fenton process performed better in DI water. When the two waters were compared there was no significant difference between the two, only for the COD in the DI water performed slightly better.



Figure 1.26 - Main reactions leading to BPA mineralization by the combined ultrasound/solar light/Fe(II) system. (Torres et al., 2008)



Figure 1.27 - BPA (118 μ mol/L) elimination by ultrasound, TiO₂ photocatalysis (PC), photo-Fenton and combined ultrasound/Fe²⁺/TiO₂ photoassisted processes applied to solutions saturated with oxygen. Fe²⁺ 100 μ mol/L; Volume: 300 mL; pH: 3; temperature: 22 ± 2 ⁰C. Ultrasound: 300 kHz/80W; solar simulator irradiation. (Torres et al., 2010)

1.2.7 DEGRADATION OF BISPHENOL A USING FERRATE (VI) AND ZERO VALENT ALUMINUM OXIDATION

The oxidation of BPA using ferrate(VI) and zero valent aluminum (ZVAI) had been studied and found that it could be a potential treatment for both drinking water and wastewater (Jiang et al., 2005; Lee et al., 2005b; Liu et al., 2011). Ferrate (VI) had been shown to be able to remove trichloroethyelene, *E. coli*, coliform organisms, bacterial, and F2 virus (Jiang and Lloyd, 2002). The ferrate (VI) ion is a very strong oxidant even stronger than ozone under acidic condition (Jiang and Lloyd, 2002). The ferrate (VI) is reduced to Fe (III) or ferric hydroxide in the process of oxidation, which would simulate the coagulant (Jiang et al., 2005). Different dosage of Fe (13-17 mg/L) had been used for a good BPA removal of 99.99%. For the removal of BPA from wastewater from $1.2\mu g/L$ to 46ng/L dosages of 1 to 5mg/L of ferrate (VI) were used. The ferrate(VI) was able to performed better than electrochemical oxidation by removing 32 % more soluble chemical oxygen demand (COD) and 20 % more total COD (Jiang et al., 2005).

Lee et al., 2005b performed Fenton processes that involved ferrate (VI) in the removal of BPA. He used potassium ferrate (K₂FeO₄) to prepare his Fe (VI) solution. Two different waters were used for the experiments, one from a lake that had a dissolved organic carbon (DOC) of 1.6mg/L, and one water from a wastewater treatment plant with a DOC of 5.3mg/L. The experiments were conducted at a BPA concentration of 0.15μ M with at contact time of 30 minutes at pH 8.0 and 25^{0} C. Five different doses of Fe (VI) were used as 0.10, 0.25, 0.5, 1.0, and 2.0mg/L. For the lake water a 0.10mg/L Fe (VI) was used for a BPA removal of about 65%, 90% at 0.25mg/L, and 0.5mg/L and higher for 100%. However, for the wastewater only 2.0 mg/L was able to achieve 100 % removal. For the 0.10, 0.25, 0.5, and 1.0mg/L Fe(VI) doses, the removal

was 15, 30, 70, and 95 %, respectively. When Fe (VI) is used in the treatment of natural water there is also a demand in the water itself for Fe(VI), thus it will compete with BPA for the Fe(VI). The ferro-sonication pre-treatment in wastewater sludge help the Fenton oxidation with the removing of BPA using Fe (II) (Mohapatra et al., 2011).

Liu et al., 2011 had investigated the oxidation of BPA using ZVAl under acidic conditions. The AOP using zero valent iron (ZVI) had been used before for organic pollutants removal (Joo et al., 2004, 2005; Noradoun and Cheng, 2005; Kang and Choi, 2009; Lee et al., 2007). The aluminum (Al³⁺/Al) has a lower redox potential of -1.67 V than of iron -0.44 V (Fe²⁺/Fe). ZVAl had been used for the removal of methyl tert-butyl ether (Lien and Wilkin, 2002), 4-chlorophenol, phenol, and nitrobenzene (Bokare and Choi, 2009). The solution of BPA (2 mg/L) and aluminum (4g/L) was studied at pH 1.5 and found that at a dose of more than 2g/L of aluminum there was no difference in the removal of BPA after 12h. The increased in pH had a negative effect on the BPA removal. The removal of BPA using ZVAl was improved with the addition of Fe²⁺ ions. The removal of BPA (2 mg/L) with ZVAl was 75% after 12h, but in the same conditions the addition of 1.0 μ M Fe²⁺ ions the removal after 8h was 99%.

1.2.8 ADSORPTION OF BISPHENOL A

Adsorption is a very important removal technology in removing different pollutants from water. A review of different processes and parameters studied are presented in Table 1.10.

Table 1.10 Parameters studied for adsorption of Bisphenol A on different adsorbents

Туре	Adsorbent	Conc. C _e Range (mg/L)	Reference
	Andesite	60-100	Tsai et al., 2006a
	Diatomaceous earth	60-100	Tsai et al., 2006a
	Titanium dioxide	60-100	Tsai et al., 2006a
	Activated bleach earth	60-100	Tsai et al., 2006a
	Hydrophobic Y type zeolite	10-90	Tsai et al., 2006b

Mineral	SMZFA F prepared from coal fly ash	0.5-100	Dong et al., 2010
	SMZFA L prepared from coal fly ash	0.5-100	Dong et al., 2010
	ZFA F prepared from coal fly ash	0.5-100	Dong et al., 2010
	ZFA L prepared from coal fly ash	0.5-100	Dong et al., 2010
	Geothite	0.3 mM	Shareef et al., 2006
	Montmorillonite	0.3 mM	Shareef et al., 2006
	Kaolinite	0.3 mM	Shareef et al., 2006
	Montmorillonite Hybrid particles PO1	22.8-54.7	Cao et al., 2009
	Montmorillonite Hybrid particles PO2	22.8-54.7	Cao et al., 2009
	Montmorillonite Hybrid particles PO3	22.8-54.7	Cao et al., 2009
	Montmorillonite Hybrid particles PO4	22.8-54.7	Cao et al., 2009
	Sediment Sample A	5-90	Zeng et al 2006
	(Pailoukou)	5 70	Zong et al., 2000
	Sediment Sample B	5-90	Zeng et al., 2006
	(Nonglinq Bridge)	0 / 0	2000g 00 uli, 2000
	Sediment Sample C	5-90	Zeng et al., 2006
	(Juzizhoutou)		6 ,
	(North Bridge)	5-90	Zeng et al., 2006
	Sediment Sample F		
	(Nanijao Park)	5-90	Zeng et al., 2006
	Sediment Huang Pu River		
	Shangai China	10-60	Li et al., 2007
Sediment	Natural Surface Coating Samples (NSCS)	10-80	Li et al., 2009
	Surficial Sediments (SS)	10-80	Shareef et al 2006
	Marine Sediment A	5-80	Xu et al., 2008
	Marine Sediment B	5-80	Xu et al. 2008
	Marine Sediment B ₂	5-80	Xu et al., 2008
	Marine Sediment B_2	5-80	Xu et al., 2008
	Marine Sediment D	5-80	Xu et al. 2008
	Marine Sediment E	5-80	Xu et al., 2008
	Yellow River Tong Guan suspending solid (TS)	11.2 µg/L	Sun et al 2005
	Yellow River San Menxia suspending solid (SS)	11.2 μg/L	Sun et al. 2005
	Yellow River Tong Guan bottom sediment (TB)	11.2 μg/L	Sun et al. 2005
	Yellow River San Menxia bottom sediment (SB)	11.2 μg/L	Sun et al. 2005
	Huan Yuankou bottom sediment (HB)	11.2 µg/L	Sun et al., 2005
Soil	Soil from experimental farm pass through 0.22mm mesh	5-130	Li et al., 2008
	Carbonaceous material prepared at 600 [°] C from by-	1 10	Nakanishi et al
	products of wood processing	1-18	2002
	Carbonaceous material prepared at 800 °C from by-	1 10	Nakanishi et al.,
Carbon	products of wood processing	1-18	2002
	Porous Carbon prepared from Moso bamboo PC ₄₀₀	1-20	Asada et al., 2004
	Porous Carbon prepared from Moso bamboo PC700	1-20	Asada et al., 2004
	Porous Carbon prepared from Moso bamboo PC ₁₀₀₀	1-20	Asada et al., 2004
	Single-walled carbon nanotubes (SWCNT)	0.1-40	Pan et al., 2008
Carbon	Multiwall carbon nanotubes MWCNT15	0.1-40	Pan et al., 2008
Nanotube	Multiwall carbon nanotubes MWCNT30	0.1-40	Pan et al., 2008
	Multiwall carbon nanotubes MWCNT50	0.1-40	Pan et al., 2008
Fullerene	Fullerene	0.1-40	Pan et al., 2008
Activated	Activated Carbon	1-20	Asada et al., 2004

Carbon	Activated Carbon from SorboNorit Charcoal (S)	50-350 50-350	Toledo et al., 2005
	Activated Carbon from Merk Charboar (N)	50-350	Talada at al. 2005
	Activated Carbon from almond shells (A)	50-550	1 oledo et al., 2005
	Activated carbon from Calgon (coconut shell base)	60-100	Tsai et al., 2006a
	Activated carbon from Calgon (bituminous coal base)	60-100	Tsai et al., 2006a
	Astivisted asthen from Takada (as assut shall based)	1 10	Nakanishi et al.,
	Activated carbon from Takeda(coconut shell based)	1-18	2002

1.2.8.1 ADSORPTION OF BISPHENOL ONTO CARBONACEOUS MATERIALS

A common adsorbent used for adsorption is activated carbon. Activated carbon has been one of the most efficient methods used for the removal of organic contaminants from water. Few studies have shown that the adsorption of BPA onto selected activated carbons or carbonaceous materials is possible. The carbon adsorbents could come from various source bases such as coconut shell-based, bituminous coal-based (Tsai et al., 2006a), coconut shells (Nakanishi et al., 2002), Moso bamboo (Asada et al., 2004), commercial charcoal-based, and almond shell (Toledo et al., 2005). Also the adsorption of BPA was also investigated onto single-walled carbon nanotubes (SWCNT), multiwalled carbon nanotubes (MWCNTs), and fullerene (Pan et al, 2008). The wide variety of so many different carbon sources made the adsorption to be very sorbent specific and had to be individually investigated.

One such experiment had been done in order to compare the surface properties of selected activated carbons and their chemically modified samples. The adsorption capacities of BPA and the effect of the operating temperature, pH, and ionic strength had been studied. Two types of commercial activated carbons were used and noted as WV A1100 (Westaco Corp. America) and F400 (Calgon Corp. America) and denoted as W20 and F20. Also treatment of these activated carbons was done using boiling nitric acid at 368K with constant temperature for 6h, and the modified activated carbons were denoted as W20A and F20A. The new modified

activated carbons were then treated under thermal treatment with a flow of N_2 , and the new compounds were named as W20N and F20N.

The treatment was done using 10 mg of carbon that was agitated at 150rpm in a thermostatic bath in a 100 mL of BPA solution (60mg/L) containing 1 mmol/L phosphate buffer solution (pH 7.0). The adsorption was done at 25 0 C (298 K) and is presented in Figure 1.28. The capacity of adsorption was in the range with other carbonaceous adsorbents. The coconut shell-based adsorbent was studied in a solution with a BPA initial concentration of 60mg/L had a capacity q_e of 238.0(mg/g) , and for the bituminous coal-based 227.3(mg/g) (Tsai et al., 2006a). However, the capacity for the bituminous coal-based was obtained after a period of 2 hours only. For other carbonaceous materials such as coconut based or byproducts of wood processing carbonized at temperatures of 873K and 1073K, the maximum capacity q_e at a final equilibrium concentration between 1 to 18mg/L was found to be only 23.5, 4.2 to 18.2, and 24.1 to 31.4 mg/g, respectively (Nakanishi et al., 2002). The experiments were run for a period of 48 hours. The range for the porous carbon material prepared from bamboo had the same range between 2.1 to 41.6 mg/g depending on the temperature of carbonization, and the experiments were conducted for a period of 24 hours (Asada et al., 2004).

For the activated carbon obtained from the same experiments was found to have a q_e of 58.2 mg/g at the final equilibrium concentrations of 1 to 20mg/L. For the charcoal based carbons from Sorbo-Norit (Sample S), Merck (Sample M), and almond based (Sample A) the adsorption capacities were found to be after 7 days 129.6, 263.1 and 188.9mg/g, respectively (Toledo et al., 2005). In the case of carbon nanotubes the single walled SWCNT performed better than the MWCNT, having an adsorption capacity of 455mg/g compared to 61.2 to 102mg/g (Pan et al.,

2008). The fullerene adsorption capacity was found to be 236 mg/g and was conducted for a period of 7 days.



Figure 1.28 – Adsorption of bisphenol A onto various activated carbons at 298 K and pH 7.0; C₀ = 60 mg/L. (Liu et al., 2009)

The increase in temperature from 288K to 318K accelerated the adsorption of BPA reducing the half-life for W20 from 5.84h to 2h and W20N from 5.38h to 1.65h, but the capacity of the adsorption was also reduces from 451 mg/g to 336.13 for W20 and 489.0 to 390.63 mg/g for W20N. For the other carbonaceous materials the effect of temperature was not investigated and the experiments were conducted at room temperature between 23 to 25 0 C.

Another important parameter that has to be taken into consideration when the adsorption of BPA is analyzed is the pH. As mentioned earlier the pKas of BPA are around 9.6 and 11.3. Because of the double deprotonation of the bisphenolate monoanion sets can take place at higher pH of around 8, the effect of the pH has to be investigated to understand its effect on the adsorption. A decrease from pH from 5 to 7 was observed, but than an increase from the pH of 7 to 11 in the half life was observed for both W20 and W20N (Liu et al, 2009). The increase in the pH from 5 to 11 resulted in a decrease in the adsorption capacity (Liu et al., 2009). The same effect was seen in the bituminous coal-based and coconut shell-based carbonaceous materials (Asada e al., 2004), charcoal and almond based carbon materials (Toledo et al., 2005), where an increase in pH created a decrease in the adsorption. This was the result of the negatively surface charge of the adsorbent, which created repulsive electrostatic interactions with the bisphenolate anions (Asada et al., 2004).

Also the increase of ionic strength showed a decrease of adsorption of 28.79% in q_e for W20 at pH 7.0 and 0.005mol/L ionic strength (Liu et al., 2009). A decrease onto both activated carbons was observed at 0.005 mol/L ionic strength, because of the Na⁺ ions adsorption onto the adsorbent under the electrostatic interactions. The small quantity of ionic strength occupied the activated sites of the activated carbons. Higher ionic strength up to 0.5 mol/L increase the q_e to 400.32 and 453.10 mg/g for W20 and W20N, respectively (Liu et al., 2009). This was done due to the screening effect of the higher ionic strength produced on the surface charged that favored the π - π dispersion interactions that resulted in a enhancement of adsorption of BPA (Liu et al., 2009; Choi et al, 2005). In the case of charcoal based carbons from Sorbo-Norit (Sample S), Merck (Sample M), and almond based (Sample A) the presence of NaCl of 0.01M and 0.1M increased for all of the adsorbents the capacity of q_e (Toledo et al., 2005). This was possible because of the screening effect that took place of the surface charge which favors adsorbate-adsorbent dispersion interactions. The Na⁺ ions were placed between the BPA molecules and the

carbon surface, thus enhancing the adsorption of BPA (Ying et al., 2003; Choi et al., 2005; Toledo et al, 2005; Ying and Kookana, 2005; Liu et al., 2009).

The increase in dosage of adsorbent doesn't always help to increase the capacity of adsorption. The increase in dosage from 50 mg/L to 250 mg/L for both the coconut shell-base and bituminous coal-based carbons source decrease the adsorption capacity from 270.3 to 227.3 mg/g and 400.0 to 238.0 mg/g, respectively (Tsai et al., 2006a). As a result the dosage is a very important parameter that should be taken into consideration when evaluating a sorbent for the adsorption of BPA.

1.2.8.2 ADSORPTION OF BISPHENOL ONTO SOILS AND SEDIMENTS

The adsorption and desorption of organic pollutants on sediments is very important for understanding the contaminant behavior such as transport and ecotoxicology risks. The evaluation of the adsorption to sediments can also help the fate modeling analysis of organic pollutants in the aqueous environment. Not too many people had mentioned the transport and transforming behavior of BPA (Nakanishi et al., 2002; Fent et al, 2003; Ying et al., 2003; Clara et al., 2004). It is known that the organic carbon content plays a role in the adsorption of BPA (Xu et al., 2008). Different environment conditions such as the presence of other pollutants, pH, temperature, and in case of marine sediment salinity plays a role in the adsorption.

The adsorption of BPA on different sediments from Xiangjiang River gave a capacity q_e between 0.15 to 0.3mg/g using an BPA initial concentration of 50 mg/L (Zeng et al., 2006). When linear model was used to fit the data the distribution coefficient K_d was between 2.2 to 8.6 (L/Kg), which was in good correlations with marine sediment from Mai Po Inner Deep Bay in Hong Kong that reported numbers between 4.43 to 8.54 (L/Kg). Even in the presence of lower

concentration, between 2 to 12 μ g/L the sorption of BPA on Yellow river sediment for the samples from the bottom sediment (SB) showed a K_d value of 4.166 (Li et al., 2008). The presence of other heavy metals into the sediments such as Cd and Pb generated a positive effect onto the sorption of BPA on sediments (Li et al., 2007). Two different concentrations of 0.15 and 0.30 mM of Cd and Pb were used. When fitted with Freundlich model the exponent n decrease from 0.945 in the absence of heavy metals to 0.77 and 0.76, after the addition of Cd and Pd, respectively. The concentration increase from 0 to 0.15mM of Cd and Pb lead to the Freundlich unit-capacity coefficient K_f to increase from 4.090 to 12.46 and 18.04, respectively (Li et al., 2007). Similar the exponent n value for the Freundlich model increased from 0.6944 to 0.8106 for the sediments in the Xiangjiang river. However, the K_f coefficients were between 0.0072 to 0.0178. The low n value <1 indicates that the adsorption capacity is low and will reduce slowly at a lower concentration (Zeng et al., 2006). The fraction of organic carbon proves to have a linear relationship with unit-capacity coefficient K_d (Xu et al., 2008).

Just like in case of carbonaceous materials, the effect of pH is important, when we are looking at the adsorption of BPA. The increase in pH has a negative effect on the adsorption of BPA from water onto sediments. The same negative effect was presented in the case of carbonaceous materials. However, depending on the sorbent the effect of pH was different. For example, in case of the sediments from Xiangjiang river there was a sudden drop in the adsorption from pH 2.5 to 6.0, than it remained constant until pH 11.0 (Zeng et al., 2006). For the sediment from Huang Pu River the same negative effect on the adsorption was observed. However, it had a more linear relationship dropping from 160 mg/Kg at pH 2.0 to 40 mg/Kg at

pH 12 (Li et al., 2007). When comparing the isotherms at different pH, with a 30psu salinity for marine sediment, the lower pH of 4.0 showed a better adsorption than those isotherms at higher pHs of 6.0, 8.0 and 10.0 (Xu et al., 2008). Because BPA is a polar compound as a result at higher alkaline solution it has higher water solubility than at acidic solution. At lower pH BPA tends to transfer itself better from liquid phase to the solid phase, which results in higher adsorption. Another effect of high pH on the sediment is that it could enhance the release of negative organic matter from the sediment into the solution and therefore decrease the BPA adsorption (Zeng et al., 2006). The deprotonated (ionic) form of BPA it would be present at higher pH and became the dominant form. This will result in electrostatic repulsion to be formed between the BPA anionic form and negatively charged sediment, which will result in a lower partition of BPA onto the sediment (Li et al., 2007).

Another important factor that could contribute greatly in the adsorption of BPA on the sediments and mostly on any adsorbent is the ionic strength. It is known that the release of other ions into the water should decrease the solubility of BPA as a result promoting adsorption. Other mechanisms could be formed and present such as the presence of low concentrations of Na⁺ ions could promote the release of native organic matter from the sediment, resulting in the decrease in adsorption of BPA (Zeng et al., 2006). Depending on the ions that are present the effect may vary. A solution containing NaNO₃ concentration of 0 to 0.8M was studied to see the effect on the BPA adsorption (Zeng et al., 2006). It showed an increase in the adsorption capacity from 0.26mg/g to 0.31mg/g when the concentration of NaNO₃ was increased from 0 to 0.8M. The Na⁺ ions are believed to react with the negative surface charges of the sediment, which created a neutral environment. The neutral environment enhanced the hydrophobic effect

of the neutral BPA species from the bulk solution as a result increasing the adsorption (Zeng et al., 2006). The same effect was observed in the presence of Ca^{2+} and NH_4^+ ions where an increase from 0.005M to 0.5M lead to an increase in the adsorption of BPA by more than 114.3% and 78.8%, respectively (Li et al., 2007). The screening effect in which the positive ions have on the negative charges of the sediment surfaces, lead to the repulsion between the BPA and sediment surface to decrease as a result to increase the adsorption of BPA (Wu et al., 2003; Burton et al., 2004; Houch et al., 2004; Tao and Tang, 2004). The effects of Ca2+ and K+ ions were also studied on the Yellow River sediment (Sun et al., 2005). The ionic strength concentrations used were 0 to 4mM. The results showed that depending on the ionic species it could increase or decrease the adsorption. In the case of Ca^{2+} the adsorption increased, but in the case of K⁺ it decreased. Also a greater effect was observed only at concentrations higher than 2 mM. During adsorption interactions such as Van der Walls, hydrogen bonding, charge transfer, ion-bonding, direct and induced ion-dipole, dipole-dipole interactions, and chemisorptions could take place (Bekbolet et al., 1999). For example in the alkaline pH conditions BPA exists as charge species, thus could engage in ion-bonding or other bonding mechanisms described above (Sun et al., 2005).

The sediment to water ratio could also play an important role in the adsorption of BPA. When comparing a series of sediment:solution (w/v) ratios of 1:250, 1:25, and 1:12.5 there was a decrease in the adsorption of BPA with an increase of sediment concentration (Zeng et al., 2006). This behavior was tried to be explained previously through the adsorption of solid phase into the system (Voice et al., 1983). It is believed that are some fractions of BPA molecules that cannot be removed through high-speed centrifuge as a result it remains in these suspended

particles in the liquid phase (Zeng et al, 2006). The same relationship was observed at lower initial concentration of 11.2μ g/L, where the ratio of water–sediment of 25:1 had a higher adsorption capacity than that of 15:1 (Sun et al., 2005).

Higher salinity of 30 psu had a negative effect on the adsorption when compare to a more diluted concentration of 5 psu. Also a higher temperature of 35 0 C had a negative effect on the adsorption when compare to that of 25 0 C.

Few papers had presented data on the adsorption of BPA onto soils at different concentration range. In one of the tests 1.5 g of soil was added into 25 ml glass bottle and 20 mL of different solutions of BPA concentrations were added, which already contained a concentration of 5 mM CaCl₂ and 100 mg/L NaN₃ (Li et al., 2008). CaCl₂ was added in order to give a more realistic and appropriate ionic strength for the background of water. The addition of NaN₃ was for the microbial inhibition. The final equilibrium concentration range was between 5 to 140 mg/L. The sorption was than fitted using Freundlich model $q = K_f Ce^n$, resulting in a nonlinear relationship with n value of 0.946. From this study the conclusion was made that the partition was not the unique mechanisms for the sorption of BPA onto soil, but adsorption also played an important role (Li et al., 2008).

In another soil adsorption test, four different soil samples were used, sample I from permanent grassland which was sandy, sample II and III from crop farming which was silt, and sample IV was used as alfalfa and was sandy (Fent et al., 2003). A soil:solution ratio of 1:20 that is 1g to 20ml of solution was used at four different BPA concentrations of 0.04, 0.20, 1, and 5.03mg/L in 0.01M CaCl₂ solution. The results were fitter using Freundlich model $q = K_f Ce^{1/n}$, resulting in K_f values of 12.57, 6.934, 17.12, and 7.409 for soil I, II, III and IV, respectively.

Also the values of 1/n were 0.7719, 0.8525, 0.7019, and 0.8414 for soils I, II, III, and IV, respectively (Fent et al., 2003).

Another representative test was conducted using sediment and water from a aquifer storage and recovery (ASR) from Bolivar, South Australia. For the adsorption of BPA 10g of sediment was added with 100 mL of groundwater at five different concentrations of 2.5, 5, 10, 15, and 20 μ g/L for a period of 16 hours (Ying et al., 2003). The results were fitter using Freundlich model q = K_fCe^{1/n} with a value of 3.89 for K_f and 0.85 for 1/n.

Adsorption of BPA on agricultural soil from South Australia collected at a depth from 0 to 15 cm from Roseworthy Campus (RC), Roseworthy Farm (RF), Terretfield (TF), and Waite Campus (WT) were performed (Ying et al., 2005). The pH of the soil was determined in a 1:2.5 w/v soil in 0.01M CaCl₂ solution. The pH values are as follows: for RC 7.2, RF 5.4, TF 7.4, and WT 5.6. Also the percentage by mass of total organic carbon was as follows: for RC 1.3, RF 0.85, TF 1.8, and WT 2.9. The sorption test were conducted using batch equilibrium method for a period of 2 hours using 2g of sediment with 200 ml of solution and an initial concentration of BPA of 25 μ g/L. By fitting the results with a linear model S = K_DC, where S was the concentration (mg/L), and K_D was the partition coefficient. The following K_D values were obtained for RC 77, RF 62, TF 78, and WT 122, which showed a direct relationship with the organic carbon present in the soil, the higher the concentration the better the adsorption (Ying et al., 2005).

1.2.8.3 ADSORPTION OF BISPHENOL ONTO MINERALS

The adsorption of BPA was also reported on different mineral surfaces such as surfactant-modified zeolite (Dong et al., 2010), andesite, diatomaceous earth, titanium dioxide, activated bleach earth (Tsai et al., 2006a), commercial hydrophobic zeolite (Tsai et al., 2006b), goethite, montmorillonite, kaolinite (Shareef et al., 2006), and polyethersulfone-organophilic montmorillonite hybrid particles (Cao et al., 2009).

For an initial concentration of 60 mg/L of BPA a dosage of 0.5 g for 2L was used , at 25 0 C, 400 rpm and pH 7.0 was used to study the adsorption on andesite, diatomaceous earth, titanium dioxide, and activated bleach earth (Tsai et al., 2006a). To characterize the minerals the BET surface area (m²/g) was determined and found to be for andesite 2.7, diatomaceous earth 3.8, titanium dioxide 50.1, and activated bleach earth 257. The adsorption results were fitted with pseudo-second order model and found a capacity concentration q_e (mg/g) of 0.53 for andesite, 0.73 for diatomaceous earth, 0.33 for titanium dioxide, and 0.86 for activated bleach earth. The capacity q_e showed a good correlation with the BET surface area with the only exception was for that of titanium dioxide, which even though had a higher BET surface area than andesite and diatomaceous earth the adsorption capacity been the lowest (Tsai et al., 2006a).

Another group of minerals studied for the adsorption of BPA was goethite, montmorillonite, and kaolinite. For the determination of adsorption 300mL of 10mM KNO₃ with an initial BPA concentration of 0.3μ M was added to 0.48g of goethite, 0.94g of montmorillonite, and 1.28g of kaolinite for a period of 10days (Shareef et al., 2006). The tests were conducted first at two different pHs for Ph of 4.0 and 10.0. For kaolinite there was a removal of about 7 % for both pHs, for montmorillonite 18 % for pH 4 and 40 % for pH 10, and for goethite about 20 % for both pHs. The only pH effect was observed for the montmorillonite, which at a pH greater than 8 the adsorption increased and stayed constant. This might happen, because the ionized molecules of BPA would interact more strongly with co-ordinated water molecules within the interlayer spaces of the mineral (Sahreef et al., 2006). Four different hybrid particles of polyethersulfone-organophilic montmorillonite were formed using a mass ratio of polyethersulfone (PES) to organophilic montmorillonite (OMMT) of 1:1, 1:2.5, 1:3 and 1:3.5 coded as PO1, PO2, PO3, and PO4 (Cao et al., 2009). The adsorption tests were performed using 0.1g of hybrid particles to 20ml of BPA solutions with initial concentrations ranging from 22.8 to 54.7mg/L. The q_e (mg/g) was obtained using the Langmuir isotherm with 20.7039, 21.7391, 23.5849, and 32.0513 for PO1, PO2, PO3, and PO4, respectively.

Zeolites are microporous aluminosilicate minerals that are commonly used as commercial adsorbents. They are multiple different types of zeolite minerals and some had been used to study the potential adsorption of BPA. For example it was found that the adsorption of BPA is effective using Y-type zeolite not with A- and F-type zeolites (Fukahori et al., 2003). For this reason studies had been done to investigate more the different type of zeolites for the purpose of adsorption of BPA. Using a commercially available hydrophobic zeolite at a dosage of 1g/2L, pH 7, 400rpm, temperature of 25 0 C, particle size = 0.223mm, and BPA initial concentrations of 10 to 90mg/L the capacity qe (mg/g) were determined using pseudo-second order model. The qe (mg/g) varied from 19.01mg/g for initial concentration of 10mg/L to 125mg/g for initial concentration of 90 mg/L of BPA. In the same study when the dosage was increased from 0.5 g/L to 1g/L, and 1.5 g/L the capacity qe (mg/g) decrease form 70.42, to 38.91, and 24.45 using

the initial BPA concentration of 20 mg/L. Also there was a negative pH effect on the adsorption when pH was greater than 9 because of the pKa values of BPA (Tsai et al., 2006a).

Zeolite that has been synthesized from coal fly ash (ZFA) had been previously investigated for the purpose of water treatment, and showed good sorption for cationic and anionic pollutants (Chen et al., 2006; Wu et al., 2006; Sui et al., 2008; Wu et al., 2008). Based on those studies surfactant modified ZFA (SMZFA) using HDTMA (bromide form) with concentration of 55 mM was formed and studied for the removal of BPA (Dong et al., 2010). Four different zeolites were formed two with high and two with low content of CaO denoted ZFA-L for low content of CaO of about 3.5 %, ZFA-F for high content of CaO of 12.10 %, and the surfactant modified for those two zeolites were denoted as SMZFA-L and SMZFA-F. Concentration of BPA ranged from 0.5 to 100mg/L, temperature 25°C, pH 11.2 and 10.5 for ZFA F and ZFA L, and 10.4 and 9.6 for SMFA F and SMFA L, and dosage of 0.5g L⁻¹. The following capacities of qe (mg/g) were obtained for SMZFA-F 114.9, SMFA-L 56.8, ZFA-F 3.5, and ZFA-L 1.4 (Dong et al., 2010). There was a positive effect as the pH increased higher than 7 to 10 for both surfactant modified zeolites with an increase for SMZFA-F and SMZFA-L from 60 to 100 mg/g, and 20 to 35mg/g, respectively. When the effect of different concentrations of NaCl of 0 to 0.4M was investigated a slightly improvement in adsorption was observed for a concentration higher than 0.2M for both surface modified zeolites. This is an indication that BPA anion was more competitive than Cl⁻ for adsorption sites onto the surface of modified zeolites. Finally the increase in temperature from 5 to 20, 35 and 50 ^oC had a negative effect on the adsorption of BPA similarly as the effect on activated carbon.

1.3 SUMMARY OF TECHNOLOGIES FOR REMOVAL OF BPA FROM WATER

A review of literature on treatment of BPA has shown that the removal of BPA is possible through different technologies or a combination of more than one technology. This is very promising taking into consideration the negative effects that BPA has on humans and animals, and especially on the reproductive system. Through different processes of oxidation using ozonation, chlorination, ultrasonication, electrochemical, bacterial degradation, photooxidation, oxidation with ferrate(VI), and zero valent aluminium, BPA can be removed from water. It could also be adsorbed onto different absorbent such as activated carbon or modified adsorbents. However, the application of each method and technique has advantages and disadvantages that limit its use.

The ozonation process is a good technology for removal of BPA since it is used in the removal or microorganisms and other organics already. The negative part of this process is the byproducts that result through the process, and the high cost of operating the system. Because of these limitations it is not widely used in the treatment of drinking water. It was argued that if the concentrations are low the concentrations of the byproducts would not be significant. But the effects and toxicity of such compounds should be also studied and evaluated. In some studies the byproducts that resulted from the degradation of BPA had a higher estrogenicity than that of BPA alone.

Chlorination is a process that had been used in the treatment of drinking water and waste water for a long period of time, in US for more than 100 years. It had been an effective and cheap disinfection process. However, the problem of byproducts is very important when it comes to the removal of BPA from water. The removal of BPA with chlorination process had many byproducts formations. BPA will have to compete with other pollutants that the chlorination process is able to remove in order to be completely removed. These byproducts could take up to 22hours to be removed, thus make it a slow process. The estrogenicity of the newly formed compounds and their interactions should be studied in depth for a better understanding.

The electrochemical process is efficient only at high concentrations. This could be a very limiting technology since the concentrations are usually low. Also a lot of pilot scale experiments had to be done for the aqueous solution in order to determine the cycle of current to be used. The building of the process chamber could be also costly. The problem of byproducts formation it is also very important since many byproducts had been reported under the electrochemical oxidation of BPA.

The photooxidation is a viable technique that has given good results only at low pH values. This is not efficient for water treatment, because the processed water in the plant is kept at approximately at a neutral pH. The process will not be able to be done to an industrial effluent because the concentrations of BPA would be high and would not be effective. Photooxidation is usually used with a combination of other processes or chemicals to have a better performance. Fenton process had been used for the formation of HO• radicals with the addition of H₂O₂. Photooxidation had been used in the presence of TiO₂ for better performance. The addition of other processes or chemicals would increase the cost of removal and will create a more complex system in which more variables would play a significant role. The problem of byproducts formation has to be taken into consideration.

The biodegradation is a process that could remove BPA, however, is not a good candidate for water treatment due to the duration. This biotechnology could be used if the bacteria would be injected before arriving to the waste water treatment plant. The most limiting factor about this technology was that some of bacteria strains in the anaerobic conditions did not perform too well, thus it cannot be used in the treatment of aquifers. Even though many bacteria, enzymes and other biological organisms had been found to biodegrade BPA, not all of them are close to at least 90% of removal. Even the mammals had been found to be able to biodegrade BPA. The degradation could be take long periods of time for a high removal, depending on the biological organisms. In the process of degradation of course there is the byproducts formation that is important to consider. The remediation could take long time and pilot scale studies would have to be done to identify and evaluate each individual specific case in order to understand the efficiency of the process to the particular case.

Ultrasonic degradation (US) of BPA, just like the photooxidation, in order to be very efficient it requires additional process or chemicals to be present. The use of US alone would not be able to obtain a high removal percentage for the BPA. Fenton process it is well known AOP that could be used in the combination of US. Even though it is effective, the Fenton process relies on the HO• radical formation, which in the process of degradation of BPA would form new byproducts. Sometimes it required even three processes such as US, Fenton, and solar irradiation to achieve a 92 % removal of BPA for a concentration of 118 µmol/L in 60 minutes. The US had been only recently started to be evaluated and more tests would have to be performed in order to find all the limiting factors that play a role in the process of BPA removal. The cost of removal could be also high, because of the addition of other processes necessary for high efficiency.

The oxidation of BPA using ferrate(VI) and zero valent aluminum (ZVAl) had been found to be a potential treatment process for drinking water and wastewater. A 0.5 mg/L Ferrate(VI) concentration was able to remove a BPA concentration of 15 μ M in 30 minutes. For the wastewater a 1mg/L ferrate (VI) was needed to obtain 95% removal. There could be a limitation for BPA treatment for higher concentrations, and for the treatment of real water because of the competition for ferrate(VI) by water itself. The ZVAI had only recently found to be able to oxidize BPA only under acidic conditions. The redox potential of aluminum is -1.67V, which is much lower than zero valent iron (ZVI) for example, which is used for the removal of many pollutants. Also the very acidic pH at which ZVAI works best, that is pH of 1.5, is a very limiting factor that has to be taken into consideration. It was found that the addition of Fe²⁺ ions could increase the efficiency of the process in the removing of BPA.

The adsorption process showed the most promising way of removing the BPA. It showed a pseudo second-order kinetic model, thus making it a fast good candidate for a water treatment plant. The technology is also a good candidate, since activated carbon is commercially available and more frequent used in regular water treatment plants for treatment of different chemical compounds. The ionic strength affected negatively only at low concentrations, the high concentrations actually helped the process. It had a better adsorption capacity at low temperatures such as 15 °C, but had a higher half time value than that at higher temperature. As a result more investigation have to be done to determine the optimum temperature at a typical ionic strength in a water treatment plant. A good advantage was the strong adsorption at a pH of 7.0 to 11.0, below this range did not perform well. The reactivation of activated carbon if it is possible should be addressed, because of the byproducts formation and the cost associated with the process. Another disadvantage of using activated carbon is that is flammable and difficult to regenerate when it needs to be reclaimed (Blocki et al., 1993).

The adsorption onto soils showed some promising aspects, but there was little investigation done and is specific to the adsorbent. The composition of soils is very important, such as high organic carbon for example. The presence of some mineral oxides help the adsorption such as Fe oxides, but Mn oxide affected in a negative way (Li et al., 2009). The soil alone is not good candidate as adsorbent, but the investigation of the adsorption to soils is good for the understanding of the behavior and transport fate of BPA in the environment.

The adsorption onto mineral surfaces looks promising because of interactions that can be achieved with the surface that could lead to reactions. Depending on the mineral, the capacities of adsorption vary greatly and acted differently at higher or lower pH. However, it showed second order kinetics as activated carbon, which makes them competitive because they are cheaper. Different types of minerals had already been investigated for the removal of BPA, and based on the studies the iron oxides were investigated for the adsorption of BPA. Different zeolites were investigated and for better performance they were modified using surfactant, which made them expensive for treatment use. Iron oxides could be better adsorbents, because of their availability and ease of recycling.

1.4 PROPOSED RESEARCH

Based on the technologies studied, adsorption may be the most cost effective and easy to manage and operate technology. It can also be incorporated into the regular treatment of water. For example the adsorbent can be added in the same manner like activated carbon in the beginning of the treatment process like the addition of powdered activated carbon (PAC) in the rapid mix tank. If a magnetic adsorbent is used, it will be easy to be removed later in the treatment process by a magnetic field. The operational process is very important for the cost. A

balance between effectiveness, ease of operation, and cost should be taken into consideration when choosing an adsorbent.

Iron oxides may serve as viable adsorbents for the adsorption of BPA from water. In addition to adsorption, oxidation or reduction of BPA may occur on the surface of iron oxide minerals. Iron oxide minerals such as hematite (Fe_2O_3) and magnetite (Fe_3O_4) have been chosen to be used for the removal of BPA from aqueous solution.

1.4.1 THE EFFECT OF ADSORBENT DOSAGE ON THE ADSORPTION OF BPA

Different dosages of adsorbent will be investigated to determine the efficiency of the adsorbent. A concentration close to the typical environmental contamination levels will be used. The concentration of 1mg/L will be investigated for different parameters, because is a more realistic concentration closer to the concentrations in the environment. The study will be done for 30 days with time periods of 1, 3, 7, 10, 14, 21, and 30 days. A concentration of 10mg/L will be also used in order to understand the adsorption at a higher concentration in case of a landfill leachate. The characterization of the initial dosage effect will be investigated using equations 25 and 26. The adsorption parameters and regression coefficients will be tabulated for comparison. It is expected that a decrease of the kinetic rate constant will occur with an increase in initial dosage concentrations (Tsai et al., 2006a; Newcombe et al., 1997).

1.4.2 ADSORPTION EQUILIBRIUM ISOTHEMS AND ADSORPTION KINETICS

In our characterization we will look at the adsorption isotherms. At equilibrium, the adsorption process will reach a maximum and will stay flat in the relationship between the adsorbate concentration on the absorbent phase and in the solution phase. The data will be analyzed according to the adsorption equilibrium equations such as the linear adsorption equation, and the nonlinear Langmuir and the Freundlich equations (Lopez-Ramon et al., 2002; Tsai et al., 2006a; Zeng et al., 2006). The linear adsorption equation is given by equation 24:

$$q_e = K_D C_e \tag{24}$$

Where, q_e and C_e are the equilibrium concentration of the analyte on the solid adsorbent (mg/kg) and in liquid solution (mg/L), respectively. The K_D is the linear coefficient of adsorption (L/kg) or the linear adsorption constant.

The Langmuir adsorption equation is (Al Duri, 1996):

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)}$$
(25)

Where, C_e is the concentration (mg/L) and q_e the amount (mg/g) of BPA absorbed at equilibrium. K_L is the direct measure of intensity of the absorption process (L/mg), and q_m is the surface constant that relates the area occupied by a monolayer of adsorbate, that reflects the sorption capacity (mg/kg). The Freundlich equation is (Zeng et al., 2006):

$$q_e = K_F C_e^n \tag{26}$$

Where, C_e is the concentration (mg/L) and q_e the amount (mg/kg) of BPA absorbed at equilibrium. K_F is the distribution coefficient and represents the general capacity of adsorbate, which is absorbed onto the absorbent for a unit equilibrium concentration, and the slope n (ranging between 0 and 1) is a measure of the absorption intensity also referred to as surface heterogeneity.

In order to characterize the effectiveness of the adsorbent as function of time, adsorption kinetics experiments and adsorption isotherm experiments have to be developed to determine the
capacity and rate of adsorption. In the first part of the adsorption kinetics we will investigate to see if the adsorption kinetics will follow a pseudo first-order model or a pseudo second-order model. Based on literature review we expect that the adsorption of BPA to follow a pseudo second-order model kinetics. The time periods that will first be determined will be 1, 3, 7, 10, 14, 21, and 30 days. The linear form of the pseudo second-order reaction is given by equation 27:

$$\frac{t}{q_t} = \frac{1}{\left(kq_e^2\right)} + \left(\frac{1}{q_e}\right)t \tag{27}$$

Where, k is the rate constant of pseudo second-order adsorption (g/mg-min) and q_e and q_t are the amount (mg/g) of the BPA adsorbed at equilibrium and at time t, respectively (Tsai et al., 2006b). This equation is very useful because the parameters such as k and q_e can be obtained directly from the graph when plotting t/q_t against t, where k is the intercept and q_e the slope. We can calculate the equilibrium concentration (i.e., C_e) using mass balance. Another important parameter is the half-life, or the half of the adsorption time that is required by the adsorbent to reduce the initial concentration of BPA to half at equilibrium. The conditions are such that $q_t = q_e/2$ at t = t_{1/2} and the equation is given as:

$$t_{1/2} = \frac{1}{kq_e}$$
(28)

The effect of adsorption with time will be investigated for a fixed concentration of 1ppm for a period of 30 days. Isotherms will be conducted as function of time for the following periods of times: 1, 3, 7, 10, 14, 21, and 30 days. This will enable us to better understand the effect on the adsorption as a function of time to investigate any changes that might occur. Also isotherms will be done using constant adsorbent dosages, but the concentration of BPA will be varied.

1.4.3 EFFECT OF pH AND IONIC STRENGTH ON THE ADSORPTION OF BPA

The effect of pH on the adsorption of BPA onto iron oxide sorbents will be also investigated. The variation is expected to reach one or more pK_a values for the BPA, at which an adsorption capacity will be found. In order to visualize this, a plot of qe (mg/kg) against pH will be plotted. The pH variation will include solution pH values of 2, 2.5, 3, 3.5, 4, 5, 6, 7, 8, 10, and 12 for a time period of 1 and 7 days. If the results give good adsorption within 1 day, shorter adsorption time periods less than 24 hours will be investigated. The various solutions with different pH values will be prepared using HCl and NaOH.

The ionic strength as seen in the literature review has an effect on the BPA adsorption. It is known that higher concentration above 2mM of Ca^{2+} for example helped the adsorption of BPA onto mineral surfaces. We will investigate difference case scenarios to simulate these conditions using water containing calcium and other ions. We will investigate which ions help or inhibit the adsorption. The effect of monovalent and divalent cations and anions on adsorption of BPA onto iron oxides will be evaluated using potassium (K⁺), calcium (Ca²⁺), chloride (Cl⁻), and bicarbonate (HCO₃⁻) ions, will be examined.

1.4.4 BPA BYPRODUCTS DEGRADATION

BPA in the environment could undergo different changes that would change the chemical structure creating new byproducts. Depending on the situation, the degradation of BPA could form many byproducts that would remain in the water and could have a negative health effect on humans. The identification of these products along with their toxicity is crucial in understanding the faith of BPA in the environment and humans. The processes and chemical mechanisms through the byproducts are formed are important in evaluating the risk that the BPA is posing for the environment and humans. We will review the current literature for the reported byproducts from BPA and try to characterize them along with the chemical mechanisms that lead to these

byproducts formation. This will enable us to better understand the behavior of BPA during the adsorption onto iron oxides minerals.

1.4.5 STATISTICAL ANALYSIS AND MULTIVARIATE LINEAR REGRESSION

The statistical analysis of our data is very important in understanding the significant of our results. The data from Chapters 2, 3, and 4 would be analyzed using Statistical Package for Social Science 20 (SPSS20). Different statistical parameters would be evaluated such as analysis of variance (ANOVA Test), coefficient of determination (R²), significance interval (p), Pearson correlation coefficient, and multivariate linear regression (MLR). All of these statistical parameters would help us in finding the independent variables that are the most important to our adsorption, which can be used in the engineering of a removal system for BPA from aqueous solutions. The MLR models will help us to predict equilibrium concentrations of BPA using different parameters values that have the most statistical significance on the adsorption.

1.4.6 REMOVAL OF HYDROQUINONE FROM WATER USING IRON OXIDES ADSORBENTS

The degradation of BPA though different environmental processes or manmade engineer processes leads to the formation of hydroquinone (HQ) and benzoquinone (BQ). These two compounds could be found in the environment from BPA degradation and other organic compounds or by point source release. BQ is the product of HQ oxidation. Both of these organic compounds had been found as a result of many anthropogenic and environmental processes. The removal capacity of these compounds by our iron oxides adsorbents will be investigated. In the case of formation of these byproducts it is important to understand their fate during the adsorption onto iron oxides is important. The adsorption of hydroquinone and benzoquinone will be evaluated for a long term study of 1, 3, 7, 10, 14, 21, and 30 days. The effect of pH and ionic strength will be investigated also.

1.4.7 RISK ASSESSEMENT OF BPA EXPOSURE

BPA had been used in the food industry through the lining of the cans. Along with the pollution of many environmental media, the BPA ingestion by humans have many exposure routes. The current blood levels of BPA in humans had already been statistically associated with the cause of many diseases such as ovarian dysfunction, recurrent miscarriage, and endometrial hyperplasia. The ingestion of BPA through outdoor and indoor air, ingestion of water, dust, and different foods at environmental relevant concentration could pose a significant health risk for the humans. The risk assessment for the ingestion of BPA through these routes exposure will be evaluated for life period of 50 years from birth. The risk assessment will also concentrate on the subpopulation such as infants. Few studies had been done in evaluating the risk assessment of BPA on humans but had been limited to few exposure routes or only to a specific subpopulation. Our study will investigate the risk assessment of BPA exposure to many routes and different subpopulations. Through the current risk assessment study we will determine the subpopulation the is most in danger and the main exposure routes for the BPA ingestion. This will help us in evaluating the risk and also enable us in finding the potential precaution steps that could be taken in order to minimize the exposure risk to BPA.

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105

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CHAPTER II

KINETIC STUDY AND SEQUENTIAL BATCH EXTRACTION 2.1 INTRODUCTION

The widespread pollution with BPA all over the world, has a negative health effect on humans and the environment, and had been addressed more through different studies in the recent years. Different technologies such as oxidation using ozonation, chlorination, electrochemical oxidation, photooxidation, bioremediation, ultrasonication, ferrate (VI) and zero valent aluminum oxidation, and adsorption had been used to remove BPA from aqueous solutions as presented in Chapter 1. After reviewing all the technologies, it was found that adsorption was a very good technology that could be used efficiently and economically.

Adsorption is a technology that had been used in water treatment for many years and is relatively easier to operate than other new emerging technologies that could also remove BPA. The adsorption of BPA had been done using different adsorbent materials. Some of the adsorbent materials that had been used for the removal of BPA are activated carbon produced from different carbon base materials such as coal (Yoon et al., 2003, Choi et al., 2005), charcoal (Bautista-Toledo et al., 2005), wood (Yoon et al., 2003, Choi et al., 2005), coconut shell (Tsai et al., 2006a; Nakanishi et al., 2002; Choi et al., 2005; Matsushita et al., 2009), bituminous (Tsai et al., 2006b), almond shells (Bautista-Toledo et al., 2005), and wastepaper (Matsushita et al., 2009); carbon nano materials such as singlewalled carbon nanotube (SWCNT), multiwalled carbon nanotube (MWCNT) (Pan et al., 2008); polymeric adsorbents which were hypercrosslinked polymeric adsorbent (MN-200 and NDA-150), aminated polymeric adsorbents (MN-100 and MN-150) (Fan et al., 2011), β -cyclodextrin derivative (polyCD) (Kitaoka and Hayashi, 2002), CD-grafted chitosan (CD-P) (Aoki et al., 2003), chitosan-bearing β -cyclodextrin (CDC) (Aoki et al., 2004), magnetic non-imprinted polymers (MNIPs), and magnetic molecularly imprinted polymers (MMIPs) based on Fe_3O_4 (Guo et al., 2011); soils (Fent et al., 2003, Ying and Kookana, 2005); sediments (Ying et al., 2003; Sun et al., 2005;Zeng et al., 2006; Xu et al., 2008); minerals such as surfactant-modified zeolite (Dong et al., 2010), andesite, diatomaceous earth, titanium dioxide, activated bleach earth (Tsai et al., 2006a), commercial hydrophobic zeolite (Tsai et al., 2006b), geothite, montmorillonite, kaolinite (Shareef et al., 2006), polyethersulfone-organophilic montmorillonite hybrid particles (Cao et al., 2009), organic-inorganic mesoporous material (Ph-MS), mesoporous silica (Kim et al., 2011), and Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007). All of these different adsorbents had been found to be able to absorb BPA from aqueous solutions. The detail adsorption properties and parameters that each of these sorbents will be discussed in Chapter 3.

After reviewing the adsorption of the different adsorbents it was found that the adsorption of BPA onto soils with different mineral oxides showed to affect the absorbance (Li et al., 2009). The presence of Fe oxides for example, showed to facilitate the adsorption of BPA, while the presence of Mn oxides inhibited the adsorption. However, there was no research done on the adsorption of BPA onto mineral oxides alone. Iron oxides had been used for environmental remediation, medical field, biomedical, catalysis and diagnostics.

Iron oxides had been used in different fields because of their magnetic and physical/chemical properties. The use of iron oxides as pure materials or composite had been studied through different research studies. The iron oxides are minerals composed of iron oxygen. One of their main characteristic is their magnetic property. For example, ferromagnetism is a mechanism where materials, such as iron or iron oxides, form permanent magnets. Magnet is referred to a material that can be magnetized through an external magnetic field and would remain magnetized after the external magnetic field is removed and can be ferrimagnetic or ferromagnetic. In a ferrimagnetic material the magnetic moments of the atoms from sublattices are opposed and unequal, as a result a spontaneous magnetization remains. This is present in sublattices that consist of different materials or ions such as Fe^{2+} and Fe^{3+} . Another magnetic property that can exist in iron oxides is antiferromagnetism. A iron oxide that has antiferromagnetism has the magnetic moments of the atoms or molecules aligned in the opposite directions on different sublattices. This makes antiferromagnetic materials to have a nonzero net magnetization. Finally the last properties that characterize iron oxides are the Neel and Curie temperatures. The Curie temperature is the temperature above which a ferromagnetic or ferrimagnetic material becomes paramagnetic. The Neel temperature (T_N) is the temperature above which an antiferromagnetic material becomes paramagnetic. A material that is paramagnetic can only be attracted only when a magnetic field is applied.

The advancements in nanotechnology had started to have applications in environmental engineering, medicine, and electronic industry. New materials had been formed as composite using iron oxide nano particles that have found applications in large areas of industry. We can see some parameters from the production of iron oxide nano particles with their applications in Table 2.1. Magnetite had been used to bind on to carbon nanotubes (CNTs) in order to give the CNTs magnetic properties and other psychical/chemical properties that without the magnetite would lack. This was done in order to increase the applications of CNTs in industry. In Table 2.2 we can the binding method, nano-magnetic particle composite, average size, and the reagent used for the CNT surface modification. As we can see from Table 2.1 and 2.2 there are few studies done already using nano iron oxide particles and some of the applications that have been found.

Table 2.1	Nanoparticles and	d composites sum	mary of iron o	oxides: synthesis,
character	ization and applic	ations		

				Avr.		
Method	Iron Oxide	Composite	Particle Shane	Part.	Application	Reference
	OMUU		Shupe	Size (nm)		
Wet- Dispersion	Fe ₃ O ₄	Hexacyaoferate	Spherical	18	Removal of Cs	Ambashta et. al, 2003.
Reverse micelle method	Fe ₃ O ₄	Octenyltrimeth- oxysilane (OcTS)	Spherical	4-15	Supermagnetic properties of the composite	Ervithayasuporn et. al, 2009.
Co- Precipitaion / chemical binding	Fe ₃ O ₄	Sodium dodecyl sulfate (SDS)	Spherical	8-12	Adsorption of porcine pancrease lipase (PPL)	Lee et. al, 2009.
Liquid- liquid phase transfer	Fe ₃ O ₄	None	Rectangular	42.2	None yet established	Bakar et. al, 2007.
Chemical binding	γ-Fe ₂ O ₃	poly-L-cysteine (PLCysn) (n=20)	Round (core)	5-25 Core	Removal of As(III), Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II)	White et. al, 2009.
Chemical binding (coated)	Fe ₃ O ₄	Cetyltrimet- hyla-mmonium bromide (CTAB)	Spherical	20-80	Removal of amaranth (AM)	Zargar et. al, 2009.
Hard- templating	γ-Fe ₂ O ₃	Sodium dodecyl sulfate (SDS)	Spherical	10	Removal of Cr(VI)	Wang et. al, 2009b.
Solvothermal	Fe ₃ O ₄	None	Hexagonal	20-100	High ferromagnetism	Zhang et. al, 2009d.
Evaporation Induced Self Asembly (EISA)	γ-Fe ₂ O ₃	SiO2	Mesoporous Plate	N.A.	Drug Targeting	Wang et. al, 2008.

Mixed Hemimicelles Solid-Phase Extraction	Fe ₃ O ₄	Alumina (Al2O3) / surface modified Sodium dodecyl sulfate (SDS)	Spherical	10-100	Trimethoprim (TMP) Detection	Sun et. al, 2009.
Solvothermal Method	Fe ₃ O ₄	None	Spherical	70	Anticancer Drug delivery of doxorubicin (Dox)	Guo et. al, 2009.
Hydrothermal and calcination	Fe ₃ O ₄	None	Hollow Spherical	220-300	Possible use as an adsorbent	Huang et. al, 2005.

Table 2.2	Nano-magnetite	particles or com	posites binding on	nto carbon nan	otubes (CNTs):

Binding Method	Nanomagnetic Particle / Composite	Surface Mod. Agent for CNT	Reference
Physical Adsorption	Magnetite- Polyacrylamide (Mag- PAAm) particles	H_2SO_4 and HNO_3 (3M : 1M) For creation of addition of functional group (-COOH)	Ko et. al, 2009.
Covalent Interaction	Fe_3O_4 nanoparticles Average Size = 50-200 nm	Polyethyleneimine (PEI)	Zhang et. al, 2009b.
Covalent Interaction	Fe_3O_4 MNPS (8 nm) , and Amineterminated MNP (MNP-NH_2).	HNO_3 for the formation oh functional group (-COOH) ; and $SOCl_2$ for the functional group (-COCl)	Xu et. al, 2008.
Hydrothermal Process under the presence of Hydrazine as a mineralizer	Fe_3O_4 nanoparticles Average Size = 20-70 nm	Potassium Persulfate (KPS) form. of func. group s potassium carboxylate (-COOK), carbonyl (-C=O) and hydroxyl (-C-OH).	Zhang et. al, 2009a.
Self Asembly	Fe_3O_4 nanobeads Average Size = 180 nm; The Fe3O4 nanoparticles Average Size = 5.8 nm	HNO ₃	Jia et. al, 2007.
Thermal decomposition	Fe ₃ O ₄ MNPS (6 nm)	Diethylene glycol (DEG) was used as a solvent medium	Wang et. al, 2009a.

Three types of iron oxides had been selected for the investigation of BPA adsorption. Two different magnetite denoted as M1 and M2, and one hematite denoted as H. Magnetite has the mineral chemical formula as iron(II, III) or Fe_3O_4 , with the common chemical name as ferrous-oxide (Ko et al., 2009). Other formula writing for magnetite is $FeO•Fe_2O_3$, which represents the one part iron oxide (FeO) and one part hematite (Fe_2O_3). The Curie temperature of magnetite is 858 K. The synthesis of magnetite nanoparticles have found applications in various fields such as biomedical-ferrimagnetic bioglass ceramics (FBC) that were used for the hypothermic treatment of bone cancer (Ikenaga et al. 1993, Ohura et al., 1991, Kokubo et al., 1992), adsorbent (Bakar et al., 2007), catalysis (Takenaka et al., 2004), passivation coatings (Ambashtaa et al., 2003), medicine, diagnostics, molecular biology, and bioinorganic chemistry.

Hematite is the mineral form of Fe(III) oxide with the chemical formula as (Fe₂O₃ or α -Fe₂O₃). The formation of hematite is done by pseudomorphosis, where the appearance and dimensions of magnetite remains the same, but through substitution process the magnetite is replaced by hematite. The production of hematite could be possible without water under volcanic activity. Hematite is antiferromagnetic with no net magnetic moment under the temperature of 260 K. The Neel temperature of hematite is 948 K.

In order to evaluate the adsorption process any model used should take into consideration the mass balance and for the isothermal system and the equilibrium adsorption (Tsai et al., 2006a, 2006b). During the adsorption process the transport stages such as external diffusion, adsorption process, and internal diffusion take place. Different theoretical models and equations that had been proposed to describe adsorption had been based on mass balance, initial boundary conditions, and pore diffusion. The use of these equations is complicated, because it requires detail information about the characteristics of the adsorbate and absorbent. These data are usually very hard to obtain and time consuming. Two of the most frequently applied models for adsorption kinetics are pseudo first-order, and pseudo second-order models (Ho et al., 2006, Tsai et al., 2003a, 2003b). These two models should be applied with great carefulness (Pan and Xing, 2010). The equation that is very often used for first order kinetics it is the equation that Lagergren proposed in 1898. The Lagergren equation was the first developed equation that described the adsorption of liquid-solid systems that was based on solid capacity (Cao et al., 2009). The pseudo first-order kinetics equation is presented in equation 1(Sui et al., 2011):

$$\ln\frac{q_e - q_t}{q_e} = -k_1 t \tag{1}$$

where, k_1 (1/min) is the pseudo first-order constant, and q_e and q_t are the amount (mg/g) of the BPA adsorbed at equilibrium and at time t, respectively.

The second model used for the investigation of kinetics studies was the pseudo secondorder model. The pseudo second-order model showed to be a better fit for most cases than the pseudo first-order model (Ho et al., 2000, Ho et al., 2001, Ho and Chiang, 2001, Wu et al., 2001). The pseudo second-order kinetics is based on the hypothesis that the adsorption rate is controlled by the chemical adsorption (Ho and McKay, 1999). The pseudo second-order equation is expressed by equation 2 (Ho and McKay, 1998, 1999):

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{2}$$

where, k_2 is the pseudo second-order adsorption constant (g/mg min), and q_e and q_t are the amount (mg/g) of the BPA adsorbed at equilibrium and at time t, respectively. By integrating
equation 2 using the following boundary conditions as t=0 to t=t and $q_t=0$ to $q_t=q_t$ results in the following equation 3:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \tag{3}$$

By rearranging equation 3 we obtained the linear form of the pseudo second-order reaction as given by:

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \left(\frac{1}{q_e}\right)t \tag{4}$$

where, k_2 is the rate constant of pseudo second-order adsorption (g/mg-min) and q_e and q_t are the amount (mg/g) of the BPA adsorbed at equilibrium and at time t, respectively. This equation is very useful because the parameters k_2 (g/mg•min) and q_e can be obtained directly from the graph when plotting t/qt against t. We can calculate the equilibrium concentration (C_e) using mass balance. Another important parameter is the half life, or the half of the adsorption time that is required by the adsorbent to reduce the initial concentration of BPA to half at equilibrium. The conditions are such that $q_t = q_e/2$ at $t = t_{1/2}$ and is given by equation 5 (Pan et al., 2010):

$$t_{1/2} = \frac{1}{k_2 q_e}$$
(5)

Finally one last parameter that could be obtained to understand the adsorption kinetics of an adsorbent is the initial adsorption rate h. The initial adsorption rate can be obtained by appling boundary conditions to equation 2 as t = 0 and $q_t = 0$, and using q_e from the fitting of equation 3 we obtained the following equation 6 (Tsai et al., 2006a):

$$h = k_2 q_e^2 \tag{6}$$

Using one or more equations from the equations 1 to 6 described above the adsorption of BPA on mesoporous carbon (Sui et al., 2011), activated carbon (Aoki et al., 2003, Tsai et al., 2006a, Liu et al., 2009), carbon nanomaterials (Pan et al., 2010), magnetic molecularly imprinted polymers (MMIPs) (Guo et al., 2011), cyclodextrins grafted chitosan (CD-P) (Aoki et al. 2003), mesoporous silica (Kim et al., 2011), polyethersulfone(PES) - organophilic montmorillonite (OMMT) hybrid particles (Cao et al., 2009), hydrophobic zeolite (Tsai et al., 2006b), and Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007) had been investigated.

Depending on the time interval studied, the time units of the equations 1 through 6 could be in minutes, hours or days. If the adsorption happens fast over a period of short time, because the adsorbent is strong, the kinetics parameters would have units in minutes or seconds. If the adsorbent is not as strong and will take long period of time to adsorb, then the unit of time could be in hours of days. Most of the studies that were mentioned above followed the pseudo secondorder better and had a fast adsorption as a result having the units of time in minutes.

2.1.1 KINETIC STUDIES DONE ON CARBONACEOUS ADSORBENT MATERIALS

The kinetics done on carbonaceous adsorbent materials such as mesoporous carbon, activated carbon, and nonmaterial had units of time of minutes and hours. Sui et al., 2011 used different AC, found that at high concentration of BPA (25mg/L) a mesoporous carbon adsorbent (CMK-3) prepared from hexagonal SBA-15 mesoporous silica and carbonized at 900 ^oC performed better than a commercial powdered activated carbon (PAC). It is important to note that the CMK-3 had a BET surface area of 920 m²/g compared to 780 m²/g of that of PAC. The study found that for both carbonaceous materials the adsorption was fitted very well by a pseudo

second-order model. The pseudo second-order parameters were: calculated qe (mg/g) equal to 180, 160, k₂ (g/mg•min) equal to 0.00049, 0.00015, t_{1/2} (min) equal to 11.3, 40.7, and h (mg/g•min) equal to 15.9 and 4 for CMK-3 and PAC, respectively. These results were lower when compared to two commercial granular activated carbons from coconut based (PCB) and bituminous coal based (BPL). The kinetics study did follow a pseudo second-order model, but the adsorption was stronger. The pseudo second-order parameters were: calculated $q_{e}\ (mg/g)$ equal to 78.13, 78.13, k₂ (g/mg•min) equal to 0.08, 0.23, t_{1/2} (min) equal to 0.16, 0.05, and h (mg/g•min) equal to 476 and 1429 for PCB and BPL, respectively. It is important to note that the BET surface area was not a lot larger that of CMK-3 with PCB equal to 916 (m^2/g) and BPL to 1060 (m²/g). However, these two commercial granulated activated carbons had a initial adsorption much higher that of CMK-3 and the half time was a lot shorter. The adsorption kinetics experiments for the PCB and BPL were conducted at initial BPA concentrations of 20 mg/L, with an adsorbent dosage of 0.5g to 2 L at an agitation rate of 400 rpm with a pH 7.0 at a temperature of 25 °C. We can conclude from the information given that the surface of the adsorbent and based material for the carbon played a significant role in the adsorption of BPA.

Other study used different types of activated carbon which required a longer time for adsorption equilibrium. The units of time in the pseudo second-order model it is hours compare to minutes to the other studies presented earlier. Two types of commercial activated carbons were used by Liu et al., 2009, the WV A1100 (Westaco Corp. America) and F400 (Calgon Corp. America) and denoted as W20 and F20. For surface modification the activated carbons were treated using boiling nitric acid (HNO₃) at 368K, with constant temperature for 6h. The new treated activated carbons were denoted as W20A and F20A. Some of the new activated carbons were then treated under thermal treatment with a flow of nitrogen gas (N₂) and the new

compounds were named as W20N and F20N. The adsorption kinetics experiments were done using 10 mg of activated carbon in a BPA solution of 60 mg/L containing 1 mmol/L phosphate buffer solution to obtain a pH of 7.0, and agitated at 150 rpm in a thermostatic bath at 25 °C (298 K). Two main transformations happened to both activated carbons. First, the treatment with HNO₃ decreased the BET surface area for W20 and F20, with the highest decrease for W20. The surface area decreased for W20 from 1,777 to 1.27 and for F20 from 996 to 900. After the N_2 treatment the area increased back for W20 to 1,760 and F20 to 1,000. Second, the treatment with HNO₃ increased the presence of hydroxyl group and carboxyl group (mmol/g) for W20 from 0.07 to 0.008 and 0.28 to 0.74 and for F20 from 0 to 0.35 and 0.002 to 1.57 for hydroxyl group and carboxyl group, respectively. After the second treatment with N₂, the W20 hydroxyl group remained the same as 0.08 mmol/g and for the carboxyl group went to 0. For the F20 adsorbent both groups went to zero. For the most part, the adsorption mechanisms for organic aromatic compounds on activated carbon, is based on the dispersion interaction that is done between the electrons from the aromatic ring from the adsorbate and those from the basal plane of the activated carbon. The increase or creation of hydroxyl and carboxyl groups on the surface of the adsorbent made the electrons to withdraw from the graphene layer and increased the activated carbons affinity towards water (Liu et al., 2009). The new groups made possible the formation of water molecular clusters through hydrogen bonding on the surface of the activated carbons. These clusters formation inhibited the adsorption of BPA on to the activated carbons. The data were fitted using pseudo first-order and pseudo second-order models. The best fit was that of pseudo second-order model having higher correlation values for R², and better agreement between the experimental qe values and calculated qe values. The pseudo second-order calculated parameters were found to be: qe (mg/g) equal to 382.12, 59.17, 432.34, k2 (g/mg•h) equal to

0.62, 2.31, 0.61, $t_{1/2}$ (h) equal to 4.22, 7.31, 3.81 and h (mg/g•h) equal to 90.65, 8.09, 113.56 for W20, W20A, and W20N, respectively. For the other activated carbon the pseudo second-order parameters were calculated and found to be q_e (mg/g) equal to 333.33, 119.05, 232.56, k_2 (g/mg•h) equal to 0.31, 0.55, 0.35, $t_{1/2}$ (h) equal to 9.77, 15.18, 12.37 and h (mg/g•h) equal to 34.13, 7.85, 18.80 for F20, F20A, and F20N, respectively.

A study was done also to see the difference between different carbon nano materials such as single walled carbon nano tube (SWCNT) with outer diameters of 1-2nm, multi walled carbon nano tube (MWCNT15) with outer diameters of 8-15nm, buckminsterfullerene fullerene (nC_{60}), and activated carbon (AC) based on wood charcoal. The BET surface area m²/g was found to be 541, 174, 7.21, and 850 for SWCNT, MWCNT15, Fullerene, and AC, respectively. The BPA concentrations used were 0.15, 2.0, and 50 mg/L, with a solid/liquid (w/v) ratios for fullerene was 1:100-1:200, for CNTs and AC 1:20,000 - 1:120,000. From the study was found that the best way to describe the adsorption of BPA onto these carbonaceous materials was by using a pseudo second-order model. Braida et al., 2003 reported that the adsorption would be inhibited by high loading of adsorbate for the AC. In the current study this was found to not be the case. However, the AC strong adsorption sites are usually attributed to the inner pores. As a result the availability of the inner pores should be a controlling factor for the adsorption rate. At higher concentrations the rate would decrease, because the availability of inner pores would also decrease (Levya-Ramos et al., 2007). This was found to be true for the AC when the concentration of BPA increased from 0.15 to 2 mg/L. The study looked at the equilibrium qe (mg/Kg) parameter and the pseudo second-order rate constant k₂. For the Fullerene the equilibrium adsorption capacity qe (mg/Kg) was 6.16, 91.4, 576, and k₂ (1/h) 0.824, 0.572, and 0.197 for 0.15, 2, and 50 mg/L, respectively. For the MWCNT the equilibrium adsorption capacity $q_e (mg/Kg)$ was 2.23x10³, 8.12x10³, 99.9 x10³, and $k_2 (1/h) 0.955$, 0.647, and 0.492 for 0.15, 2, and 50 mg/L, respectively. For the SWCNT the equilibrium adsorption capacity $q_e (mg/Kg)$ was $5.39x10^4$, $7.36x10^4$, $36.3x10^4$, and $k_2 (1/h) 1.076$, 0.716, and 0.824 for 0.15, 2, and 50 mg/L, respectively. For the AC the equilibrium adsorption capacity $q_e (mg/Kg)$ was $0.123x10^5$, $2.03x10^5$, $4.89x10^5$, and $k_2 (1/h) 2.728$, 0.391, and 0.940 for 0.15, 2, and 50 mg/L, respectively. We can see for both Fullerene and MWCNT that the rate decreased as the concentration of BPA increased from 0.15 to 50 mg/L.

2.1.2 KINETIC STUDIES DONE ON MINERALS

The adsorption of BPA had been found to be possible onto inorganic adsorbents such as minerals. Different raw minerals or modified trough different process had been used for the adsorption of BPA. Kinetics studies had been conducted on minerals such as andesite, diatomaceous earth, titanium dioxide, activated bleach earth (Tsai et al., 2006a), commercial hydrophobic zeolite (Tsai et al., 2006b), polyethersulfone-organophilic montmorillonite hybrid particles (Cao et al., 2009), organic-inorganic mesoporous material (Ph-MS), mesoporous silica (Kim et al., 2011), and Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007).

The BET surface area (m²/g) of the minerals had been reported as follows: andesite 2.7, diatomaceous earth 3.8, titanium dioxide 50.1, activated bleach earth 257 (Tsai et al., 2006a), hydrophobic zeolite 504.5 (Tsai et al., 2006b), Fe(III)/Cr(III) hydroxide 156, mesaporous silica (MCM-41) 1030, and organic-inorganic hybrid mesoporous material (Ph-MS) 750. For the polyethersulfone(PES) - organophilic montmorillonite (OMMT) hybrid particles with mass ratios of PES to OMMT of 1:0, 1:1, 1:2.5, 1:3, and 1:3.5, which were denoted as PO, PO₁, PO₂, PO₃, and PO₄ the BET surface area was not reported. The pore volume (PV) (cm³/g) was

calculated based on the formulas presented in Deng et al., 2007. From the data presented in Deng et al., 2007 a linear relationship between the pore volume and BET surface area was established for the polyethersulfone (PES)-activated carbon (AC) hybrid particles with a correlation R^2 of 0.9595. The linear equation was used to estimate the BET surface area for the PO₁ to PO₄ hybrid particles. The BET surface area (m^2/g) was estimated to be equal to 167, 184, 173, and 183 for PO, PO₁, PO₂, PO₃, and PO₄, respectively.

In all of the studies presented earlier, it was found that the adsorption followed better for four studies the pseudo second-order model, the study that used the Fe(III)/Cr(III) hydroxide for most of the initial concentrations the second-order model was better or at least as good as the first-order model. We can conclude that for the adsorption of BPA onto minerals the pseudo second-order model was a better fit just like in the case of carbonaceous materials. The minerals of andesite, diatomaceous earth, titanium dioxide, and activated bleach earth kinetics studies were done using a BPA initial concentration of 20 mg/L, absorbance dosage of 0.5g:2L, pH 7.0, agitation rate of 400 rpm, and temperature of 25 ^oC. The pseudo second order parameters were as follows: equilibrium adsorption capacity q_e (mg/g) was 0.53, 0.73, 0.33, 0.86 the k_2 (1/min) 12.0, 7.46, 48.01, 4.02, the $t_{1/2}$ (min) 0.16, 0.18, 0.06, 0.29, the h (mg/g•min) 3.36, 3.95, 5.23, 2.98 for andesite, diatomaceous earth, titanium dioxide, and activated bleach earth, respectively. We can see that there was not a very good correlation of the BET surface area to the adsorption capacity of the adsorbent.

For the Fe(III)/Cr(III) hydroxide kinetic study a 500 mg to 50 mL of solution was used at a pH of 6.5, temperature 35 0 C, and BPA concentrations of 10, 20, 30, 40, and 50 mg/L. The equilibrium time for 10 to 40 mg/L was 80 minutes and 100 minutes for 50 mg/L. The pseudo second-order model for all the initial concentrations had a better fit than the first-order and

120

Elovich model. The second-order parameters for Fe(III)/Cr(III) hydroxide were: the equilibrium adsorption capacity q_e (mg/g) 0.409, 0.750, 1.081, 1.541, 1.667 and k_2 (g/mg•min) 0.693, 0.253, 0.141, 0.077, and 0.0655 for 10, 20, 30, 40, and 50 mg/L, respectively.

The kinetic adsorption experiments were conducted using a 0.1g of sorbent to 20 mL of aqueous solution with different BPA concentrations of 100, 150, 200, and 240 μ mol/L at 25 ^oC. For the polyethersulfone (PES) - organophilic montmorillonite (OMMT) hybrid particles PO₁, PO₂, PO₃, and PO₄. The pseudo second-order parameters were as follows: equilibrium adsorption capacity q_e (mg/g) was 20.83, 21.41, 22.83, 29.59 and the k₂ (g/mg•min) 0.00388, 0.00387, 0.00464, and 0.00221 for PO₁, PO₂, PO₃, and PO₄, respectively. The study also evaluated the relationship between the adsorption amount and the sorption time using an equation presented by Manohar et al., 2006. The adsorption of BPA onto PES-OMMT was found to better fit a pseudo second-order model. The intraparticular mass transfer diffusion was expected to be the rate limiting factor.

The adsorption of BPA onto organic-inorganic phenyl-functionalize mesoporous silica (Ph-MS) and mesoporous silica (MCM-41) followed a pseudo second-order also. The synthesis of the Ph-MS was done in the laboratory. The addition of 50 mg of sorbent to 250 mL of aqueous solution with BPA concentration of 20 mg/L, shaking at 200 rpm at 25 0 C for 6h and at a pH of 6.2 to 7.2 found to follow a second-order adsorption. The pseudo second-order parameters were as follows: equilibrium adsorption capacity q_e (mg/g) was 1.91, 42.2 and the k₂ (g/mg•min) 0.0336, and 0.0037 for MCM-41, and Ph-MS, respectively. The high affinity of BPA towards the Ph-MS was believed to be due to the hydrophilic hydroxyl groups and hydrophobic

phenyl groups. These two groups could lead to strong hydrogen bonding with the hydroxyl groups and strong π - π interactions with the benzene rings of the BPA.

Finally the BPA adsorption kinetics studies were conducted onto Y-type hydrophobic zeolite. The adsorption affinity of BPA on to the zeolite found to be stronger than other minerals such as andesite, diatomaceous earth, titanium dioxide, and activated bleach earth. The adsorption of BPA on the zeolite was found to follow a pseudo second-order model. The kinetic experiments were conducted using a 1g of sorbent with average particle size of 0.223mm to 2 L of aqueous solution with BPA concentrations of 10 to 90 mg/L, agitation speed of 400 rpm at 25 $^{\circ}$ C for 2h at pH 7.0. The pseudo second-order parameters were as follows: equilibrium adsorption capacity q_e (mg/g) was 19.01, 38.91, 57.47, 80.56, 92.59, 107.53, 116.28, 123.46, 125.0 the k₂ (g/mg•min) 1.107, 0.315, 0.050, 0.017, 0.008, 0.005, 0.004, 0.004, 0.002 the t_{1/2} (min) 0.05, 0.08, 0.34, 0.73, 1.31, 1.99, 2.19, 2.19, 3.93 for 10, 20, 30, 40, 50, 60, 70, 80, and 90 mg/L, respectively. It was concluded from the study that the adsorption was due to the London force mechanism, and that the adsorption depended greatly on the adsorption dosage and initial BPA concentrations and the half time (t_{1/2}) increased from 0.05 to 3.93 minutes.

2.1.3 KINETIC STUDIES DONE ON POLYMERS

Guo et al., 2011 was able to synthesize magnetic molecularly imprinted polymers (MMIPs) and magnetic non-template imprinted polymers (MNIPs) that were based on kaolinite and magnetite (KLT/Fe₃O₄). The kaolinite/Fe₃O₄ serves as a support and functional monomer. The KLT/Fe₃O₄ modification was done in two steps according to Gai et al., 2010 and Zhang et al., 2009c. The BET surface area (m^2/g) was 142.90 and 150.80 having a average particle size of

3.16 μ m and 3.29 μ m for MMIPs and MNIPs, respectively. The kinetics studies for the lab created polymeric adsorbents MMIPs and MNIPs was done in a solution of 100 mg/L BPA at a pH 3.0 with a agitation speed of 300 rpm, for a duration of 12h, and with a adsorbent ratio to solution at 0.01g to 10mL at 25 ^oC. The equilibrium time was found to be 360 minutes and 640 minutes for MMIPs and MNIPs, respectively. Both the MMIPs and MNIPs followed a pseudo-second order kinetics model. The pseudo second-order parameters were as follows: equilibrium adsorption capacity q_e (mg/g) was 46.73, 60.61, the k₂ (g/mg•min) 7.202, 9.836, the t_{1/2} (min) 1.572, 3.612 the h (mg/g•min) 29.71, 16.78 for MNIPs and MMIPs, respectively. From the data we can see that the MMIPs had higher adsorption capacity and rate constant, but had a slower adsorption and smaller initial adsorption than that of MNIPs. However, as contact time increased the MMIPs manage to have a smaller equilibrium time than MNIPs as stated earlier.

2.2 RESEARCH OBJECTIVE

The objective of the research presented in Chapter 2 was done in order to establish the adsorption kinetics of all the mineral adsorbents like the Hematite (H), and Magnetite (M1 and M2). The adsorption kinetics study determines the initial adsorption rate (h), equilibrium time of adsorption (t), equilibrium capacity (q_e), adsorption rate constant (k_2), and half life of adsorption ($t_{1/2}$). All these parameters help us to better understand the behavior of the adsorbent, the limiting steps of the adsorption, and possible mechanisms of adsorption. The kinetics experiments were done using two concentrations of BPA (1.2 mg/L and 10 mg/L) at a fixed adsorbent to aqueous solution ratio of 5g to 50 mL for a period of 30 days.

In the second part of the study in this chapter, the effect of pH was investigated. The pH of the solution is a very important parameter and many times a limiting one. The pH of the

solution could increase or decrease the adsorption, depending on the adsorbent and adsorbate. Many studies that were done on the adsorption of BPA onto different adsorbents also studied the effect of pH as well. Some of the adsorbents that were also investigated for the effect of pH, were mesoporous carbon (Sui et al., 2011), activated carbon (Tsai et al., 2006a, Liu et al., 2009, Toledo et al., 2005, Asakura and Matsubo, 2009), Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007), Y-type hydrophobic zeolite (Tsai et al., 2006b), magnetic molecularly polymers (MMIPs) and magnetic non-template imprinted polymers (MNIPs) (Guo et al., 2011), β -cyclodextrin derivative (polyCD) (Kitaoka and Hayashi, 2002), hypercrosslinked polymers (Fan et al., 2011), surfactant-modified zeolite (Dong et al., 2010), geothite, montmorillonite, kaolinite (Shareef et al., 2006), marine sediments (Xu et al., 2008), and river sediment (Zeng et al., 2006, Li et al., 2007). The effect of pH in this chapter was investigated in order to observe any effect on the adsorption for all three adsorbents H, M1, and M2. The most effective adsorbent was than further investigated in Chapter 3. In Chapter 4 the extensive effect of pH was investigated along with other parameters such as ionic strength.

Finally in the last part of Chapter 2 the extraction of sorbed BPA from the adsorbent was investigated. The extraction of BPA may be obtained from the mass balance. If extraction of the BPA from the adsorbent is possible the process could be used on BPA as a regeneration tool for the adsorbent. If the adsorbent could be washed and the BPA removed, then that adsorbent could be reused for adsorption. With an extractant our main focus of the study was to investigate the mass balance, because we could easily regenerate the adsorbent using a high temperature furnace. If the BPA was present on the adsorbent surface the high temperature from the furnace would be able to remove it. This process would not produce byproducts like in the case of other adsorbents. The extraction results presented in Chapter 2 are for the solvents that we had a

successful extraction. However, many solvents and techniques have been investigated for the adsorption of BPA.

2.3 MATERIALS AND METHODS

2.3.1 CHEMICALS

All the chemicals used for these experiments are presented in Table 3.

Chemical	Specification	Source		
Methyl <i>tert</i> -butyl ether (MTBE)	HPLC grade	Fisher Chemicals, Fairlawn, NJ		
Acetone	Certified ACS	Fisher Chemicals, Fairlawn, NJ		
6N Hudrochloric A aid (HCl)	ACS Reagent	RICCA Chemical Company,		
on Hydrochione Acid (HCI)	grade	Arlington, TX		
Bisphenol A (BPA)	\geq 97 %	Sigma-Aldrich, St.Louis, MO		
Hematite (H) Fe_2O_3 ,	\leq 5 micron and \geq	Sigma-Aldrich, St.Louis, MO		
	99%			
Magnetite (M1) Fe ₃ O ₄ ,	Laboratory Grade	Fisher Chemicals, Fairlawn, NJ		
Magnetite (M2) Fe ₃ O ₄ ,	325 Mesh Powder	Alfa Aesar, Ward Hill, MA		

Table 2.3 Chemicals

2.3.2 TIME STUDY EXPERIMENTS

The time study experiments were done for two separate BPA concentrations of 1.2 mg/L and 10 mg/L. All the three adsorbents H, M1, and M2 were used with a solid to solution ratio of 5g:50mL. The experiments were carried out with deionized water (DI) in 125 mL serum bottles. A blank bottle with no adsorbent was also used. The purpose of the blank was to determine if any BPA transferred from the water phase to the air phase or was adsorbed to the glass walls of the serum bottle. After the addition of water, the serum bottles were capped with butyl rubber septa and crimped with aluminum seals. The serum bottles were than shaken and placed in a rotating tumbler at 16 rounds per minute (rpm) in the dark for mixing at 25 ^oC. The experiments were carried out for a period of 1, 3, 7, 10, 14, 21, and 30 days. All experiments were carried out

in triplicate. The data were fitted using the assumption that follows a completely mixed batch reactor (CMBR) as a results the reactions equations for reaction order of zero, first and second order were obtained and are presented in equations 7, 8, and 9, respectively (Crittenden, 2005).

$$C = C_0 - kt 7$$

$$C = C_0 e^{-tk} 8$$

$$\frac{1}{C} = \frac{1}{C_0} + kt 9$$

where, C is the final BPA concentration (mg/L), C_0 is the initial BPA concentration (mg/L), t is the time of adsorption (days), and k is the adsorption rate constant having units depending on the order of the equation, with units of mole/L•s, s⁻¹ and L/ mole•s for zero , first and second order, respectively. To obtain a linear relationship the zero order was plotted as C vs time, first order as ln(C) vs time, and second order as 1/C vs time. For all plots, the slope was equal to k. The data were analyzed using Statistical Package for the Social Sciences (SPSS) and parameters such as coefficient of determination R^2 and statistical significance value p were obtained.

2.3.2.1 ROUTINE ANALYSIS

After removal of serum bottles from the rotating tumbler, 50mL of the sample was transferred from the bottle into a 50mL Teflon centrifuge tube, and centrifuged for 10 minutes at 7100 rpm using a Eppendroft centrifuge 5810R. The solution was then transferred in two different vials. Approximately 15 mL of the solution was transferred into a 20 mL glass vial, and the rest in a 40 mL glass vial. The 20 mL vial was used or the measurement of total dissolved solids and pH, and the 40 mL vial was used for the BPA analysis.

2.3.2.2 TDS AND pH ANALYSIS

The analysis of total dissolve solids (TDS) was done using Orion conductivity meter model 150 with an Orion conductivity cell 013005D and the pH analysis was performed using Thermo Orion pH/mV/temperature meter 720 using an Orion comb. pH probe model 915600. The instrument was calibrated for the pH using pH standards of 4.0, 7.0, and 10.0. The calibration of TDS was done using TDS standards with a conductivity of 1413µs and 12.9 ms.

2.3.2.3 LIQUID-LIQUID EXTRACTION (LLE)

Exactly 10 mL of samples were transferred from the 40 mL vial or from the diluted sample from the volumetric flask into a 15 mL glass test tube. After the water sample was transferred, a volume of 75 μ L of 2,4,6-tribromophenol (TBP) from a stock solution of 1,000 ppm prepared in acetone was added using a 250 μ L syringe. After adding one drop of concentrated hydrochloric acid (HCl) into the test tube, the test tube was then closed and shaken gently twice. After the shaking of test tubes, 2 mL of methyl *tert*-butyl ether (MTBE) were added. The test tube was then shaken for 30 seconds vigorously and then followed by 2-3 minutes of slow mixing. After the mixing, enough time was allowed for the two phase to separate, and then about 1 mL of the MTBE from the upper phase was pipetted using a 1 mL Eppendorf pipetter into a 2 mL gas chromatography (GC) vial.

2.3.2.4 BPA ANALYSIS

The MTBE sample obtained from the LLE step was analyzed on a Agilent Model 6890 GC. The GC was equipped with a flame ionization detector (FID). The injection was done using an auto sampler by direct injection of 1.0 μ L of MTBE sample at an inlet temperature of 250 °C, while the detector temperature was maintained at 300 °C. For the separation of BPA and TBP, a DB-5 (J&W) widebore capillary GC column with dimensions 30m x 320 μ m x 0.25 μ m was

used. The oven temperature in the beginning was set at 100 $^{\circ}$ C. The temperature was then ramped from 100 $^{\circ}$ C to 265 $^{\circ}$ C at 20 $^{\circ}$ C/min and held at 265 $^{\circ}$ C for 1 minute. Helium (ultra high purity), was the carrier gas with a flow rate of 5.8 mL/min and at an inlet pressure of 25 psi. The other gases used were dry grade air, hydrogen (H₂), and the makeup gas nitrogen (N₂). The flow rates for the other gases were 400 mL/min, 10 mL/min, and 35 mL/min, respectively.

The BPA was identified by the retention time from the BPA standard calibration that was prepared in MTBE. The BPA calibration was done using an internal standard calibration with the BPA concentrations of 0.1, 0.2, 0.5, and 1 mg/L. TBP was used as an internal standard with a concentration of 7.5 mg/L.

2.3.3 EFFECT OF pH AND BATCH EXTRACTIONS

To study the effect of pH on adsorption, all three of the adsorbents H, M1, and M2 were used. The adsorbent to the solution of deionized water was 5g:50 mL (DI) in a 125 mL serum bottle with a BPA concentration of 1.2 mg/L. Just like in the kinetics study, there was a blank system with no adsorbent added, in order to determine if there was any BPA escaped from the water phase to the air phase or adsorbed to the serum bottle glass walls. After the addition of water, the serum bottles were capped with butyl rubber septa, and crimped with aluminum seals. The serum bottles were than shaken and placed in a rotating tumbler at 16 rotation per minute (rpm) in the dark for mixing at 25 ⁰C. The experiments were conducted for 1 day. The different pHs used were as follows: 2, 4, and 6 for adsorbent M1, 2, 4, 6, 10, and 12 for adsorbent M2, and 2, 2.5, 3, 3.5, 4, 5.6, 10, and 12 for adsorbent H. All the experiments were performed in triplicate.

The routine, pH, TDS, and BPA analysis, as well as LLE were conducted for the most part the same as for the kinetics experiments. The difference was for the BPA analysis of the extracts and the batch extraction of BPA from the adsorbent.

For batch extraction of adsorbent the 5g of adsorbent was transferred from the 50mL Teflon centrifuge tube after centrifugation for 10 minutes at 7100 rpm using a Eppendroft centrifuge 5810 R. The 5g adsorbent remaining in the 50 mL Teflon tube was mixed with 20 mL of DI water at pH 3. The Teflon tubes were then gently shaken until the adsorbent mixed well with the DI water and placed in a rotating tumbler at 16 rpm in the dark for mixing at 25 °C for duration of 24 hours. After 24 hours the Teflon tubes were then centrifuged at 7100 rpm for 10 minutes and the water was transferred into a 20 mL glass vial. After the centrifugation, 25 mL of acetone was then added to the adsorbent, after which gently shaken until the adsorbent mixed well with the acetone and placed in a rotating tumbler at 16 rpm in the dark for mixing at 25 °C for for a duration of 24 hours. The Teflon tubes were then centrifuged for 5 minutes at 6400 rpm and the acetone was transferred in a 20 mL glass vial and stored at 4 °C after it was injected in GC for BPA analysis.

The acetone extracts were analyzed using a BPA calibration with an internal standard calibration and BPA concentrations of 0.2, 0.4, 0.8, 1, and 2 mg/L. TBP was used as an internal standard with a concentration of 40 ppm. The acetone extracts and calibration samples were diluted in a volumetric flask in acetone and transferred into a 2 mL gas chromatography (GC) vials. The extract DI extracts were injected using the BPA calibration was done using an internal standard calibration with the BPA concentrations of 0.1, 0.2, 0.5, and 1 mg/L. TBP was used as an internal standard with a concentration of 7.5 mg/L.

2.4 RESULTS AND DISCUSSION

In the first part of the study, kinetics experiments were done, using a 1.2 mg/L BPA concentration as presented earlier in the chapter. From Figure 2.1 (a) through (c) we can see the total BPA concentration remaining in the aqueous solution and adsorbent after a period of 30 days for all three adsorbents. From the graphs we can see that magnetite M2 had the best mass balance for BPA. The hematite H had a drop to 1.03mg/L in the first day, which remained mostly constant and reached 0.94 mg/L after 30 days. Finally M1 had the biggest drop to 0.53 mg/L after 30 days. From Figure 2.2 (a) through (c), and 2.3 (a) through (c) we can see the fitting for zero, first and second order for magnetite M1 and hematite H, respectively. Because, there was almost no drop in the total concentration of BPA for magnetite M2, the data were not analyses using SPSS. We can see that the data for magnetite M1 had a good significance interval with a pvalue of 0.001 for all the three cases: the zero, first and second order. However, the first order had the highest R^2 value. For the hematite H, the p-values were higher than 0.05 with the lowest value for second order of 0.06. Also the second order had the highest R^2 value of 0.539. We can concluded from our data, that it did not followed very well the model using the CMBR assumption, and when compare the second order we obtained a better fit.

As a result, to better interpret the data, the water BPA concentrations were plotted against the time (days), fitted with Sigma Plot, and analyzed statistically with SPSS. From Figure 2.4 (a) through (c) we can see the water concentration remaining in the aqueous solution after a period of 30 days for all the three adsorbents. From the graphs we can see that magnetite M2 had a good mass balance for BPA. The hematite H had a drop to 0.94 in the first day, which remained mostly constant and reached 0.83 mg/L after 30 days. Finally, M1 had the biggest drop to 0.30 mg/L after 30 days. From Figures 2.5 (a) through (c), and 2.6 (a) through (c) we can see the fitting for zero, first and second order for magnetite M1, and hematite H, respectively. The fitting using SPSS found out to be similar to that of total BPA concentration for hematite H. However, both the R^2 values and p-values were worse, when compare to those of total BPA concentration. The same conclusion can be found that the model for the adsorbent hematite H, which did not fit well our data. From the total water BPA concentration fits for hematite H, the zero order had a better fit when compare all three orders, having an R^2 of 0.464 and p-value of 0.92. For magnetite M1, the R^2 and p-value were higher for the total water BPA concentration against the time. In the case of M1 the second order had the better R^2 and p-value of 0.844 and 0.003, respectively.

We can see the linear regression parameters, R^2 and p-value for both the magnetite M1 and hematite H for total BPA concentration and water concentration in Table 2.4 and 2.5, respectively. From Table 2.6 and 2.7 we can see the tabulated pH and TDS values for all the three adsorbents cases for the total period of 30 days. Figure 2.7 (a) through (c) presents the pH variation as a function of time for all three adsorbents. For magnetite M2, the pH stayed constant for all the 30 days with a small drop about 0.3 from an average pH of around 7.9 for blank solution. The pH of hematite H fluctuated from a 7.4 to 7.9. An average there was a drop to around a pH of 7.6. Magnetite M1 had the greatest affect an the pH. The drop after only one day was to a pH of 5.3 and went down to about 4.6 after 30 days. For a WTP the drop would be significant to influence the chemistry of the water. From Table 2.7 we can see the TDS values where we observed that magnetite M1 had the highest effect, followed by magnetite M2 and hematite H. For magnetite M1 the TDS increases to 844 from 261 mg/L after one day and stayed in that range with a highest value of 892 at 30 days. Magnetite M2 increases the TDS to about 460 and remained constant with slightly variations of about 5 mg/L, and for the hematite H the TDS remained constant to about 273.



Figure 2.1 Total BPA concentration as a function of time:
C₀ = 1.2 mg/L, 5g sorbent : 50mL solution
a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)



Figure 2.2 Total BPA concentration as a function of time for Magnetite (M1): $C_0 = 1.2 \text{ mg/L}, 5g \text{ sorbent} : 50 \text{mL solution}$ a) Zero order, b) First order, and c) Second order



Figure 2.3 Total BPA concentration as a function of time for Hematite (H): $C_0 = 1.2 \text{ mg/L}, 5g \text{ sorbent} : 50 \text{mL solution}$ a) Zero order, b) First order, and c) Second order



Figure 2.4 Water BPA concentration as a function of time: C₀ = 1.2 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)



Figure 2.5 Water BPA concentration function for Magnetite (M1):
C₀ = 1.2 mg/L, 5g sorbent : 50mL solution
a) Zero order, b) First order, and c) Second order



Figure 2.6 Water BPA concentration function for Hematite (H): $C_0 = 1.2 \text{ mg/L}, 5g \text{ sorbent} : 50 \text{mL solution}$ a) Zero order, b) First order, and c) Second order



Figure 2.7 pH variation as a function of time: C₀ = 1.2 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)

Sarbart	Equation	$\mathbf{y} = \mathbf{z}$	nx +b	\mathbf{P}^2	n	
Sorbeit	Fit	а	b	ĸ	h	
Magnetite (M1)	Zero Order	-0.010	0.852	0.878	0.002	
Magnetite (M1)	First Order	-0.015	-0.152	0.897	0.001	
Magnetite (M1)	Second Order	0.022	1.143	0.895	0.001	
Hematite (H)	Zero Order	-0.002	1.005	0.500	0.075	
Hematite (H)	First Order	-0.002	0.004	0.535	0.062	
Hematite (H)	Second Order	0.002	0.996	0.539	0.060	

Table 2.4 Total BPA concentration linear regression parameters for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution

Table 2.5 Water BPA concentration linear regression parameters for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution

Sorbont	Equation	$\mathbf{y} = \mathbf{z}$	ax +b	\mathbf{P}^2	n	
Sorbent	Fit	а	b	ĸ	þ	
Magnetite (M1)	Zero Order	-0.010	0. 595	0.781	0.008	
Magnetite (M1)	First Order	-0.021	-0.511	0.827	0.004	
Magnetite (M1)	Second Order	0.050	1.614	0.844	0.003	
Hematite (H)	Zero Order	-0.003	0.910	0.464	0.092	
Hematite (H)	First Order	-0.003	-0.095	0.419	0.116	
Hematite (H)	Second Order	0.004	1.101	0.414	0.119	

Before	After									
Blank	Time	Blank		Magnetite (M1)		Magnetite (M2)		Hematite (H)		
pН		pН	Stdv	pН	Stdv	pН	Stdv	pН	Stdv	
7.998	1Day	8.082	0.018	5.279	0.061	7.987	0.015	7.756	0.013	
7.895	3Days	7.958	0.103	5.022	0.051	7.570	0.056	7.906	0.034	
7.720	7Days	7.977	0.048	4.810	0.012	7.786	0.116	7.577	0.079	
7.926	10 Days	7.962	0.065	4.883	0.040	7.763	0.085	7.643	0.052	
8.006	14 Days	8.168	0.003	4.850	0.144	7.941	0.080	7.699	0.018	
7.945	21 Days	8.026	0.050	4.727	0.145	7.746	0.010	7.415	0.024	
7.865	30 Days	8.020	0.021	4.588	0.106	7.828	0.039	7.684	0.026	

Table 2.6 Solution pH values for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution

Table 2.7 Solution TDS values for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent : 50mL solution

Before	After								
Blank	Time	Blank		Magnetite (M1)		Magnetite (M2)		Hematite (H)	
TDS		TDS	Stdv	TDS	Stdv	TDS	Stdv	TDS	Stdv
259.00	1Day	262.00	1.00	844.67	13.01	454.33	4.93	272.00	2.65
260.00	3Days	261.67	1.53	866.33	13.05	456.67	10.79	274.00	2.00
262.00	7Days	259.67	0.58	870.67	2.52	464.00	3.46	275.00	1.00
261.00	10 Days	261.00	1.00	875.00	5.57	461.33	4.16	274.33	1.53
260.00	14 Days	261.67	0.58	885.00	12.49	465.33	1.53	273.33	0.58
261.00	21 Days	260.33	0.58	858.67	25.58	464.33	1.53	272.33	2.52
260.00	30 Days	258.67	1.15	892.00	13.11	465.00	1.00	274.67	1.15

In the second part of the kinetic experiments, studies were done using a 10 mg/L BPA concentration to investigate the adsorption of a industrial effluent or landfill leachate that could have this high concentration. From Figure 2.8 (a) through (c) we can see the total BPA concentration remaining in the aqueous solution and adsorbent after a period of 30 days for all the three adsorbents. From the graphs, we can see that magnetite M2 had a good mass balance for BPA, and there was no significant drop over time in the total BPA concentration. The

hematite H had a drop to 9.11 in the first day which remained mostly constant and reached 8.56 mg/L after 30 days. Finally M1 had the biggest drop to 4.95 mg/L after 30 days. From Figure 2.9 (a) through (c), and 2.10 (a) through (c) we can see the fitting for zero, first and second order for magnetite M1, and hematite H, respectively. Because there was almost no drop in the total concentration of BPA for magnetite M2, the data were not analyzed statistically using SPSS. We can see that the data for magnetite M1 had a very good significance interval with a p-value of 0.000 for all the three cases of zero, first and second order. For hematite H the p-values showed a good significance interval with values of 0.000 and the zero order had the highest R^2 value of 0.970. We can conclude that our data did follow very well the model using the CMBR assumption for both the adsorbents magnetite M1 and hematite H.

Just like in the case of 1.2 mg/L BPA concentration, the results were also plotted using the water BPA concentration against the time (days), fitted with Sigma Plot, and analyzed statistically with SPSS. From Figure 2.11 (a) through (c) we can see the water concentration remaining in the aqueous solution after a period of 30 days for all three adsorbents. From the graphs we can see that magnetite M2 had the best mass balance for BPA, with just a small decreases to about 8.9mg/L after 30 days. The hematite H had a drop to 8.6 in the first day, which remained mostly constant and reached 8.15 mg/L after 30 days. Finally M1 had the biggest drop to 4.3 mg/L after 30 days. From Figure 2.12 (a) through (c), and 2.13 (a) through (c) we can see the fitting for zero, first and second order for magnetite M1, and hematite H, respectively. The fitting using SPSS found out to be similar to that of total BPA concentration for hematite H. For the water BPA concentration fits for hematite H, the zero order had a better fit when all the three orders were compared, having an R^2 of 0.881 and p-value of 0.002. For magnetite M1 both the R^2 and p-value were slightly higher for the total BPA water concentration

142

fits, with values of 0.924 and 0.001, respectively. The data followed a first order model just like the model fittings for the total BPA concentration.

We can see the linear regression parameters, R^2 and p-value for both the magnetite M1 and hematite H for total BPA concentration and water concentration in Table 2.8 and 2.9, respectively. From Table 2.10 and 2.11 we can see the tabulated pH and TDS values for all the three adsorbents cases for the 30 day study. Figure 2.14 (a) through (c) presents the pH variation as a function of time for all three adsorbents. For magnetite M2 the pH stayed constant for all the 30 days with a small drop about 0.2 from an average pH of around 8.2 for the blank solution. The pH of hematite H fluctuated from a 7.78 to 7.94. An average there was a drop to around a pH of 7.83 for hematite H. Magnetite M1 had the greatest affect on the pH with a drop after only one day to a pH of 5.14 and continued to decrease to about 4.92 after 30 days. For the treatment of leachate or industrial water effluent, the drop would be significant to influence the chemistry of the aqueous solution. From Table 2.9 we can see the TDS values from which we observed that magnetite M1 had the highest effect, followed by magnetite M2, and hematite H. For magnetite M1 the TDS increases to 832 from 250 mg/L after one day and stay in that range, with a highest increase of 871 after 30 days. The solutions with magnetite M2 had an increase in the TDS to about 450 and remained constant, with slightly variations of about 20 mg/L. The TDS for the solution containing hematite H remained constant to about 265 mg/L.



Figure 2.8 Total BPA concentration as a function of time: C₀ = 10 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)



Figure 2.9 Total BPA concentration function for Magnetite (M1): $C_0 = 10 \text{ mg/L}, 5g \text{ sorbent} : 50 \text{mL solution}$ a) Zero order, b) First order, and c) Second order



Figure 2.10 Total BPA concentration function for Hematite (H): $C_0 = 10 \text{ mg/L}, 5g \text{ sorbent} : 50 \text{mL solution}$ a) Zero order, b) First order, and c) Second order



Figure 2.11 Water BPA concentration as a function of time: C₀ = 10 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)



Figure 2.12 Water BPA concentration function for Magnetite (M1): $C_0 = 10 \text{ mg/L}, 5g \text{ sorbent} : 50 \text{mL solution}$ a) Zero order, b) First order, and c) Second order



Figure 2.13 Water BPA concentration function for Hematite (H): $C_0 = 10 \text{ mg/L}, 5g \text{ sorbent} : 50 \text{mL solution}$ a) Zero order, b) First order, and c) Second order


Figure 2.14 pH variation as a function of time: C₀ = 10 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)

Sorbont	Equation	$\mathbf{y} = \mathbf{a}$	nx +b	P ²	n
Sorbent	Fit	а	b	K	þ
Magnetite (M1)	Zero Order	-0.104	10.443	0.958	0.000
Magnetite (M1)	First Order	-0.012	2.353	0.959	0.000
Magnetite (M1)	Second Order	0.001	0.094	0.957	0.000
Hematite (H)	Zero Order	-0.034	9.204	0.970	0.000
Hematite (H)	First Order	-0.004	2.221	0.966	0.000
Hematite (H)	Second Order	0.000	0.108	0.962	0.000

Table 2.8 Total BPA concentration linear regression parameters for the 30 days time study, $C_0 = 10$ mg/L, 5g sorbent : 50mL solution

Table 2.9 Water BPA concentration linear regression parameters for the 30 days time study, $C_0 = 10$ mg/L, 5g sorbent : 50mL solution

Sorbent	Equation	$\mathbf{y} = \mathbf{a}$	nx +b	\mathbf{P}^2	n
Sorbent	Fit	а	b	ĸ	þ
Magnetite (M1)	Zero Order	-0.102	7.239	0.922	0.001
Magnetite (M1)	First Order	-0.018	1.999	0.924	0.001
Magnetite (M1)	Second Order	0.003	0.132	0.919	0.001
Hematite (H)	Zero Order	-0.020	8.687	0.881	0.002
Hematite (H)	First Order	-0.002	2.162	0.875	0.002
Hematite (H)	Second Order	0.000	0.115	0.875	0.002

Before		After								
Blank	Timo	Bla	ank	Magne	tite (M1)	Magnet	tite (M2)	Hemat	ite (H)	
pН	1 1110	pН	Stdv	pН	Stdv	pН	Stdv	pН	Stdv	
8.047	1Day	8.108	0.025	5.146	0.052	8.065	0.019	7.829	0.007	
8.122	3Days	8.224	0.033	5.022	0.039	8.096	0.023	7.796	0.028	
8.198	7Days	8.282	0.027	4.997	0.089	8.026	0.080	7.781	0.033	
7.846	10 Days	8.122	0.013	4.928	0.045	8.006	0.008	7.945	0.011	
7.987	14 Days	8.280	0.015	4.832	0.099	7.980	0.030	7.836	0.017	
8.073	21 Days	7.988	0.023	4.637	0.038	7.857	0.033	7.861	0.005	
8.192	30 Days	8.279	0.020	4.924	0.114	7.981	0.083	7.826	0.005	

Table 2.10 Solution pH values for the 30 days time study, $C_0 = 10 \text{ mg/L}$, 5g sorbent : 50mL solution

Table 2.11 Solution TDS values for the 30 days time study, $C_0 = 10 \text{ mg/L}$, 5g sorbent : 50mL solution

Before	After								
Blank	Timo	Bla	Blank		ite (M1)	Magnet	Magnetite (M2) Hematite		
TDS	1 11110	TDS	Stdv	TDS	Stdv	TDS	Stdv	TDS	Stdv
249.00	1Day	249.00	1.00	832.67	2.52	454.67	7.37	262.00	0.00
248.00	3Days	247.67	0.58	827.67	8.02	470.33	2.52	262.33	0.58
249.00	7Days	249.00	0.00	840.33	5.13	445.33	8.96	263.33	1.15
254.00	10 Days	253.33	0.58	848.00	2.65	451.67	2.52	263.00	1.00
255.00	14 Days	253.33	0.58	851.00	1.00	453.33	1.53	269.67	2.08
250.00	21 Days	257.00	1.00	859.67	6.11	454.00	1.00	271.67	3.06
254.00	30 Days	254.00	1.00	871.33	7.09	454.33	1.53	270	1.528

The pH could have a significant role in the adsorption of BPA as the waster chemistry and behavior of BPA molecule changes. The pH effect on the adsorption of BPA onto different adsorbents have been studied on sediments (Zeng et al., 2006, Li et al, 2007, Xu et al., 2008), mesoporous carbon (Sui et al., 2011), activated carbon (Asakura and Matsubo, 2009, Toledo et al., 2005, Tsai et al., 2006a), minerals (Shareef et al., 2006, Dong et al., 2010, Tsai et al., 2006a), Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007), and polymer adsorbents (Fan et al., 2011, Kitaoka and Hayashi, 2002, Guo et al., 2011). For most of the adsorbents presented above an increase in the pH would result in a decrease in the adsorption capacity of the adsorbent. The only two exceptions were for mineral montmorillonite and surfactant-modified zeolite, for which an increase in the adsorption was observed for a pH above 7.0. In order to determine any affect of the pH, all three adsorbents were analyzed at different pHs. From Figure 2.15 (a) through (c) and Figure 2.16 (a) through (c) we can the effect of pH for all the three adsorbents for total BPA concentration, and water concentration, respectively. We can see that the pH had only a small effect on the magnetite M1 and M2, and a significant effect on hematite H. The total BPA concentration was obtained to find if there was any reaction occurring during the adsorption. We can see that there was a possible reaction under pH 4 for hematite H, and that there was a significant drop in the BPA concentration under pH 6. From Figure 2.16 (c) we can see a drop from about 1.19 mg/L to 0.06 mg/L, which is a removal of about 94.95 %. It is possible to achieve a much better adsorption at lower pH using hematite H. As a result more experiments were conducted to see the extend of the pH effect along with other parameters, and the results were presented in Chapter 3 and 4.

To investigate for a possible reaction, desorption experiments were conducted for the adsorbents. The extractions of the BPA from the different adsorbents were done using different solvents. After several trials, the best extraction was found to be 25 mL of acetone to 5g of sorbent for a period of 24h in a rotating tumbler at 16 rotation per minute (rpm) in the dark at 25 ^oC. DI water was found to be able to extract some of the BPA, but was insignificant and only worked for magnetite M1 and hematite H. We can see the extraction of the samples at different pH and the partition in Figure 2.17 (a) through (c) for all the three adsorbents. In this part of the study a aqueous solution of 2.5mM sodium bicarbonate NaHCO₃, 1.5mM calcium chloride (CaCl), and 1.7 mM magnesium chloride (MgCl₂) was also used in the adsorption and desorption

experiments. The buffer aqueous solution with 2.5mM NaHCO₃ was investigated in order to see the effect on the adsorption of the ionic strength in a aqueous synthetic water solution.

From Table 2.12 we can see the concentration of BPA remaining in the solution and extracts, along with their standard deviations for magnetite M1. For magnetite M1 the pH of the DI extracts changes slightly from the solution pH of 2 to a pH of 3 and remained the same for the solution with a pH of 4 as we could see in Table 2.13. In Table 2.14 we can see the TDS for the solutions and DI water extracts for magnetite M1. We can see that there is a decrease in the TDS for the DI water extracts because iron would not dissolved as much as in the second aqueous to adsorbent interaction. The solution and extract BPA concentrations, pH and TDS for magnetite M2 are presented in tables 2.15, 2.16, and 2.17, respectively. We can see that the mass balance is very good for magnetite M2. There was only a small amount of BPA that was adsorbed onto the adsorbent magnetite M2, which could be the reason that the total amount was able to be desorbed. The magnetite M2 lowered the pH of the solution if the pH is above 9.0, and raised the pH if it was below 9.0, and there was no effect to the solution pH at a pH of 8.0. The solution and extracts BPA concentrations, pH and TDS for hematite H are presented in Table 2.18, 2.19, and 2.20, respectively. We can see that the BPA concentration from the DI water extracts are minimal and probably would have been removed with acetone if the extraction with acetone contact time would had been longer. The pH of the solution increased after the addition of hematite H for a pH lower than 7.5 and decreased pH for a higher pH than 7.5. From the Table 2.20 we can see that the TDS of the solution is affected at very acidic or basic conditions in the presence of hematite H. In the pH range of 3.0 to 5.6 there was no change in the TDS of the solution, and the TDS of the DI water extracts decreases significantly.



Figure 2.15 Total BPA concentration as a function of pH: C₀ = 1.2 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)



Figure 2.16 Water BPA concentration as a function of pH: C₀ = 1.2 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)



Figure 2.17 Total BPA concentration distribution as a function of pH: C₀ = 1.2 mg/L, 5g sorbent : 50mL solution a) Magnetite (M1), b) Magnetite (M2), and c) Hematite (H)

Sample	Rlank	Solution	Acetone Extracts	DI Water Extracts
F	Dialik	BPA	BPA	BPA
pH 2	1.20	0.60 ± 0.01	0.50 ± 0.02	0.12 ± 0.00
pH 4	1.19	0.51 ± 0.02	0.42 ± 0.02	0.05 ± 0.02
pH 5.6 (DI)	1.22	0.61 ± 0.02	0.43 ± 0.03	0.03 ± 0.01
2.5mM	1.18	0.67 ± 0.03	0.46 ± 0.02	

 Table 2.12 BPA concentration (mg/L) as function of pH for Magnetite (M1)

 Table 2.13
 pH
 for Magnetite (M1) and Deionized Water (DI) extracts

Comula		Solu	tion	DI Water	Extracts
Sample	рН	рН pH Std		рН	Stdv
Blank pH 2	2.080	2.455	0.006	3.072	0.011
Blank pH 4	4.031	4.067	0.206	4.063	0.016
Blank pH 5.6 (DI)	5.624	4.453	0.231		
Blank 2.5mM	7.869	4.642	0.123		

Table 2.14 TDS for Magnetite (M1) and Deionized Water (DI) extracts

Sample		Solution		DI Water Extracts		
	TDS	TDS	Stdv	TDS	Stdv	
Blank pH 2	1940	1420	10.00	260	3.78	
Blank pH 4	18	664	7.37	117	1.00	
Blank pH 5.6 (DI)	1	670	6.81			
Blank 2.5mM	294	722	5.43			

Sample	Blank	Solution BPA	Acetone Extracts BPA
pH 2	1.20	1.09 ± 0.06	0.15 ± 0.02
pH 4	1.19	1.12 ± 0.09	0.23 ± 0.02
pH 5.6 (DI)	1.22	1.14 ± 0.04	0.23 ± 0.02
pH 10	1.22	1.15 ± 0.04	0.25 ± 0.04
pH 12	1.21	1.18 ± 0.01	0.23 ± 0.02
2.5mM	1.18	1.16 ± 0.01	0.19 ± 0.02

 Table 2.15 BPA concentration (mg/L) as function of pH for Magnetite (M2)

 Table 2.16 pH for Magnetite (M2)

Somula		Solution		
Sample	рН	pН	Stdv	
Blank pH 2	2.080	2.498	0.024	
Blank pH 4	4.031	7.448	0.079	
Blank pH 5.6 (DI)	5.624	7.573	0.051	
Blank pH 10	9.950	7.756	0.109	
Blank pH 12	12.080	11.936	0.014	
Blank 2.5mM	7.869	7.816	0.074	

Samula		Solu	tion
Sample	TDS	TDS	Stdv
Blank pH 2	1940	1087	15.28
Blank pH 4	18	254	1.53
Blank(DI) pH 5.6	1	251	1.53
Blank pH 10	11	252	3.46
Blank pH 12	1440	1290	10.00
Blank 2.5mM	294	478	3.21

Table 2.17 TDS for Magnetite (M2) and Deionized Water (DI) extracts

 Table 2.18 BPA concentration (mg/L) as function of pH for Hematite (H)

Sample	Dlaule	Solution	Acetone Extracts	DI Water Extracts
Bampic	ыапк	BPA	BPA	BPA
pH 2	1.18	0.60 ± 0.01	0.69 ± 0.17	0.06 ± 0.01
pH 3	1.20	0.62 ± 0.02	0.16 ± 0.08	0.03 ± 0.01
рН 3.5	1.19	0.67 ± 0.05	0.14 ± 0.00	0.03 ± 0.01
pH 4	1.19	0.75 ± 0.04	0.31 ± 0.06	0.03 ± 0.00
pH 5.6 (DI)	1.22	1.00 ± 0.03	0.17 ± 0.03	
pH 10	1.22	1.07 ± 0.01	0.30 ± 0.02	
pH 12	1.21	1.11 ± 0.02	0.27 ± 0.02	
2.5mM	1.18	0.94 ± 0.03	0.17 ± 0.06	

S 1 -		Solution pH pH Stdv		DI Water Extracts	
Sample	рН			рН	Stdv
Blank pH 2	2.080	2.219	0.014	3.010	0.026
Blank pH 3	2.986	5.306	0.148	5.086	0.108
Blank pH 3.5	3.547	6.499	0.133	6.251	0.275
Blank pH 4	4.031	6.738	0.062	6.569	0.016
Blank pH 5.6 (DI)	5.624	6.976	0.032		
Blank pH 10	9.950	7.243	0.039		
Blank pH 12	12.080	12.002	0.010		
Blank 2.5mM	7.869	7.590	0.154		

 Table 2.19 pH for Hematite (H) and Deionized Water (DI) extracts

Table 2.20 TDS for Hematite (H) and Deionized Water (DI) extracts

Commle		Solu	tion	DI Water Extracts				
Sample	TDS	TDS	Stdv	TDS	Stdv			
Blank pH 2	1940	1467	5.77	189	3.06			
Blank pH 3 34 34	34	0.58	7	0.58				
Blank pH 3.5	28	28	0.00	4	0.00			
Blank pH 4	18	26	0.58	5	0.00			
Blank pH 5.6 (DI)	1	25	0.00					
Blank pH 10	11	28	0.58					
Blank pH 12	1440	1287	5.77					

2.5 CONCLUSIONS

When compare the total BPA concentration for magnetite M1 for 1.2 mg/L the kinetics showed to followed a first order kinetics model, however for the total BPA water concentration it followed a second order model. The kinetics model using the total BPA water concentration is a better fit to investigate the adsorption, since the BPA desorption is playing an important role in calculating the total BPA concentration. For the hematite H at the lower BPA concentration of 1.2 mg/L the second order was a better fit for the total BPA concentration and the zero order for the total BPA water concentration. However, in both cases the significance interval is above 0.05, as a result from a statistical point of view is insignificant. Also the correlation R^2 is very low showing that the model assumption could not interpret the data to well. Because of the small adsorption on magnetite M2 there was no statistical analysis performed on the data.

When compared to the higher BPA concentration of about 10 mg/L, the results were different. The adsorption for magnetite M1 followed the first order kinetic model for both the total BPA concentration and total BPA water concentration. At a higher pH there was a significant correlation for adsorbent hematite H, having a zero order model fit for both the total BPA and total water BPA concentrations. When compared the pH for magnetite M1 the drop of pH in the solutions followed the same trend at both initial concentrations of 1.2 and 10 mg/L. For the solutions with the lower BPA concentration of 1.2 mg/L the beginning pH was lower than that for the 10 mg/L BPA solutions. The trend for both magnetite M2 and hematite H was the same for both concentrations, with a pH decrease after the equilibrium with the adsorbent.

The desorption with acetone prove to be efficient for the BPA when using the iron oxides adsorbents. Based on the results we can see that there was a significant pH effect on the adsorbent hematite H. When compared the extractions for the batch extractions we can see close to 100 % recovery for most of the pH for all the three adsorbents. For hematite H from the recovery data for pH below 4.0 might suggest that there could be a possible reaction taking place between the hematite H and BPA molecules. This formation of byproducts should be further investigated to evaluate the possible byproducts and their estrogenic activity not to be higher than that of the BPA alone.

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CHAPTER III

ADSORPTION OF BISPHENOL A ONTO MINERAL OXIDES

3.1 INTRODUCTION

Pharmaceuticals and personal care products (PPCPs) consists of wide range of chemicals such as sunscreen agents, veterinary and human drugs, and the endocrine disrupting compounds (ECDs). The EDCs are considered to be one type of PPCPs (Pan et al., 2009). Bisphenol A (BPA) is known to be one of the EDCs (Krishnan et al., 1993), with a initial reported acute toxicity of 1-10 μ g/mL to the aquatic organisms from fresh water and marine water species (Alexander et al., 1988). For children and adults the BPA reference dose (RfD) of 50 µg/Kg/day was determined by United States Environmental Protection Agency (USEPA, 2011), and 10 µg/Kg/day by European Commission Scientific Committee on Food (Schecter et al., 2010). However, since 1988 there had been a lot more studies done which showed adverse health effects at much lower concentrations such as 0.02 µg/L and 0.025 µg/Kg/day (Sall and Hughes, 2005; Crain et al., 2007; Fleisch et al., 2010). EDCs can produce harm to humans and wildlife in interfering with their reproductive system, by blocking or mimicking the activity of natural hormones (Harrison et al., 1997; Snyder et al., 2003). They had been labeled as emerging organic pollutants (Daughton and Ternes, 1999). The United States Environmental Protection Agency (USEPA) has defined EDCs as compounds that interfere with the "synthesis, secretion, transport, binding action, or elimination of natural hormones in the body that are responsible for the maintenance of homeostasis, reproduction, development, and/or behavior" (USEPA, 1997). Some of the effects on humans that have been reported are an increase in the incidence of testicular, ovarian, and breast cancer and also reduce fertility (Colborn et al., 1993; Harrison et al., 1997; Cheek et al., 1998). As a result significant effort has to be done in order for the BPA to be removed from the aqueous phase.

BPA is a monomer that is widely used in the production of epoxy resins and polycarbonate in the plastic industry. The contamination of the environment with BPA was done through multiple sources. The pollution of the aqueous phase with BPA is posing the most significant threat to human and wildlife, because there is no alternative way of bypassing the exposure. If BPA is found in canned foods, the exposure can be reduced or even eliminated by eating less or not eating at all any canned food. The contamination from the aqueous phase and from the wastewater and drinking water treatment plants is very important to be taken care off. The contamination from the fresh body of water, marine, groundwater, and landfill leachate have to be addressed. The release of BPA into the environment could be done through sewage treatment effluents, landfill leachate, or natural degradation of polycarbonate plastics (Crain et al., 2007). The leachate of BPA from sewage treatment plants, landfill leachate, and industrial effluents are considered point sources pollution. The leachate of BPA through watershed runoffs from epoxy resins and polycarbonate plastics debris are considered non-point sources pollution.

The landfill leachate is one of the main sources of pollution for the PPCPs as significant amounts of dispose compounds are dumped and get concentrated in the leachate. Municipal landfills are becoming a significant concern because they are a source of new and emerging pollutants such as PPCPs (Eggen et al., 2010), with concentrations of BPA up to 17,200 μ g/L reported in one study (Yamamoto et al., 2001). The leachate can infiltrate and contaminate the ground water, which can end up in the water treatment plants or drinking water wells. Other BPA concentrations has been reported for concentrations as high as 370 μ g/L for wastewater effluent (Huang et al., 2012), 3.2 μ g/L for river water (Huang et al., 2012), 12.2 μ g/L wastewater (Hohne and Puttmann, 2008), and 10,500 ng/g for river sediments (Huang et al., 2012).

Both the surface and raw water supply of the drinking water treatment plants had been contaminated (Jin et al., 2004, Suzuki et al., 2004; Crain et al., 2007; Loos et al., 2010; Huang et al., 2012; Kuch and Ballschmiter, 2001; Ignatius et al., 2010; Rodriguez-Mozaz et al., 2005). This contamination is posing a serious health risk especially to the reproductive system and fecundity of the humans and aquatic animals (Crain et al., 2007; Nakamura et al., 2010). Traces of BPA had been found all over the world in the environment in river water (Belfroid et al., 2002; Crain et al., 2007; Huang et al., 2012; Crain et al., 2007; Voutsa et al., 2006; Vigano et al., 2006; Ko et al., 2007; Yoon et al., 2010; Ribeiro et al., 2009; Jonkers et al., 2010; Rodriguez-Mozaz et al., 2005; Zhang et al., 2007; Kuch and Ballschmiter, 2001; Ignatius et al., 2010; Loos et al., 2010; Ignatius et al., 2010; Kolpin et al., 2002), estuaries and seawater (Belfroid et al., 2002; Crain et al., 2007; Huang et al., 2012; Klecka et al., 2009; Jonkers et al., 2010), ground water (Rudel et al., 1998; Crain et al., 2007; Huang et al., 2012), wastewater and sludge (Rudel et al., 1998; Larsson et al., 2000; Lee and Peart, 2000b; Jeannot et al., 2002; Hernando et al., 2004; Lee et al., 2005; Mauricio et al., 2006; Kim et al., 2007a,b; Gibson et al., 2007; Hu et al., 2007; Furhacker et al., 2000; Zhang et al., 2008; Hohne and Puttmann, 2008; Stasinakis et al., 2008; Sodre et al., 2010; Jonkers et al., 2010; Vega-Morales et al., 2010; Wang et al., 2010; Nie et al., 2011; Huang et al., 2012), river and freshwater sediment (Khim et al., 1999; Bolz et al., 2001; Fromme et al., 2002; Stachel et al., 2003; Liu et al, 2004b; Burkhardt et al., 2005;

Hachimoto et al., 2005; Peng et al., 2006; Lei et al., 2008; Klecka et al., 2009), marine sediments (Kawahata et al., 2004; Stuart et al., 2005; Klecka et al., 2009), dust (Rudel et al., 2003; Wilson et al., 2007; Volkel et al., 2008; Geens et al., 2009), and atmosphere (Wilson et al., 2001; Berkner et al., 2004; Matsumoto et al., 2005; Fu and Kawamura, 2010).

When a proposed ranking system was done for pharmaceuticals, PPCPs and EDCs or EOCs out of 100 chemicals the overall priority for BPA was second place and 17β -estridol came only in seventeen place for the overall score (Kumar and Xagoraraki, 2010). The ranking system was done by taking into consideration the occurrence (BPA was in third place), and the ecological and health effects. Thus the presence of BPA in the aquatic system could lead to negative effect on the wildlife and humans. For the aquatic system in aerobic systems such as rivers, the half lives of BPA had been reported to be between 4.5-4.7 days (Cousins et al., 2002). For aerobic conditions in marine sediments a half-life of 14.5 days had been reported for BPA (Ying et al., 2003). The degradation of BPA has been done mainly by bacteria (Kang and Ha, 2002). Under anaerobic conditions the biodegradation of BPA has been limited (Ike et al., 2006).

The removal of BPA from aqueous solutions had been investigated through different studies using oxidation with ozonation (Alum et al., 2004; Irmak et al., 2005; Deborde et al., 2008; Zhang et al., 2008; Garoma and Matumoto, 2009), chlorination (Hu et al., 2002; Yamamoto and Yasuhuru, 2002; Gallard et al., 2004; Lee et al., 2004; Korshin et al., 2006), electrochemical oxidation (Boscoletto et al., 1994; Tanaka et al., 2002; Andreescu et al., 2003; Ngundi et al., 2002; Gozmen et al., 2003; Kuramitz et al., 2004; Murugananthan et al., 2008), photooxidation(Ohko et al., 2001; Chiang et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2006b, 2007; Torres et al., 2010; Yap et al., 2010), biodegradation (Dorn et al., 1987; Lobos et al., 1992; Spivack et al., 1994; Staples et al., 1998; Furhacker et al., 2000; Ike et al., 2000; Klecka et al., 2001; West et al., 2004; Kang and Kondo, 2002a; 2002b; Kang et al., 2004; Kang et al., 2006; Torres et al., 2007a; 2007b; Torres et al., 2008a, 2008b; Guo and Feng, 2009;), ferrate(VI) and zero valent aluminum oxidation(Jiang et

al., 2005; Lee et a., 2005; Liu et al., 2011), and adsorption (Nakanishi et al., 2002; Asada et al., 2004; Toledo et al., 2005; Sun et al., 2005; Shareef et al., 2006; Tsai et al., 2006a; 2006b; Zeng et al., 2006; Li et al., 2007; Xu et al., 2008; Li et al., 2008; Pan et al., 2008; Cao et al., 2009; Li et al., 2009; Dong et al., 2010). All of these processes had been used to remove BPA from waste and drinking water. Each process or technology has advantages and disadvantages that limit its use when removing BPA from the aqueous phase. The cited literature on the treatment of BPA has shown that through a process or technology or in combination of more than one, the removal of BPA is possible.

When a technology or process is taking into consideration for the removal of BPA it is important that it should be both economical and efficient. In order to be economical for the most part has to be a conventional technology or process for water treatment that is well established, practical and easy to manage. A new technology or process could be very effective in removing BPA. However, if it is very expensive or very hard to manage, the application in large scale becomes impractical or even impossible. It may take many years until the new technology or process to become both economically feasible and practical. The process of BPA removal should to be sustainable and as green as possible. The production of byproducts and waste during the removal of BPA should also be taking into consideration.

The ozonation process has been used in the WTP for many years for treatment of odor, taste, disinfection, and for the wastewater disinfection (Klavarioti et al., 2009). Ozonation studies had been conducted on the site of WTP (Ternes et al., 2002; Hua et al., 2006; Jasim et al., 2006; Vieno et al., 2007), and wastewater treatment plants (WWTPs) (Ternes et al., 2003; Huber et al., 2005; Nakada et al., 2007). As stated above the removal of BPA using ozonation had been studied in few studies since 2004. One of the negative effects of this process is the byproducts

formation and the high cost of operating that is associated with ozonation. Because of these two reasons it is not widely used in the treatment of drinking water especially in United States (US). Because the BPA concentrations are low it was argued that the byproducts formation would not be significant. However, their estrogenic activity should be investigated to don't exceed that of BPA alone. In few studies the removal of BPA from water in WTP using conventional treatment processes leads to byproducts formation that could have higher estrogenic activity than BPA (Niwa et al., 2002; Stackelberg et al., 2004; Korshin et al., 2006).

The chlorination process has been used in the treatment of drinking water and waste water in US for more than 100 years. When compare to other disinfection processes, chlorination, has been effective and relatively cheap. However, the removal of BPA using chlorination process has many byproducts formation (Hu et al., 2002). The BPA has to compete with other pollutants to be removed, and the byproducts formed during the process could take up to 22 hours to disappear. It was reported that some of the byproducts formed during BPA removal through their synergistic and additive effects had a higher estrogen activity than BPA alone (Hu et al., 2002).

The electrochemical process is not a conventional process for WTP or WWTP and is efficient only at high concentrations; this is a very limiting technology since the concentrations of BPA are usually low. The byproducts are also formed during this process and a lot of current cycles have to be done in order to find the most efficient cycle. The building and management of the process chamber could also be very costly.

The photooxidation process has given good results at low pH and low BPA concentration, which would limit the process. The photooxidation process was used usually in combination with other processes or chemicals to be able to have high removal efficiency. The

addition of hydrogen peroxide facilitated the formation of HO• radicals using Fenton process, which helped the efficiency of BPA removal. The addition of other processes or chemicals, such as titanium dioxide, would increase the cost of removal. The photooxidation process leads to byproducts formation during the removal of BPA.

Another non conventional process for WTP is the biodegradation. Biodegradation, if efficient, could be used in the treatment of aquifers and WWTP. Depending on the biological organisms BPA could be removed. Organism such as bacteria, fungi and planktons could remove BPA to a certain percentage depending on the strains. Enzymes found from different sources could also biodegrade BPA. Not all the organisms are able to biodegrade BPA above 90 %. The half lives of BPA could range from 3 to 14.5 days. Bacteria under anaerobic conditions did not perform well for the degradation of BPA, thus making it not viable for aquifers treatment. The biotechnology could be used if the bacteria would be injected before arriving to the wastewater treatment plant in the wastewater collecting sewer system. However, this has to be further investigated to see if BPA has no competition from other organic pollutants. The degradation could be take long periods of time for a high removal depending on the biological organisms, thus the use for WWTP could be very limited. Byproducts had also been identified during the biodegradation of BPA.

Ultrasonic (US) process could be used to remove BPA effectively with additional process or chemicals. Fenton process it is well known AOP that could be used in the combination of US. One of the process that is often used in combination with US is the Fenton process that releases HO• radicals that could remove BPA. A BPA concentration of 118 μ mol/L it took three processes such as US, Fenton, and solar irradiation to achieve a 92 % removal in 60 minutes (Torres et al., 2008b). During the US the removal of BPA leads to byproducts formation. US had to be coupled with ozonation for a BPA removal to zero in 60 minutes using 20 ml/min O_3 flow rate (Guo and Feng, 2009). The cost of removal could be high, because of the additional processes necessary for high efficiency.

The oxidation of BPA using ferrate (VI) and zero-valent aluminum (ZVAI) had been found to be potential treatment process for drinking water and wastewater. For the removal of BPA (15 μ M) a concentration of 0.5 mg/L of Ferrate(VI) and 1 mg/L in 30 minutes was used for lake water and wastewater, respectively (Lee et al., 2005). Ferrate (VI) could be a strong oxidant, stronger the ozone, under acidic conditions (Jiang and Lloyd, 2002). The ZVAI had only recently found to be able to oxidize BPA only under acidic conditions (Liu et al., 2011). The redox potential of aluminum is -1.67 V, and works efficiently at pH 1.5. The very low pH could be a limiting factor. The addition of Fe²⁺ increases the efficiency of the process in the removing of BPA.

In some studies done from 1999 until 2002 for the removal of some selected groups of EDC/PPCPs, herbicides, and pesticides found that there was minimal removal during coagulation, sedimentation and filtration (Zang and Emary, 1999; Petrovic et al., 2010; Adams et al., 2002; Ternes et al., 2002). Coagulation was found to don't be effective in removing trace levels of organic pollutants (Montiel and Welte, 1992). Adsorption is a very important removal technology that had been used for treatment of drinking water and other polluted effluents. Some of the popular sorbents are granular activated carbon (GAC) and powder activated carbon (PAC). Activated carbon had been found to be able to remove many organic pollutants (Crittenden et al., 1999). The adsorption processes for many of the sorbents including activated carbon showed a pseudo-second order kinetic model, being most promising way of removing the BPA from water. The adsorption of BPA was found to be possible onto minerals, sediments, soils,

carbon, porous carbon, activated carbon, fullerene, carbon nanotubes, and polymeric adsorbents. BPA had been also been removed by filtration through physical separation or chemical binding on the membrane. Some of the membranes were able to filtrate BPA are hybrid membranes of polyethersulfone molecular that were imprinted with polymer spheres (MIP) (Son et al., 2011). When six membranes made of polyethersulfone, polysulphone and regenerated cellulose were investigated found that the membrane made of polysulphone was the most efficient (Su-Hua et al., 2010). Nanofiltration (NF) had been also used to removed BPA at very low concentrations such as 1-10ppb (Kim et al., 2008) and higher concentrations of 2 mg/L (Zhang et al., 2006). Kim et al., 2008 found that NF alone was only able to remove only 72 % of BPA. Many of the sorbents used are good candidates since are commercially available or easily available to be excavated. During the adsorption process the pollutant chemical of interest is attached to the surface of a sorbent through different adsorption mechanisms. The organic pollutants structure may react with the surface of the sorbent, resulting in a byproduct formation. The formations of the byproducts have to be address, in order to determine if the new byproducts are adsorbed to the sorbents as well. We can see a review of different research papers that studied different sorbents and parameters for the removal of BPA presented in Table 3.1.

Table 3.1 Parameters studied for adsorption of Bisphenol A on different adsorbents

Туре	Adsorbent	Adsorbent dosage	Conc. C _e Range (mg/L)	q _e ¹ (mg g ⁻¹)	рН	T ⁰ C	Time	Mixing rate (rpm)	Adsorption Model ¹ Freundlich Model Q=K _f C _e ⁿ ,K _f C _e ^{1/n}	Reference
	Andesite Diatomaceous earth Titanium dioxide Activated bleach earth	0.05-0.25 (g/L)	60-100	$\begin{array}{c} 0.53^2 \\ 0.73^2 \\ 0.33^2 \\ 0.86^2 \end{array}$	3-11	25	2h	200-600	K_{f} , n – N.A.	Tsai et al., 2006a
	ZFA F prepared from coal fly ash ZFA L prepared from coal fly ash SMZFA F prepared from coal fly ash SMZFA L prepared from coal fly ash	0.05g/100mL	0.5-100	$3.5^{3} \\ 1.4^{3} \\ 114.9^{3} \\ 56.8^{3}$	2.5-10.5	25	24h	N.A.	K_f , n – N.A.	Dong et al., 2010
	Geothite Montmorillonite Kaolinite	0.48g/300mL 0.94g/300mL 1.28g/300mL	684 µg/L	$\frac{15-20\%^4}{10-40\%^4}$ 2-8\% ⁴	3-12	25	21d	N.A.	K_{f} , n – N.A.	Shareef et al., 2006
	Hydrophobic Y type zeolite	0.5-1.5	10-90	111.11 ⁵	3-11	25	2h	400	$K_f = 67.20^5$ $1/n = 0.22^5$	Tsai et al., 2006b
Mineral	Mesoporous silica MCM-41 Phenyl-functionalized mesoporous silica (Ph-MS)	50mg/ 250mL	10-260	9 ⁶ 351 ⁶	6.2-7.2	25	6h	200	$K_{\rm f}, n-N.A.$	Kim et al, 2011
	Fe(III)/Cr(III) hydroxide-untreated Fe(III)/Cr(III) hydroxide-pretreated	100-800mg/50mL	10-50	3.47 ⁷ 3.67 ⁷	4-10	32-60	2.3- 3.3h	160	$\begin{split} K_{\rm f} &= 0.132 \\ n &= 1.379 \\ K_{\rm f} &= 0.128 \\ n &= 1.367 \end{split}$	Namasivayam and Sumithra et al., 2007
	Montmorillonite Hybrid particles PO1 ⁸ Montmorillonite Hybrid particles PO2 ⁸ Montmorillonite Hybrid particles PO3 ⁸ Montmorillonite Hybrid particles PO4 ⁸	0.1g/20mL	22.8-54.7	20.7039 ⁸ 21.7391 ⁸ 23.5849 ⁸ 32.0513 ⁸	N.A.	25	8h	N.A.	$\begin{split} K_f &= 2.4618^j \\ 1/n &= 2.1164^j \\ K_f &= 4.1491^j \\ 1/n &= 5.6302^j \\ K_f &= 7.3023^j \\ 1/n &= 3.6258^j \\ K_f &= 5.9073^j \\ 1/n &= 2.5221^j \end{split}$	Cao et al., 2009
Soil	Soil from experimental farm pass through 0.22mm mesh	1.5g/20mL	5-130	2.5 ⁹	7.0	25	24h	Waterba- th	K _f , N.A. n = 0.946	Li et al., 2008

Soil	Roseworthy Campus (RC) Roseworthy Farm (RF) Terretfield (TF) Waite Campus (WT)	2g/200mL	25 µg/L	N.A. ¹⁰	7.0	20	2h	Mechani- cal shaker	K_f , $n - N.A$.	Ying and Kookana, 2005
	Laacher Hof AXXa Laacher Hof AIII Hofchen Mußbach	1g/20mL	0.04-5.0	N.A. ¹¹	6.9-8.13	3 20-25	72h	Overhe- ad Shaker	$\begin{split} K_f &= 12.57 \\ 1/n &= 0.7719 \\ K_f &= 6.934 \\ 1/n &= 0.8525 \\ K_f &= 17.12 \\ 1/n &= 0.7019 \\ K_f &= 7.409 \end{split}$	Fent et al., 2003
				12					$\frac{1/n = 0.8414}{K_f = 0.0178}$	
	Sediment Sample A (Pailoukou)			0.28^{12}					n = 0.8106	
	Sediment Sample B (Nonglinq	1:12.5 ^d	5-90 ^d	0.22^{12}	2-11 2				$K_f = 0.0146$ n = 0.7684	Zeng et al., 2006
	Bridge)			0.20^{12}		25	01	200	$K_{\rm f} = 0.0143$	
	Sediment Sample D (North Bridge)			0.20 0.175 ¹²			011	200	$\begin{array}{l} n = 0.6944 \\ K_{f} = 0.0090 \\ n = 0.7869 \end{array}$	
	Sediment Sample E (Nanjiao Park)			0.170^{12}					$K_f = 0.0072$ n = 0.7124	
Sediment	Sediment Huang Pu River Shangai China	2g/20mL	10-60	0.15 ¹³	2-12	25	24h	N.A.	$K_{\rm f} = 4.090 \\ n = 0.954$	Li et al., 2007
	Natural Surface Coating Samples (NSCS) Surficial Sediments (SS)	0.5g/20mL	10-80	0.4^{14} 0.3^{14}	7	25	24h	200	K_f , $n - N.A$.	Li et al., 2009
	Marine Sediment A Marine Sediment B_1 Marine Sediment B_2 Marine Sediment B Marine Sediment D Marine Sediment E	0.5g/20mL	5-80	$8.54^{15} \\ 6.76^{15} \\ 4.96^{15} \\ 5.22^{15} \\ 4.65^{15} \\ 4.43^{15} \\ \end{cases}$	4-10	25	12h	100	K _f , n – N.A.	Xu et al., 2008

Sediment	Yellow River Tong Guan suspending solid (TS) Yellow River San Menxia suspending solid (SS) Yellow River Tong Guan bottom sediment (TB) Yellow River San Menxia bottom sediment (SB) Huan Yuankou bottom sediment (HB)	15:1 25:1	2-12µg/L	$\begin{array}{c} 52 \text{ ng/g}^{16} \\ 76 \text{ ng/g}^{16} \\ 30 \text{ ng/g}^{16} \\ 58 \text{ ng/g}^{16} \\ 19 \text{ ng/g}^{16} \\ 27 \text{ ng/g}^{16} \\ 17 \text{ ng/g}^{16} \\ 26 \text{ ng/g}^{16} \\ 23 \text{ ng/g}^{16} \\ 42 \text{ ng/g}^{16} \end{array}$	7.5-8.5	25	14h	2h water bath	Only For SB: $K_f = 6.248$ n = 1.278 For SS $K_f = 8.869$ n = 1.245	Sun et al., 2005
	Sediment from a aquifer storage and recovery (ASR) from Australia	10g/100mL	2.5-20 μg/L	40µg/Kg ¹⁷	7.9	25	16h	Mechani- cal shaker	$\begin{array}{l} K_{\rm f}=25\\ 1/n=0.24 \end{array}$	Ying et al., 2003
Carbon	Carbonaceous material prepared at 600 ⁰ C from by-products of wood processing Carbonaceous material prepared at 800 ⁰ C from by-products of wood processing	N.A.	1-18	4-18.2 ¹⁸ 24-31.4 ¹⁸	N.A.	25	48h	N.A.	$\begin{split} K_{\rm f} &= 1\text{-}7 \\ 1/n &= 0.25\text{-}0.53 \\ K_{\rm f} &= 11.5\text{-}18.0 \\ 1/n &= 0.26 \end{split}$	Nakanishi et al, 2002
Porous Carbon	Porous Carbon prepared from Moso bamboo PC_{400} Porous Carbon prepared from Moso bamboo PC_{700} Porous Carbon prepared from Moso bamboo PC_{1000}	0.01g/100mL	1-20	2.1 11.4 41.8	N.A.	23	24h	Incubator shaker	$\begin{split} K_{\rm f} &= 0.30 \\ 1/n &= 0.53 \\ K_{\rm f} &= 0.14 \\ 1/n &= 1.4 \\ K_{\rm f} &= 25 \\ 1/n &= 0.24 \end{split}$	Asada et al., 2004
	CMK-3 prepared from silica based	10mg/200mL	25	296 ¹⁹	3-13	10-40	1h	135	$\begin{array}{l} K_{\rm f} = 55.1 \\ 1/n = 0.45 \end{array}$	Sui et al., 2010
	Powdered Activated Carbon PAC	50mg/ 250mL	10-260	337 ⁶	6.2-7.2	25	бh	200	K_f , $n - N.A$.	Kim et al, 2011
Activated Carbon	Powdered Activated Carbon PAC	10mg/200mL	25	178 ¹⁹	6.8	25	8h	135	$K_{\rm f}, n-N.A.$	Sui et al., 2010
	Norit 20B - Huron River Water AC800 - Huron River Water (Both coal based)	5 and 15 mg/L	100nM	$\begin{array}{c} 10.5 \&\\ 3.4\%^{20}\\ \hline 3.4 \&\\ <\!\!1.0\%^{20} \end{array}$	5.8-8.3	N.A.	1-5h	N.A.	$K_{f} = 2.85$ 1/n = 0.37 $K_{f} = 1.66$ 1/n = 0.42	Yoon et al., 2003

	Activated Carbon (Wako Pure Chemicals- Osaka, Japan)	0.01g/100mL	1-20	57.0	N.A.	23	24h	Incubator shaker	$\begin{array}{c} K_{\rm f} = 9.9 \\ 1/n = 0.71 \end{array}$	Asada et al., 2004
	Activated carbon from Calgon (coconut shell base) Activated carbon from Calgon (bituminous coal base)	0.05-0.25	60-100	263.2 ²¹ 328.3 ²¹	3-11	25	2h	200-600	K_f , $n - N.A$.	Tsai et al., 2006a
	Activated carbon from Takeda(coconut shell based)	N.A.	1-18	23.5 ¹⁸	N.A.	25	48h	N.A.	$K_{\rm f} = 9.2$ 1/n = 0.27	Nakanishi et al, 2002
	Activated Carbon	0.01g/100mL	1-20	58.2	N.A.	23	24h	Incubator shaker	$K_{\rm f} = 9.9$ 1/n = 0.71	Asada et al., 2004
	AC from SorboNorit Charcoal (S) AC from Merk Charcoal (M) AC from almond shells (A)	0.1g/100mL	50-350	$129.6^{22} \\ 263.1^{22} \\ 188.9^{22}$	2-13	25	7d	Thermos -tatic bath	K_{f} , n – N.A.	Toledo et al., 2005
Activated Carbon	AC from Westvaco W20 AC W20A - treated with NO ₃ AC W20N - treated with N ₂ AC from Calgon F20 AC F20A - treated with NO ₃ AC F20N - treated with N ₂	10mg/100mL	60	$\begin{array}{c} 382.12^{23} \\ 59.17^{23} \\ 432.34^{23} \\ 333.33^{23} \\ 119.05^{23} \\ 232.56^{23} \end{array}$	5-11	15-45	7d	150	K _f , n – N.A.	Liu et al., 2009
	Purified Water PW Leachate sample 1 AW Leachate sample 2 BW	100-1300mg/500ml	2-200 (μg/mg)	N.A.	5-9	20	6h	180	$\label{eq:Kf} \begin{array}{c} K_{\rm f} = 0.24 \\ 1/n = 0.38 \\ K_{\rm f} = 0.45 \\ 1/n = 0.37 \\ K_{\rm f} = 0.10 \\ 1/n = 0.30 \end{array}$	Asakura and Matsubo, 2009
	Coal Base-0 years of prior use		0.001-0.4	105					K_f , n – N.A.	Choi et al., 2005
	Coal Base-2.2 years of prior use		0.1-0.4	80					$K_{f} = 12$ 1/n = 0.623 $K_{f} = 8$	
	Coal Base-5.9 years of prior use		0.3-0.4	25					1/n = 0.470	
	Coconut Base-0 years of prior use	N.A.	0.03-0.3	70	N.A.	N.A.	N.A.	N.A.	$K_{\rm f} = 28$ 1/n = 0.783	
	Coconut Base-3.1 years of prior use	(0.025-0.4	30					$K_{f} = 12$ 1/n = 0.578 $K_{c} = 18$	
	Wood Base-0 years of prior use		0.03-0.3	50					$R_{\rm f} = 10$ 1/n = 0.593 $K_{\rm f} = 11$	
	Wood Base-3.1 years of prior use		0.15-0.4	70					1/n = 0.58	

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Fullerene	Fullerene	$1:100-1:200^{24}$	0.1-40	236	N.A.	23	7d	30	$K_{\rm f}$, $n - N.A$.	Pan et al., 2008
Carbon Nanoma- terials	Single-walled carbon nanotubes (SWCNT) Multiwall carbon nanotubes MWCNT15 ²⁴ Multiwall carbon nanotubes MWCNT30 ²⁴ Multiwall carbon nanotubes MWCNT50 ²⁴	1:20,000-1:120,000 ^k	0.1-40	455 102 61.6 73.9	N.A.	23	7d	30	K _f , n – N.A.	Pan et al., 2008
	MN-200 Purolite International Co. 15^{0} C, 30^{0} C, 45^{0} C MN-100 Purolite International Co. 15^{0} C, 30^{0} C, 45^{0} C MN150 Purolite International Co. 15^{0} C, 30^{0} C, 45^{0} C NDA-150 Jiangsu N&G Env. Tech. 15^{0} C, 30^{0} C, 45^{0} C	0.05g/100mL	20-100	$\begin{array}{c} 2.09(mm \\ ol/g)^{25} \\ 1.75(mm \\ ol/g)^{25} \\ 1.69(mm \\ ol/g)^{25} \\ 1.22(mm \\ ol/g)^{25} \end{array}$	6.5-7.5	15-45	72h	130	K _f , n – N.A.	Fan et al., 2011
	Chitosan-bearing b-cyclodextrin- CDC	3-40mg/ 10mL	0.1-100	98 ²⁶	N.A.	25	24h	90	K_{f} , $n - N.A$.	Aoki et al., 2004
Polymeric Adsorbents	Magnetic molecularly polymers (MMIPs) 25 ^o C 35 ^o C			46.73 ²⁷ 42.74 ²⁷ 36.90 ²⁷					$\begin{split} K_{f} &= 4.681 \\ 1/n &= 0.594 \\ K_{f} &= 2.261 \\ 1/n &= 0.678 \\ K_{f} &= 2.485 \\ 1/n &= 0.500 \end{split}$	
	45 C Magnetic non-template imprinted polymers (MNIPs) 25 ⁰ C	10mg/ 10mL	0.1-100	60.61 ²⁷	3	25	12h	300	$K_{\rm f} = 4.483$ 1/n = 0.534	Guo et al., 2011
	35 [°] C 45 [°] C			49.50 ²⁷ 40.65 ²⁷					$\begin{split} & K_{\rm f} = 4.434 \\ & 1/n = 0.486 \\ & K_{\rm f} = 4.859 \\ & 1/n = 0.444 \end{split}$	

¹Maximum sorption capacity (q_e)was obtained from Langmuir model or from the sorption capacity at the highest initial concentration, most of the time the pH was 7.0 and Temperature 25 ^oC. The Adsorption parameters reported for the Freundlich Model were the strength of adsorption K_f, and 1/n which is the slope that measures of the adsorption intensity. ²Concentration of 60 mg/L, mixing rate 400 rpm, Temperature 25^oC, pH 7.0 and dosage of 0.5g 2L⁻¹. ³ Concentration of BPA 0.5-100 mg/L, Temperature 25^oC, pH 11.2 and 10.5 for ZFA F and ZFA L, and 10.4 and 9.6 for SMFA F and SMFA L, dosage of 0.5g L⁻¹. ⁴Sorption of BPA was done at pH 4,7, and 10, however the data was presented for pH 4 and 10 because

for the pH of 7 was identical to that of pH 4. The experiments were run for a period of 21days, but most of the adsorption occurred after 10 minutes for geothite and kaolinite and 2 days for montmorillonite. ⁵Concentration of BPA 10-90mg/L, mixing rate 400 rpm, Temperature 25⁰C, pH 7.0 and dosage of 0.250g/L ⁶The data was obtained from Langmuir equations. ⁷The data was obtained from Langmuir equation. ⁸The concentration of BPA was 45.6 mg/L, Temperature 25^oC, for the ge the Langmuir isotherm was used. Polyethersulfone-organophilic montmorillonite hybrid particles were prepared using modified organoclay with hexadecyl trimethyl ammonium bromide (HDTMA) abrevieted as OMMT with polyethersulfone (PES). The following ratios of PES to OMMT were used 1:1, 1:2.5, 1:3, and 1:3.5 and the particles were coded as PO1, PO2, PO3, and PO4. ⁹The experiments were done in an ionic strength solution of 5 mmol/L of CaCl₂ as a background for groundwater and 100 mg/L of NaN₃ to inhibit the microbial degradation. ¹⁰The adsorption isotherms experiments were fitted using S = KDC, where S was the concentration of BPA adsorbed by soil (mg/Kg), KD is the sorption coeficient, and C isth equilibrium solution concentration of BPA (mg/L). The following sorption coefficients had been reported as $K_D=11, 2, 22$, and 44 for RC, RF, TF, and WT soil, respectively. ¹¹The isotherm experiments were conducted in the presence of 0.01 M CaCl₂ as an ionic strength soultion. ¹²Sediment concentration (sediment:solution, w/v), the C_e is the equilibrium final concentration used for the isotherms. The q_e data reported was for concentration of 50 mg/L, initial pH 7.0, Time 8h, Temperature 25^oC. ¹³The experiments were done in the presence of 0.005M CaCl₂ as a groundwater background and 100 mg/L of NaN₃ to inhibit the microbial degradation. The q_e was obtained from the graph of q_e vs. C_e. ¹⁴The q_e was obtained from the graph of q_e vs. C_e. ¹⁵Concentration of BPA 5-80mg/L, mixing rate 100 rpm, Temperature 25^oC, pH 8.0 and dosage of 0.5g/20mL.¹⁶The q_e was obtained from the graph of q_e vs. C_e and the initial concentration of BPA was 11.2 μ g/L.¹⁷The q_e was obtained from the graph of q_e vs. C_e.¹⁸The variation in the q_e is due to the different source of the wood chips. ¹⁹For silica CMK-3 adsorbent the q_e was obtained from Langmuir from experiments done at 25^oC. For the PAC the maximum qe was obtained from the pseudo second-order plots from which the CMK-3 had an q_e of 180 (mg/g).²⁰The total contact time was 4hours and the adsorbent dosage used was 5 and 15 mg/L.²¹Concentration of 60-100mg/L, mixing rate 400 rpm, Temperature 25°C, pH 7.0 and dosage of 0.5g 2L⁻¹. ²²The study was done at a pH of 6.5-7.5. ²³The q_e was obtained from the pseudo second-order model which was conducted at a pH of 7.0 and a temperature of 25 °C. ²⁴The outer diameters for MWCNT15, MWCNT30, MWCNT50 8-15,20-30, and 30-50 nm, respectively. With the solid/water (w/v) ratios as reported in the table. ²⁶The highest qe was obianed using the lowest adsorbent (CDC) dosage of 3.04 mg/10mL. ²⁷The q_e was obtained from Langmuir plots of the data.

3.2 ADSORPTION OF BISPHENOL A ONTO CARBONACEOUS MATERIALS

3.2.1 ADSORPTION OF BPA ONTO CARBON AND POROUS CARBON

Carbonaceous adsorbents had been fabricated trough different techniques to produce different adsorbents that were efficient in removing organic pollutants. The carbonization temperature of carbonaceous material had been found to affect the adsorption properties of the carbonaceous adsorbent (Asada et al., 2004). One of the main advantages that charcoal adsorbents have over other adsorbents is the large surface area that can be obtained through activation by developing a pore structure. Through the Brunauer-Emmett-Teller (BET) method the surface area can be calculated, with some carbonaceous adsorbents having a BET surface area range of 2.5 to 1350 m²/g and total pore volume range of 0.01 to 0.605 ml/g (Asada et al., 2004). Carbonaceous by-products had been used through carbonization to create carbon adsorbents from Sugi chip, Sugi sawdust, Hinoki chip, and Kenaf sawdust, from which the defibrated Kenaf bast and Kenaf fiber were formed (Nakanishi et al., 2002). The carbonization temperature used could reached up to 1000 °C. The adsorption of common organic chemicals had been found to be directly proportional with the BET surface area. For very low concentrations that are usually at trace levels, it had been presumed that the affinity between adsorbate and adsorbent is more important than the pore volume or surface area. We can see equation 1, which is used to study the adsorption of chemicals, is the Freundlich equation (Zeng et al., 2006):

$$q_e = K_F C_e^n \tag{1}$$

where, C_e is the equilibrium concentration (mg/L) of adsorbate, q_e the amount (mg/kg or mg/g) of BPA absorbed at equilibrium, K_F is the distribution coefficient or adsorption parameter related to bonding energy, and represents the general capacity of adsorbate which is absorbed onto the
absorbent for a unit equilibrium concentration $([(mg/g)(L/mg)]^n)$, and the slope n (ranging between 0 and 1) is a measure of the absorption intensity also referred to as surface heterogeneity (unitless). The slope n measures the interaction between the surface of the absorbent and adsorbate, while K_F is a measurement of both interaction and adsorption capacity. When compared to activated carbon, which is more expensive adsorbent, the carbonized carbon byproduct at the temperature of 800 0 C had similar values for both 1/n (0.26-0.27) and K_F (11.5-12.1) values. Actually the absorbance was even better than that of activated carbon that had a BET surface area of 1119 m²/g and pore volume of 0.566 ml/g (Nakanishi et al., 2002). The conclusion is that the carbonaceous by-products could be successfully used as adsorbents and that the temperature of carbonization it is important for the affinity of the adsorbate and absorbent. The equilibrium concentrations range were from 1 to 18 mg/L of BPA after 48 hours of shaking in a bath, with the highest amount of BPA adsorption of 34.1 mg/g of Sugi sawdust carbonized at 800 °C (Nakanishi et al., 2002). Asada et al., 2004 studied the difference of different porous carbons that were carbonized at 400, 700, and 1000 ⁰C (PC₄₀₀, C). When compare the BET surface area with a commercially available activated carbon (AC) it was 2.5, 251, 300 and 1350 for PC₄₀₀, PC₇₀₀, PC₁₀₀₀, AC, respectively. Since it was found that the surface area influences the affinity between the adsorbate and absorbent a Fourier Transform-Infrared Spectrometry (FT-IR) was done in order to indentify the surface functional groups. It was found for PC₄₀₀ and AC that contain functional groups of C=O, C=C, and O-H. The PC₇₀₀ and PC₁₀₀₀ adsorbents showed minimal functional groups, where PC₄₀₀ and AC showed presence of carboxyl groups. The decrease of carboxyl groups as an increased in carbonization temperature lead to a surface polarity decrease, and the surface hydrophobicity also increased. As a result it was presumed that the affinity between the adsorbent and a hydrophobic adsorbate such as BPA to be

strong. The explanation given was that the PC_{1000} was able to absorb more than AC at low equilibrium concentrations up to 5 mg/L even though the surface area of PC_{1000} was smaller than that of AC (Asada et al., 2004). Sui et al., 2011 using a different AC, found that at high concentration of BPA (25mg/L), a mesoporous carbon adsorbent (CMK-3) prepared from hexagonal SBA-15 mesoporous silica and carbonized at 900 0 C performed better than the AC. It is important to note that the CMK-3 had a BET surface area of 920 m²/g compared to 780 m²/g of that of AC.

3.2.2 ADSORPTION OF BPA ONTO ACTIVATED CARBON

Activate carbon had been produced from different carbon base materials such as coal (Yoon et al., 2003, Choi et al., 2005), charcoal (Bautista-Toledo et al., 2005), wood (Yoon et al., 2003, Choi et al., 2005), coconut shell (Tsai et al., 2006a; Nakanishi et al., 2002; Choi et al., 2005; Matsushita et al., 2009), bituminous (Tsai et al., 2006a;), almond shells (Bautista-Toledo et al., 2005), and wastepaper (Matsushita et al., 2009). Activated carbon had been produced in the lab in small scale from different carbon sources; however when the term of Activated Carbon is being used to describe the adsorbent it is very possible that was actually purchased commercially and not produced in the lab. Two types of activated carbon had been used in the treatment of water, which are powder activated carbon (PAC) that is added in the rapid mix tank and granular activated carbon (GAC) that is used in columns. Both PAC and GAC can be bought in bulk for water treatment purposes. Whenever the term lab AC will be used, it is meant to provide the indication that the actual AC was produced in the lab and is not available in bulk commercially. At equilibrium, the adsorption process will reach a maximum capacity and will stay flat in the relationship between the adsorbate concentration on the absorbent phase and in

the solution phase. Besides Freundlich equation there is the nonlinear Langmuir equation that is used to better understand the adsorption. The Langmuir adsorption equation is (Al Duri, 1996):

$$q_e = \frac{q_m K_L C_e}{(1 + K_L C_e)} \tag{2}$$

where, C_e is the concentration (mg/L) and q_e the amount (mg/g) of BPA absorbed at equilibrium. K_L is the direct measure of intensity of the absorption process (L/mg), and q_m is the surface constant that relates the area occupied by a monolayer of adsorbate, that reflects the sorption maximum capacity (mg/g). We can see in Table 2 a relationship between the BET surface area of different PAC and their Freundlich and Langmuir parameters.

		Langmuir			Freundlich				
Adsorbent	Area (m ² /g)	$\begin{array}{c} & K_L \\ q_m (mg/g) \\ & \\ (L/mg) \end{array}$		R ²	\mathbf{R}^2 $\mathbf{K}_{\mathbf{F}}^1$		R ²	Reference	
PAC	780	296	0.121	0.918	55.1	0.45	0.951	Sui et al., 2011	
AC-PCB	916	263.2	1.81	0.854	206.1	0.07	0.963	Tsai et al., 2006a	
AC-BPL	1060	328.3 4.97		0.770	253.8	0.14 0.951		Tsai et al., 2006a	
AC-M	1084	263.1 0.153		N.A.	N.A.			Toledo et al., 2005	
AC	1119	N.A.			9.2	0.27	0.995	Nakanishi et al., 2002	
AC	1150	N.A.			0.24	0.38	N.A.	Asakura and Matsubo, 2009	
AC-A	1216	188.9	0.071	N.A.	N.A.			Toledo et al., 2005	
AC-S	1225	129.6 0.038		N.A.	N.A.			Toledo et al., 2005	
AC-CO0	1260	N.A.			28 0.783 N.A.		N.A.	Choi et al., 2005	
AC	1350	N.A.			9.9	9.9 0.71 0.980		Asada et al., 2004	
AC-WB0	1610	N.A.			18	18 0.593 N.A.		Choi et al., 2005	
PAC	1780	337 0.1095		0.984	N.A.			Kim et al., 2011	

 Table 3.2 BET Surface Area, Langmuir, and Freundlich parameters for activated carbon

¹The unit of K_F was $(mg/g(L/mg)^{1/n})$. ²The unit of K_F was $(\mu g/mg (L/\mu g)^{1/2})$ with equilibrium concentration of BPA in water in the units of $\mu g/L$.

From Table 3.2 we can see that a higher value in BET surface area does not necessarily mean a higher adsorption of BPA. As stated earlier, the functional groups on the surface of the adsorbent plays a significant role for the adsorption of BPA. The adsorption mechanisms of

aromatic compounds, such as BPA, are generally based on π - π dispersion interactions between the aromatic ring electrons from the adsorbate and those of the activated carbon (Liu et al., 2009). For the most part, an increase in BET surface area did increase the adsorption of BPA since the adsorptive sites had increased. However, at high concentrations AC sorbents may not work as efficient, because the pores may by swell by the adsorbate (Braida et al., 2003). Adsorbents with low surface polarity is effective for the adsorption of high hydrophobic substances, and high BET surface area of AC is effective as the solubility in the water of the pollutant increases (Asada et al., 2004). Toledo et al., 2005 studied three different AC sorbents, two commercially available from charcoal based (AC-S and AC-M) and one lab created from almond shells (AC-A). All three samples of AC were analyzed for the chemical characteristics. For the determination of acid and basic groups on the surface of the AC he used a procedure described by Boehm, 1996, and for the pH of the point of zero charged (pH_{PZC}) was used the procedures described by Newcombe et al., 1993 and Ferro-Garcia et al., 1998 by using pH shift analysis. The AC sample M had a pH_{PZC} of 7.5 which was similar to that of the solution pH 7.0, which will produce a surface charge density close to zero. Sample S had a pH_{PZC} of 12.0, which will produce a positive charge density. The AC sample A had a value between the AC sample M and S with a pH_{PZC} of 10.1. The adsorption capacity followed this pattern for AC sample M, A, and S, with $q_m (mg/g)$ of 263.1, 188.9, 129.6, respectively. The dispersion interactions between the adsorbent and adsorbate were present for AC samples A and S, as a result the $q_{e}\xspace$ is reduced when compare to that of sample M. Another important factor for the adsorption that was found is the source of carbon for the AC, different carbon sources with similar BET surface areas performed differently.

For better performance the AC had been treated through different process in order to increase its effectiveness. The treatment in some case produced the exact opposite effect, reducing the amount of BPA removal. For example AC treated with nitric acid produced an increase in the amount of carboxyl and hydroxyl groups in the surface of the adsorbent. The increase in the affinity of the AC towards water was due to the H-bonding that formed on the surface of the AC with the water molecules (Liu et al., 2009). The formation of the new bonds inhibited the adsorption of BPA. From the two different AC treated with nitric acid, one of them showed a significant decreased from 1,777 m²/g to 1.76 m²/g in the available surface area for adsorption.

Because the adsorbent phase is organic carbon based, the log K_{OW} plays a significant role in the adsorption of BPA onto AC sorbents. When six different AC were used for the removal of BPA, 17 β -estradiol (E2), and 17 α -ethynyl estradiol (EE2) with log K_{OW} of 3.3, 3.1-4.0, 3.7-3.9, respectively. For all the six AC, the adsorption order of removal was E2>EE2>BPA, where the octanol-water partition coefficient (K_{OW}) was believed to play a significant role. More studies done on other organic pollutants found that the increase in the K_{OW} increases the adsorption capacity (Liu and Qian, 1995, Poerschmann et al., 2000, Rao and Asolekar, 2001).

All of the AC studied found that it followed a pseudo-second-order kinetics adsorption equation.

3.2.3 ADSORPTION OF BPA ONTO CARBON NANOMATERIALS

The creation of nanomaterials and with that the carbon nanomaterials (CNMs) had been recognized as one of the most promising new materials in our century (Nowack and Bucheli, 2007, Mauter and Elimelech, 2008). The increasing production of CNMs had also increased the release in the environment during production, applications and disposal. Because the CNMs have

a strong interaction with the organic pollutants due to its hydrophobic surface (Pan and Xing 2008), the organic pollutants behavior in the environment could be affected. Mauter and Elimelech, 2008 had proposed the used of CNMs in the water treatment. The CNMs had found to have high adsorption capacity of natural organic matter (Su and Lu, 2007), pesticides (Pyrzynska et al., 2007), fluoride (Li et al., 2003), heavy metals (Li et al., 2002), and polyaromatic hydrocarbons (Yang et al., 2006).

Pan et al., 2008 studied the adsorption of BPA using different CNMs, which included carbon nanotube of which one singlewalled (SWCNT), three multiwalled (MWCNTs), and fullerene. The MWCNTs were designated as MWCNT15, MWCNT30, and MWCNT50 for having the outer diameter of 8-15, 20-30, and 30-50 nm, respectively. The BPA concentrations used were 100 - 40,000 µg/L, and the solid/water ratio for fullerene was 1:100-1:200 and for the CNTs 1:20,000 - 1:120,000. The SWCNT performed the best with $q_e \ (mg/g)$ of 600, the MWCNTs had a qe 61-102, and finally fullerene had a qe of 236. The equilibrium adsorption was obtained after 7 days. As stated above the π - π bond have been found to play a significant role in the adsorption of BPA onto carbon organic materials, and also to any aromatic compound to the adsorption onto CNMs (Gotovac et al., 2006, Chen et al., 2007). The π - π bonds are strong for donor-acceptor systems, but weak as a pair of acceptor or donors (Zhu et al., 2004, Chen et al., 2007). The π - π bond between BPA and CNMs is a donor-acceptor system which is very strong. Pan and Xing, 2010 studied the kinetics of SWCNT, MWCNT15, and AC which was wood charcoal based. Their results came in good accordance with previous studies which found that the absorption of BPA onto carbonaceous materials follows a pseudo-second order equation. However, in their study they could not found a clear pseudo-second order kinetics for the adsorption onto the AC. The high capacity adsorption for AC as discussed earlier, relies on the

high surface area that is generally in the inner pores of the sorbent. The adsorption on the AC was found to be diffusion controlled, thus the availability of the inner pores would be a controlling factor. With an increase in the concentration of the solid-phase, the rate of adsorption will decrease (Leyva-Ramos et al., 2007). The decreased in the adsorption could also be attributed if two organic pollutants are present. Depending on their chemical and structural properties different organic pollutants could over compete others. For example, in one study the BPA out competed EE2 when the concentration of BPA increased. One of the reasons was believe to be the butterfly structure of BPA that facilitates the adsorption more than that of EE2, which is an irregular three-dimensional structure (Pan and Xing, 2010).

3.2.4 ADSORPTION OF BPA ONTO POLYMERIC ADSORBENTS

Polymeric adsorbents had been investigated for the removal of BPA having high surface area, good surface chemistry, and large pore size. The polymeric adsorbents could also be regenerated using solvents such as methanol, acetone, and ethanol (Valderrama et al., 2007). Some of the polymers used for BPA adsorption could be bought commercially; others had been manufactured in the laboratory. Commercially polymer adsorbents that had been used for the BPA adsorption are hypercrosslinked polymeric adsorbent MN-200 and NDA-150, aminated polymeric adsorbents MN-100, and MN-150 (Fan et al., 2011). Other polymer sorbents had been prepared in the lab such as β -cyclodextrin derivative (polyCD) (Kitaoka and Hayashi, 2002), CD-grafted chitosan (CD-P) (Aoki et al., 2003), chitosan-bearing β -cyclodextrin (CDC) (Aoki et al., 2004), magnetic non-imprinted polymers (MNIPs), and magnetic molecularly imprinted polymers (MMIPs) based on Fe₃O₄ (Guo et al., 2011). When we compared the commercial hypercrosslinked polymeric adsorbents, we cans see that MN-200 which had a greater BET surface area of 1156 m²/g than that of NDA-150 with a BET surface area of 836 m²/g. The MN-

200 performed better than that of NDA-150 having a maximum absorbance of 2.09 mmol/g for MN-200 compare to that of 1.75 for NDA-150 at 30 °C. Based on these results we could conclude that the surface of hypercrosslinked polymeric adsorbents and micropore area could be key factors for the BPA adsorption affinity. The MN-150 had lower BET and micropore area than that of MN-100. The BET surface area for MN-150 was 850 m^2/g and 815 m^2/g for MN-100. For the aminated polymeric adsorbents it was found that the functional groups on the surface of the adsorbent would play a significant role in the adsorption. The maximum adsorption at 30 °C was found to be only 1.22 mmol/g for MN-100 compared to that of 1.69 mmol/g for MN-150. For the pH range of 1 to 7 the adsorption remained relatively the same around 425 mg/g for MN-200, and 330 mg/g for MN-150 at 30 ^oC. One of the things that was found during this study was the contribution that π - π bonds formed between the BPA and polymeric adsorbents with the benzene rings. The carbon atom in the polymeric adsorbent has a π electron orbit that is perpendicular to the polymeric surface. As a result the BPA, which has two benzene rings, would have a stronger adsorption with the benzene rings to the polymer surface than other organic pollutants with one benzene ring. Using the FTIR spectrometry it was determined that the MN-100 and MN-150 showed presence of tertiary amino groups. The nitrogen-containing groups that are present on the polymeric adsorbent surface may form hydrogen bonding by the -OH substitution on the BPA.

For the lab created polymeric adsorbents MMIPs and MNIPs the adsorption experiments were done in a solution of 100 mg/L BPA in a pH 3.0 with an agitation speed of 300 rpm for duration of 12h with an adsorbent ratio to solution of 0.01g to 10mL. Using the Langmuir equation the capacity of both MMIPs and MNIPs were lower than those of commercial polymer adsorbents MN-200 and MN-150, having a maximum absorbance of 142.9 and 112.4 for MMIPs

and MNIPs, respectively. Both the MMIPs and MNIPs followed pseudo-second order kinetics (Guo et al., 2011).

The lab created polymer adsorbent polyCD was used to remove BPA from aqueous solution (Kitaoka and Hayashi, 2002). The removal was done from a 0.2mM BPA solution, neutralized at pH 7.0 using 20mM 3-(N-morpholino)propanesulfonic acid (MOPS) buffer at 20 ⁰C with a concentration of 1mg/mL of polyCD being able to remove 92 % and 97 % after 2h and 18h, respectively. The removal capacity was found to be 84 mg/g being equal to 0.65 mol of BPA for 1 mol of CD in polyCD. In a different study a 4.8 x 10⁻⁴ M of BPA was used with 50 mg of lab created CD-grafted chitosan (CD-P) at 25 ^oC and stirred at 90 rpm for a duration of 50h (Aoki et al., 2003). The equilibrium time was found to be around 5 hours, with 80 % of BPA adsorbed from the solution. The amount of BPA adsorbed at equilibrium was found to be in a molar ration from the amount of CD moiety in the CD-P to be equal to 0.85/1.0 mol of CD/BPA. Aoki et al., 2004 presented an improved method of synthesizing chitosan-bearing β -cyclodextrin (CDC) from 4-(4, 6-dimethoxy-1, 3, 5-triazin-2-yl)-4-methylmorpholinium chloride (DMT-MM) and was used for the adsorption of BPA. When the equilibrium concentration of BPA was higher than 10 mg/L the amount absorbed on the CDC was 85mg/g, and when the equilibrium concentration of BPA was lower than 1 mg/L the amount of BPA adsorbed was a lot smaller of about 0.1 mg/g.

3.2.5 ADSORPTION OF BPA ONTO SOILS

The adsorption of BPA onto soils had been also investigated in order to understand the behavior of BPA in the environment. The BPA exposure to soils is through the sewage sludge that is added to the soil for farming purposes that could be contaminated with BPA, or through the leachate from landfills that contains BPA. The contamination from landfill leachate could be

very important because the highest concentrations of BPA had been reported in landfill leachates. Different soils had been used to study the sorption or adsorption of BPA onto them. Soil from a agricultural land from South Australia taken from 0 to 15 cm were denoted as Roseworthy Campus (RC), Roseworthy Farm (RF), Terretfield (TF), and Waite Campus (WT). The soil sample that is very well represented in South Australia was a sandy loam (RF), which was collected from Roseworthy Farm, was used in degradation studies also (Ying and Kookana, 2005). The percentages of organic carbon reported were 1.3, 0.85, 1.8, and 2.9 for the RC, RF, TF, and WT, respectively. Fent et al., 2003 used soils from North-Rhine Westphalia, and Rhineland-Palatinate from Germany. Some of the properties of the soils were sandy loam with organic carbon (OC) percentage of 1.35, loamy silt with OC % of 1.09, Loamy Silt with OC % of 2.11, and Sandy loam with OC % of 0.92 for Laacher Hof AXXa, Laacher Hof AIII, Hofchen , and Mußbach, respectively. The sorption of BPA on soils can be correlated depending on the carbon content in the soil. The sorption of organic pollutants had been found to be well correlated to the amount of organic carbon present in the soils, the higher the percentage the higher the adsorption. In order to quantify the sorption the following equations 3 and 4 had been used:

$$S = K_D C \tag{3}$$

$$K_{OC} = \frac{K_D \times 100}{\% \text{ org. C}}$$
(4)

where, S is the concentration of the BPA adsorbed by the soil (mg/Kg), K_D is the sorption coefficient, C is the equilibrium concentration (mg/L), K_{OC} is the organic carbon sorption coefficient.

The soils from South Australia were used in a ratio of 2g to 200 mL of water with a BPA concentration of 25 μ g/L and agitated for a duration of 2 h in a mechanical shaker. The K_D

values followed a good correlation to the percentage of organic carbon in soils. The following order was obtained WT > TF > RC > RF with the values of 44, 22, 11, 2 and 1,507, 1,210, 881, 251 for K_D and K_{OC}, respectively. For the soils in Germany a ratio of 3g to 20 mL of 0.01 M CaCl₂ solution with a BPA concentration of 5 mg/L was shaken for duration of up to 70 h in overhead shaker. The order of adsorption was as following for Hofchen > Laacher Hof AXXa > Mußbach > Laacher Hof AIII, with the values of 17.12, 12.57, 7.4, 6.9 and 811.2, 930.9, 805.3, 636.1 for K_D and K_{OC}, respectively. It is important to state the K_D values had followed for the most part well the organic carbon content in the soils, with the only difference was for the soils Mußbach and Laacher Hof AIII, which had close percentages of 0.92 and 1.09. Even though the soil from Mußbach had a lower organic carbon percentage of 0.92 it had a higher K_D value than the soil of Laacher Hof AIII, however their percentages were close to each other. Based on the following results we can see that according to McCall et al., 1980 the presence of BPA in soils would be moderately mobile in the RF soil and have a low mobility for all the rest of the samples from South Australia or Germany. McCall et al., 1980 classified the organic compounds with values of K_{OC} between 150-500 and 500-2,000 to have moderately mobility and low mobility, respectively.

3.2.6 ADSORPTION OF BPA ONTO SEDIMENTS

The presence of BPA in the aquatic system is well known as presented in the introduction of Chapter 3. BPA had been identified in the surface water, wastewater effluents, landfill leachate, and industrial wastewaters. The presence of BPA in the surface waters and the fact that is a hydrophobic chemical makes it a good candidate to accumulate in the sediment. The BPA sorption on sediments would influence other process such as degradation or bioaccumulation (Xu et al., 2008). The source of drinking water plant or other utilization could be an aquifer, which could become contaminated through landfill leachate. As a management for fresh water in Australia in particular, but other countries also, uses the aquifer storage and recovery (ASR) (Ying et al., 2003, Dillon et al., 1999). The ASR is used by utilizing injection wells to recharge a confined aquifer to be available for recovery when needed (Vanderzalm et al., 2006). The introduction of the effluent from a sewage treatment plant into aquifer could pose a risk, because of the potential contamination of that water. Different studies had been conducted to evaluate the sorption of BPA onto sediments (Ying et al., 2003; Sun et al., 2005;Zeng et al., 2006; Xu et al., 2008).

The main parameters that had been investigated for the sorption of BPA onto sediments were the Freundlich, K_D , and K_{OC} parameters. Zeng et al., 2006 took six different sediment samples from Xiangjiang river and denoted them A, B, C, D, and E. The organic carbon percentage for the soils were 6.69, 5.64, 4.88, 2.63, and 2.06 for A, B, C, D, and E, respectively. Using different masses of soil and concentration of BPA using the Freundlich equation the K_F parameter was found. The K_F parameter could be used as a relative indicator of adsorption capacity. As a result it is assumed that the higher the organic carbon, the higher the K_F would be. This was found to be the case when the K_F increased from sample E with a value of 0.0072 to 0.0178 for sample A, which had the highest level of organic carbon. Also the K_D (L/Kg) was from 2.2 for sample E and 8.6 for sample A. The results were in good correlation with the results from the soils.

The study of BPA sorption was conducted using marine sediments by Xu et al., 2008. A total of six marine sediments were collected from Mai Po Inner Deep Bay from Hong Kong. The sediments were than dried and pass through a series of sieves. The sediment that passes through a 60-mesh (250 μ m) sieve and retained by a 100-mesh (150 μ m) sieve was used for the

adsorption. There was 5g of dry weight sediment used at 25 0 C, followed by the addition of 0.02 % by weight of sodium azide for the inhibition of bacterial growth. A 20 mL of aqueous solution with different BPA initial concentrations (5-80 mg/L) added in a 50-mL Erlenmeyer flask. The pH was adjusted at 8.0 and the samples were placed in a temperature-controlled S150 shaking incubator at 100 rpm for duration 12h. The aqueous solution was prepared at 30 psu according to Zhao et al., 2001. To better see the effect of the organic carbon, the same six sediments were also treated with hydrogen peroxide (H₂O₂) oxidant and the experiments were conducted again. After the oxidation with H₂O₂ about 80-90 % of the organic carbon had been removed. The initial percentage of organic carbon were 1.28, 1.34, 1.23, 1.27, 1.22, 1.21 and the final percentage of organic carbon after the H₂O₂ treatment were 0.25, 0.24, 0.18, 0.21, 0.16, and 0.14 for the soil samples A, B₁, B₂, B₃, D, and E, respectively. The K_D values for the marine sediments were

similar to those reported by Zeng et al., 2006 for the marine sediments. However, for the treated sediments the values of K_D were equal to the lower range. The K_D (L/Kg) values were 8.54, 6.76, 4.96, 5.22, 4.65, 4.43 and for the treated sediments the values were 3.54, 3.00, 2.37, 2.46, 2.31, 2.14 for A, B₁, B₂, B₃, D, and E, respectively. The results were similar to those reported by Sun et al., 2005 when using sediments from Yellow River from San Menxina bottom sediment with a BPA concentration between 2 to 12 µg/L. The adsorption parameters found for Freundlich and linear isotherms were $K_f = 6.248$, 1/n = 0.782, and $K_D = 4.116$. Ying et al., 2003 reported similar numbers for sediment collected from aquifer material with an organic content of only 0.5 %. The K_D was reported to be equal to 3.89 L/Kg, showing a small adsorption of BPA on sediments.

3.2.7 ADSORPTION OF BPA ONTO MINERALS

The adsorption of BPA had been found to be possible on inorganic adsorbents such as minerals. Different raw minerals or modified through different process had been used for the adsorption of BPA. Such minerals are surfactant-modified zeolite (Dong et al., 2010), andesite, diatomaceous earth, titanium dioxide, activated bleach earth (Tsai et al., 2006a), commercial hydrophobic zeolite (Tsai et al., 2006b), geothite, montmorillonite, kaolinite (Shareef et al., 2006), polyethersulfone-organophilic montmorillonite hybrid particles (Cao et al., 2009), organic-inorganic mesoporous material (Ph-MS), mesoporous silica (Kim et al., 2011), and Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007). The parameters and equations that had been used to characterize and evaluate the adsorption of BPA such as Freundlich, Langmuir equations, pseudo first and second order parameters or BET surface area had been used.

The minerals that had the lowest adsorption of BPA are andesite, diatomaceous earth, titanium dioxide, and activated bleach earth. The study with all this four minerals had been conducted by Tsai et al., 2006a. The BET surface area of the minerals had been reported of being 2.7, 3.8, 50.1, and 257 for andesite, diatomaceous earth, titanium dioxide, and activated bleach earth, respectively. Using a BPA initial concentration of 20 mg/L, absorbance dosage of 0.5g:2L, pH 7.0, agitation rate of 400 rpm, and temperature of 25 °C a pseudo second order kinetic model relationship was established. The maximum adsorption capacity using the pseudosecond order model were 0.53, 0.74, 0.33, and 0.86 mg/g for andesite, diatomaceous earth, titanium dioxide, and activated bleach earth, respectively. We can see there could not be a very good correlation of the BET surface area to the adsorption capacity of the adsorbent. For the titanium dioxide the adsorption was lower than expected if we were to take into consideration just the BET surface area as the main factor of adsorption. The same case applies when we compare the activated bleach earth that had a BET surface area of about 260 m²/g to that of and esite and diatomaceous earth that had a BET surface area of 3 and 4 m^2/g , respectively. We would expect a lot larger maximum adsorption capacity from the activated bleach earth compare

to that of andesite and diatomaceous earth. However, we can see that there was no significant difference between them, having values for all three between 0.53 to 0.86 mg/g. When looking at the adsorption is important to note that the physical characteristics such as surface area or pore volume are not the only important characteristics of the adsorbent. The chemical characteristics of the adsorbent such as surface polarity charge should be also taken into consideration. In the case for the BPA, which is hydrophobic, would have an electrostatic repulsion with the mineral adsorbent if the charge of the adsorbent would be a negative surface charge. The surface properties had been found to play a significant role in the adsorption of BPA especially at low trace level concentrations in other adsorbents.

Geothite, montmorillonite, and kaolinite are minerals that also showed weak adsorption capacity for BPA (Shareef et al., 2006). Different amount of mineral adsorbents were added to 300 mL of solution in order to obtain a surface area of 100 m²/L. The mass of the minerals were 0.48g, 0.94g, and 1.28g for geothite, montmorillonite, and kaolinite, respectively. The study was conducted with a BPA concentration of 0.3 μ M, pH4 and 10, at temperature of 25 ⁰C, and duration of 10 days. The pH was adjusted to the required value by adding 10 mM HNO₃ or KOH. The adsorption of BPA was only 10-40 %, with the montmorillonite at pH 10 having 40 % and the rest being under 20 %. The difference for the montmorillonite was believed to be due to the surface area of the interlayer region. The BET surface area takes into consideration only the external surface area. However, for the clays the potential surface area taking into consideration the interlayer regions also could be as high as 800 m²/g.

Using the Langmuir isotherm for the maximum adsorption capacity q_e (mg/g) in the range of 1.4 to 9 had been found for zeolite synthesized from coal fly ash (ZFAL and ZFAF), mesoporous silica (MCM-41), treated and untreated Fe(III)/Cr(III) hydroxide. Synthesized

zeolite had been used to remove trivalent Chromium Cr(III) (Sui et al., 2008, Wu et al., 2008), and phosphate (Wu et al., 2008). In the past it was found that the adsorption of BPA was only effective using Y-type zeolite not with A- and F-type zeolite (Fukahori et al., 2003a, 2003b). Recently zeolite synthesized from fly ash had been study for the removal of BPA (Dong et al., 2010). The main chemical composition differences for the fly ashes were the content of calcium oxide (CaO). The zeolite that was synthesize from the fly ash with high content of CaO (12.5 %) was denoted ZFAF, and for the one that was with low CaO (3.5%) was denoted ZFAL. The BET surface area for ZFAF was 2.8 m^2/g and for ZFAL was 1.0 m^2/g . For the sorption tests 0.05g to 100 mL of solution with concentrations of BPA ranging from 0.5 to 100 mg/L was used in a 250 mL conical flask was then placed in a orbital shaker at 25 °C, for a duration of 24 h. The maximum adsorption concentrations were found to be 1.4 and 3.5 mg/g for the ZFAL and ZFAF, respectively. Similar adsorption capacities had been found using Fe(III)/Cr(III) hydroxide. The adsorption of BPA using Fe(III)/Cr(III) hydroxide was investigated, because the adsorbent is produced in a effluent of treatment plants. The treatment of Cr(VI) using Fe(II) reduction created an effluent of Fe(III)/Cr(III) hydroxide. The Fe(III)/Cr(III) hydroxide had been already studied for the removal of pesticides (Namasivayam et al., 1994b), heavy metals (Namasivayam and Senthilkumar, 1998), dyes (Namasivayam et al., 1994a), and nickel (Namasivayam and Ranganathan, 1994c). The BET surface area for Fe(III)/Cr(III) hydroxide was found to be 156 m^2/g , which was a lot larger than that of ZFAF and ZFAL. But the maximum adsorption capacity was not too much different. The parameters studied for the adsorption experiments were 500 mg to 50 mL of aqueous solution at 160 rpm. The effect of dosage was analyzed for 100-800 mg and BPA concentrations of 10-50 mg/L. It was found that the adsorption follows a pseudo-second order model. Using the Langmuir equation it was found the maximum adsorption of capacity was only 3.47 mg/g for the untreated sorbent, and 3.67 mg/g for the pretreated sorbent at different pH using HCl and NaOH. For the commercially available mesoporous silica MCM-41 the adsorption of BPA did not follow a very good regression for a pseudo-second order model. Using a 50 mg of sorbent to 250 mL of aqueous solution with BPA concentrations of 10 to 260 mg/L, shaking at 200 rpm at 25 0 C for 6h at a pH of 6.2 to 7.2 it was modeled using Langmuir isotherm. The maximum adsorption capacity was found to be only 9 mg/g.

The adsorption of BPA was investigated on polyethersulfone(PES) - organophilic montmorillonite (OMMT) hybrid particles with mass ratios of PES to OMMT of 1:0, 1:1, 1:2.5, 1:3, and 1:3.5, which were denoted as PO, PO₁, PO₂, PO₃, and PO₄, respectively (Cao et al., 2009). The porosity of the sorbents was between 75 to 89 %. The study found that the adsorption followed a pseudo-second order model. The adsorption experiments were conducted using a 0.1g of sorbent to 20 mL of aqueous solution with different BPA concentrations of 100, 150, 200, and 240 μ mol/L at 25 °C. For the adsorption isotherms study, different adsorbent dosages of 0.003 to 0.1 g to 20 mL of aqueous solution with BPA fixed concentration of 200 μ mol/L at a temperature of 25 °C was done. The maximum absorbance q_e (mg/g) and Langmuir parameter K_L was obtained using the Langmuir isotherm and Freundlich parameter K_F and 1/n was obtained using Freundlich isotherm with q_e = 20.70, K_L = 0.0502, K_F = 2.46, 1/n = 0.472; q_e = 21.74, K_L = 0.0785, K_F = 4.15, 1/n = 0.380; q_e = 23.58, K_L = 0.130, K_F = 7.30, 1/n = 0.276; q_e = 32.05, K_L = 0.0836, K_F = 5.91, 1/n = 0.396 for PO1, PO2, PO3, and PO4, respectively.

The adsorption of BPA onto different minerals with higher adsorption capacity ranging from 56.8 to 351 mg/g had been investigated. The minerals that had a highest adsorption capacity were surface modified zeolite prepared from fly ash (Dong et al., 2010), hydrophobic Y-type zeolite (Tsai et al., 2006b), and organic-inorganic hybrid mesoporous material (Ph-MS)

(Kim et al., 2011). For the modified zeolite experiments two different fly ashes had been used to first synthesize the zeolite. The zeolites were presented above as ZFAL and ZFAF depending on the initial CaO concentrations in the fly ash. The surface modification of minerals had been found to enhance the adsorption of organic pollutants (Dong et al., 2010). The surface modification was done using Hexadecyltrimethylammonium (HDTMA). The two surface modified zeolites were denoting as SMZFAL and SMZFAF. The FTIR test found that the SMZFAs have presence of symmetric and asymmetric vibrations of C-C from the alkyl chain of HDTMA. This was the result of the bi-layer micelles that formed, rather than monolayer coverage that the HDTMA formed. For the sorption tests 0.05g to 100 mL of solution with concentrations of BPA ranging from 0.5 to 100 mg/L was used in a 250 mL conical flask that was placed in an orbital shaker at 25 °C, for duration of 24 h. The maximum adsorption concentrations q_e (mg/g) increased with the surface modification from 1.4 to 56.8 for the zeolite synthesized from the low CaO concentration and increased from 3.5 to 91.5 for the zeolite synthesized from high CaO concentration. The BET surface area (m^2/g) also increased with the surface modification from 1 to 50.6 and 2.8 to 91.5 for the SMZFAL and SMZFAF, respectively.

The adsorption of Y-type hydrophobic zeolite had also found to be more effective than other minerals with a maximum adsorption concentration of 111.11 mg/g (Tsai et al., 2006b). The BET surface area of the zeolite was found to be 504 m²/g. The adsorption of BPA on the zeolite was found to follow a pseudo-second order model. Using a 1g of sorbent with average particle size of 0.223mm to 2 L of aqueous solution, with BPA concentrations of 10 to 90 mg/L, agitation speed of 400 rpm at 25 $^{\circ}$ C for 2h at pH 7.0 it was modeled using Langmuir and Freundlich isotherms. The Langmuir parameter K_L was found to be 3.103 (L/mg), and Freundlich parameters were K_F = 67.20, and 1/n = 0.22. It was concluded from the study that the

adsorption was due to the London force mechanism, and that the adsorption depended greatly on the adsorption dosage and initial BPA concentration.

Finally the highest adsorption capacity out of the minerals was found to be to that of phenyl-functionalize mesoporous silica (Ph-MS) that was synthesized in the laboratory. Using a 50 mg of sorbent to 250 mL of aqueous solution with BPA concentrations of 10 to 260 mg/L, shaking at 200 rpm at 25 0 C for 6h at a pH of 6.2 to 7.2 it was modeled using Langmuir isotherm. The adsorption followed a pseudo-second order model and found to have a maximum adsorption capacity of 351 mg/g.

3.3 RESEARCH OBJECTIVE

The research presented in Chapter 3 was conducted in order to establish the adsorption capacities of all three mineral adsorbents hematite (H), magnetite (M1), and magnetite (M2). This was very important for the next steps of the research when the effect of ionic strength, pH, adsorbent dosage, and BPA concentrations will be all taken into consideration for the strongest adsorbents. The most important characteristics of any adsorbent are to be inexpensive and effective. If a sorbent is able to absorb well a certain pollutant, but it is very expensive, than it would become impractical. If a sorbent is a weak sorbent, but is able to be regenerated and relatively inexpensive, could be more practical from a financial and environmental point of view.

The research objective in the first part was to obtain the maximum adsorption capacity at 1 day and 7 days at the optimal parameters found from the research from Chapter 2. The best adsorbent was hematite H at pH 2. The data was than analyzed using Langmuir and Freundlich isotherms in order to better interpret the data.

In the second part of the study, the effect of time on an adsorption was determined by keeping the concentration of BPA fixed at 1.2 mg/L. A low concentration of BPA was chosen, because the levels of BPA reported in the environment were not very high. This time the pH was not adjusted and only the 5g to 50 mL ratio was evaluated. The study was looking to see the effect on the Freundlich parameters with time at the low BPA concentration. For this study all three iron oxide mineral adsorbents have been used.

3.4 MATERIALS AND METHODS

3.4.1 CHEMICALS

All the chemicals used for these experiments are presented in Table 3.

Chemical	Specification	Source		
Methyl <i>tert</i> -butyl ether (MTBE)	HPLC grade	Fisher Chemicals, Fairlawn, NJ		
6N Hudrochloric Acid (HCl)	ACS Reagent	RICCA Chemical Company,		
	grade	Arlington, TX		
Bisphenol A (BPA)	≥ 97 %	Sigma-Aldrich, St.Louis, MO		
Hematite (H) Fe_2O_3 ,	\leq 5 micron and \geq	Sigma-Aldrich, St.Louis, MO		
	99%			
Magnetite (M1) Fe ₃ O ₄ ,	Laboratory Grade	Fisher Chemicals, Fairlawn, NJ		
Magnetite (M2) Fe ₃ O ₄ ,	325 Mesh Powder	Alfa Aesar, Ward Hill, MA		

 Table 3.3 Chemicals

3.4.2 ADSORPTION CAPACITY

Different amounts of 1g, 2g, and 5g of hematite were added to 50 mL of deionized water (DI) in 125 mL serum bottles with different BPA concentrations. For the blank system there was no adsorbent added. The purpose of the blank was to determine if there was any BPA transfer from the water phase to the air phase or adsorbed to the glass of serum glass bottle. After the addition of BPA solution and adsorbent, the serum bottles were capped with butyl rubber septa, and crimped with aluminum seals. The serum bottles were then shaken and placed in a rotating tumbler at 16 rpm in the dark for mixing at 25 0 C. For the 1g:50mL solid solution loading, the BPA aqueous concentrations were 0.4, 0.8, 1, 2, 4, 6, 8, 10, 12, 15, 17, 20, 25, 33, 40, and 50 mg/L. For the 2g:50mL loading, the BPA aqueous concentrations were 0.4, 1, 2, 4, 6, 8, 10, 15, 17, 20, 25, 33, 40, 45, 50, 60, 70 and 80 mg/L. For the 5g:50mL loading, the BPA aqueous concentrations were 1, 2, 4, 6, 8, 10, 20, 25, 40, 50, 65, 85, 100, 115, 130, 150, 180 and 200 mg/L. The experiments were carried out for a period of 1 and 7 days.

3.4.2.1 ROUTINE ANALYSIS

After removal of serum bottles from the rotating tumbler, 50mL of the sample was transferred from the bottle into a 50mL Teflon centrifuge tube, and centrifuged for 10 minutes at 7100 rpm using an Eppendroft centrifuge 5810R. The solution was then transferred in two different vials. Approximately 15 mL of the solution was transferred into a 20 mL glass vial, and the rest in a 40 mL glass vial. The 20 mL vial was used or the measurement of total dissolved solids and pH, and the 40 mL vial was used for the BPA analysis.

3.4.2.2 TDS AND pH ANALYSIS

The analysis of total dissolve solids (TDS) was done using Orion conductivity meter model 150 with an Orion conductivity cell 013005D and the pH analysis was performed using Thermo Orion pH/mV/temperature meter 720 using an Orion comb. pH probe model 915600. The instrument was calibrated for the pH using pH standards of 4.0, 7.0, and 10.0. The calibration of TDS was done using TDS standards with a conductivity of 1413µs and 12.9 ms.

3.4.2.3 LIQUID-LIQUID EXTRACTION (LLE)

Exactly 10 mL of samples were transferred from the 40 mL vial or from the diluted sample from the volumetric flask into a 15 mL glass test tube. After the water sample was transferred, a volume of 75 μ L of 2,4,6-tribromophenol (TBP) from a stock solution of 1,000

ppm prepared in acetone was added using a 250 μ L syringe. After adding one drop of concentrated hydrochloric acid (HCl) into the test tube, the test tube was then closed and shaken gently twice. After the shaking of test tubes, 2 mL of methyl *tert*-butyl ether (MTBE) were added. The test tube was then shaken for 30 seconds vigorously and then followed by 2-3 minutes of slow mixing. After the mixing, enough time was allowed for the two phase to separate, and then about 1 mL of the MTBE from the upper phase was pipetted using a 1 mL Eppendorf pipetter into a 2 mL gas chromatography (GC) vial.

3.4.2.4 BPA ANALYSIS

The MTBE sample obtained from the LLE step was analyzed on a Agilent Model 6890 GC. The GC was equipped with a flame ionization detector (FID). The injection was done using an auto sampler by direct injection of 1.0 μ L of MTBE sample at an inlet temperature of 250 °C, while the detector temperature was maintained at 300 °C. For the separation of BPA and TBP, a DB-5 (J&W) widebore capillary GC column with dimensions 30m x 320 μ m x 0.25 μ m was used. The oven temperature in the beginning was set at 100 °C. The temperature was then ramped from 100 °C to 265 °C at 20 °C/min and held at 265 °C for 1 minute. Helium (ultra high purity), was the carrier gas with a flow rate of 5.8 mL/min and at an inlet pressure of 25 psi. The other gases used were dry grade air, hydrogen (H₂), and the makeup gas nitrogen (N₂). The flow rates for the other gases were 400 L/min, 10 L/min, and 35 L/min, respectively.

The BPA was identified by the retention time from the BPA standard calibration that was prepared in MTBE. The BPA calibration was done using an internal standard calibration with the BPA concentrations of 0.1, 0.2, 0.5, and 1 mg/L. TBP was used as an internal standard with a concentration of 7.5 mg/L.

3.4.3 TIME STUDY

For the time study different masses of hematite (H), and magnetite (M1) were added to 25 or 50 mL of deionized water (DI) in a 125 mL serum bottle with a BPA concentration of 1.2 mg/L. Also there was a blank system with no hematite added, in order to determine if there was any BPA escaped from the water phase to the air phase or adsorbed to the glass of serum glass bottle. After the addition of BPA solution, the serum bottles were capped with butyl rubber septa, and crimped with aluminum seals. The serum bottles were then shaken and placed in a rotating tumbler at 16 rpm in the dark for mixing at 25 0 C. For the hematite (H) the masses used for 50 mL of solution were 0.2, 0.5, 0.65, 1, 2, and 5g. The masses of hematite (H) used for 25 mL of solution, were 4, 5, 7.5 and 10 g. The experiments were conducted for 1, 3, 7, 10, 14, and 21 days. For the magnetite (M1) the masses used for 50 mL of solution were 0.2, 0.5, 0.65, 1, 2, and 30 days.

The routine, pH, TDS, and BPA analysis, as well as LLE were conduct the same as for the adsorption capacity experiments.

3.5 RESULTS AND DISCUSSION

From Figure 3.1 and 3.2 we can see that the Langmuir is a very good fit for the Hematite for all three adsorbent dosages of 1g, 2g, and 5g. The results were as expected in good correlation with the those presented for minerals such as andesite, diatomaceous earth, activated bleach earth (Tsai et al., 2006a), and sediments (Zeng et al., 2006). For all the minerals and sediments the adsorption of BPA was a weak adsorption. From Figure 3.1 (a) through (c) and Figure 3.2 (a) through (c) the adsorption fitted with Langmuir isotherm found that the maximum

adsorption qe (mg/g) and K_L (L/mg) parameter increased from 1 day to 7 days for all the adsorbent dosages 1g, 2g, and 5g. For the Figure 3.3 (a) through (c) and Figure 3.4 (a) through (c) all the three adsorbent dosages 1g, 2g, and 5g for were analyzed using Freundlich isotherm. We can see from the Figure 3.3 (a) through (c) and Figure 3.4 (a) through (c) that the Freundlich parameter K_F increased for all the adsorbent dosages from 1day to 7 days. However, the unitless parameter n decreased from 1 to 7 days. The parameter n shows the affinity of the adsorbate to the absorbent, the higher the n the more favorable the adsorption was. From the K_F we can see that the affinity decreased we observed that the capacity increased. From Table 3.4 we can see all the parameters tabulated for both Langmuir and Freundlich isotherms. We can see that for the 1 day study that the Langmuir had a better correlation R^2 value than that of the Freundlich isotherm for 1g, and 2g dosage and almost equal for 5g. For the 7 days however the Freundlich isotherm had slightly better R^2 values for the fit. However, we can see from the Figure 3.3 (a) through (c) and Figure 3.4 (a) through (c) that the Freundlich isotherm overestimated the adsorption after equilibrium concentration of 30, 45, and 140 mg/L for the1g, 2g, and 5g, respectively.

From both the Langmuir and Freundlich isotherms we can see corroboration in results, which showed a stronger and more intense adsorption at lower adsorbent dosage and a higher capacity with increase in time and dosage as a result of the surface area increased. The Langmuir isotherms parameters were more meaningful for describing the adsorption. From the regression coefficient R^2 we can see that there was strong correlation for both the Langmuir and Freundlich isotherms.



Figure 3.1 Langmuir isotherms for 1 day pH 2: a) 1g sorbent : 50mL solution, b) 2g sorbent : 50mL solution and c) 5g sorbent : 50mL solution



Figure 3.2 Langmuir isotherms for 7 days pH 2: a) 1g sorbent : 50mL solution, b) 2g sorbent : 50mL solution and c) 5g sorbent : 50mL solution



Figure 3.3 Freundlich isotherms for 1 day pH 2: a) 1g sorbent : 50mL solution, b) 2g sorbent : 50mL solution and c) 5g sorbent : 50mL solution



Figure 3.4 Freundlich isotherms for 7 days pH 2: a) 1g sorbent : 50mL solution, b) 2g sorbent : 50mL solution and c) 5g sorbent : 50mL solution

Sorbent Mass	Time	q _{max} (mg/Kg)	K _L (L/mg)	\mathbf{R}^2	$K_{\rm F}$ [(mg/Kg)(L/mg) ⁿ]	n	\mathbf{R}^2
1g	1 Day	253.1	0.376	0.973	95.534	0.272	0.903
2g	1 Day	273.4	0.243	0.993	91.659	0.269	0.945
5g	1 Day	302.0	0.122	0.963	78.732	0.275	0.969
1g	7 Days	337.1	0.639	0.946	148.141	0.250	0.961
2g	7 Days	343.4	0.395	0.922	136.342	0.240	0.974
5g	7 Days	395.8	0.239	0.938	142.505	0.221	0.968

Table 3.4 Langmuir and Freundlich constants for Hematite (H) as a function of time with
pH 2 and 50 mL solution

The time study was done in order to see the effect of time on the Freundlich parameters for all the three iron oxides. The adsorbent dosage to a fix BPA concentration of 1.2 mg/L solution volume ratios can been seen in Table 3.6, 3.9, and 3.12 for M1, M2, H, respectively. Figure 3.5 (a) through (g) shows the adsorption of BPA onto magnetite M1 for a period of 1 to 30 days. Figure 3.6 (a) through (e) shows the adsorption of BPA onto magnetite M2 for a period of 1 to 14 days. Figure 3.7 (a) through (f) shows the adsorption of BPA onto hematite H for a period of 1 to 21 days.

The interpretations of the results were hard to make due to the fluctuation of the data there was no trend observed. From Figure 3.5 (a) through (g) we can see for magnetite M1 that after the first day there is an increase in n until 10 days, followed by a decrease and increase in the 30 days. Overall if we take the numbers as approximation it could be said that there is an increase in the n with an increase in the time for adsorption. As a result it can be implied that the affinity of adsorbate to the absorbent increases with time. The correlation value of R^2 was in the range of 0.872 to 0.965. The adsorption capacity does follow the trend of n values by increasing and decreasing afterwards. At the end of the 30 days, however the maximum adsorption capacity and highest affinity is found. All the tabulated Freundlich coefficients for magnetite M1 are found in Table 3.5. Over time there was no big fluctuation in the pH or TDS from the original values after 1 day. This is a sign that the equilibrium for pH and TDS was reached after 24h. The pH range was from 4.201 to 7.679 for the 10g:25mL to 200 mg:50 mL, respectively. The TDS (mg/L) range was from 282 to 2550 for the 200 mg:50 mL and 10g:25mL, respectively.



Figure 3.5 Freundlich isotherms as a function of time with $C_0 = 1.2 \text{ mg/L}$ a) 1 day, b) 3 days and c) 7 days



Figure 3.5 cont. Freundlich isotherms as a function of time with $C_0 = 1.2 \text{ mg/L}$ d) 10 days, e) 14 days and f) 21 days



Figure 3.5 cont. Freundlich isotherms as a function of time with $C_0 = 1.2 \text{ mg/L}$ g) 30 days

Time	$K_{\rm F}$ [(mg/Kg)(L/mg) ⁿ]	n	\mathbf{R}^2
1 Day	21.133	1.198	0.893
3 Days	0.999	1.000	0.828
7 Days	20.841	1.418	0.965
10 Days	113.884	2.290	0.903
14 Days	96.391	2.283	0.933
21 Days	30.667	1.907	0.872
30 Days	119.390	2.643	0.952

Table 3.5 Freundlich constants for Magnetite (M1) as a function of time with DI, and $C_0 = 1.2 \text{ mg/L}$

 Table 3.6 pH Variation for Magnetite (M1)

Mass	Volume	1Day	3Days	7Days	10 Days	14 Days	21 Days	30 Days
Blank	50mL	8.159	7.739	7.896	7.946	8.145	7.756	7.941
10g	25mL	4.201	4.319	4.249	4.291	4.195	4.295	4.337
7.5g	25mL	4.254	4.352	4.317	4.329	4.254	4.297	4.306
5g	25mL	4.52	4.498	4.427	4.343	4.363	4.404	4.398
4g	25mL	4.431	4.58	4.496	4.516	4.43	4.678	4.724
5g	50mL	4.653	4.99	4.813	4.782	5.032	5.123	5.297
2g	50mL	6.533	6.542	6.513	6.62	6.475	6.42	6.476
1g	50mL	7.051	7.121	7.085	7.285	7.146	7.088	6.886
650mg	50mL	7.309	7.318	7.369	7.309	7.368	7.32	7.184
500mg	50mL	7.391	7.432	7.439	7.489	7.518	7.459	7.282
200mg	50mL	7.679	7.676	7.672	7.692	7.756	7.726	7.595

 Table 3.7 TDS Variation for Magnetite (M1)

Mass	Volume	1Day	3Days	7Days	10 Days	14 Days	21 Days	30 Days
Blank	50mL	261	261	260	260	260	260	261
10g	25mL	2550	2490	2490	2530	2470	2480	2470
7.5g	25mL	2040	1980	1950	2020	1970	2010	2020
5g	25mL	1480	1450	1430	1460	1430	1450	1440
4g	25mL	1250	1230	1190	1220	1200	1210	1200
5g	50mL	897	865	871	875	864	875	871
2g	50mL	509	494	496	498	493	510	504
1g	50mL	375	366	369	368	372	372	377
650mg	50mL	332	326	331	328	327	330	331
500mg	50mL	314	310	312	312	312	313	314
200mg	50mL	282	283	280	281	279	280	281

The results of magnetite M2 followed to some respect the trend of those of magnetite M1. We can see from Figure 3.6 (a) through (e) the adsorption of BPA onto magnetite M2. The Freundlich parameter n first decreases with time and increased for the final days of 10 and 14 to about 2.3. The correlation for 1 and 3 days was not that great having a R^2 value of around 0.7. However, it increased to as much as 0.965 after that. The K_F parameter showed a continuous increase in the adsorption capacity from 14 to about 100. All the tabulated Freundlich coefficients for magnetite M2 are found in Table 3.8. Over time there was no big fluctuation in the pH or TDS from the original values after 1 day just the same as for M1. We can conclude the same that the equilibrium for pH and TDS was reached after 24h. For M2 the pH range was not that wide and it ranged from 7.911 to 8.074 for the 10g:25mL to 650mg:50 mL, respectively. We can conclude that the hematite H affected very little the pH of the solution from the original blank solution with a pH of 8.159. The TDS (mg/L) range for the M2 was from 270 to 1050 for the 200 mg:50 mL and 10g:25mL, respectively. We can see that M2 did not increase as much as M1 the TDS of the solution. Actually at the highest adsorbent to solution ratio of 10g:25mL the TDS for M2 was more than half of that of M1.



Figure 3.6 Freundlich isotherms as a function of time with $C_0 = 1.2 \text{ mg/L}$ a) 1 day, b) 3 days and c) 7 days


Figure 3.6 cont. Freundlich isotherms as a function of time with $C_0 = 1.2 \text{ mg/L}$ d) 10 days and e) 14 days

Time	K _F [(mg/Kg)(L/mg) ⁿ]	n	R ²
1 Day	14.776	6.466	0.762
3 Days	17.614	3.862	0.704
7 Days	20.841	1.418	0.965
10 Days	113.884	2.290	0.903
14 Days	103.464	2.222	0.894

Table 3.8 Freundlich constants for Magnetite (M2) as a function of time with DI, and $C_0 = 1.2 \text{ mg/L}$

 Table 3.9 pH Variation for Magnetite (M2)

Mass	Volume	1Day	3Days	7Days	10 Days	14 Days
Blank	50mL	8.159	7.739	7.896	7.946	8.145
10g	25mL	7.911	7.741	7.79	7.884	7.862
7.5g	25mL	7.958	7.877	7.805	7.955	7.91
5g	25mL	8.021	7.911	7.768	8.003	7.974
4g	25mL	8.037	7.981	7.865	8.05	8.022
5g	50mL	7.947	7.938	7.86	7.969	7.976
2g	50mL	8.028	7.972	7.909	8.035	8.071
1g	50mL	8.037	7.981	7.956	8.059	8.077
650mg	50mL	8.074	8.018	8.009	8.045	8.126
500mg	50mL	8.071	8.026	7.983	8.047	8.162
200mg	50mL	8.045	8.067	7.968	7.911	8.176

 Table 3.10 TDS Variation for Magnetite (M2)

Mass	Volume	1Day	3Days	7Days	10 Days	14 Days
Blank	50mL	261	261	260	260	260
10g	25mL	1050	1190	1020	1050	1010
7.5g	25mL	865	854	841	866	848
5g	25mL	675	662	652	669	661
4g	25mL	593	584	585	593	581
5g	50mL	474	467	465	481	466
2g	50mL	350	346	340	354	347
1g	50mL	307	303	302	307	303
650mg	50mL	290	287	290	291	288
500mg	50mL	284	282	278	282	283
200mg	50mL	270	269	268	271	267

The results of hematite H were also similar to that of the other iron oxides of M1 and M2. We can see from Figure 3.7 (a) through (f) the adsorption of BPA onto hematite H. The Freundlich parameter n first increased and then decreased. However if we do not take the 7 days results into consideration the n value was about the same to about 2. The correlation for all the days did not change too much having R^2 values in the range of 0.833 to 0.961. The K_F parameter showed an slightly increase in the adsorption capacity from the first day to the last day of the experiment. However, there were two days, which is day 3 and 21 that showed an unusual high value. All the tabulated Freundlich coefficients for hematite H are found in Table 3.11. Over time there was no big fluctuation in the pH or TDS from the original values after 1 day like the other adsorbents M1 and M2. We can conclude that the equilibrium for pH and TDS was reached after 24h. For hematite H the pH range was not that wide just like M2, and it ranged from 7.827 to 8.057 for the 5g:50mL to 500mg:50 mL, respectively. We can conclude that the hematite H just like magnetite M2, affected very little the pH of the solution from the original blank solution with a pH of 8.159. The TDS (mg/L) range for the hematite H was from 260 to 301 for the 1g:50 mL to 10g:25mL, respectively. We can see that hematite H did slightly affected the TDS of the solution.



Figure 3.7 Freundlich isotherms as a function of time with $C_0 = 1.2 \text{ mg/L}$ a) 1 day, b) 3 days and c) 7 days



Figure 3.7 cont. Freundlich isotherms as a function of time with $C_0 = 1.2 \text{ mg/L}$ d) 10 days, e) 14 days and f) 21 days

Time	K _F [(mg/Kg)(L/mg) ⁿ]	n	\mathbf{R}^2
1 Day	33.418	2.627	0.804
3 Days	326.069	2.019	0.833
7 Days	19.586	8.708	0.871
10 Days	41.622	1.642	0.948
14 Days	47.349	2.161	0.931
21 Days	762.917	2.268	0.961

Table 3.11 Freundlich constants for Hematite (H) as a function of time with DI, and $C_0 = 1.2 \text{ mg/L}$

 Table 3.12 pH Variation for Hematite (H)

Mass	Volume	1Day	3Days	7Days	10 Days	14 Days	21 Days
Blank	50mL	8.159	7.739	7.896	7.946	8.145	7.756
10g	25mL	7.854	7.716	7.668	7.752	7.833	7.945
7.5g	25mL	7.909	7.787	7.744	7.949	7.871	7.915
5g	25mL	7.994	7.843	7.774	8.109	7.936	7.946
4g	25mL	7.875	8.027	7.761	8.103	7.976	7.952
5g	50mL	7.827	7.814	7.749	7.945	7.874	7.832
2g	50mL	7.947	7.954	7.832	8.026	7.978	7.917
1g	50mL	7.987	7.967	7.925	8.065	8.045	7.938
650mg	50mL	8.002	7.977	7.949	8.12	8.098	7.956
500mg	50mL	8.057	7.991	7.952	8.113	8.093	7.946
200mg	50mL	8.013	8.015	7.968	8.117	8.146	8.028

 Table 3.13 TDS Variation for Hematite (H)

Mass	Volume	1Day	3Days	7Days	10 Days	14 Days	21 Days
Blank	50mL	261	261	260	260	260	260
10g	25mL	301	298	298	297	296	304
7.5g	25mL	287	285	286	286	285	289
5g	25mL	274	274	274	273	271	280
4g	25mL	265	265	264	268	267	275
5g	50mL	266	265	266	268	267	268
2g	50mL	261	260	257	261	260	263
1g	50mL	260	260	261	261	259	262
650mg	50mL	260	259	261	261	260	262
500mg	50mL	261	260	262	260	260	263
200mg	50mL	261	261	264	261	260	263

3.6 CONCLUSSIONS

Based on the adsorbents studied, it was found that for the most part the activated carbon or carbonaceous adsorbent materials had the highest adsorption capacity. However, different treatment of inorganic minerals for example, was able to have a maximum adsorption capacity close to many organic adsorbents even higher than many activated carbons (Kim et al. 2011). Most of the carbonaceous adsorbent materials showed to follow a pseudo second-order kinetic model, making them a good candidate for a water treatment plant. The GAC or PAC has been used in the water treatment industry. However, the cost of operation or recharge is not low and the cost had played a significant role in using this technology. Not all the carbonaceous adsorbents had the same adsorption capacity and varied depending on the source of the carbon as we can see from Table 3.1.

Different treatment to the activated carbon had been applied in order to increase the efficiency of the AC adsorbents. Depending on the AC, the treatment would help or hurt the efficiency of the adsorbent (Liu et al., 2009). The AC used for the adsorption, not all the time had been purchased commercially, and was produced in the lab. This could be a very limiting factor for the use in large quantities such as a water treatment plant. It was found from different studies that were done in the production of adsorbent, that the carbonization temperature played a significant role in the adsorption properties of the adsorbent. The higher the temperature the better the adsorption of adsorbent was found. In general the high BET surface area had been reported as the major factor for good adsorption of organic pollutants for carbonaceous adsorbent materials. From Table 3.2 we can see that a higher BET surface area not always meant a higher adsorption. It was found that the functional groups along the surface of the adsorbent also played a significant role in the adsorption (Asada et al., 2002).

Novel carbon based materials that had been more recently found and manufacture such as fullerene and carbon nanotubes had been also used as an adsorbent for BPA. The single-walled carbon nanotubes(SWCNT) showed the best adsorption capacity with 455 mg/g (Pan et al., 2008). The rest of the nano materials did not showed more significant adsorption efficiency than other activated carbons.

Polymeric adsorbents were also used successfully in removing BPA from aqueous solutions. Just like the activated carbons, the polymeric adsorbents, were purchased from a commercially supplier or lab manufactured. Some of the polymeric adsorbents had a capacity equal to that of some activated carbon adsorbents. The highest capacity of any of the polymeric adsorbents that was found was 98 mg/g (Aoki et al., 2004).

The adsorption of the BPA onto soil had been found to be very strong and to be dependent on the amount of the organic carbon present in the soil. The higher the organic carbon the higher the adsorption of BPA was observed. From the study of different soils it was found that BPA would have a low to moderate mobility in soils (Fent et al., 2003). The presence of different mineral oxides in the soil showed to affect the absorbance of BPA (Li et al., 2009). The presence of Fe oxides for example showed to facilitate the adsorption of BPA, while the presence of Mn oxides inhibited the adsorption. The adsorption of BPA onto sediments had been found to follow similar behavior as that of soils. The adsorption of BPA was influence by the amount of organic carbon present in the sediments (Zeng et al., 2006). The marine sediments that were studied showed a higher capacity for the adsorption of BPA (Xu et al., 2008). The adsorption of BPA onto aquifer material with only 0.5 % organic carbon showed a similar adsorption as the marine sediments. Compared to the AC the adsorption onto soil and sediments was weak.

Minerals had also found to be able to remove BPA using adsorption. Depending on the time of the mineral, the adsorption capacity varied from 0.33 to 351 mg/g. This wide variation makes the minerals adsorbent very case specific. It is important to note that the mineral that had the highest adsorption capacity was not bought commercially but lab produced. Some of the mineral adsorbents showed a low capacity, while other had capacities higher than many activated carbon adsorbents. Some of the minerals used in the adsorption that had comparable adsorption capacities with activated carbons had high BET surface areas.

The objective of the first part of this chapter was to determine the capacity of hematite. The mineral oxide that was evaluated in the first part of the study as hematite H showed to be a weak adsorbents for BPA. The adsorption capacities were obtained from Langmuir model fits for both 1 and 7 days isotherms. The weak absorbance was expected and was in good correlation with those presented for minerals such as andesite, diatomaceous earth, activated bleach earth (Tsai et al., 2006a), and sediments (Zeng et al., 2006). We can see the capacities of adsorption in Table 3.4 ranging from 0.253 to 0.301 (mg/g) for 1 day and 0.337 to 0.395 (mg/g) for 7 days. For the 1 day studies the Langmuir had a better fit for the data and Freundlich for the 7 days. However, for the Freundlich fits the adsorption in the higher equilibrium concentrations had been overestimated for both 1 and 7 days. Even though Langmuir had a slightly lower R² value for 7 days it was concluded that was a better fit for both days.

Freundlich parameters were obtained from the time studies and presented in Table 3.5, 3.8, and 3.11 for magnetite M1, M2, and hematite H, respectively. From the time studies it was found that in general an increase of capacity is expected with time. For magnetite M1 and hematite H the capacity increased than dropped and finally at the end of the study increased. For magnetite M2 it increases constantly with a small difference in the last days of the study. Based

from the time study it was also found that the two magnetites and one hematite acted differently under the similar circumstances. Magnetite M1 for example dropped the pH of the solution from around 8.159 to about 4.201 for a 10g to 25 mL adsorbent to solution ratio. For the other two adsorbents the pH remained for the most part unaltered at the same ratio of 10 g to 25 mL adsorbent to solution ration. We can see the effect of pH for the time study at different adsorbent to solution ratios in Tables 3.6, 3.9, and 3.12 for magnetite M1, magnetite M2, and hematite H. The total dissolved solids (TDS) of the solution were presented in Tables 3.7, 3.10, and 3.13 for magnetite M1, magnetite M2, and hematite H, respectively. The TDS of the solution was also greatly affected by magnetite M1, with a lower effect done by magnetite M2, and with almost no effect done by hematite H, respectively. The study of these parameters it is very important for a water treatment plant settings, because it changes the chemistry of the water, and the chemical interactions would be different under different conditions.

Even though the adsorption onto the mineral oxides was not very strong compared to other adsorbents, it still has it advantages against other adsorbents such as AC. The price of GAC or PAC is still generally high, which is a major limiting factor for the use of AC. The regeneration of AC is also impractical because of the cost associated with it. There is also the production of byproducts that could be generated through the regeneration process of AC or other carbonaceous adsorbents that has to be taken into consideration. The regeneration of minerals oxides used in this study should be less expensive and be able to be done in a blast furnace. There is the advantage of not having the concern of byproducts formation in the process of regeneration. Also, the cost of mineral oxides is expected to be lower than other carbonaceous adsorbent materials because no special processes have to be used in the production of them. The mineral oxides are natural occurring minerals that just have to be excavated.

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CHAPTER IV

THE EFFECT OF pH AND IONIC STRENGTH VARIATION

4.1 INTRODUCTION

The existence of chemical organic pollutants is posing an immediate harm to the environment and humans. The toxicity and availability of these pollutants, as well as the possible migration in the environment, makes each pollutant distinct and case specific. The amount of harm due to the presence of an organic pollutant in water for example, is governed by many chemical physical interactions that would be very specific for each pollutant. The amount that an organic pollutant could be available in water depends on its solubility in the aqueous solution. The solubility of an organic pollutant would be affected by the other chemicals present in that aqueous solution, the pH of the solution, surface charge of the pollutant and many other properties for both the aqueous solution and organic pollutant. Some of the most important parameters that have to be taken into consideration when investigating the removal of an organic pollutant from an aqueous solution are the pH and ionic strength.

First, when we investigate the removal of an organic pollutant, in our case bisphenol A (BPA) is founding a suitable removing technology. The removal of BPA from aqueous solutions had been investigated through different studies using oxidation with ozonation (Alum et al., 2004; Irmak et al., 2005; Deborde et al., 2005; Deborde et al., 2008; Zhang et al., 2008; Garoma and Matumoto, 2009), chlorination (Hu et al., 2002; Yamamoto and Yasuhuru, 2002; Gallard et al., 2004; Lee et al., 2004; Korshin et al., 2006), electrochemical oxidation (Boscoletto et al., 1994; Tanaka et al., 2002; Andreescu et al., 2003; Ngundi et al., 2002; Gozmen et al., 2003; Kuramitz et al., 2004; Murugananthan et al., 2008), photooxidation(Ohko et al., 2001; Chiang et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Lee et al., 2004; Zhou et al., 2004; Katsumata et al., 2004; Peng et al., 2006; Chen et al., 2004; Peng et al., 2004; Peng et al., 2006; Chen et al., 2004; Peng et al., 2006; Peng et al., 2006;

al., 2006b, 2007; Torres et al., 2010; Yap et al., 2010), biodegradation (Dorn et al., 1987; Lobos et al., 1992; Spivack et al., 1994; Staples et al., 1998; Furhacker et al., 2000; Ike et al., 2000; Klecka et al., 2001; West et al., 2001; Kang and Kondo, 2002a, 2002b; Kang et al., 2004; Suzuki et al., 2004; Kang and Kondo, 2005), ultrasonication (Kiajima et al., 2006; Torres et al., 2007a, 2007b; Torres et al., 2008a, 2008b; Guo and Feng, 2009;), ferrate(VI) and zero valent aluminum oxidation(Jiang et al., 2005; Lee et a., 2005; Liu et al., 2011), and adsorption (Nakanishi et al., 2002; Asada et al., 2004; Toledo et al., 2005; Sun et al., 2005; Shareef et al., 2006; Tsai et al., 2006a, 2006b; Zeng et al., 2006; Li et al., 2007; Xu et al., 2008; Li et al., 2008; Pan et al., 2008; Cao et al., 2009; Li et al., 2009; Dong et al., 2010). All of these processes had been used to remove BPA from waste and drinking water. The cited literature on the treatment of BPA has shown that through a process or technology and in combination of more than one in some cases, the removal of BPA is possible. Even though all the processes mentioned earlier had been able to remove BPA from aqueous solutions, each process or technology has advantages and disadvantages that limit its use when removing BPA from the aqueous phase. Each process or technology would behave differently under different pH and ionic strengths.

One of the main reasons that the pH and ionic strengths plays a significant role in the removing of BPA from aqueous solution is that BPA would act differently under acidic or alkaline conditions. BPA is a polar organic compound that under alkaline solutions would have higher solubility. The BPA has two pKa of 9.6 and 10.2 (Staples et al., 1998) above which the BPA would be deprotonated and formed bisphenolate anions. The surface of adsorbent would change with the change of pH, as a result would influence the adsorption of BPA that is governed by the adsorbent-adsorbate electrostatic interactions (Toledo et al., 2005). The presence of different ionic species such as calcium Ca^{2+}, NH_4^+ or K⁺ ions would be able to diminish the

effect of negative charge of an adsorbent surface and be able to decrease the repulsion of the BPA and the adsorbent. This was found to be true for some organic pollutants and sediments (Liu et al., 2001, Burton et al., 2004). The presence of the ionic species would decrease the solubility of organic compounds and enhance the sorption onto sediments for example (Wu et al, 2003, Houch, 2004). The pH and ionic strength would influence the adsorption of BPA from the aqueous solution onto the hematite H. The influence of both pH and ionic strength were studied in Chapter 4.

4.2 THE INFLUENCE OF pH ON THE REMOVAL OF BPA USING DIFFERENT REMOVAL PROCESSES

The pH of the solution is a very important parameter that could increase or decrease the adsorption, depending on the adsorbent and adsorbate physical chemical properties. Different processes and technologies that have found to be able to removed BPA from aqueous solutions have investigated the effect of pH. The electrochemical oxidation of the urban wastewater showed that is affected by the pH of the solution (Zorpas, 2011). As the pH increases the chemical oxygen demand (COD) decreases more rapidly. The increase in the pH from 6 to 8 had a positive effect on the urban wastewater electrochemical oxidation. The effect of pH on the electrochemical oxidation of BPA had been also investigated by Kuramitz et al., 2001 and Chen, 2004. Kuramitz et al, 2001 found that the peak current for the removal of BPA at pH 5.8 was proportional to the scan rate, and for the pH 12.0 was proportional to the square root of the scan. This finding is indicating that the electrochemical oxidation process for the removal of BPA is controlled by the diffusion at pH 12.0 and adsorption at pH 5.8. As a result, the inactivation of the electrode is made possible by the oxidation of BPA, which can occur at acidic, neutral, and medium alkaline solutions. The same effect was observed by Chen, 2004, which the

electrochemical treatment increased for the acidic conditions and decreased under the alkaline conditions. When the conductivity was high there was no significant pH effect taking place.

The enzymatic treatment of BPA using soybean peroxidase from glysine (SBP) obtained from Sigma was found to be possible (Watanabe et al., 2011). The removal of BPA is possible using reaction pathways of peroxidase-catalysis in the presence of hydrogen peroxide (H_2O_2). The reaction that occurs in the presence of H_2O_2 creates a water-insoluble oligomer. The optimum pH for the BPA removal was found to be 7.0. From previous studies the optimum pH for phenols was found to be pH 6.0 and 7.0 (Wright and Nicell, 1999, Bodalo et al., 2006). The optimum pH found by Watanabe et al., 2011 was in good accord with the previous studies that were done using phenol. The study done on BPA removal showed that the enzymatic treatment was able to remove most of the derivates that formed through the process also. The byproducts derivates formation would be addressed in detail in Chapter 5.

Another process that relies on the hydrogen peroxide for the production of hydroxyl radicals (HO•) is the photo-Fenton reaction. The Fenton reaction relies on the photolysis of iron aquacomplex Fe(OH)²⁺, that is followed by subsequent reactions that produces more HO• radicals which happens in the presence of hydrogen peroxide. The Fenton process has been used to degrade the BPA (Katsumata et al., 2004). The optimum pH for the Fenton process that degrades BPA was found to be 4.0. Zhou et al., 2004 conducted initial control experiments using photooxidation by using Fe(III)-OH complexes for the production of HO• radicals for the removal of BPA. Fe(III)-OH complexes had been used before using photooxidation to oxidize organic compounds (Deng et al., 1996, Bajt et al., 2001). It found that there was an increase of 41.6% removal efficiency in water at pH 3.0. Also, it was found that the addition of Fe(III)-oxalates had a higher yield of HO• radicals in the presence of oxygen in water than that of

Fe(III)-OH complexes. The optimum pH interval was found to be lower than pH 4.0 with no significant difference after pH 3.5. There was a significant degradation drop in efficiency from pH of 4.0 to 6.0. At pH 8.0 it was found that there was almost no degradation with a small difference from the degradation that was recorded at pH 6.0. Lee et al., 2004 investigated the effect of pH on the photodegradation of BPA with titanium dioxide (TiO₂) immobilized on glass tubes. A lower pH of 3.0 had a higher degradation than that of pH 7.0 and 10.0. At the pH of 10.0 there was almost no degradation of BPA. Oxidation of BPA under natural and wastewater conditions using ferrate (Fe(VI)) have found to be pH dependent, with an optimum pH of 6.0 and decreased with an increase in the pH.

The treatment of water using ozone (O_3) by the process of ozonation had been used to remove multiple organic pollutants. The oxidation of BPA using ozonation is affected by the pH (Deborde et al., 2005, Garoma and Matsumoto, 2009). The oxidation of BPA is possible by the decomposition of aqueous ozone that reacts with hydroxide ion (OH⁻), which leads to the production of HO• radicals. Deborde et al., 2005 found to have minima at a pH lower than 5.0 and maxima above pH of 10.0. The same pH effect is presented by Garoma and Matsumoto, 2009 found that there was an increase in the oxidation of BPA with an increase in pH. At pH 2.0 there were only 53 % removals, which increase to 79 and 92% for pH 5.0 and 7.0, respectively. It was found that there was no significant increase in the removal of BPA with the increase of pH above 7.0 to 10.0.

4.2.1 THE INFLUENCE OF pH ON ADSORPTION

Many studies that were done on the adsorption of BPA onto different adsorbents studied the effect of pH as well. Some of the adsorbents that were also investigated for the effect of pH are mesoporous carbon (Sui et al., 2011), activated carbon (Tsai et al., 2006a, Liu et al., 2009, Toledo et al., 2005, Asakura and Matsubo, 2009), Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007), Y-type hydrophobic zeolite (Tsai et al., 2006b), magnetic molecularly polymers (MMIPs) and magnetic non-template imprinted polymers (MNIPs) (Guo et al., 2011), β -cyclodextrin derivative (polyCD) (Kitaoka and Hayashi, 2002), hypercrosslinked polymers (Fan et al., 2011), surfactant-modified zeolite (Dong et al., 2010), geothite, montmorillonite, kaolinite (Shareef et al., 2006), marine sediments (Xu et al., 2008), and river sediment (Zeng et al., 2006, Li et al., 2007).

The BPA adsorption onto sediments had found to be pH dependent with a dramatic decrease in the adsorption from pH 2.0 to 6.0 (Zeng et al., 2006). The BPA is a polar organic compound that has higher water solubility in an alkaline solution than the acidic solution. The BPA at low pH values would favorable transfer from the aqueous phase to the solid phase; as a result there would be a higher adsorption. Li et al., 2007 found that there is a decrease in the amount of BPA adsorbed onto sediment with an increase in pH. However, the decrease is not as drastic as in the case found by Zeng et al., 2006. As the solution pH increases, the anionic deprotonated form of BPA increases, and becomes the dominant form of BPA. The charge of the anionic form of BPA is negative, thus creating an electrostatic repulsion to the negative charged sediment. The decrease on the adsorption onto sediments with the increase of pH was also found by Xu et al., 2008.

As presented earlier in Chapters 1, 2, and 3 the organic carbon adsorbents had been presented as a very strong adsorbent in many cases. Different organic adsorbents had been used to removed BPA such as mesoporous organic carbon (Sui et al., 2011) and activated carbon (Toledo et al., 2005, Tsai et al., 2006a, Asakura and Matsuto, 2009). The activated carbon produced from different organic based products such as commercial charcoal-based carbons

(Sample S and Sample M), lab created from almond shells (Sample A), coconut shell (PCB), and bituminous coal (BPL). The results showed that the source of the organic carbon for the adsorbents was very important and the pH effect was different for each individual case. The activated carbon samples A, S, and M showed a strong decrease in the adsorption of BPA above pH 8.0 (Toledo et al., 2005). The BPL and PCB adsorbents showed a slight decrease when the pH would increase from 9.0 to 11.0 and for the adsorption in the range of pH of 3.0 to 9.0 there was no effect. Asakura and Matsumoto, 2009 found that there was no pH effect in the range of 5.0 to 9.0 for the activated carbon. The mesoporous carbon CMK-3 produced from hexagonal SBA-15 mesoporous silica found that there was a dramatic decrease in the amount of BPA adsorbed at a pH above 8.5. The amount of BPA (mg) per amount of adsorbent (g) adsorbed went down from around 200 mg/g at pH 8.5 to 80 mg/g at pH 12.0.

Different polymeric adsorbents had been used as presented earlier to remove the BPA such as magnetic non-template imprinted polymers (MNIPs) (Guo et al., 2011), β -cyclodextrin derivative (polyCD) (Kitaoka and Hayashi, 2002), hypercrosslinked polymers, and aminated polystyrene (Fan et al., 2011). The polymeric adsorbents showed similar behavior as other adsorbents presented earlier. All showed a decrease in the absorbance with the increase in the pH. For the MNIPs the absorbance decreases from a q_e of 50 mg/g at pH 7.0 to 20 mg/g at pH 10.0. There was a small decrease in the absorbance from pH 2.0 to 7.0. For the polyCD adsorbent there was no significant difference for the pH range of 2.0 to 5.0, with a small decrease until pH 9.0 and a more drastic decrease from 90% to 50% from pH 9.0 to 11.0. For the both of hypercrosslinked polymers MN-200 and aminated polystyrene MN-150 there was a decrease in the adsorption above pH 8.0. However, the MN-200 had a higher BET surface area of 1155 m²/g compare to that of MN-150 with a BET surface area of 815 m²/g. The q_e for MN-200 drop from

425 mg/g, which was maintained at the pH range of 1.0 to 8.0, to 250 mg/g at pH 11.0. The q_e for MN-150 was 330 mg/g and dropped for the pH range of 1.0 to 8.0 to 225 mg/g at pH 11.0.

The pH effect had been investigated for the adsorption of BPA onto different minerals. Two surfactant-modified zeolites SMZFAF, which had a higher concentration of CaO content, and SMZFAL, which had a low concentration of CaO content, had been investigated (Dong et al., 2010). There was an increase in the adsorption for both the surface-modified zeolite adsorbents above a pH of 7.0. For the SMZFAL there was small increase in the adsorption from 20 mg/g from pH 7.0 to 35 mg/g for pH 9.7. However, for the SMZFAF there was a much stronger pH effect on the adsorption with an increase from 50 mg/g from pH 7.0 to 95 mg/g at pH 10.0. The same effect of higher adsorption at high pH is seen for montmorillonite, where a pH above 7.0 showed to increase the BPA removal from 20 to 40 % at pH 10.0. For the remaining minerals, geothite and kaolinite, there was no pH effect on the adsorption in the study conducted by Shareef et al., 2006. Not all the minerals had a higher adsorption at higher pH. The Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007) and Y-type hydrophobic zeolite (Tsai et al., 2006b) had a lower adsorption above pH 7.0 for Fe(III)/Cr(III) hydroxide and above pH 8.5 for the Y-type hydrophobic zeolite. For both the minerals the decrease in the adsorption was not that significant. For the Fe(III)/Cr(III) hydroxide there is a decrease from 45 to 40 % removal, and from 40 mg/g to 32 mg/g for Y-type hydrophobic zeolite.

4.3 THE INFLUENCE OF IONIC STRENGTH ON THE REMOVAL OF BPA

The influence of ionic strength had been studied just in few studies, with many studies conducted in deionized water (DI). The oxidation of BPA using ferrate Fe(VI) were conducted with natural water having alkalinity of 2.5 mM as bicarbonate ions HCO_3^- (Lee et al., 2005). The influence of bicarbonate ion concentration had been investigated under the treatment of
ozonation. Garoma and Matsumoto, 2009 investigated the ionic strength using 1, 2, 4, and 8 mM HCO_3^- ions concentration. It was found that there was no significant effect on the removal of BPA using HCO_3^- ions. The ionic strength effect was studied for surfactant-modified zeolite SMZFAF and SMZFAL is in the presence of sodium chloride (NaCl). There was only a small increase in the adsorption of BPA at a 0.2M NaCl. The influence of NaCl had also been investigated in removal of BPA using activated charcoal-based carbon (Sample S and M), and almond-shell based lab created adsorbent (Sample A) (Toledo et al., 2005). The effect of ionic concentrations of 0.01 and 0.1M NaCl had been investigated on the three activated carbons Sample S, M, and A. The greatest ionic strength effect was observed on Sample M with a lowest effect on Sample A and Sample S.

The effect of ionic strength on the adsorption of BPA onto sediments had been investigated using sodium nitrate (NaNO₃) (Zeng et al., 2006), calcium chloride (CaCl₂), and ammonium chloride (NH₄Cl) (Li et al., 2007). The ionic strengths of NaNO₃ of 0 to 0.8M had been investigated and found to increase the adsorption of BPA with the increase of Na⁺ ions. The positive Na⁺ ions react with the negative surface charge of the sediment, which creates a neutral environment enhancing the hydrophobic effect of neutral BPA species as a result increasing the adsorption. Li et al., 2007 investigated the effect of the Ca²⁺ and NH₄⁺ using 0.005 to 0.5M ionic strengths which increased the adsorption by 114.3% and 78.8%, respectively. Just like in the study of Zeng et al., 2006 the Ca²⁺ and NH₄⁺ ions would screen the negative effect on the sediment surface which could enhanced the adsorption (Liu et al., 2001, Burton et al., 2004). The increase in the Ca²⁺ and NH₄⁺ ions could also create a salting effect by decreasing the solubility of BPA in the aqueous solution, as a result enhancing the adsorption onto the sediment (Wu et

al., 2003, Houch, 2004). The pH of the solution did not change significantly for both the Ca^{2+} and NH_4^+ ions for all the ionic strengths of 0.005 to 0.5M.

4.4 MATERIALS AND METHODS

4.4.1 CHEMICALS

All the chemicals used for these experiments are presented in Table 4.1.

Т	ab	le 4	4.1	Che	emi	cal	S

Chemical	Specification	Source		
Methyl <i>tert</i> -butyl ether (MTBE)	HPLC grade	Fisher Chemicals, Fairlawn, NJ		
6N Hudrochloric Acid (HCl)	ACS Paggant grada	RICCA Chemical Company,		
on Hydroemone Acid (HCI)	ACS Reagent grade	Arlington, TX		
Bisphenol A (BPA)	\geq 97 %	Sigma-Aldrich, St.Louis, MO		
Hematite (H) Fe_2O_3 ,	\leq 5 micron and \geq 99%	Sigma-Aldrich, St.Louis, MO		
Magnetite (M1) Fe ₃ O ₄ ,	Laboratory Grade	Fisher Chemicals, Fairlawn, NJ		
Magnetite (M2) Fe ₃ O ₄ ,	325 Mesh Powder	Alfa Aesar, Ward Hill, MA		
Calcium Chloride (CaCl ₂)	ACS Reagent grade	Fisher Chemicals, Fairlawn, NJ		
Potassium Chloride (KCl)	ACS Reagent grade	Fisher Chemicals, Fairlawn, NJ		
Sodium Bicarbonate (NaHCO ₃)	ACS Reagent grade	Fisher Chemicals, Fairlawn, NJ		

4.4.2 THE pH EFFECT STUDY

Different amounts of 1g, 2g, and 5g of hematite H were added to 50 mL of deionized water (DI) in 125 mL serum bottles with different BPA concentrations. For the blank system there was no hematite added. The purpose of the blank was to determine if there was any BPA transfer from the water phase to the air phase or adsorbed to the glass of serum glass bottle. The BPA concentrations for 1g hematite H, were 1.2, 20 and 50 mg/L, for 2g for hematite H were 1.2, 13 and 80 mg/L, and for 5g hematite H were 1.2, 13, 130 and 200 mg/L. The pH range studied for all the adsorbent dosages and BPA concentrations were 2, 2.5, 3, 3.5, 4, 5, 7, and 10. All the pH experiments were done in triplicates. After the addition of BPA solution and adsorbent, the serum bottles were capped with butyl rubber septa and crimped with aluminum

seals. The serum bottles were then shaken and placed in a rotating tumbler at 16 rpm in the dark for mixing at 25 0 C. The experiments were carried out for a period of 1 day.

4.4.2.1 ROUTINE ANALYSIS

After removal of serum bottles from the rotating tumbler, 50mL of the sample was transferred from the bottle into a 50mL Teflon centrifuge tube, and centrifuged for 10 minutes at 7100 rpm using an Eppendroft centrifuge 5810R. The solution was then transferred in two different vials. Approximately 15 mL of the solution was transferred into a 20 mL glass vial, and the rest in a 40 mL glass vial. The 20 mL vial was used or the measurement of total dissolved solids and pH, and the 40 mL vial was used for the BPA analysis.

4.4.2.2 TDS AND pH ANALYSIS

The analysis of total dissolve solids (TDS) was done using Orion conductivity meter model 150 with an Orion conductivity cell 013005D and the pH analysis was performed using Thermo Orion pH/mV/temperature meter 720 using an Orion comb. pH probe model 915600. The instrument was calibrated for the pH using pH standards of 4.0, 7.0, and 10.0. The calibration of TDS was done using TDS standards with a conductivity of 1413µs and 12.9 ms.

4.4.2.3 SOLUBLE CALCIUM AND IRON ANALYSIS

The soluble iron and calcium concentrations in solution were measured using flame atomic absorbance spectrometry with an AAnalyst 800 (PerkinElmer). For both metals, a six point external standards calibration of 0.5, 1, 2, 3, 4 and 5 mg/L was prepared from a 1000 mg/L standard stock solution. The calibration standards were freshly prepared in a 2% HNO₃ dionized water (DI) solution each day of injection. If dilution was necessary, the sample was diluted in a 2% HNO₃ DI solution using volumetric flasks.

4.4.2.4 LIQUID -LIQUID EXTRACTION (LLE)

Exactly 10 mL of samples were transferred from the 40 mL vial or from the diluted sample from the volumetric flask into a 15 mL glass test tube. After the water sample was transferred, a volume of 75 μ L of 2,4,6-tribromophenol (TBP) from a stock solution of 1,000 ppm prepared in acetone was added using a 250 μ L syringe. After adding one drop of concentrated hydrochloric acid (HCl) into the test tube, the test tube was then closed and shaken gently twice. After the shaking of test tubes, 2 mL of methyl *tert*-butyl ether (MTBE) were added. The test tube was then shaken for 30 seconds vigorously and then followed by 2-3 minutes of slow mixing. After the mixing, enough time was allowed for the two phase to separate, and then about 1 mL of the MTBE from the upper phase was pipetted using a 1 mL Eppendorf pipetter into a 2 mL gas chromatography (GC) vial.

4.4.2.5 ZETA POTENTIAL MEASURMENTS

The zeta potential was analyzed using an Zeta-Meter System 3.0+ (Zeta Meter, Inc., Staunton, VA) equipped with a type GT-2 electrophoresis cell. The GT-2 electrophoresis cell was equipped with molybdenum anode and platinum cathode. Two different suspension solutions were prepared for the recording of the zeta potential of hematite H. The solution was prepared in DI water. Ten zeta potential readings were recorded for a period of no more than 2 minutes.

4.4.2.6 BPA ANALYSIS

The MTBE sample obtained from the LLE step was analyzed on a Agilent Model 6890 GC. The GC was equipped with a flame ionization detector (FID). The injection was done using an auto sampler by direct injection of 1.0 μ L of MTBE sample at an inlet temperature of 250 $^{\circ}$ C, while the detector temperature was maintained at 300 $^{\circ}$ C. For the separation of BPA and TBP, a

DB-5 (J&W) widebore capillary GC column with dimensions $30m \times 320 \ \mu m \times 0.25 \ \mu m$ was used. The oven temperature in the beginning was set at $100 \ ^{0}$ C. The temperature was then ramped from $100 \ ^{0}$ C to $265 \ ^{0}$ C at $20 \ ^{0}$ C/min and held at $265 \ ^{0}$ C for 1 minute. Helium (ultra high purity), was the carrier gas with a flow rate of 5.8 mL/min and at an inlet pressure of 25 psi. The other gases used were dry grade air, hydrogen (H₂), and the makeup gas nitrogen (N₂). The flow rates for the other gases were 400 L/min, 10 L/min, and 35 L/min, respectively.

The BPA was identified by the retention time from the BPA standard calibration that was prepared in MTBE. The BPA calibration was done using an internal standard calibration with the BPA concentrations of 0.1, 0.2, 0.5, and 1 mg/L. TBP was used as an internal standard with a concentration of 7.5 mg/L.

4.4.3 IONIC STRENGTH EFFECT STUDY

For the study of ionic strength on adsorption of BPA, calcium (Ca²⁺), potassium (K⁺) and bicarbonate (HCO_3^-) were investigated. The Ca²⁺ ions were studied using CaCl₂ at concentrations of 0.001, 0.005, 0.05, 0.1 and 0.5M. All the ionic strengths experiments were performed using three different BPA concentrations of 1.3, 13, and 130 mg/L. The adsorbent dosage used was 5g to 50 mL of aqueous solution. For the CaCl₂ there were three different cases: case I with just the CaCl₂, case II with all the ionic strengths mentioned earlier with the addition of 1mM of sodium bicarbonate (NaHCO₃), and finally case III having all CaCl₂ ionic strengths of 0.005, 0.05, 0.1 and 0.5M with the pH aqueous solution adjusted to 2.0 using 6N hydrochloric acid (HCl).

The K^+ ions were studied using KCl concentrations of 0.001, 0.005, 0.05, 0.1 and 0.5M. All the ionic strength experiments were performed using three different BPA concentrations of 1.3, 13, and 130 mg/L. The routine analysis, pH, TDS, soluble calcium and iron, BPA analysis, zeta potential, as well as LLE were conduct the same as for the pH effect study.

4.5 RESULTS AND DISCUSSION

The average zeta potential of hematite H can be found in Figure 4.1 and found to be 14.09 ± 2.2 , drops to an average of -22 to -27 for the -28.20 \pm from pH 2.0, to the pH range of 7.0 to 10.0, respectively. Two other studies had investigated the zeta potential of the adsorbent for the removal of BPA. One study investigated a mesoporous carbon prepared from hexagonal SBA-15 mesoporous silica (Sui et al., 2011) and the second study investigated a Y-type hydrophobic zeolite (Tsai et al., 2006b). For both the organic and inorganic adsorbents showed both a decrease in the adsorption with an increase in the pH and decrease of zeta potential with the increase of the pH. Based on the previous studies it was expected that at a lower pH to have a less negative charge and even to become positive. Based on these results is expected that the adsorption to be stronger at acidic conditions and be less under alkaline conditions. The decrease in the adsorption capacity at higher pH could be due to the more negative charge of the adsorbent, having an electrostatic repulsion to the negative charge of bisphenol anion. This had been found in the previous studies mentioned earlier in the case of BPA and with other organic compounds and different adsorbents.

The adsorptions of BPA as a function of pH were plotted using a power function with the y axis for the adsorption capacity q and the x axis for the pH. The form of the power function is presented in equation 1:

$$q = a \ (pH)^n \tag{1}$$

Where, q is the amount (mg/Kg) of BPA absorbed, a is power function coefficient which can be

seen as a general capacity adsorbate that was absorbed onto the adsorbent, and the slope n can been interpreted as an adsorption intensity.

The pH effect for 1g to 50mL for the BPA concentrations of 1.2, 20, and 50 mg/L had been investigated and the results are presented in Figure 4.2 (a) trough (c). The tabulated power function parameters are presented in Table 4.2. From Table 4.2 we can see a decrease in the power function coefficient n from -1.633 to -1.961 as the concentration of BPA increases from 1.2 to 20 mg/L. However, there is a decrease in the adsorption capacity and affinity for a BPA concentration of 20 to 50 mg/L. We can see that the more negative the n was the strongest the pH effect was. As a result we can see from Figure 4.2 that at the BPA concentration of 20 mg/L the pH had the highest effect on the adsorption. The increase in the BPA initial concentration could reach the adsorption capacity of the adsorbent, and no further increase in the adsorption could be obtained. The same effect has been found for the removal of BPA by Fe(III)/Cr(III) hydroxide (Namasivayam and Sumithra, 2007). The increase in the initial BPA concentration decreased the total BPA adsorption. From Table 4.3 we can see the initial and final pH along with the standard deviations for 1g to 50 mL solutions for all three BPA concentrations of 1.2, 20, and 50 mg/L. There is an increase in the pH from initial pH for the pH range of 2 to 7 and decrease in the pH from initial pH for the pH of 10.0. The tabulated TDS can be seen in Table 4.4. There is an decrease in the TDS from initial TDS for the pH range of 2 to 4 and 10, and also an increase in the TDS from initial TDS for the pH of 5 and 7. From Table 4.5 we can see as expected that there is a higher soluble iron at a low pH of 2.0 due to the acidic conditions. We can see that there is no significant information from the soluble iron data, just an apparent increase of the soluble iron for the solution of BPA with the increase in concentration from 1.2 mg/L to 50 mg/L.







Initial BPA C ₀ (mg/L)	a	n	R ²
1.2	169.749	-1.633	0.939
20	988.184	-1.961	0.927
50	708.951	-1.523	0.977

Table 4.2: Power function constants for Hematite (H) as a function of pH, and 1g sorbent:50 mL solution

Table 4.3: pH for Hematite 1g:50 mL

Sample pH	1	.2 mg/L	2	20 mg/L	50 mg/L		
	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH	
2	1.982	2.066 ± 0.001	1.994	2.075 ± 0.012	2.012	2.104 ± 2.012	
2.5	2.549	2.593 ± 0.005	2.532	2.602 ± 0.009	2.512	2.635 ± 2.512	
3	2.957	3.224 ± 0.004	2.984	3.403 ± 0.214	3.021	3.301 ± 3.021	
3.5	3.548	4.445 ± 0.018	3.521	4.486 ± 0.009	3.486	4.577 ± 3.486	
4	3.976	6.000 ± 0.077	4.021	6.086 ± 0.011	4.001	6.173 ± 4.001	
5	4.939	6.559 ± 0.037	5.032	6.668 ± 0.021	4.969	6.743 ± 4.969	
7	6.983	6.782 ± 0.043	6.975	7.580 ± 0.033	6.987	7.870 ± 6.987	
10	9.959	7.921 ± 0.245	9.965	8.503 ± 0.044	9.982	9.328 ± 9.982	

Table 4.4: TDS for Hematite 1g:50 mL

Sample	1	1.2 mg/L			20 mg/L			50 mg/L			
pH	Initial TDS	Final TDS	Stdv	Blank	Final TDS	Stdv	Blank	Final TDS	Stdv		
2	2030.0	1932.0	3.5	2020.0	1873.3	5.8	2030.0	1860.0	2030.0		
2.5	594.0	516.0	5.0	596.0	507.0	1.0	596.0	502.0	596.0		
3	207.0	134.7	1.5	205.0	130.7	1.2	206.0	124.3	206.0		
3.5	59.0	16.0	0.0	58.0	14.3	0.6	58.0	12.7	58.0		
4	28.0	14.3	0.6	28.0	13.3	0.6	28.0	11.3	28.0		
5	3.0	6.0	0.0	3.0	5.7	0.6	3.0	5.3	3.0		
7	1.0	6.0	0.0	1.0	5.7	0.6	2.0	6.3	2.0		
10	15.0	14.0	0.0	16.0	15.3	0.6	18.0	17.0	18.0		

Sample	1.2 n	ng/L	20 n	ng/L	50 mg/L		
рĤ	Fe	Stdv	Fe	Stdv	Fe	Stdv	
2	2.643	0.055	2.690	0.159	2.440	0.026	
2.5	0.086	0.021	0.227	0.012	0.060	0.010	
3	0.037	0.006	0.200	0.026	0.050	0.000	
3.5	0.027	0.006	0.073	0.012	0.057	0.006	
4	0.027	0.006	0.067	0.015	0.050	0.000	
5	0.020	0.000	0.050	0.010	0.047	0.006	
7	0.030	0.000	0.060	0.010	0.053	0.006	
10	0.030	0.000	0.040	0.010	0.047	0.006	

Table 4.5: Soluble Iron (Fe) for Hematite 1g:50 mL

The pH effect for 2g to 50mL with the BPA concentrations of 1.2, 13, and 80 mg/L had been investigated, and the results are presented in Figure 4.3 (a) through (c). The tabulated power function parameters are presented in Table 4.6. From Table 4.6 we can see an decrease in the power function coefficient n from -0.402 to -1.409 as the concentration of BPA increases from 1.2 to 80 mg/L. There is an increase in the adsorption capacity and affinity for a BPA concentration of 1.2 to 80 mg/L. In the case of 1g the increase in the initial BPA concentration from 20 to 50 mg/L decreased the total BPA adsorption and affinity. For the adsorbent dosage of 2g, the maximum capacity had not been reach for an initial BPA concentration of 50 mg/L. At the BPA concentration of 80 mg/L the pH had the highest effect on the adsorption. From Table 4.7 we can see the initial and final pH along with the standard deviations for 2g to 50 mL solution ratios for all the three BPA concentrations of 1.2, 13, and 80 mg/L. There is an increase in the pH from initial pH for the pH range of 2 to 7, and decrease in the pH from initial pH for the pH of 10. The TDS tabulated values can be seen in Table 4.8. There is a decrease in the TDS from initial TDS for the pH range of 2.0 to 4.0, and an increase in the TDS from initial TDS for the pH range of 5.0 to 10.0. From Table 4.9 we can see as expected, that there is a higher soluble iron at a low pH of 2.0 due to the acidic conditions just in the case of 1g to 50 mL solution. The

soluble iron was higher for 2g at the highest BPA concentration of 80 mg/L, but lower to the other two BPA concentrations. We can see that there is a trend for the soluble iron data, with an increase for the solution of BPA with 1.2 mg/L to that of 80 mg/L.



Figure 4.3 Power function as a function of pH: 2g sorbent: 50mL solution a) $C_0 = 1.2 \text{ mg/L}$, b) $C_0 = 13 \text{ mg/L}$, and c) $C_0 = 80 \text{ mg/L}$

Initial BPA C ₀ (mg/L)	a	n	\mathbf{R}^2
1.2	37.871	-0.402	0.909
13	337.131	-1.104	0.955
80	877.855	-1.409	0.958

Table 4.6: Power function constants for Hematite (H) as a function of pH, and 2g sorbent:50 mL solution

Table 4.7: pH for Hematite 2g:50 mL

Sampla	1	l.2 mg/L]	13 mg/L		80 mg/L		
pH	Initial pH	itial Final pH oH		Initial pH	Initial pH	Final pH		
2	1.963	2.125 ± 0.006	1.963	2.100 ± 0.008	1.966	2.042 ± 1.966		
2.5	2.467	2.730 ± 0.014	2.477	2.627 ± 0.012	2.465	2.645 ± 2.465		
3	3.000	3.970 ± 0.014	3.018	4.021 ± 0.032	2.984	3.968 ± 2.984		
3.5	3.512	5.232 ± 0.048	3.502	5.269 ± 0.026	3.516	5.303 ± 3.516		
4	3.954	6.453 ± 0.067	3.964	6.428 ± 0.069	4.032	6.536 ± 4.032		
5	4.969	7.284 ± 0.019	5.012	7.326 ± 0.015	5.006	7.385 ± 5.006		
7	6.989	7.466 ± 0.018	7.024	7.541 ± 0.021	7.019	7.747 ± 7.019		
10	9.568	6.825 ± 0.001	9.592	7.278 ± 0.256	9.740	9.069 ± 9.740		

 Table 4.8: TDS for Hematite 2g:50 mL

Sampla	1.2 mg/L				13 mg/L			80 mg/L		
pH	Initial TDS	Final TDS	Stdv	Blank	Final TDS	Stdv	Blank	Final TDS	Stdv	
2	1940.0	1716.7	5.8	1950.0	1726.7	5.8	2020.0	1790.0	2020.0	
2.5	599.0	432.3	1.5	603.0	431.7	2.5	623.0	436.7	623.0	
3	170.0	58.0	0.0	170.0	50.0	0.0	178.0	54.0	178.0	
3.5	36.0	25.7	0.6	37.0	24.3	0.6	38.0	22.3	38.0	
4	29.0	20.0	1.7	27.0	20.0	0.0	13.0	13.7	13.0	
5	4.0	7.3	0.6	4.0	7.7	0.6	5.0	7.7	5.0	
7	2.0	13.7	1.5	2.0	15.3	0.6	2.0	18.0	2.0	
10	11.0	19.0	0.0	12.0	20.7	0.6	21.0	26.0	21.0	

Sample	1.2 n	ng/L	20 n	ng/L	50 mg/L		
pН	Fe	Stdv	Fe	Stdv	Fe	Stdv	
2	2.283	0.068	2.493	0.055	3.190	0.255	
2.5	0.113	0.006	0.250	0.010	0.453	0.031	
3	0.070	0.000	0.113	0.006	0.400	0.010	
3.5	0.073	0.006	0.130	0.000	0.397	0.006	
4	0.073	0.006	0.133	0.006	0.410	0.010	
5	0.073	0.006	0.147	0.012	0.403	0.006	
7	0.073	0.006	0.137	0.032	0.400	0.000	
10	0.097	0.006	0.403	0.006	0.403	0.006	

Table 4.9: Soluble Iron (Fe) for Hematite 2g:50 mL

The pH effect for 5g to 50mL for the BPA concentrations of 1.2, 13, 130, and 200 mg/L had been investigated and the results presented in Figure 4.4 (a) trough (d). The tabulated power function parameters are presented in Table 4.10. From Table 4.10 we can see a decrease in the power function coefficient n from -1.270 to -2.050 as the concentration of BPA increased from 1.2 to 13 mg/L. The n increased to -1.648 for the BPA concentration of 130 mg/L with a further increase to -0.724 for the BPA concentration of 200 mg/L. The adsorption constant n continued to increase for the BPA concentration of 130 mg/L, and then decreased for the BPA concentration of 200 mg/L. At the BPA concentration of 13 mg/L the pH had the highest effect on the adsorption. The decrease in the adsorption capacity q was lower for higher initial BPA concentrations of 130 and 200 mg/L. From the result we can conclude that the removal of BPA from industrial effluents with high BPA concentrations is not as pH sensitive. From Table 4.11 we can see the initial and final pH along with the standard deviations for 5g to 50 mL solutions for all the four BPA concentrations of 1.2, 13, 130, and 200 mg/L. There is an increase in the pH from initial pH for the pH range of 2.0 to 7.0, and a decrease in the pH from initial pH for the pH of 10.0. For the TDS, the opposite of pH trend is seen as in the case of 1g, and 2g to 50 mL solution and the results are tabulated in Table 4.12. There is a decrease in the TDS from initial TDS for the pH range of 2.0 to 3.5, and an increase in the TDS from initial TDS for the pH range of 4.0 to 10.0. From Table 4.13 we can see as expected, that there is a higher soluble iron at a low pH of 2.0 due to the acidic conditions just in the case of 1g and 2g to 50 mL solution. The soluble iron was similar to the values of 2g to 50 mL solution with only the 130 mg/L solution having the highest concentration of soluble iron. When compared to the 1g and 2g to 50 mL solution are similar to those of 2g in the BPA solution of 80 mg/L.



Figure 4.4 Power function as a function of pH: 5g sorbent : 50mL solution a) $C_0 = 1.2 \text{ mg/L}$, b) $C_0 = 13 \text{ mg/L}$, and c) $C_0 = 130 \text{ mg/L}$



Figure 4.4cont. Power function as a function of pH: 5g sorbent : 50mL solution d) $C_0 = 200 \text{ mg/L}$

Table 4.10: Power function constants for Hematite (H) as a function of pH, and 5g sorbent:50 mL solution

Initial BPA C ₀ (mg/L)	a	n	\mathbf{R}^2
1.2	30.0317	-1.270	0.926
13	497.637	-2.050	0.879
130	1115.949	-1.648	0.930
200	611.1836	-0.724	0.966

Sampla	1	.2 mg/L	1	l3 mg/L	1.	30 mg/L		200 mg/L
pH	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH	Initial pH	Final pH
2	2.012	2.275 ± 0.022	1.975	2.222 ± 0.020	1.947	2.194 ± 0.008	1.923	2.161 ± 0.009
2.5	2.487	3.262 ± 0.014	2.512	3.223 ± 0.012	2.469	3.142 ± 0.021	2.432	3.089 ± 0.005
3	2.987	5.540 ± 0.032	2.946	5.541 ± 0.005	3.021	5.545 ± 0.018	2.961	5.573 ± 0.052
3.5	3.504	6.483 ± 0.016	3.479	6.509 ± 0.004	3.465	6.527 ± 0.004	3.447	6.537 ± 0.064
4	4.067	6.849 ± 0.015	4.072	7.008 ± 0.075	3.978	7.044 ± 0.008	3.985	7.058 ± 0.003
5	4.997	6.934 ± 0.020	4.927	6.988 ± 0.010	4.957	7.115 ± 0.015	5.036	7.178 ± 0.030
7	7.024	6.933 ± 0.031	6.975	6.985 ± 0.016	7.039	7.189 ± 0.019	7.019	7.251 ± 0.026
10	10.014	7.243 ± 0.039	9.995	7.156 ± 0.329	9.945	9.148 ± 0.018	9.988	9.292 ± 0.056

 Table 4.11: pH for Hematite 5g:50 mL

Table 4.12: TDS for Hematite 5g:50 mL

Sample	1.2 mg/L		13 mg/L		130 mg/L			200 mg/L				
pН	Blank	TDS	Stdv	Blank	pН	Stdv	Blank	pН	Stdv	Blank	pН	Stdv
2	1940.0	1646.67	5.77	1950.0	1653.33	5.77	1960.00	1683.33	5.77	1960.0	1700.00	10.00
2.5	638.0	236.33	1.53	642.0	237.67	0.58	648.00	238.00	1.00	651.0	239.00	1.00
3	175.0	39.33	0.58	175.0	38.67	0.58	179.00	37.67	0.58	182.0	37.33	0.58
3.5	58.0	29.67	0.58	59.0	28.33	0.58	60.00	27.67	0.58	60.0	27.33	0.58
4	18.0	26.33	0.58	23.0	31.67	0.58	25.00	27.00	1.00	17.0	26.00	0.00
5	5.0	25.00	0.00	5.0	25.00	0.00	5.00	25.67	0.58	6.0	27.33	0.58
7	3.0	28.00	1.00	3.0	27.67	0.58	4.00	28.33	0.58	4.0	29.00	0.00
10	11.0	28.67	0.58	15.0	31.33	0.58	28.00	34.67	0.58	37.0	50.00	0.00

Sample	1.2 mg/L		13 mg/L		130 mg/L		200 mg/L	
pН	Fe	Stdv	Fe	Fe	Stdv	Stdv	Fe	Stdv
2	2.163	0.072	1.893	0.015	4.290	0.122	3.157	0.121
2.5	0.407	0.006	0.420	0.010	0.510	0.060	0.470	0.017
3	0.400	0.000	0.397	0.006	0.407	0.006	0.447	0.023
3.5	0.410	0.000	0.400	0.000	0.403	0.006	0.460	0.026
4	0.410	0.010	0.403	0.006	0.400	0.000	0.467	0.015
5	0.407	0.012	0.423	0.015	0.403	0.006	0.433	0.012
7	0.407	0.012	0.443	0.031	0.417	0.021	0.423	0.006
10	0.407	0.006	0.400	0.000	0.407	0.006	0.430	0.017

Table 4.13: Soluble Iron (Fe) for Hematite 5g:50 mL

To better see the effect of initial BPA concentrations on the different adsorbent dosages at pH 2, 2.5, 3, 3.5, 4, 5, 7, and 10 bar figures were plotted and the results are presented in Figure 4.5 (a) through (h), Figure 4.6 (a) through (h), and Figure 4.7 (a) through (h) for 1g, 2g, and 5g, respectively. From Figure 4.5 (a) through (h) we can see that at an initial BPA concentration of 1.2 mg/L there is a BPA removal a lot higher than that at 20 and 50 mg/L at pH of 2.0. As the pH increased the difference between the BPA removals for all the three concentrations decreased. At pH of 4.0 the difference in the BPA removal between the 20 and 50 mg/L becomes the same. At pH 10 all the three initial BPA concentrations had the same removal close to one percent. Table 4.14 presents the tabulated values of the removal percentage for the 1g to 50 mL solution at different pH, and initial BPA concentrations.



Figure 4.5 BPA percentage removal as a function of pH: 1g sorbent : 50mL solution a) pH = 2, b) pH = 2.5, and c) pH = 3



Figure 4.5cont. BPA percentage removal as a function of pH: 1g sorbent : 50mL solution d) pH = 3.5, e) pH = 4, and f) pH = 5



279

g) pH = 7, and h) pH = 10

Sample pH	1.2 ppm	20 ppm	50 ppm	
Sumple pii	% Removal	% Removal	% Removal	
2	83.65 ± 0.66	24.04 ± 1.83	9.44 ± 0.48	
2.5	69.67 ± 0.71	18.94 ± 1.13	7.14 ± 0.38	
3	52.24 ± 0.71	14.57 ± 1.50	6.23 ± 0.50	
3.5	43.07 ± 0.87	10.90 ± 0.72	4.39 ± 0.38	
4	18.42 ± 0.88	2.96 ± 1.15	3.22 ± 0.52	
5	14.00 ± 1.40	1.47 ± 0.31	2.01 ± 0.46	
7	9.53 ± 1.61	0.71 ± 0.63	1.02 ± 0.60	
10	1.01 ± 0.24	0.70 ± 0.51	0.57 ± 0.55	

Table 4.14: Total Bisphenol A (BPA) removal with Hematite (1g:50 mL) as function of pH

Figure 4.6 (a) through (h) shows that at initial BPA concentration of 1.2 mg/L there was a higher BPA removal than that at 13 and 80 mg/L at pH of 2.0. As the pH increased the difference between the BPA removals for all the three concentrations decreased. At pH of 5.0 there is no more difference in the BPA removals for the 1.2 and 13 mg/L. Above the pH 5.0 the adsorption removal stays the same for 1.2 and 13 mg/L even at pH 10. Table 4.15 presents the tabulated values of the removal percentage for the 2g to 50 mL solution at different pHs and initial BPA concentrations.



Figure 4.6 BPA percentage removal as a function of pH: 2g sorbent : 50mL solution a) pH = 2, b) pH = 2.5, and c) pH = 3



Figure 4.6cont. BPA percentage removal as a function of pH: 2g sorbent : 50mL solution d) pH = 3.5, e) pH = 4, and f) pH = 5



g) pH = 7, and h) pH = 10

Sample pH	1.2 ppm	13 ppm	80 ppm	
	% Removal	% Removal	% Removal	
2	86.19 ± 0.48	44.97 ± 1.05	15.18 ± 0.76	
2.5	71.52 ± 0.45	38.05 ± 1.39	13.09 ± 0.63	
3	58.95 ± 0.42	35.12 ± 0.54	10.25 ± 0.37	
3.5	48.73 ± 1.21	27.69 ± 0.57	8.26 ± 0.34	
4	28.43 ± 0.58	23.13 ± 0.78	6.06 ± 0.49	
5	14.87 ± 1.01	14.69 ± 0.10	4.48 ± 0.56	
7	9.86 ± 1.73	8.91 ± 0.89	1.17 ± 0.78	
10	6.53 ± 1.12	6.12 ± 0.45	0.55 ± 0.70	

Table 4.15: Total Bisphenol A (BPA) removal with Hematite (2g:50 mL) as function of pH

Figure 4.7 (a) through (h) shows that at initial BPA concentration of 1.2 mg/L there is a only a small difference in the BPA removal than that of 13 mg/L for pH 2.0 and 2.5. However, there was a larger difference in the total removal of BPA for the concentration of 130 and 200 mg/L at pH of 2.0 to 3.5. As the pH increases the difference between the BPA removals was different than that of 1g and 2g to 50 mL solution results. At pH 3.0 the difference between the 1.2 mg/L starting solution and that of 13 mg/L started to increase. As for the initial BPA concentration of 130 and 200 mg/L the difference in the BPA removal was not significant. As the pH increased there was actually a slight higher adsorption removal for the initial BPA concentration of 200 mg/L than the adsorption for the initial BPA concentration of 130 mg/L. Table 4.16 presents the tabulated values of the removal percentages for the 5g to 50 mL solution at different pHs, and initial BPA concentrations.



Figure 4.7 BPA percentage removal as a function of pH: 5g sorbent : 50mL solution a) pH = 2, b) pH = 2.5, and c) pH = 3



Figure 4.7 cont. BPA percentage removal as a function of pH: 5g sorbent : 50mL solution d) pH = 3.5, e) pH = 4, and f) pH = 5



Figure 4.7 cont. BPA percentage removal as a function of pH: 5g sorbent : 50mL solution g) pH = 7, and h) pH = 10

Sample	1.2 ppm	13 ppm	130 ppm	200 ppm % Removal	
рН	% Removal	% Removal	% Removal		
2	95.18 ± 0.87	81.69 ± 0.23	26.92 ± 0.49	18.75 ± 0.35	
2.5	89.60 ± 1.21	80.19 ± 0.20	22.86 ± 0.45	16.47 ± 1.12	
3	67.46 ± 1.28	44.72 ± 0.32	12.20 ± 2.58	12.38 ± 0.80	
3.5	56.64 ± 0.44	23.39 ± 0.75	10.32 ± 0.93	11.59 ± 0.18	
4	47.74 ± 1.22	8.29 ± 0.48	6.19 ± 0.18	11.14 ± 0.27	
5	19.44 ± 0.56	5.19 ± 0.87	5.94 ± 0.27	9.29 ± 0.10	
7	12.75 ± 0.52	4.28 ± 1.06	5.91 ± 0.50	8.38 ± 0.57	
10	9.40 ± 1.88	3.56 ± 1.38	4.82 ± 0.65	5.82 ± 0.26	

Table 4.16: Total Bisphenol A (BPA) removal with Hematite (5g:50 mL) as function of pH

Another examination of the data was done in order to see the difference of the adsorbent dosage at a fixed initial BPA concentration of 1.2 mg/L at different pHs of 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, 7.0, and 10.0. Bar figures were plotted and the results are presented in Figure 4.8 (a) through (h). From Figure 4.8 (a) through (h) we can see that the 5g of adsorbent has the highest removal as expected and that there was not a high difference in the BPA removal for a pH above 5.0.



Figure 4.8 BPA fraction removal as a function of pH: $C_0 = 1.2 \text{ mg/L}$ a) pH = 2, b) pH = 2.5, and c) pH = 3



Figure 4.8 cont. BPA fraction removal as a function of pH: $C_0 = 1.2 \text{ mg/L}$ d) pH = 3.5, e) pH = 4, and f) pH = 5



Figure 4.8 cont. BPA fraction removal as a function of pH: $C_0 = 1.2 \text{ mg/L}$ g) pH = 7, and h) pH = 10

	1g		2g		5g	
Sample pH	Fraction Removal	Stdv	Fraction Removal	Stdv	Fraction Removal	Stdv
2	0.84	0.01	0.86	0.00	0.95	0.01
2.5	0.70	0.01	0.72	0.00	0.90	0.01
3	0.52	0.01	0.59	0.00	0.67	0.01
3.5	0.43	0.01	0.49	0.01	0.57	0.00
4	0.18	0.01	0.28	0.01	0.48	0.01
5	0.14	0.01	0.15	0.01	0.19	0.01
7	0.10	0.02	0.10	0.02	0.13	0.01
10	0.01	0.00	0.07	0.01	0.09	0.02

Table 4.17: Removal of BPA with Hematite, C₀=1.2 mg/L

The ionic strength effect of the Ca²⁺ ions was studied using CaCl₂ ionic strengths of 0.001, 0.005, 0.05, 0.1 and 0.5M. All the ionic strengths were done using three different BPA concentrations of 1.3, 13, and 130 mg/L for a 5g to 50 mL adsorbent to aqueous solution ratio. The three different cases results are presented in Figure 4.9 (a) through (c) for CaCl₂ ionic strengths of 0.001 to 0.5 M, Figure 4.9 (d) through (f) for the CaCl₂ ionic strengths of 0.001 to 0.5 M with a 1mM of NaHCO₃, and finally Figure 4.9 (g) through (i) for the CaCl₂ ionic strengths of 0.001 to 0.5 M with the aqueous pH solution adjusted to 2.0. From Figure 4.9 (a) through (c) we can definitely see that there is an ionic strength effect on the adsorption of BPA onto hematite H. As the ionic strength increases the removal of BPA also increases. After an ionic strength higher than 0.005M there is the same effect for both the 1.3 and 13 ppm initial concentration of BPA in the aqueous solution. The solution with the highest initial BPA concentration had the lowest removal of BPA as expect due to the adsorption capacity of the adsorbent. We can see the results of the pH for all the three different cases represented by bar charts in Figure 4.10 (a) through (c), and tabulated values in Table 4.18, 4.19, and 4.20 for the ionic strengths of CaCl₂, 1 mM NaHCO₃ addition, and adjusted pH of 2.0, respectively.
The results in Figure 4.9 (d) through (f) for the 1 mM of NaHCO₃ addition follows very closely the same pattern and values as in the case of CaCl₂ ionic strength solutions. However, the percentage removal is slightly lower than the system with only the Ca²⁺ ions. This is believe to be due to the pH effect on the solution. The pH effect on the solution had been investigated and presented earlier in other chapters, where we see a decrease in the adsorption with an increase in the pH. For the buffer system with the 1 mM of NaHCO₃ we can see that the pH is slightly higher than the system with no NaHCO₃.

For the system with the adjusted pH to 2.0 we can see from Figure 4.9 (g) through (i) that there was little effect for the initial BPA concentration of 1.2 and 13 mg/L. For both cases there was almost no significant effect for all the ionic strengths. This was due to the fact that at acidic conditions the BPA is in its neutral form and surface charge of the adsorbent is not highly negative and may even be positive. As a result the Ca^{2+} ions would not have a big effect on the adsorption due to the low initial concentration of BPA. We could also see from Table 4.20 that there is little change in the pH of the solution with a slight increase only for the case of 0.5M. For the case of initial BPA concentration of 130 mg/L we can see an effect above the ionic strength of 0.1M. This was due to the high concentration of BPA in the solution, which created a salting effect decreasing the solubility of the BPA in the aqueous solution as a result increasing the adsorption.

The concentrations of soluble iron are presented in bar charts in Figure 4.11 (a) through (c) and in tabulated form in Table 4.21, 4.22, and 4.23 for the ionic strengths of CaCl₂, 1 mM NaHCO₃ addition, and adjusted pH of 2.0, respectively. From the results we can see that the initial BPA concentration had no effect on the soluble iron of the solution. For the case where Ca^{2+} ions were present only at the second case with the addition of 1 mM NaHCO₃, the soluble

iron concentration followed the same trend and had similar values for all the different ionic strengths and BPA initial concentrations. For both cases the soluble iron increased with the increase in the ionic strength. As expected in the acidic conditions with the pH adjusted to 2.0 there was an increase in the soluble iron concentration and it decreases with an increase in the ionic strength. The initial BPA concentration, the pH of the solution, and the addition of NaHCO₃ had no effect on the soluble Ca²⁺ ions concentration. The concentration of the Ca²⁺ ions increased with the increase in the ionic strength which was expected.



Figure 4.9 BPA percentage removal as a function of CaCl₂ ionic strength: 5g sorbent : 50mL solution
a) C₀ = 1.3 mg/L, b) C₀ = 13 mg/L, and c) C₀ = 130 mg/L



Figure 4.9 cont. BPA percentage removal as a function of $CaCl_2 + 1mM$ NaHCO₃ ionic strength: 5g sorbent : 50mL solution d) $C_0 = 1.3$ mg/L, e) $C_0 = 13$ mg/L, and f) $C_0 = 130$ mg/L



Figure 4.9 cont. BPA percentage removal as a function of CaCl₂ ionic strength at pH 2.0: 5g sorbent : 50mL solution
g) C₀ = 1.3 mg/L, h) C₀ = 13 mg/L, and i) C₀ = 130 mg/L



Figure 4.10 pH variation as a function of ionic strength: 5g sorbent : 50mL solution a) CaCl₂, b) CaCl₂ + 1mM NaHCO₃, and c) CaCl₂ at pH 2



Figure 4.11 Soluble iron (Fe) variation as a function of ionic strength: 5g sorbent : 50mL solution a) CaCl₂, b) CaCl₂ + 1mM NaHCO₃, and c) CaCl₂ at pH 2

Ionic Strength	Samula	1.3 ₁	1.3ppm		13ppm		ppm
Tome Strength	Sample	pН	Stdv	pН	Stdv	pН	Stdv
	Blank	6.055	0.000	5.917	0.000	5.990	0.000
	Solution	7.103	0.051	6.935	0.060	7.041	0.058
0.005M CaCl ₂	Blank	6.435	0.000	5.927	0.000	6.032	0.000
	Solution	6.886	0.049	6.792	0.034	6.470	0.121
	Blank	5.967	0.000	6.132	0.000	6.092	0.000
0.051v1 CaCl ₂	Solution	6.540	0.027	6.553	0.006	6.621	0.015
	Blank	5.932	0.000	5.954	0.000	6.408	0.000
$0.1M \text{ CaCl}_2$	Solution	6.489	0.033	6.488	0.042	6.520	0.009
0.5M CaCl ₂	Blank	5.565	0.000	6.299	0.000	6.218	0.000
	Solution	6.337	0.020	6.324	0.016	6.696	0.035

Table 4.18: pH for Hematite 5g:50 mL as a function of CaCl₂

Table 4.19: pH for Hematite 5g:50 mL as a function of CaCl₂ + 1mM NaHCO₃

Ionic Strength	Samula	1.3p	1.3ppm		13ppm		opm
ionic Strength	Sample	pН	Stdv	pН	Stdv	pН	Stdv
0.001M CaCl ₂	Blank	7.975	0.000	7.986	0.000	7.889	0.000
+1mM NaHCO ₃	Solution	7.525	0.026	7.476	0.007	7.495	0.006
0.005M CaCl ₂	Blank	7.961	0.000	7.949	0.000	7.914	0.000
+1mM NaHCO ₃	Solution	7.367	0.040	7.413	0.011	7.373	0.020
0.05M CaCl ₂	Blank	7.614	0.000	7.585	0.000	7.485	0.000
+1mM NaHCO ₃	Solution	7.040	0.033	7.033	0.014	7.004	0.050
0.1M CaCl ₂	Blank	7.507	0.000	7.524	0.000	7.527	0.000
+1mM NaHCO ₃	Solution	7.022	0.010	7.066	0.010	7.088	0.005
0.5M CaCl ₂	Blank	7.055	0.000	6.963	0.000	6.844	0.000
+1mM NaHCO ₃	Solution	6.697	0.054	6.707	0.008	6.696	0.035

Table 4.20: pH for Hematite 5g:50 mL as a function of CaCl₂ at pH 2

Ionic Strength	Sample	1.3 p	1.3ppm		13ppm		opm
ionie birengen	Sample	pН	Stdv	pН	Stdv	pН	Stdv
0.005M CaCl ₂	Blank	2.029	0.000	2.045	0.000	2.055	0.000
@ pH 2	Solution	2.014	0.027	2.037	0.021	2.052	0.020
0.05M CaCl ₂	Blank	2.064	0.000	2.054	0.000	2.062	0.000
@ pH 2	Solution	2.084	0.018	2.045	0.023	2.007	0.022
0.1M CaCl ₂	Blank	1.987	0.000	1.985	0.000	1.986	0.000
@ pH 2	Solution	2.136	0.007	2.111	0.006	2.090	0.015
0.5M CaCl ₂	Blank	1.982	0.000	1.996	0.000	1.982	0.000
@ pH 2	Solution	2.334	0.013	2.348	0.003	2.336	0.013

Ionic Strength	Sample	1.3ppm		13p	pm	130ppm		
	-	Fe	Stdv	Fe	Stdv	Fe	Stdv	
0.001M CaCl ₂	Solution	N.D.		N.D.		N.D.		
0.005M CaCl ₂	Solution	0.010	0.000	0.010	0.010	0.020	0.000	
0.05M CaCl ₂	Solution	0.120	0.010	0.120	0.010	0.120	0.020	
0.1M CaCl ₂	Solution	0.150	0.010	0.150	0.000	0.130	0.020	
0.5M CaCl ₂	Solution	0.590	0.010	0.570	0.010	0.580	0.010	

Table 4.21: Soluble iron (Fe) for Hematite 5g:50 mL as a function of CaCl₂

Table 4.22: Soluble iron (Fe) for Hematite 5g:50 mL as a function of CaCl₂ + 1mM NaHCO₃

Ionic Strength	Sample	1.3	ppm	13p	pm	130p	130ppm	
	-	Fe	Stdv	Fe	Stdv	Fe	Stdv	
0.001M CaCl ₂ +1mM NaHCO ₃	Solution	N.D.		N.D.		N.D.		
0.005M CaCl ₂ +1mM NaHCO ₃	Solution	0.020	0.000	0.020	0.000	0.020	0.000	
0.05M CaCl ₂ +1mM NaHCO ₃	Solution	0.120	0.010	0.100	0.000	0.110	0.000	
0.1M CaCl ₂ +1mM NaHCO ₃	Solution	0.190	0.010	0.180	0.000	0.180	0.010	
0.5M CaCl ₂ +1mM NaHCO ₃	Solution	0.700	0.010	0.700	0.010	0.700	0.000	

Table 4.23: Soluble iron (Fe) for Hematite 5g:50 mL as a function of CaCl₂ at pH 2

Ionic Strength	Sample	1.3ppm		13p	pm	130ppm		
	_	Fe	Stdv	Fe	Stdv	Fe	Stdv	
0.005M CaCl ₂ @ pH 2	Solution	2.210	0.020	2.200	0.040	2.180	0.020	
0.05M CaCl ₂ @ pH 2	Solution	1.570	0.020	1.480	0.030	2.000	0.060	
0.1M CaCl ₂ @ pH 2	Solution	1.430	0.100	1.500	0.090	1.630	0.080	
0.5M CaCl ₂ @ pH 2	Solution	1.050	0.050	1.030	0.010	1.010	0.010	

Ionia Strongth		1.3ppm			13ppm			130ppm	
Iome Strength	Blank	Hematite	Stdv	Blank	Hematite	Stdv	Blank	Hematite	Stdv
0.001M CaCl ₂	45.50	44.40	0.40	45.60	44.70	0.70	44.80	44.60	0.40
0.001M CaCl ₂ +1mM NaHCO ₃	44.50	40.40	0.30	46.50	41.40	0.90	45.50	44.90	0.70
0.005M CaCl ₂	223.70	223.97	2.50	218.90	223.50	1.97	205.20	205.50	0.82
0.005M CaCl ₂ +1mM NaHCO ₃	243.60	227.37	1.06	231.30	220.20	1.01	213.50	214.63	2.27
0.005M CaCl ₂ @ pH 2	231.90	223.37	1.92	228.60	214.00	4.70	210.60	213.27	7.29
0.05M CaCl ₂	2326.00	2325.00	33.00	2342.00	2351.00	22.00	2370.00	2283.00	62.00
0.05M CaCl ₂ +1mM NaHCO ₃	2298.00	2221.00	27.87	2256.00	2238.33	13.58	2405.00	2315.00	14.11
0.05M CaCl ₂ @ pH 2	2212.00	2082.30	79.78	2285.00	2118.70	40.67	2280.00	2126.67	33.61
0.1M CaCl ₂	4487.00	4017.00	120.07	4672.00	4174.00	35.00	4431.00	4083.00	23.80
0.1M CaCl ₂ +1mM NaHCO ₃	4383.00	4044.00	150.01	4403.00	4110.00	69.58	4460.00	4135.00	30.12
0.1M CaCl ₂ @ pH 2	4468.00	4088.00	23.03	3770.00	3761.33	57.35	4487.00	4105.33	18.50
0.5M CaCl ₂	21300.00	20317.00	186.10	20850.00	21163.00	117.19	21680.00	20553.00	100.17
0.5M CaCl ₂ +1mM NaHCO ₃	21260.00	19770.00	370.00	21490.00	20423.00	361.16	21670.00	20370.00	285.13
0.5M CaCl ₂ @ pH 2	20790.00	20593.00	150.44	21380.00	20633.33	560.03	20690.00	20816.67	158.22

Table 4.24: Calcium (mg/L) concentration for Hematite 5g:50 mL as a function of ionic strength

The ionic strength effect of the K⁺ ions was studied using KCl ionic strengths of 0.001, 0.005, 0.05, 0.1 and 0.5M. All the ionic strengths were done using three different BPA concentrations of 1.3, 13, and 130 mg/L for a 5g to 50 mL adsorbent to aqueous solution ratio. The results are presented in Figure 4.12 (a) through (c), from where we can see that the effect of the K⁺ ions was a lot lower than that of Ca²⁺ ions. In the case for an ionic strength above 0.05M there is only slight effect on the adsorption of BPA for both the 1.3 and 13 mg/L initial BPA concentrations. However, the BPA removal was lower for the initial BPA concentration of 13 mg/L when compared to that of 1.3 mg/L. In the case of Ca²⁺ ions the removal was the same above 0.05M which also indicates that Ca²⁺ ions have a greater effect on the adsorption of BPA. The removal of the BPA for the initial concentration of 130 mg/L was also less than 1.3 and 13 mg/L initial concentration as expected, due to the adsorption capacity of the adsorbent.

We can see the results of the pH and soluble iron results for all the three different cases of initial BPA concentration represented by bar charts in Figure 4.13 and 4.14 and tabulated values in Table 4.25 and 4.26. From Figure 4.13 we can see that the equilibrium pH after one day was around 7.0 in all the cases. As a result we can see that the effect on the removal of BPA was only due in part of the addition of K^+ ions and the pH of the solution did not play a significant role. From Figure 4.14 we can see that there was also a slight increase in the soluble iron above the ionic strength of 0.005M with a considerable increase at 0.5M.



Figure 4.12 BPA percentage removal as a function of ionic strength: 5g sorbent : 50mL solution a) $C_0 = 1.3$ mg/L, b) $C_0 = 13$ mg/L, and c) $C_0 = 130$ mg/L



Figure 4.13 pH variation as a function of ionic strength: 5g sorbent : 50mL solution



Figure 4.14 Soluble iron (Fe) variation as a function of ionic strength: 5g sorbent : 50mL solution

Ionic Strength	Samula	1.3p	1.3ppm		13ppm		ppm
Tome Strength	Sample	pН	Stdv	pН	Stdv	pН	Stdv
	Blank	6.696	0.000	6.369	0.000	6.346	0.000
	Solution	7.104	0.006	7.139	0.027	7.146	0.023
0.005M KCl	Blank	6.363	0.000	6.208	0.000	6.341	0.000
	Solution	7.014	0.069	7.038	0.005	7.089	0.090
0.05M KCI	Blank	5.944	0.000	5.771	0.000	6.869	0.000
0.05101 KCI	Solution	7.004	0.005	7.006	0.019	7.039	0.019
	Blank	5.855	0.000	5.724	0.000	5.774	0.000
U.IIVI KUI	Solution	7.000	0.015	7.061	0.019	6.872	0.003
0.5M KCl	Blank	5.669	0.000	5.603	0.000	5.715	0.000
	Solution	7.069	0.036	7.087	0.011	7.071	0.048

Table 4.25: pH for Hematite 5g:50 mL as a function of KCl

Table 4.26: Soluble iron (Fe) for Hematite 5g:50 mL as a function of KCl

Ionic Strength	Sample	1.3ppm		13p	pm	130ppm		
8	-	Fe	Stdv	Fe	Stdv	Fe	Stdv	
0.001M KCl	Solution	N.D.		N.D.		N.D.		
0.005M KCl	Solution	0.030	0.010	0.053	0.006	0.040	0.020	
0.05M KCl	Solution	0.030	0.010	0.053	0.006	0.023	0.006	
0.1M KCl	Solution	0.073	0.021	0.120	0.026	0.033	0.023	
0.5M KCl	Solution	0.387	0.031	0.680	0.026	0.380	0.070	

4.6 CONCLUSIONS

The study done in chapter 4 found that the adsorption of BPA onto hematite H is very pH sensitive. The more acidic the solution was the better the adsorption. From the results on the pH effect we can see that there was a adsorption capacity that the adsorbent reached, above which the removal did not increase anymore with the increase in the BPA concentration. If the adsorption capacity for the adsorbent was not reached, both power function parameters increased the adsorption capacity constant a and n parameter increased. If the BPA concentration is raised above the adsorption capacity of the adsorbent both power functions a and n decreased.

The effect of the initial BPA concentration was found to be limited at a pH lower than 2.0. When the adsorption was strong the difference in BPA concentration had a significant effect. However, if the pH is high and the adsorption is not as strong the removal of BPA is the same and does not depend so much on the initial concentration of BPA. The same effect was seen in the case of different adsorbent dosages. The main different in the adsorbent dosage was at lower pH and as the pH increase the difference was diminished.

The adsorption of BPA was also found to be influenced by the ionic strength. The Ca^{2+} ions had a stronger effect on the adsorption than that of K⁺ ions. The effect of ionic strength had a small effect when the solution was acidic at a pH of 2.0. The buffer solution with the bicarbonate ions only influenced the adsorption at a higher BPA concentration of 130 mg/L. At higher initial concentration of BPA the effect of the bicarbonate ions helped the adsorption due to the salting effect, which decreases the solubility of BPA in aqueous solution. The most important factor was found to be the pH when compare to the ionic strength. For the solution of where the pH was adjusted at 2.0 the removal of BPA was only influenced significantly for the highest BPA concentration and at 0.5M ionic strength of CaCl₂.

The removal of BPA from wastewater or from a natural body of water could be higher than that from DI alone due to the presence of different other species in the water based on the study of the ionic strength. However, this has to be investigated further because the other species in water could also outcompete with BPA and adsorbed onto the hematite H.

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CHAPTER V

BPA BYPRODUCTS DEGRADATION

5.1 INTRODUCTION

Over the past decade the use of pharmaceuticals and personal care products (PPCPs) had increased and consists of wide range of chemicals such as sunscreen agents, veterinary and human drugs, and endocrine disrupting compounds (ECDs). One type of PPCPs are the EDCs (Pan et al., 2008), and Bisphenol A (BPA) is known to be one of the EDCs (Krishnan et al., 1993). By blocking or mimicking the activity of natural hormones, the EDCs that escaped in the environment can produce harm to wildlife and humans, by interfering with their reproductive system (Harrison et al., 1997; Snyder et al., 2003). Because of the side effects that have been reported to humans are an increase in the incidence of testicular, ovarian, and breast cancer and also reduce fertility (Colborn et al., 1993; Harrison et al., 1997; Cheek et al., 1998), significant efforts have been done in order for the BPA to be removed from the aqueous phase.

BPA is mostly known for being used in the plastic industry for the production of epoxy resins and polycarbonate. Currently, the capacity production of BPA is the highest in the US and had increased over the years all over the world (Jiao et al., 2008). However, China is becoming a big consumer of BPA with an increase in usage from 106,000 tonnes in 2001 to 570,000 tonnes in 2008 (Yu and Jia, 2008). The contamination of the environment with BPA was done through multiple sources and traces of BPA had been found in: river water, estuaries and seawater, ground water, wastewater and sludge, river and freshwater sediment, marine sediments, dust particles, and atmosphere. The pollution of the aqueous phase with BPA is posing the most significant threat to humans and wildlife, because there is no alternative way of bypassing the exposure. If the aqueous phase is consumed or the wild life is living in that aqueous phase the exposure to BPA cannot be avoided. Some of the BPA contaminations of the aqueous phase in

the environment are done through sewage treatment effluents, landfill leachate, or natural degradation of polycarbonate plastics (Crain et al., 2007).

When compared to other pharmaceuticals, PPCPs and EDCs out of 100 chemicals the overall priority for BPA was found to be in second place for the overall score, which took into consideration the occurrence, ecological effect, and health effects. (Kumar and Xagoraraki, 2010). Each inorganic and organic chemical have different physical chemical properties that influences its behavior in the environment. As a result some chemicals would degrade more easily and other not by bacteria or other chemical reactions that take places in the environment. As a result of these chemical transformations the occurrence of byproducts takes place. BPA could also be transformed through different process and form different chemical byproducts. The study of the newly formed byproducts is very important in evaluating the risk that the BPA has on the environment and humans. Few studies done on the removal of BPA from water in water treatment plant (WTP) using conventional treatment processes lead to byproducts formation that could have higher estrogenic activity than BPA (Niwa et al., 2002; Stackelberg et al., 2004; Korshin et al., 2006). During the water disinfection or bleaching the paper during recycling the chlorination of BPA takes place. Toxicity studies of the chlorinated derivates of BPA had suggested that their estrogenic activity is stronger than that of BPA alone (Takemura et al., 2005). Different technologies that are currently used or could be used in the future for the WTP and waste water treatment plants (WWTPs) have been investigated and found that BPA could produce byproducts. Also biological process done by different bacteria had been found to be able to produce byproducts. The purpose of this chapter is to find the byproducts that could be formed from BPA as a result of different process that are present in the environment or are in use in different industries.

5.2 ENVIRONMENTAL FATE OF BISPHENOL A

The presence of BPA in different environmental media has been presented in the beginning of this chapter and in detail in Chapters 1 and 3. Most of the BPA contamination had been presented to be in the aqueous phase. The highest concentrations of BPA had been reported to be in the landfill leachate, wastewater effluents, and industrial effluent discharge. In order to evaluate the persistence of BPA in the environment and the medium of greatest concern a multimedia assessment of BPA was conducted (Cousins et al., 2002). The environmental fate analysis on BPA was very extensive and used many models in order to understand the transport and behavior of BPA in the environment.

It is important to note that the multimedia assessment study was done more than a decade ago, and since then better data are available in regards to concentrations and half lives of the BPA. As a result the study can help us to predict the behavior of BPA and not give us definitive percentage for the fate of BPA in the environment. Also it is important to state that the study had been sponsored by the Society of the Plastic Industry (SPI) and one of the authors' works for Dow Chemical Company. As a result many of the input parameters that were chosen were not in the conservative side. One example is the half lives used for the water and soil used in this study compared to the one used by the European Union System for the Evaluation of Substances (EUSES). The present study had half lives of 4.5 days for both water and soil while the EUSES recommends using 15 and 30 days for water and soil, respectively. The half life used in this study was obtained from the study done by Klecka in 2001, which is one of the current authors that conducted the research sponsored by the same Society of Plastic Industry.

One of the main important factors that influence the partition of a chemical in the environment is the point of discharge. Depending on where a pollutant is release the partition of the pollutant in different media would depend greatly on the discharged media. The multimedia assessment done by Cousins et al., 2002, takes in to consideration four different release models from which one model is based just on engineering emissions factors rather than actual environmental measurements for that reason it was ignored. The remaining three models estimated that the release would be done mostly in the surface water. The study argues that probably the best realistic model gives us an actual 90 % release in the surface water and 10 % in the atmosphere with a total 20,930 kg/year release. The lowest percentage release of BPA to the water phase was 82% and the highest 98%. Based on the data presented in Chapters 1 and 3 we can conclude that the major release in the environment is in the surface water, where most of the BPA pollution had been reported and the highest concentrations of BPA reported.

To evaluate fate of BPA the study conducted by Cousins et al., 2002 used the Equilibrium Criterion Model (EQC), which is described in detailed by Mackay et al., 1996. The EQC model uses a representative are of 100,000 km² that is equal to that of the state of Ohio. The computer model has three level of fate comparison using different principles that are described in Mackay, 2001.

5.2.1 LEVEL I ASSESSMENT OF BPA USING EQUILIBRIUM CONDITIONS

The model used was Level I EQC, which modeled the BPA partition under equilibrium based on the chemical physical properties of BPA. The media taken into consideration in this model were air, soil, water, sediment, suspended sediment, and fish. Based on these results we can see that 98% of the total BPA concentration was partitioned into soil or surface water with 67.9% and 20.5%, respectively. BPA is moderately hydrophobic and moderately soluble in water, having an fugacity capacity for soil 50 times than that of water. Due to the fact that the volume of water in the EQC model is $2x10^{11}$ m³ and the soil $9x10^9$ m³ the percentage in water was still substantial. Similarly, the sediment has a large fugacity than that of water, however due to the smaller volume compared to that of water in the EQC model the distribution is only 1.5%.

The distribution in biota was not high even though a bioconcentration factor (BCF) of 125 was used. Previous study done using Level I partition by Staples et al, 1998, showed a partition of 25% in the soil, 52% in the water, and 23% in the sediment. The ratio used for the model by Cousins et al., 2002 of sediment:soil:water:air was 1:90:2000:1,000,000, where the ratio used by Staples et al., 1998 was 1:2:333:286,000. The model used by Staples et al., 1998 is more realistic due to the fact that BPA is mostly discharged in the surface water. We can see in Figure 5.1 the diagram for Level I EQC modeling done by Cousins et al., 2002.



Figure 5.1 - Level I EQC modeling diagram. (Cousins et al., 2002)

5.2.2 LEVEL II ASSESMENT OF BPA USING ENVIRONMENTAL LOSS PROCESSES

The next evaluation was done using an Level II EQC modeling, where there was additional information added to the equilibrium partition system. In this new model the half lives for the each of the media such as air, soil, water, and sediment where added in the model. The biota and suspended sediments were taken off the model. The purpose of the Level II EQC model evaluation was to determine the routes through which the BPA would be lost under equilibrium partition and steady state conditions. The loss could be done through reaction in the different partition media and through advection forces. As mentioned earlier the results of the data depends greatly on the input parameters of the half lives of BPA, by using more conservative values proposed by the EUSES the persistence of BPA in the environment would have been longer. We can see the diagram for the Level II EQC modeling in Figure 5.2.



Figure 5.2 - Level II EQC modeling diagram. (Cousins et al., 2002)

From Figure 5.2 we can see that the major loss routes of BPA in the environment would be the reaction that is responsible for about 29.6 % and 65.8% loss for water and soil, respectively. The advection loss is significant in water and is about 4.6%. The current model predicts an overall residence time of about 6.3 days, with an reaction residence of 6.6 days, and advection residence of 136 days. Based on this model the persistence of BPA does not seem to be significant and the reaction is the dominant persistence factor. Also we can conclude that the advection of BPA and transport in the atmosphere is very low, and the water phase is having the greatest potential for transport.

5.2.3 LEVEL III ASSESMENT OF BPA USING NONEQUILIBRIUM STEADY STATE

The Level III EQC modeling is very important because it is able to determine the overall environmental fate of BPA based on the media effects on the release. During the Level III modeling a nonequilibrium steady state is used to calculate the fugacity as a result a lot of importance is put on the transport and transformation processes. The Level III assessment has the most realistic calculations that simulate real environmental process that could be done using EQC model. Using this model the tendency for a pollutant to migrate to different media can be calculated by modeling emissions to each individual compartment and calculating the amount present in each media at steady state conditions. Four different case scenarios were used with individual emissions of 1000 kg/h to the water, air and soil media comportments, and simultaneous emissions of 1000 kg/h to each of the media compartments. We can see the BPA distribution in each media compartment for all the 4 cases in Table 5.1 for the EQC Level III assessment. In Figure 5.3 we can see the results for the Level III EQC modeling diagram for the case 4, where the simultaneous emissions of 1000 kg/h to each of the media compartments of air, water, and soil was released.



Figure 5.3 - Level III EQC modeling diagram (100kg/h released simultaneously to air, water and soil). (Cousins et al., 2002)

Table 5.1.	EQC Level III results:	BPA	distribution	in each	medium	comportment	based on
single and	multiple emissions.						

Emission medium	ImissionAmount at steady state (kg)Residencenedium(percent in brackets)(withinin				Residence time (d) (without advection in brackets)
	Air	Water	Soil	Sediment	in brackets)
	35	13 600	139 000	741	6.4
Air	(<0.1)	(8.8)	(90.7)	(0.5)	(6.5)
	< 0.1	135 000	< 0.1	7 354	5.9
Water	(<0.1)	(94.8)	(<0.1)	(5.2)	(6.7)
	< 0.1	212	156 000	12	6.5
Soil	(< 0.1)	(0.1)	(99.9)	(<0.1)	(6.5)
	35	149 000	295 000	8 107	6.3
All three	(<0.1)	(32.9)	(65.3)	(1.8)	(6.6)

case scenarios. We can see that if the BPA is released only in the air the 8.8%, 90.7%, and 0.5%would migrate to the water, soil, and sediment, respectively. From these results we can conclude that if the BPA emission would be in air it will not remain in air but transfer to soil mostly and water. The much higher rate of deposition to the soils is due to the EQC large surface for the soil media compartment, which would receive a large atmospheric deposition. If the emission is done only in water then we can see that 94.8% of the BPA will remained in water and the remaining 5.2% would transfer to the sediment media compartment. The transfer from water to soil and air is negligible. This finding is very important because the second case, with the emission in water, is the most realistic environmental scenario. If the emission of BPA occurs in soil only, than 99.9% would remained in the soil and 0.1% of the BPA would migrate into the water media, probably because of the rain runoff. As a result we can conclude that if the emission of BPA is to the water and soil most of the BPA would remained into the media that was emitted and a small percentage would transferred to the sediment for the water emission. Finally for the forth case the emission was simultaneously done in air, soil and water. We can see the results in the diagram for the forth case in Figure 5.3. We may see that the distribution at steady state is mostly present in the soil with 65.3% followed by water media with 32.9%, sediment 1.8% and the air phase was negligible. Also we can see that the transfer from the air to the soil is much larger than to that of air to water as expected. Also there was a small transition from soil to water and water to sediment. The transfer from soil to air and water to air are negligible. Even though is a small transfer from sediment to the water it is half of the transferred that occurs from water to the sediment. The remaining half of the BPA transferred from water to the sediment is lost through advection and reaction. As a result we can see that there is no BPA accumulation in the sediment

and that the BPA would be transferred back into water or lost through reaction and advection. Another important aspect in the forth case is that there is no BPA transferred from water to the soil only from the soil to the water. There is also a significant loss due to the reaction for both soil and water. As a result the residence times for all the 4 cases are around 6.2 days. Based on all the 4 cases we can conclude that the emission rates and also the media are very important and we need to evaluate the environmental fate and exposure of BPA. In order to do an accurate risk assessment and fate for BPA, the emission rates to the various media compartments have to be very accurately quantified.

If we would compare the results from the Level III EQC modeling to different regulations worldwide we can conclude from our data that BPA is not a persistent chemical. Rodan et al., 1999 says that single media half-life criteria is used to determined if a chemical is persistent in the environment by regulators worldwide. The United Nations Environment Program (UNEP) that was created for the international action on persistent pollutants established a guidelines for half-life above which a pollutant would be considered persistent. The guidelines for the UNEP that was chosen was 2 days, 2 months, 6 months, and 6 months for air, water, soil and sediments, respectively (Cousins et al., 2002). For the same media the Canadian Environment department in 2000 used 2 days, 6 months, 6 months, and 1 year (Gouin et al., 2000). Gouin et al., 2000 also suggested a persistence predicted by a multimedia model for 58 to 83 days for a chemical. In United States if there is no sufficient data available for a chemical pollutant a screening for persistent, bioaccumulative, and toxic (PBT) substances are determined based on their half-life. In US two different agencies published thresholds that were similar to determine if a chemical is persistent in the environment. First policy was the Premanufacture Notices (PMNs) there was submitted under the section 5 of the Toxic Substances Control Act (TSCA). A second rule was

also added under section 313 of the Emergency Planning and Community Right-to-Known Act (EPCRA). For both the TSCA and EPA final rule on the Toxic Release Inventory (TRI) was that a chemical is persistent if the half-life in water, soil, and sediment is above 60 days. Also the EPA considers a chemical very persistent if the half-life was above 180 days. For the bioaccumulation there was similar agreement for both the agencies, for a BCF factor higher than 1000 a chemical was considered bioaccumulative and higher than 5000 very bioaccumulative.

Another important factor when considering the environmental fate of a chemical is the potential for long-range transport (LRT). The LRT is controlled by two main factors: the persistence of the chemical and "stickiness" which is the propensity of chemical to partition to the sediment if is transported in the water or to the land surface if is transported in the air. To calculate LRT the TaPL3 model can be used, which is a modification of the EQC model with no advection present (Beyer et al., 2000). Using the TaPL3 Cousins et al., 2002 found that the traveled distance of BPA in air was 0.51 km and for water 561 km. As a result it can be concluded that in the case of air emission the BPA will stay close to its point source and in the case of a water emission BPA could traveled few hundred kilometers from the point source pollution.

Based on the information and data obtained from the environmental fate of BPA, we can concluded that the reaction process that take place in the environment are very important due to the fact that a large portion of BPA is lost due to different reactions. The study of possible reaction pathways depending on the environmental or design process is very important in understanding the environmental fate of BPA and risk assessment of its byproducts. As a result a detailed review of different process that could degrade BPA should be conducted in order to better understand the estrogenic activity and pathways formation of new BPA byproducts.

5.3 BPA BYPRODUCTS FORMATION UNDER ULTRASOUND

Ultrasonic (US) treatment is able to generates HO• radicals through a process of acoustic cavitation (Torres et al., 2007b) and is considered to be an advance oxidation process (AOP). During the ultrasonic process the bubbles from the cavitation act as microreactors that are growing, pulsating, and then collapsing. During the collapse or pulsation the process occurs very fast adiabatically, as a result there is a hot nucleus that has high pressures in hundreds of atmospheres and temperatures that reach thousands of degrees (Crum, 1995). The process of US is affected by the power, frequency, and dissolved gases present, which would have an effect on the reaction rate and byproduct distribution (Petrier et al., 1994, Nagata et al., 1996, Goel et al., 2004). Torres et al., 2007b performed ultrasound irradiation of a 300 mL with a 118 μ mol/L BPA concentration at 300 kHz. The process worked under the presence of hydrogen peroxide (H₂O₂) and oxygen (O₂), and we can see the first step of BPA degradation under sonochemical process in Figure 5.4.



Oxidation products

Figure 5.4 - Monohydroxylated BPA formation and perhydroxyl generation from BPA reaction with •OH radical in oxygenated medium. (Torres et al., 2007b)

The formation of perhydroxyl radical (•OOH) could lead to more H_2O_2 formation by combination of •OOH (Zhou et al., 2004). From Torres et al., 2007a and Torres et al, 2008a we can see more detailed information about the US process used to degrade BPA and the pathway of byproducts formation from US process. With an increase in the electrical powers from 20W to 80W the degradation of BPA increased as a result in higher H_2O_2 formation and increase in collapsing cavities. We can see the main byproducts formed by US indentified with HPLC/MS electrospray in Table 5.2.

Table 5.2 Main intermediates formed by ultrasound and identified by HPLC/MC electrospray (Torres et al., 2008a).

	Structure	Retention time (min)	ES positive $M+H$	ES negative $M-H$	Molecular weight (<i>M</i>)
А	H ₃ C H ₂ C OH	3.30	151	149	150
В	H ₃ C H ₂ C OH	4.84	135		134
С	Н3С ОН	6.98		135	136
D	$HO \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ OH \end{array} OH HO \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \\ OH \\ OH \end{array} OH$	12.10		259	260
Е	$0 = \underbrace{\begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ OH \end{array}} OH O OH O OH OH OH OH OH OH OH OH OH OH$	12.10	259	257	258
F	HO-CH3 CH3 OH	13.22		243	244
G	$o = \underbrace{-}_{CH_3}^{CH_3} \underbrace{-}_{OH}^{CH_3} o$	13.22	243	241	242
BPA	$HO \longrightarrow CH_3 \longrightarrow OH$	14.76		227	228

From Table 5.2 and Figure 5.5 we can see that the main degradation of BPA was done through HO• radical reactions, with the formation of monohydroxylated BPA, hydroquinone, and 4-isopropenyl phenol after the first HO• radicals reactions with the BPA. After additional hydroxylation of 4-isopropenyl phenol the byproduct were monohydroxylated 4-isopropenyl phenol, and the hydroxylation of monohydroxylated BPA lead to the formation of
dihydroxylated BPA. The oxidation of dihydroxylated BPA and monohydroxylated BPA produced different quinone of both compounds. The oxidation of 4-isopropenyl phenol lead to the formation of 4-hydroxyacetophenone. Subsequent oxidations lead to the formation of some aliphatic, oxalic, acetic and formic acids at the end of the experiment. The remaining byproducts have low volatility and are very hydrophilic. We can also see the change in the BPA byproducts as a function of time in Figure 5.6. As a result these final byproducts compounds would remain in the solution as a result of the HO• radicals short lifetime, which would recombine before reaching them. The removal of these final byproducts would be accomplished by the combination of US process with UV irradiation (Torres et al., 2008a).



Monohydroxylated 4-isopropenylphenol

Figure 5.5 - Main sonochemical degradation pathways of Bisphenol A. 300 kHz, 80W and oxygen saturating gas (Torres et al., 2008a).



Figure 5.6 - Change in BPA by-products during ultrasonic treatment of a solution saturated with oxygen. Frequency: 300 kHz; power: 80W; volume: 300mL; temperature: 20 ± 1^{0} C. Monohydroxylated-4-isopropenylphenol (A), 4-isopropenylphenol(B), 4-hydroxyacetophen-one(C), dihydroxylatedbisphenolA(D), quinone of dihydroxylated bisphenolA (E), monohydroxylated bisphenol A (F) and quinone of monohydroxylated bisphenol A (G). (Torres et al., 2008a).

Mohapatra et al., 2011 performed US, Fenton oxidation (FO), and ferro-sonication (FS) on wastewater sludge (WWS) samples spiked with BPA. Under these processes HO• radicals are formed, which reacts with the BPA molecule. Some of the byproducts that are formed through these processes are 3-hydroxybisphenol A, hydroquinone, and 4-hydroxyacetophenone. We can see a byproduct formation from BPA and the region of attack for the hydroxyl radicals in Figure 5.7 a and b (Mohapatra et al., 2011). From Figure 5.7b we can see that the ultimate byproducts of the BPA under the hydroxyl radical reaction are the formation of carbon dioxide CO_2 and water (H₂O). The continuous reaction with the radicals will be able to induce aromatic cleavage as a result producing lightweight hydrocarbons such as formic, propionic acids, and formaldehyde.



CO₂ and H₂O

Figure 5.7 - BPA degradation during ultrasonic, Fenton's oxidation and ferro sonication pre-treatment of WWS: a) Proposed region of attack (a - the site of intraenol ring cleavange) and b) proposed pathway of degradation based on m/z ratios obtained furing LC-MS/MS analysis (Mohapatra et al., 2011).

Two of the main limitations of the US degradation of BPA using HO• radicals reaction is that are short-lived and is not very effective at very low concentrations. If the organic pollutant would not be around the bubble bulk, than at low concentrations would remain in the solution. As a result different studies tried to produce a salting effect by adding anions that are normally present in natural waters. The hypothesis was that by producing a salting effect, the organic pollutant will be pushed towards the bubble bulk solution interference as a result enhancing the

332

degradation. Based on previous studies some authors found that the addition of anions would have positive effect on degradation (Torress et al., 2007a), while other studies found no significant effect over the US treatment (Cost et al., 1993, Gultekin and Ince, 2008). Based on those studies Petrier et al., (2010) investigated the effect of different anions to the US removal of BPA. At an initial BPA concentration of 300µM, a 300mL solution, pH 8.3, temperature of 21°C, and at a power of 80W showed no significant effect for a addition of bicarbonate ions for a concentration range of 12-500 mg/L. However, at a lower BPA concentration there was an positive effect observed with the addition of bicarbonate ions. Higher concentration of bicarbonate ions produced a better removal of BPA. The removal rate of 0.02μ M/min during the first 2 minutes of US without any anions was obtained, and in the presence of 500 mg/L (6mM) bicarbonate ions the initial degradation rate was found to be 0.05 µM/min. The effect of various anions such as Cl^{-} , SO_4^{2-} , HPO_4^{2-} , HCO_3^{-} was investigated using the following inorganic salts: sodium chloride (NaCl), sodium phosphate (Na₂HPO₄), sodium sulfate (Na₂SO₄), and sodium bicarbonate (NaHCO₃). From Figure 5.8 we can see that the solution with sodium bicarbonate had the best removal of BPA under US.

The improvement of BPA degradation under US in the presence of bicarbonate anions is believe to be due to the formation of carbonate radical $(CO_3^{-\bullet})$ that is a reactive intermediate that has previously found when a advance oxidative process was applied to carbonated water (Mazellier et al., 2002, Mazellier et al., 2007), and had an electron oxidant of 1.78 V at pH 7.0 (Petrier et al., 2010). The pK_a of $CO_3^{-\bullet}$ has found to be under pH 0 as a result there could be no protonation in the pH range of 0-10, as a result the only specie expected to be present would be the $CO_3^{-\bullet}$.



Figure 5.8 - The effect of inorganic ions on the rate of BPA sonochemical degradation. (initial BPA concentration 0.12 μ M; 300 kHz; 300 ml; 80 W; pH 8.3; T = 21 0 C in absence or presence of 6 mM inorganic salts NaCl, Na₂SO₄, Na₂HPO₄, or NaHCO₃). (Petrier et al., 2010).

The best effect was observed at a low BPA concentration of 0.022 µmol and only reacted with the non-ionic form of BPA. The experiments were conducted at pH 8.3, which is lower than the first BPA pK_a of 9.6. Based on the mechanisms that were proposed by Busset et al., 2007 while investigating the reaction of $CO_3^{-\bullet}$ with phenol, Petrier et al., 2010 proposed a primary intermediate formation for the $CO_3^{-\bullet}$ reaction with BPA to be phenoxyl radical. After the formation of phenoxyl radical, due to its unstable nature, it would continue to react with oxygen. The new byproducts that would result from this reaction would be mono-hydroxylated BPA [2-(4-hydroxyphenyl)-2-(30,40-dihydroxyphenyl)propane] and quinone of monohydroxylated BPA, which were identified using HPLC-MS analysis. The pathway proposed by Petrier et al., 2010 for the compete BPA reaction with the $CO_3^{-\bullet}$ can be seen in Figure 5.9



Figure 5.9 - Reaction pathway proposed for the first intermediates formation in the case of the reaction of $CO_3^{-\bullet}$ with BPA. (Petrier et al., 2010)

Chlorination had been used in the last 100 years for disinfection of drinking and waste water. As a result of chlorination, during the process of disinfection, the presence of halomethanes had been reported. Halomethane are compounds that are derived from methane (CH₄) which has one or more hydrogen atoms replaced with other halogenated atoms such as fluorine (F), chlorine (Cl), bromine (Br) and Iodine (I). In the case of chlorination the presence of tetracholoromethane (CCl₄) or also known as carbon tetrachloride is expected. Guo and Feng, 2009 hypothesis that the presence of CCl₄ would help the removal of BPA under US. They based their assumption on the fact that CCl_4 is a hydrogen scavenger that would react with. During the US process the formation of hydrogen atom, which is the hydroxyl atom, would be followed with a reaction of the CCl_4 with the hydrogen atom. This step is very important due to the fact that the hydrogen atom could react back with the hydroxyl atom, which is the key factor in removing BPA using US process. During their study Guo and Feng, 2009 used a BPA concentration of 100 µg/L (0.439 µmol/L) which was lower than most of other US studies. Guo and Feng, 2009 used a mixture of 50mL with a BPA concentration of 100µg/L with CCl_4 concentration of 25µg/L using ultrasonic intensity of 60W/cm² and ultrasonic frequency of 20kHz at pH 6.5 and 25 ⁰C for 2h. We can see the main pathway of BPA degradation using US only in Figure 5.10.



Figure 5.10 - Main degradation pathways of low-concentration BPA during US treatment. (Guo and Feng, 2009)

The main advantage of the CCl₄ addition is not only the reaction with the hydrogen atom,

but also the subsequent chain reactions that follows, which produces different oxidants that

contains chlorine. The oxidants that are produce are HClO and three chlorine containing radicals such as •Cl, •CCl₃, and: CCl2. During the US the production of •Cl radicals is also more favorable due to the fact that the bond energy for the H-OH bond is 119 kcal/mol and for the C-Cl bond is only 73kcal/mol, which can be easier broken. This leads to the formation of big amounts of •Cl radicals and the subsequent formation of the other oxidants presented earlier. It is important to note that the pH of the solutions decreased from 6.5 to 4.6 after 2h of US irradiation due to the formation of HCl and HClO during the degradation, which was found also by Rajan et al., 1998. Just like in the case of Torres et al, 2008a few intermediates were found during the degradation and are presented in Table 5.3.

Compound list	Retention time (min)	Main fragment ions (m/z)	Molecular weight before and molecular weight after silylation	Molecular structure
BPA	35.10	372, 357, 207, 73	228, 372	HO-CH3 CH3 CH3
A	36.85	460, 445, 357, 207, 73	244, 460	HO-C-C-OH
В	11.20	166, 151, 77, 73	94, 166	но
с	19.20	206, 191, 91, 73	134, 206	HO-CCH3 CH2
D	20.02	254, 239, 108, 73	110, 254	но-Он
E	23.50	208, 193, 151, 89, 73	136, 208	HO-CCH3
F	11.62	147, 117, 73	90, 234	О ОН ССНСН ₃ НО
G	17.18	205, 147, 73	92, 308	$\begin{array}{ccc} H_2C &CH &CH_2 \\ 2 & & & \\ OH & OH & OH \end{array}$

 Table 5.3 The Main intermediates during the BPA ultrasonic irradiation alone (Guo and Feng, 2009)

The main pathway presented in Figure 5.10 and the intermediates from Table 5.3 were obtained using the degradation of BPA alone in a 100μ g/L solution under a sonic irradiation of 1

hour. As a result the main reaction was with that of HO• radicals. When the results are compared to those of Torres et al., 2008a, four of the intermediates found in this study were also found previously using US processes which were: monohydroxylated BPA, hydroquinone, 4-isopropenylphenol and 4-hydroxyacetophenone. In addition to those four in the current study glycerol, 2-hydroxypropionic acid, and phenol were also found. We can see from Figure 5.10 the first reaction of BPA with the HO• radicals lead to the formation of monohydroxylated BPA, and the breaking of the C-C bond between the benzene ring and isopropyl produced $\bullet C_6H_5OH$ and $\bullet C(CH_3)_2C_6H_4OH$ radicals. The radicals were then converted to 4-isopropenylphenol led to the generation of hydroquinone and 4-hydroxylated of phenol and 4-isopropenylphenol led to the generation of hydroquinone and 4-hydroxylated between the formation of 2-hydroxypropionic acid and glycerol.



Figure 5.11 - Concentrations of the intermediates during BPA ultrasonic irradiation. BPAconcentration:100 μ g/L; ultrasonicfrequency: 20kHz; ultrasonicintensity:60W/cm2; pH:6.5; temperature:25±0.5 ⁰C. (\circ) Monohydroxylated BPA; (\blacktriangle)phe-nol; (\triangle)4-isopropenylphenol; (\blacksquare)hydroquinone; (\Box)4-hydroxyacetophenone; (\blacklozenge)2-hydroxypropionic acid; (\Diamond) glycerol. (Guo and Feng, 2009)

From Figure 5.11 we can see the remaining intermediates in the solution after the sonic irradiation of 2 hours. From Figure 5.11 we can see that monohydroxylated BPA had the highest concentration of 16.1 μ g/L after 45 minutes of irradiation. And the glycerol and 2-hydroxypropionic acid had the lowest concentration with the peak concentration of 2 μ g/L after 60 minutes of sonic irradiation.

Ultrasonic (US) process could be used to remove BPA effectively with additional process or chemicals. AOP could be used in the combination of US for a better removal. Processes such as Fenton process, photo degradation, and electro chemical process could be used in combination with US to perform a better removal for BPA. All the three processes could also degrade BPA alone and will be discuss later in the chapter. The Fenton process utilizes the addition of hydrogen peroxide H_2O_2 , Fe^{2+} , and Fe^{3+} under UV light to produce HO• radicals. The photocatalysis is a AOP that also uses the UV light to excite an electron, for example from titanium dioxide (TiO₂) and in combination with hydrogen peroxide is able to produce HO• radicals (Torres et al., 2010). In Figure 5.12 we can see the removal of a BPA concentration of 118 µmol/L using different combinations of US, TiO₂ photocatalysis (PC), photo-Fenton and combined US/Fe²⁺/TiO₂ photoassisted processes were done in a saturated oxygen solution with an Fe²⁺ ions concentration of 100µmol/L in a 300mL volume, at a pH 3.0 and temperature of 22^{0} C using an ultrasound frequency of 300 kHz and ultrasound intensity of 80 W/cm². It is important to note that the US used by Torres et al., 2010 is very strong and could be very costly. The total duration of the study was done for 4 hours. From Figure 5.12 we can see that the combination of the US, Fe^{2+} , and TiO₂ photoassisted process had the greatest effect on the BPA removal. During this study the degradation of BPA was also concluded to be done because of the HO• radicals attacks. The removal of BPA using TiO₂ alone showed the least degradation.



Figure 5.12 - BPA (118 μ mol/L) elimination by ultrasound, TiO₂ photocatalysis (PC), photo-Fenton and combined ultrasound/Fe²⁺/TiO₂ photoassisted processes applied to solutions saturated with oxygen. (Torres et al., 2010)

The successive attacks of HO• radicals on the BPA using all the three treatments led to the formation of different aliphatic acids such as acetic, formic, and oxalic acid. The process formation of these acids and subsequent mineralization to carbon dioxide (CO₂) followed two stages. In the first stage the BPA is degraded to monohydroxylated BPA followed by dihydroxylated BPA, than in stage two, to the formation of aliphatic acids such as oxalic, formic, and acetic acid to the complete mineralization to CO₂.

In previous study done by Torres et al., 2008b used a photo-Fenton process for the degradation of a solution with initial BPA concentration of 118 μ mol/L, in a 600mL volume, at neutral pH and temperature of 22^oC was saturated with oxygen and used an ultrasonic frequency of 300kHz and intensity of 89W/cm² with Fe²⁺ ions concentration of 100 μ mol/L and H₂O₂ concentration of 96 μ mol/L. We can see the BPA, total organic carbon (TOC), monohydroxylated BPA, and aliphatic acids production and degradation in Figure 5.13. We can also see the main reactions that leaded to the BPA mineralization in Figure 5.14.



Figure 5.13 - Changes in levels of BPA, total organic carbon (TOC), monohydroxylated BPA, and aliphatic acids during BPA (118 μ mol/L) degradation by photo-Fenton. (Torres et al., 2008b)



Figure 5.14 - Main reactions leading to BPA mineralization by the combined ultrasound/solar light/ Fe(II) system. (Torres et al., 2008b)

Removal of BPA using electrochemical (EC) treatment had showed to be possible by Zhou et al., 2004. The oxidation can be done by a direct oxidation with a carbon-based anodes or metal (Andreescu et al., 2003, Kuramitz et al., 2004), or it can be degraded indirectly using strong oxidants such as ozone (O3) and HO• radicals, that could be indirectly produced using electrochemical produced transformations with the presence of boron doped diamond electrodes or transition metal oxides (Boscoletto et al., 1994; Tanaka et al., 2002; Gozmen et al., 2003; Murugananthan et al., 2008). Different intermediates had been have been found during the electrochemical oxidation including hydroquinone, hydroxylated BPA, phenol, benzoquinone, resorcinol, isopropenylphenol, catechol, and isopropylphenol (Boscoletto et al., 1994, Gozmen et al., 2003). Other aliphatic acids intermediates were found due to the aromatic cleavage were tartaric, maleic, formic, and citric acids (Tanaka et al., 2002, Gozmen et al. 2003).

Cui et al., 2009 performed electrochemical treatment of BPA using four different types of anodes, titanium / boron doped diamond (Ti/BDD), titanium / antimony-tin dioxide (Ti/Sb-SnO₂), titanium/ruthenium (IV) oxide (Ti/RuO₂), and platinum (Pt). Initially for the electrolysis testing a 80 ml of solution with a BPA concentration of 100 mg/L was placed in a cell containing an 0.1M Na₂SO₄ as electrolyte. Two different current intensities of 10 and 50 mA/cm² were investigated. From the initial investigation was found that degradation of BPA using Ti/RuO₂ anode too. The best degradation was found using 10 mA/cm² obtained with Ti/BDD electrode and for the 50mA/cm² was the Ti/Sb-SnO₂ electrode. For the 10mA/cm² the pH was found to decrease initially than was followed by an increase for Ti/BDD, Pt, Ti/Sb-SnO₂ anodes with the exception of Ti/RuO₂ anode, which showed just a slight decrease in pH. We can see the EC reaction byproducts concentrations in Figure 5.15 and reaction pathway in Figure 5.16.



Figure 5.15 - Concentration of the intermediates products of EC degradation of BPA at current density of 10 mA/Cm² on the a) Pt, b) Ti/RuO₂, c)Ti/Sb-SnO₂ and d) Ti/BDD (Cui et al., 2009)



Figure 5.16 - Reaction pathway of electrochemical BPA degradation(Cui et al., 2009)

Gozmen et al., 2003 investigated the effect of indirect electrochemical treatment of BPA using the Fenton process. Previous studies found that the organic compounds that had aromatic rings and had been attacked by hydroxyl radicals were forming cyclohexadienyl radical. Also the cyclohexadienyl radical in the presence of other oxidizing agents such as Cu^{2+} , O_2 and Fe³⁺ was degraded to hydroxylated derivates. Based on these studies Gozmen et al., 2003 expected the BPA degradation in the presence of hydroxyl radical generated by EC treatment in combination with Fenton process to occur according to Figure 5.17.



Figure 5.17 - Expected BPA degradation pathway. (Gozmen et al., 2003)

Gozmen et al., 2003 studied the degradation of BPA under high concentration of 0.7mM (160 mg/L) and used different cuprous, cupric, ferrous, and ferric ions ratios to the BPA concentrations. The ratios were 1.42, 2.86, 4.28, and 7.14 for both ions. When the Cu^{2+} was used at the ratio of $[Cu^{2+}]/[BPA_0] = 4.28$ the meta-monohydroxylated byproduct, which is identified in Figure 5.17 with **II**, was dominant over the ortho-monohydroxylated byproduct (**III**), in the presence of Fe²⁺ ions the opposite was true. The intermediates were found using different instruments such as LC-MS, HPLC, and GC-MS. Some of the intermediates appeared in more than one instrument, while others just in one of them. We can see the intermediates from the EC degradation of BPA in the presence of cuprous/cupric ions and ferrous/ferric ions in Table 5.4

	345
t al.,	2003)

compound	chemical structure	methods
m-monohydroxylated BPA	$HO \longrightarrow CH_3 OH OH$	LC-MS
o-monohydroxylated BPA	но-С-С-С-ОН СН3 ОН	LC-MS
dihydroxylated BPA	HO-CH ₃ OH CH ₃ OH CH ₃ OH OH	LC-MS
phenol	Он	GC-MS
catechol	ОН ОН	HPLC and GC-MS
hydroquinone	но-Он	HPLC and GC-MS
benzoquinone		HPLC and GC-MS
resorcinol	он ОН	HPLC and GC-MS
4-isopropenylphenol	CH_2 CH_2 CH_3 OH	GC-MS
4-hydroxy mandelic acid	но он	GC-MS
4-hydroxy benzoic acid	но сн	GC-MS
butendionic acid	HOOC-CH=CH-COOH	GC-MS
4-oxobutenoic acid	0 HOOC-CH=CH-C-H	GC-MS
acetic acid	СН ₃ СООН	HPLC and GC-MS
formic acid	НСООН	HPLC

 Table 5.4
 Identified BPA Conversion and Degradation Products (Gozmen et al., 2003)

From Table 5.4 we can see the ortho-monohydroxylated and metha-monohydroxylated byproducts as expected from Figure 5.17. The tests were performed in a 200 mL volume solution. It was found that the combination of cuprous/cupric ions pair was able to degrade the BPA and mineralized faster than the ferrous/ferric ions pair. However, the ferrous/ferric ions pair prove to be more efficient method of mineralizing the BPA not consuming so much electricity as the cuprous/cupric ions pair did. As a result, it was found that the use of Cu^{2+} for the mineralization of BPA or similar compounds using Fenton and EC processes would be unfeasible due to the economical and technical reasons. For the Fe²⁺ it was found that at ratios of 3 to 4 it would be sufficient for an efficient mineralization using Fenton and EC processes in a aqueous medium. It is important to note that the concentration of BPA was a lot higher than relevant environmental concentrations, which could pose a significant obstacle for these processes to work using the current parameters presented by Gozmen et al., 2003.

Poerschmann et al., 2010 performed the degradation of BPA was also done at a lower concentration of 10mg/L (44 μ M) in amber glass reactors with volume capacity of 100mL, which were sealed with Teflon lined septa. The reactors were kept at room temperature of around 25^oC and the oxygen concentration was measured to be about 8mg/L. The pH of the solution was acidified to a pH of 3.0. Two different ferrous ions concentrations were used, which were equal to 10 μ M for system I and 20 μ M for system II. The equivalent molar ratios of [Fe²⁺]/[BPA₀] were equal to 0.23 and 0.45 for system I and II, respectively. The acidic conditions were chosen in order for the Fe²⁺ reagent to be regenerated in a cyclic way and the Fe³⁺ formation to be avoided. For the Fenton process to take place the addition of hydrogen peroxide H₂O₂ was added in both systems with concentration of 100 μ M and 200 μ M for system I and II, respectively. The amounts of H₂O₂ were

smaller to the expected H_2O_2 oxidant required for a complete mineralization of BPA if added alone. The molar requirement was 36moles of H_2O_2 for each mole of BPA. The reaction was carried for a period of 60 minutes and at 180 rpm in a orbital shaker, and was than quenched by adding 5 mM of t-butanol, which is known to react readily with the hydroxyl radical having a rate constant of $k = 6 \times 10^8 M^{-1} s^{-1}$. The intermediates were able to be found using GC-MS instrument.

In Table 5.5 we can see the intermediates with molecular size lower than BPA generated using Fenton reaction in system I. Some of the intermediates that were found during photosensitized degradation (Katsumate et al., 2004, Zhan et al., 2006) or by enzyme-catalyzed Fenton oxidation (Huang and Weber, 2005) had been found to be formed by the oxidation of BPA using Fenton process in the presence of ferrous ions and hydrogen peroxide (Poerschmann et al., 2010). The intermediates found in all of the photosensitized and enzyme-catayzed studies that were present during the system I study and their retention times are: phenol (8.78 min), glycerol (12.22 min), 4-isopropenylphenol (13.29 min), catechol (13.60), hydroquinone (13.83 min), 4-hydroxyacetophenone (14.67 min), including threitol/erythritol (15.49), 4-(1-hydroxy-1methylethyl)phenol (15.68 min), 4-isopropylenecatechol (16.01 min), 4-hydroxybenzoic acid (16.56 min), naphthyldiol (20.56 min), hydroxy-1-phenoxy-2-isopropyl-4-phenol (23.38 min), 4,40-dihydroxy methyl stilbene (23.57 min) and 4-isopropyl-1-phenoxy-2-isopropyl-4-phenol (23.94 min). From the above mentioned intermediates the 4-isopropenylphenol and 4hydroxyacetophenone were the most abundant with 3.77% and 4.65 %, respectively. Ring opening byproducts found were lactic acid (9.40), and dicarboxylic acids such as oxalic (10.15 min), succinic (12.67 min), fumaric (13.04 min), and glutaric acid (13.78 min). The lactic acid was found to be the abundant intermediate that had an open ring, with an abundance of 1.55 %.

Retention time (min) ^a	Intermediate "family" (see text)	MW ^b	Tentative structure	Concentration c (%, referred to $c_{0,BPA}$)
7.41		108	0	0.31
8.78		94 (166)	OH	0.46
9.40		90 (234)	СН ₃ —СН—СООН	1.55
			OH	
10.15		90 (234)	НООС—СООН	0.05
12.22		92 (308)	HO—CH ₂ —CH—CH ₂ —OH	0.07
12.67		118 (262)	OH HOOC—(CH ₂) ₂ —COOH	0.05
13.04		116 (260)	HOOC—CH=CH—COOH	0.08
13.29		134 (206)	CH ₃	3.77
			ноС	
13.60 + 13.83		110 (254)	HO	1.4 + 9.7
		()	но + но - Он	
13.78		132 (276)	HOOC—(CH ₂) ₃ —COOH	0.08
14.67		136 (208)	✓ C—CH ₃	4.65
			НОО	
15.19		164 (308)	С—СН ₂ — СН ₂ — ОН	1.12
15.49		122 (410)	HO CH (CHCOLD) CH OH	0.06
15.45		152 (200)	$HO - CH_2 - [CH(OH)]_2 - CH_2 - OH$	0.30
15.68		152 (296)		0.70
			ICH ₃	
16.01		150 (294)	HO CH ₃	0.12
			но-с	
16.56		138 (282)	НО-СООН	0.01
17.24		152 (296)	но-СН2-СООН	0.08
20.56		160 (304)	ноОн	0.11
22.4-22.6	A	228 (372)	CH ₃	49.7
			но-С-С-С-Он	
22.20			CH ₃	5.00
23.38	В	244 (388)	CH ₃	5.32
			но-С-с-о-С-он	
22.57	D	226 (270)	CH ₃	0.22
23.57	D	226 (370)	CH ₃	0.55
			но-	

 Table 5.5
 Identification of Intermediates. (Poerschmann et al., 2010)

Retention time (min)"	Intermediate "family" (see text)	MW ^b	Tentative structure	Concentration c (%, referred to $c_{0,BPA}$)
23.63	A	244 (460)	HO CH ₃	2.94
			но-С-Он	
23 79	A	244 (460)	CH ₃	0.85
23.75	<i>N</i>	244 (400)		0.05
			но-с-с-с-он	
23.94	С	270 (342)	CH ₃ CH ₃	0.07
			но-С-о-Сн	
			CH ₃ CH ₃	
24.43	В	260 (476)	CH ₃	0.06
			но-с-о-он	
24 76	В	260 (476)	OH CH ₃	0.06
21170	5	200 (110)		0.00
			HO-C-O-OH CH ₂ OH	
24 39 + 24 47	C	286 (430)		0.05 ± 0.08
	-			
24.28	562	274 (562)	CH ₂ —OH	0.35
			НО-С-С-ОН	
			СООН	
24.49	D	242 (458)	HQ CH ₃	0.12
			но сн с он	
24.54		276 (402)		0.06
24.34		270 (492)	CH ₃ CH—COOH	0.00
			CH ₃ CH CH—COOH	
24.73		260 (548)	HO CH ₃ OH	0.15
			но с он	
			CH-	
25.22	D	258 (546)	но, СН ₃ ОН	0.11
25.39		286 (502)	CH ₂	0.51
			ĊH ₂	
			С—ОН	
			CH ₃ CH ₃	
25.21 + 25.50	D	302 (518)	OH CH_3 OH CH_3	0.1 + 0.05
25.22 25.39 25.21 + 25.50	D	258 (546) 286 (502) 302 (518)	$HO \qquad CH_3 \qquad OH \qquad CH_2 \qquad OH \qquad CH_2 \qquad OH \qquad CH_2 \qquad OH \qquad CH_3 \qquad CH_3 \qquad OH CH \\ OH CH CH CH CH CH CH CH $	0.11 0.51 0.1 + 0.05

Table 5.5 (continued) (Poerschmann et al., 2010)

Another groups of different intermediates were denoted in Figure 5.5 with A through D. Group A which also included BPA itself with its monohydroxylated (23.63 min and 23.79 min) and dihydroxylated intermediates (24.73 min); group B was composed of 4-hydroxy-1-phenoxy-2-isopropyl-4-phenol (23.38 min) with its monohydroxylated intermediates (24.43 min, 24.76 min); group C had 4-isopropyl-1-phenoxy-2-isopropyl-4-phenol (23.94 min) with monohydroxylated (24.39 min, 24.49 min) and dihydroxylated inermediates (25.21 min,25.50 min); finally group D was composed of 4,40-dihydroxy-methylstilbene (23.57 min) with its monohydroxylated (24.49 min) and dihydroxylated intermediates (25.22 min).

The second group of intermediates that had the molecular size higher than that of BPA are presented in Table 5.6. The total concentration of all the intermediates from Table 5.6 is about 9% of the initial BPA concentration. The intermediates listed in Table 5.6 are a result of Fenton sub-stoichiometric coupling oxidative coupling reactions of the stabilized radicals, which occurs in the substrate of the BPA structure. These intermediates are persistent.

Based on the literature, the electrophilic attack of hydroxide radical ions on the organic substrate happens through hydrogen abstraction or though the addition (hydroxylation) to double bonds, which has a significant electron densities like in the case of aromatic substrates (Duesterberg and Waite, 2007). The addition of the HO• radicals to the BPA resulted in the formation of the hydroxycyclohexadienyl radical as could be seen in bottom of the Figure 5.18. A third possible reaction mechanisms is the electron transfer, which will result in the formation of radical cations (BPA^{*+}). The elimination of hydroxycyclohexadienyl radical from water would lead to the formation of a very reactive and strong oxidizing phenoxy radical (C₆H₅O[•]) that would be stabilized by mesomeric structures 1 through 3 seen in top of Figure 5.18, where we can see that the electron can be located in different positions.

Retention time (min) ^a	MW ^b		Tentative structure
27.75	336 (624)	2-4	CH ₃ CH ₃
			но С ОН
28.24	336 (552)	1–6	HO' CH ₃
28.80	226 (552)	1.5	но сн
20.00	550 (552)	-5	но
28.53	320 (464)	1-2	CH ₃ CH ₃
			но
29.04	362 (578)		сн ₃ но-с-с-он
			CH ₃ CH ₃ CH ₃
29.13 + 29.95	334 (550)		ОН СН3
			HO-CH ₂ -CH ₂ -C-C-OH CH ₃ OH
31.42	350 (566)		но
32.57	454 (742)	3-3	OH CH ₃
			но-С-С-Он
			но-С-С-С-ОН
33.68	470 (830)	Monohydroxylated isomer of the 3–3 or 3–7 combination	но-СН3 СН3 он
			но-с-он
33.85	454 (670)	1–3	
			о-С-С-Он СН3 СН3
34.69	454 (670)	1-6	но с на сна сна он
			о-С-с-он
35.52	470 (758)	1–7	но о сна сна он
			но-с-с-он

Table 5.6 Identification of Intermediates based on oxidative coupling reaction leading to products greater than that of BPA (Poerschmann et al., 2010)



Figure 5.18 - The central role of the hydroxycyclohexadienyl radical of BPA in the degradation pathway of the BPA substrate. "R" denotes the C_6H_5OH moiety. (Poerschmann et al., 2010)

The phenoxyl radical can also be formed by the hydrogen abstraction from the BPA molecule. This phenoxyl radical can also be stabilized by resonance as seen in the structure 4 through 7 in Figure 5.18. The hydroxycyclohexadienyl radical can undergo different reactions; however the most important one is the addition of molecular oxygen and the formation of dioxygen radical. The electron-donating substituent such as alkyl groups to a lesser extent and the hydroxyl can follow the reaction presented in Figure 5.19 and Figure 5.18 for radicals 4 and 7, which are represented in Figure 5.19 through pathways I and II, respectively. We can see from Figure 5.19 that some expecting intermediate for pathway I is 2-(2,4-hydroxyphenyl)-20-(4-hydroxyphenyl)propane and for pathway II is 2-(3,4-hydroxyphenyl)-20-(4-hydroxyphenyl) propane. After the abstraction of the hydrogen atom from the methyl group followed by a reaction with the oxygen or HO• radicals lead to pathway III from Figure 5.19 and the formation of 4-isopropenylphenol (13.29 min) and 2,2-bis(4-hydroxyphenyl)-1-propanol (23.79 min).

From the study presented by Poerschmann et al., 2010 we can conclude that the Fenton oxidation of BPA with even low concentration of oxidant leads to the formation of many intermediates. Some of the intermediates such as the diphenyl ether- and biphenyl types are posing a potential ecotoxicological risk. The intermediates that have high hydroxylation degree are usually more easily biodegradable than BPA (Moeder et al., 2004).

Other AOP processes that use Fenton processes for the degradation of BPA are ozonation, oxidation using zero valent aluminum, and photooxidation. Just like the EC these process produces intermediates that have to be taken into consideration when the degradation of BPA is perform. Ozonation for example had been used in the water treatment plant for removal of different organic pollutants.



Figure 5.19 - Intermediate formation proceeding from resonance-stabilized radicals (see Figure 5.18) along with the assignment of the identified analytes (Poerschmann et al., 2010)

5.5 BPA BYPRODUCTS FORMATION UNDER PHOTOOXIDATION

Photooxidation of BPA had been reported to be able to degrade BPA. The photooxidation process could happen in water or in atmosphere by either direct photolysis or photooxidation. The half-lives of BPA in atmosphere and water as a result of photooxidation are between 0.74 h to 7.4 h and 66 h to 160 h, respectively (Staples et al., 1998). Photooxidation sometimes is couple to other processes such as Fenton for a better efficiency. Fe (III)–oxalate complexes had been used as a catalyst in the photodegradation of BPA (Zhou et al., 2004). When dissolved in water BPA has no adsorption to the light for a wavelength above 365 nm. The hydroxyl radical (HO•) which is able to oxidize BPA as mention above could be formed in the presence of UV light, hydrogen peroxide and Fe²⁺ or Fe³⁺ ions according to the equations 6 to 8 from Chapter 1. Another chemical compound that is used for the photocatalysis in water is titanium dioxide (TiO₂) (Devipriya and Yesodharan, 2005; Malato et al., 2007). The wavelength of the UV light needed for the reaction is lower or equal to 387nm. Oxygen (O₂) and H₂O₂ addition to the aqueous solution also helps the process of degradation according to the equation 10 to 15 from Chapter 1.

Studies had been done and showed the potential photodegradation of BPA using titanium dioxide (TiO₂) (Ohko et al., 2001, Chiang et al. 2004, Rodriguez et al., 2010); platinized TiO₂ (Chiang et al. 2004); nitrogen-doped titanium dioxide/activated carbon (TiO₂/AC) composite (Yap et al., 2010); ultraviolet radiation (UV) and UV/hydrogen peroxide combination (Rosenfeldt and Linden, 2004); using natural humic substances (HS) under solar irradiation and the presence of oxygen, Fe(III) and hydrogen peroxide (Zhan et al., 2006); using simulated lake water containing algae (*Chlorella vulgaris* and *Anabaena cylindrica*), humic acid and ferric ions

(Peng et al., 2006); using different combinations of titanium dioxide, hydrogen peroxide, and Fe^{2+} ions (Torres et al., 2010).

Based on few studies on the degradation of BPA under different AOP some of the main degradation products of BPA were resulted from hydroxylation of the BPA aromatic rings, which leads to the formation of quinones and through further oxidation to aliphatic acids and at the end to carbon dioxide and inorganic ions (Rodriguez et al., 2010). Following this path we can see the main steps during the BPA degradation under the photocatalysis in Figure 5.20 that was presented in the study performed using different combinations of titanium dioxide, hydrogen peroxide, and Fe²⁺ ions (Torres et al., 2010).



Figure 5.20 - Main steps during BPA degradation by photocatalysis (Torres et al., 2010)

One of the most important pathways of degradation for BPA under photolysis would be in an aqueous solution that is similar to the lake water. Because of the environmental pollution of surface waters with BPA, the treatment of BPA in water treatment plants or waste water treatment plants is important. However, the photo degradation of BPA could take place naturally in the environment under the solar light irradiation. Zeng et al., 2006 performed the degradation of BPA at an initial concentration of 2mg/L under simulated lake water. The irradiation was carried out with a 250W metal halide lamp that concentrated the wavelength at 368 and 380 nm, which falls into the UV light irradiation of the solar spectrum of 280-400 nm, that hits the surface of the earth.

Different case scenarios combinations were performed and was found that the best degradation of BPA occurred when the Fe³⁺ ions, humic acid (HA), and *Chlorella vulgaris* (CV) algae when present in the same time. Using a 2 mg/L BPA solution, HA of 4 mg/L, Fe³⁺ of 20 μ mol/L and CV of 5 x 10⁹ cells/L at a pH 6.5 resulting in a 35 % removal after 4 hours. The effect of Fe³⁺ ions at pH 6.5 was seen only in the presence of CV or HA, probably because of the formation of different complexes.

The increase in the CV cells help the degradation in the presence of both the Fe^{3+} ions and HA. Also the increase in the Fe^{3+} ions concentration helped the degradation in the presence of CV and HA. The increase of HA was also attributed to an increase in the degradation. However, the increase in the BPA concentration from 2 to 4, 6, and 8 mg/L lead to a removal decrease in the degradation from 35% for the 2 mg/L to 22%, 15%, and 14%, respectively. We can see the pathway of BPA photodegradation in the presence of CV only in Figure 5.21. The byproducts are expect to be similar to other AOP that used the HO• radicals or other radicals in the oxidation of BPA.



Figure 5.21 - Pathway of BPA photodegradation in the solution containing only algae. (Peng et al., 2006)

Zhan et al., 2006 also investigated the photodegradation of BPA that involved the reactive oxygen in the presence of humic substances. Four different types of humic substances were used such as Fluka humic acid (FLHA), Suwannee river fulvic acid (SRFA), and Nordic lake fulvic and humic acid (NOFA, NOHA). The concentration of BPA used in this study was equal to 44 μ mol/L (10 mg/L) and the humic substances had a concentration of 10 mg/L. With the increase in the BPA concentration from 4.4 μ mol/L to 88 μ mol/L the pseudo first-order rate constant *k* for the BPA degradation changed from 0.0080 min⁻¹ to 0.0056 min⁻¹ for SRFA. The change in the rate constant showed that there was no significant difference in the degradation, with the increase in BPA concentration from 1 to 20 mg/L. This finding was different that that reported by Peng et al., 2006, however in this current study the fluvic acid was investigated and not humic acid. The effect of dissolved oxygen (DO) was also investigated. For the fluvic acid (FA) there was an increase in the degradation of BPA with an decrease in the DO for both SRFA

and NOFA. For the HA the opposite was observer, which showed an decrease in the degradation of BPA with an increase in the DO. For the SRFA there was a 52.9% enhancement in the degradation of BPA in the absence of DO and nitrogen purged solution, while for the NOHA there was a 33.3% increase in the degradation of BPA in the air-aerated solution than that of nitrogen purged.

In the process of photo degradation in the presence of humic substances different reactions took place. We can see the mechanism proposed for the degradation of BPA in the presence of DO and humic substances in Figure 5.21.



Figure 5.22 - The scheme of proposed mechanism of photosensitized degradation of BPA involved oxygen in HS solution (Zhan et al., 2006)

It been found that the natural humic substances (HS) are capable to reach an excited triplet state (3 HS*) through solar light adsorption and as a result through electronic energy, hydrogen or electron atom transfer the degradation of phenols could be induced (Zhan et al., 2006). One of the reasons was that the 3 HS* could be deactivated by transferring the energy to the ground state oxygen in order to form single oxygen (1 O₂). Because of the inhibition of BPA degradation for the system with SRFA and BPA present it was believed that the energy

transferred from the ³SRFA* to BPA took place, leading to the excitation of BPA (BPA*) which followed further degradation. For the NOHA system with the BPA present the BPA helped the degradation. One reason could be that the H-donor molecule such as BPA would give up its hydrogen atom to the ³NOHA* leading to the formation of phenolic radical. The hydrogen atom would have been afterwards transferred to the dioxygen to form superoxide anion $(O_2^{\bullet-})$ or hydroperoxyl radical (HO[•]₂).

The addition of 20 µmol/L Fe (III) ions to the NOFA and BPA solution showed no significant effect on the degradation. For the degradation of BPA in the presence of SRFA the pathway is presented in Figure 5.22. The main byproducts identified in the BPA degradation were 2-Hydroxy-propanoic acid, glycerol, 4-isopropenylphenol, p-hydroquinone, and mono-hydroxylated BPA.



Figure 5.23 - Proposed photodegradation pathway of BPA in SRFA solution under simulated solar irradiation (Zhan et al., 2006)

5.6 BPA BYPRODUCTS FORMATION UNDER BIOLOGICAL DEGRADATION

One of the main pathways for the formation of byproducts from BPA happens in the environment through biodegradation processes. BPA can be biodegraded by aerobic and anaerobic bacteria in the aqueous solutions such as rivers, estuaries or underground water. The degradation of BPA is performed better under aerobic conditions, because the anaerobic bacteria is not cable of biodegrading the BPA as efficient under anoxic conditions. The degradation of BPA in the environment could also be done by enzymes and fungus.

5.6.1 BPA BYPRODUCTS FORMATION UNDER BACTERIAL DEGRADATION

The aqueous medium is the most polluted environmental medium and because of its physical chemical properties the BPA would not transferred to a different medium from a aqueous medium. As a result most of the expected byproducts formation from BPA in the environment is expect to be present in the aqueous medium. Some of those processes happen in a water treatment plant or wastewater treatment plant, because of the processes used to treat the water. Other biodegradation happens in the natural body of waters such as rivers, oceans, estuaries and ground water through the presence of different bacteria that are capable of degrading BPA.

Ike et al., 2000 studied the biodegradation of BPA using bacteria on 3 different activated sludge and 44 river water samples. The three activated sludge samples were denoted as S, L and G, where samples S was obtained from a regular domestic wastewater treatment plant and sample G from a wastewater treatment plant that receives mainly only BPA containing discharge from an epoxy resin manufacturing plant. Finally the sample L was obtained from a laboratory activated sludge that has been presented in Fujita et al., 1994. The river waters samples were obtained from 15 sites of 7 different rivers from Japan. The quality of water samples range from

A to E from most clean to heavily pollute on the environmental water quality standards. One of the typical BPA-degrading bacterium identified was *Pseudomonas* sp. FJ-4, which has also been found and characterized by Ike et al., 1995.

The removal of BPA in the activated sludge sample S, which had been acclimated to BPA, biodegraded BPA in 24 hours without any lag period. The sludge samples L and G, which had been not acclimated to BPA, degraded the BPA under the detection limit with lag period of 35 and 40hours after 48 and 56 hours, respectively. The initial BPA concentration used in the studies were from 40 to 50 mg/L. The required degradation time for a BPA concentration of 50mg/L was at least 24 hours, which is a lot larger than the actual hydraulic residence time in a wastewater treatment plant of 5 hours (Schroeder, 1997).

For the river water out of 44 tested samples 4 showed no degradation, 34 partial degradation, and 6 had complete degradation. It is important to note that out of the 6 river samples which had the least pollution, 3 samples had no degradation and the other 3 partial degradation. On the other hand, from the 13 water samples of the rivers that were heavily polluted 9 samples had partial degradation and 4 samples complete degradation. This is a important factor in understanding the fate of BPA in the environment since most of the surface waters in the US are not heavily polluted or have very high concentrations of BPA. In order to monitor the BPA degradation, the total organic carbon (TOC) was monitored. The experiments for the river water were conducted for a period of 15 days. Out of 44 river samples, 41 samples were able to lower the TOC concentration after a lag period of 2 to 5 days. It took about 14 days to have a complete TOC removal. We can see the possible metabolic pathway for the BPA in Figure 5.23. The BPA degrading bacterium that were identified were from genera *Arthrobacer*, *Pseudomonas*, and *Enterobacteriaceae*.



Figure 5.24 - Possible metabolic pathway of BPA (Ike et al., 2000)

From Figure 5.23 we can see the metabolites that were identified during the BPA degradation. The main byproducts that were accumulated during the biodegradation processes were the p-hydroxyacetophenone (HAP) and p-hydroxybenzoic acid (HBAL). In the beginning of degradation approximately 0.8 moles of HAP and HBAL were formed for each mole of BPA, and at the end both were continued to be degraded via p-hydroxybenzoic acid (HBA). The other compounds presented in Figure 5.23 appeared only in small percentages. The three byproducts that could not be degraded and could accumulated are 2,3-bis(4-hydroxyphenyl)-1, 2-propaneidol and p-hydroxybenacyl alcohol, which can only be degraded if additional bacteria

are present that are capable of degrading such compounds. The toxicity of these byproducts had been investigated and found that they are not higher than that of BPA (Ike et al., 2000). It was also found that HAP might have a weak estrogenicity activity, which was not yet studied nor reported.

The biodegradation of BPA under aerobic conditions had been found by others since 1987. Dorn et al., 1987 found that 15-25 % of the total BPA concentration of around 3.0 mg/L from a chemical plant effluent degraded after 48 hours. After a period of 5 days the BPA was reduced to under 0.1mg/L, which was the detection limit at that time. Two other studies done under aerobic conditions which found some of the similar intermediates as Ike et al., 2000 were done by Lobos et al., 1992 and Spivack et al., 1994. Both studies used a gram negative aerobic bacteria (MV1) that was isolated from sludge coming from a wastewater treatment plant at a plastic manufacturing facility. We can see the production of the major byproducts for a period of 8h in Figure 5.24 from the study done by Lobos et al., 1992.



Figure 5.25 - Bisphenol A degradation and metabolite formation during resting-cell assay with strain MV1 cells grown on bisphenol A. Symbols: •, BPA; \Box , 4-HBA; \circ , 4-HAP; Δ , BHPP; **•**, BHPPD. (Lobos et al., 1992)
From Figure 5.24 we can see that the byproducts HBA and HAP are also found in Ike et al., 2000, but two other major byproducts not present in the previous presented study were 2,2-bis(4-hydroxyphenyl)-1-propanol (BHPP) and 2,3-bis(4-hydroxyphenyl)-1, 2-propaneidol (BHPPD). The biodegradation of BPA by MV1 bacterial strain pathway is presented in Figure 5.25. We can see that there was a major pathway accounted for 85 % of the degradation and a minor one that accounts for the 15 % of the degradation. The byproducts identified from the biodegradation of BPA by MV1 presented in Figure 5.25 are: *I*, 2,2-bis(4-hydroxyphenyl)-1-propanol; *II*, 1,2-bis(4-hydroxyphenyl)-2-propanol ; *III*, 4,4'-dihydroxy- α -methylstilbene; *IV*, 2,2-bis(4-hydroxyphenyl)propanoic acid; *V*, 2,3-bis(4-hydroxyphenyl)-1,2-propanediol; *VI*, 4-hydroxyphenacyl alcohol; *HBAL*, 4-hydroxybenzaldehyde; *HBA*, 4-hydroxybenzoic acid; *HAP*, 4-hydroxyacetophenone.

Suzuki et al., 2004 also investigated the biodegradation of BPA under aerobic conditions using the MV1 bacterium strain and found similar pathway of degradation as previous studies. The pathway presented by Suzuki et al., 2004 is found in Figure 5.26 along with some of its intermediates that were found as 3,cis-4,4'-dihydroxy- α -methylstilbene (DHMS cis) and trans-4,4'-dihydroxy- α -methylstilbene (DHMS trans); 4, 4-hydroxybenzaldehyde (HBAL) ; 5, 4hydroxyacetophenone (HAP); 6, 4-hydroxybenzoic acid (HBA); 7, 2,2-bis(4-hydroxyphenyl)-1propanol (BPA-OH); 8, 2,2-bis(4-hydroxypheny1)propanoic acid (BPA-COOH). The intermediates presented above were found for BPA concentrations of 1 and 10 mg/l. The major byproducts present in the solution after 3days were BPA-OH, BPA-COOH, and HAP. The half lives of BPA were found to be 0.4 and 1.1 d for the initial concentration of 1 and 10 mg/L, respectively. The degradation of both BPA concentrations followed first order kinetics. The detection limit for the BPA-OH and BPA-COOH was 2 μ g/L.



Figure 5.26 - Metabolic pathway for BPA biodegradation by strain MV1 (Spivack et al., 1994)



Figure 5.27 - Metabolic pathway for BPA by bacterium strain MV1 (Suzuki et al., 2004)

BPA-OH and BPA-COOH were also found in one of the sampling river in concentrations from 1-40 ng/L depending on the season and byproduct. The only intermediate that was present all year long at higher concentrations was BPA-COOH. Under the laboratory condition the removal of BPA under detection limit was 6 and 14 days for initial BPA concentration of 1 and 10 mg/L, respectively. For the initial BPA concentration of 10 mg/L the byproducts that remained in the solution even after 14 days were BPA-OH, BPA-COOH, and HAP. For the 1 mg/L solution from all those three intermediates only BPA-COOH remained in the solution after 14 days.

BPA would only transfer very little to different media of the environmental from the water phase as explained earlier in the chapter. A highest percentage of that transfer is to the sediment medium. Once the BPA is transferred to the sediment it could be under aerobic or anaerobic conditions depending on the depth that it traveled. Ying and Kookana, 2003 investigated the degradation of BPA in seawater under aerobic and anaerobic conditions. The degradation of BPA in seawater alone, from a initial concentration of 5 μ g/L, took about 57 days to bring the concentration down to about 0.3 μ g/L, with a lag period of about 37 days and half live of 39 days. The degradation of BPA in the sediment under aerobic conditions from a initial concentration of 1.2 μ g/L took about 25 days, with a half life of 14.5 days. However, under anaerobic conditions there was no observed degradation after a period of 70 days. For the anaerobic degradation the results were in accordance with Voordeckers et al., 2002, which found no loss of BPA in estuaries sediments after a period of 162 days. The study done by Voordeckers et al., 2002 used conditions to promote sulfate-reduction, iron(III)-reducion, methanogenesis, and nitrate-reduction conditions to no avail. As a conclusion the BPA would accumulate in marine sediment under anoxic conditions.

5.6.2 BPA BYPRODUCTS FORMATION UNDER ENZYME DEGRADATION

Enzymes had been used as a biocatalytic elimination of endocrine disrupting compounds (EDCs) such as BPA. Different types of enzymes such as laccase, manganese peroxidase (MnP), lignin peroxidase (LiP), and crude enzymes from different fruits had been investigated for the degradation of BPA.

One of the most studied enzymes for the removal of BPA has been laccase. Laccase has been isolated from fungus such as *Coriolopsis polyzona* (Cabana et al., 2007), family *Chaetomiaceae* (Saito et al., 2004), white rot basidiomycete *Trametes villosa* (Fukuda et al., 2001), and *Phanerochaete chrysosporium* ME-446, and *Trametes versicolor* IFO7043 (Tsutsumi et al., 2001). Other studied look at the degradation of both the laccase and MnP together (Tsutsumi et al., 2001) or the degradation of MnP alone (Hirano et al., 2000). For a mixture of 0.22mM of BPA it took about 12 hours for the complete removal of estrogenic activity of BPA. In the presence of laccase alone the main byproduct found to be 4-isopropenylphenol (Fukuda et al. 2001). The proposed pathway for the BPA degradation by MnP is seen in Figure 5.27. The byproducts obtanined from the enzyme degradation of BPA by MnP seen from Figure 5.27 were pehnol (II), 4-isopropenylphenol (III, IV), and hexestrol (di-TMS) (V).

Xuan et al., 2002 studied the oxidation of BPA using crude enzymes from different fruits and vegetables. The crude enzymes that came from potato (*Solanum tuberosum*) was found to be the most effective one at pH of 8.0 and at a temperature of 37 0 C. From Figure 5.28 we can see the proposed pathway for the oxidation of BPA using crude enzymes from potato along with its byproducts as product A as 4[1-(4-hydroxyphenyl)-1-methylethyl]-benzene-1, 2-diol, and product B as 4[1-(4-hydroxyphenyl)-1-methyl-ethyl]-benzene-1, 3-diol. After a duration of 60 minutes all the initial BPA concentration of 0.6 mM and byproducts had been reduced to zero.



Figure 5.28 - Proposed pathway for BPA degradation by MnP (Hirano et al., 2000)



Polymer

Figure 5.29 -The oxidation of BPA by crude enzyme prepared from potato (Xuan et al., 2002)

5.7 BPA BYPRODUCTS FORMATION UNDER OZONE OXIDATION

Ozone had been used for water treatment plants (WTPs) all over the world as a disinfection process. However, due to its operational cost has not been used so widely. The process works on the production of ozone (O_3) and injecting it in the water. The molecular O_3 than reacts directly with the organic compounds, or with a hydroxyl radicals (HO•), forms from the decomposition of the O_3 in water. Under acidic conditions the direct reaction with the molecular O_3 dominates and in the basic conditions the reaction with the HO• radicals dominate (Irmak et al., 2005).

Previously in the chapter the ozone was presented as in combination with other process such as photooxidation. Ozonation is one of the advance chemical processes (AOP) that had been used to oxidize BPA and other EDCs (Esplugas et al 2007). Few experiments had been done in investigating the oxidation of BPA with O_3 (Deborde et al., 2008, Irmak et al., 2005, Alum et al. 2004). Irmak et al., 2005 found that at an initial BPA concentration of 0.1mmol a time of 80 minutes was necessary to oxidize completely the BPA with an O_3 to BPA mole ratio of 14.94. Alum et al., 2004 observed an increase in estrogenic activity after 5 minutes of ozonation and stabilization afterwards, which was explained as a complete transformation of BPA to byproducts. Seven different byproducts had been identified during the oxidation of BPA through ozonation by Deborde et al., 2008. The proposed pathway for the byproducts formation during the ozonation could be seen in Figure 5.29 for the first five byproducts noted as B1 to B5, and in Figure 5.30 for the byproducts noted as b2 and b3. For a complete removal of BPA from the solution an ozone dose of about 4 to 4.5 times higher than that of the initial BPA concentration of 100 μ M was needed. For a ozone dose higher than 570 μ M was found to be

necessary for the complete removal of the byproducts as well for an initial BPA concentration of $100 \ \mu M$.

As a result it was concluded that further ozonation at a higher dose the new organic chemicals would be oxidize to smaller polar compounds such as acids or aldehydes. The major byproducts formation from the ozonation of BPA would be orthoquinone, catechol and muconic acid derivate, orbenzoquinone and 2-(4-hydroxyphenyl)-propan-2-ol.



Figure 5.30 - Proposed reaction pathways for the formation of products B1-B5 (Deborde et al., 2008)



Figure 5.31 - Proposed reaction pathways for the formation of products b2 and b3 (Deborde et al., 2008)

5.8 BPA BYPRODUCTS FORMATION UNDER CHLORINATION

The most important engineer process that could lead to byproducts formation during the BPA removal is chlorination. Because of lower cost of operation chlorination is the most used process for disinfection for both wastewater and water treatment plants. Chlorination had been used in the last 100 years for disinfection of drinking and waste water. The chlorination of BPA in water leads to the formation of byproducts and chlorinated BPA molecules (Gallard et al. 2004; Gallart et al., 2007; Yamamoto and Yasuhara, 2002; Hu et al., 2002; Fukazawa et al., 2001; Lee et al., 2004; Alum et al., 2004). The same behavior has been observed for the chlorination of phenols (Gallard et al., 2002), which could be a byproduct of BPA.

The major byproducts reported during the chlorination of BPA were monochlorobisphenol A, dichlorobisphenol A, trichlorobisphenol A, and tetrachlorobisphenol A. A proposed pathway for chlorination reaction with BPA is found in Figure 5.31. The position of the chlorine atom is also important, because two different molecules could have the same molecular weight, but their geometry is different depending on the location of the chlorine atom.



Figure 5.32 - Presumed chlorination reaction scheme of BPA. (Yamamoto and Yasuhara, 2002)

Depending on the amount of chlorine used, the BPA could be consumed rapidly or remain in the solution after even 60 minutes of contact time. For a chlorine concentration of 10.24 mg/L using sodium hypochlorite solution at a mole ratio to BPA of 58.7, the BPA was consumed in the first 5 minutes of chlorination. However, if a lower concentration of chlorine was used as 1.03 mg/L with a molar ratio to BPA of 6.56, some fraction of BPA remained in the solution even after 60 minutes of contact time. Depending on the total time of chlorination different byproducts formed immediately during the chlorination and others later on. During in the early stage of chlorination 2-chlorobisphenol A, 2,6-dichlorobisphenol , 2,2'-

dichlorobisphenol A , 2, 2',6-trichlorobisphenol A and 2,2',6,6'-tetrachlorobisphenol A were formed. After further chlorination other byproducts were formed such as 2,4,6-trichlorophenol, 2,6-dichloro-1; 4-benzoquinone, 2,6-dichloro-1; 4-hydroquinone, $C_9H_{10}Cl_2O_2$, $C_9H_8Cl_2O$ and $C_{10}H_{12}Cl_2O_2$ (Yamamoto and Yasuhara, 2002).

The concentration of BPA from 8 to 370 μ g/L was found in the final effluents from 8 paper recycling plants. In the same effluents concentration from 0.2 to 1.4 μ g/L of mono-, di-, tri-, and tetrachlorobisphenol A were also found (Fukazawa et al., 2001). During the chlorination of BPA it was found that the estrogenic activity decreased after 24 hours of chlorination and only the byproduct trichlorophenol (2,4,6-TCP) was persistent after that time. The decrease of estrogenic activity after chlorination of BPA has been also been reported by Alum et al., 2004. The presence of TCP after 24 hours had been also found by Hu et al., 2002. In Figures 5.32 and 5.33 we can see the proposed pathway substitution and the formation of polychlorinated phenoxyphenols, respectively. Hu et al., 2002 also used sodium hypochlorite for the chlorination experiments of BPA and found 13 different byproducts.



Figure 5.33 - Pathways of chloro-substitution reaction between bisphenol A and HOCl. (Hu et al., 2002)



Figure 5.34 - Formation of polychlorinated phenoxyphenols. (Hu et al., 2002)

The concentration of BPA used by Hu et al., 2002 was 500µg/L and a sodium hypochlorite of 1.46mg/L at a pH of 7.5. Both tetrachlorobisphenol A and trichlorophenol increased with increase in the chlorination contact time up to 60 minutes. The presence of tetrachlorobisphenol A in the solution after a chlorination time of 60 minutes was also found by

Gallard et al., 2004 in a solution of initial BPA concentration of 5 μ M and chlorine concentration of 2.7 mg/L in ultra-pure water. The increase in the chlorine concentration from 0.2 to 2.0 mg/L showed to improve the removal of BPA, and there was a decrease in the half live of BPA with an increase in the pH from 5.0 to 9.0. The chlorination of BPA (500nM) in synthetic river water was also carried out in the presence of humic substances. There were two concentrations of natural organic matter (NOM) of 0.5 and 1 mg/L and chlorinated with 0.54 and 1.05 mg Cl₂/L. We can see the formation of byproducts and their slow disappearance in Figure 5.34. We can see that the BPA disappeared in the first 4h of chlorination and that the byproducts formed stayed in the solution for about 10-20 hours at a low chlorine dose of 0.5 to 1 mg/L. As a result to eliminate the presence of these chlorinated byproducts from the drinking water a high chlorine residue is needed.



Figure 5.35 - Chlorination of BPA in synthetic water. Insert in figure 5.35a shows the consumption of chlorine vs. time (Gallard et al., 2004)

5.9 CONCLUSIONS AND DISCUSSION

The objective of this chapter was to evaluate the fate of BPA in the environment and find possible byproducts that would result from the degradation of BPA in the environment through natural or engineer processes. The major pollution of BPA is found to be in the aquatic system and especially in the surface waters. The pollution from landfill leachate infiltration in the underground water is a very possible scenario also. The newly engineer landfills have better designs for the leachate collection pipes and membranes that would prevent major leachate infiltration. However, some of the old landfill designs did not have all the safety features and the total volume of leachate infiltration had been greater. As a result the landfill leachate could pose a serious danger to the pollution of groundwater aquifers. Even though there would be a dilution in the BPA concentration, the landfill leachate has the highest concentrations of BPA reported and the anoxic systems are very limited in the biodegradation of BPA.

The pollution of the aquatic medium was found to be very important in the fate of the BPA in the environment due to its chemical physical properties. If the emission of BPA is done in water medium at steady state conditions about 95 % of the total emission would remain in the water and not transfer to other medium such as soil or air. As a result due to the current pollution with BPA in the environment, it is expect that most of the pollution to be present in water, where it was initially released through different sources. Another important finding that was obtained from the EQC modeling was that the major loss of BPA in the environment happens through different reactions. BPA is not considering as a persistent pollutant, because of its residence time close to about 7 days in most of the environmental medium. The reaction of BPA, which leads to the creation of different organic pollutants, have to be further investigated. The deposition of BPA in the sediment through intermedia exchange could lead to the accumulation of BPA in the anoxic part of the sediment due to very low or no biodegradation of BPA. As a result, BPA

could become persistent in sediments. The increase of yearly production of BPA over the years increased the BPA pollution all over the world even though it has a low residence time.

The wastewater treatment influent is one aqueous medium where BPA had been easily found. The mostly used process for disinfection for both wastewater and water treatment plants is chlorination. Other emerging technologies such as electrochemical oxidation, ultrasonication, photooxidation, biodegradation, ozonation, and Fenton processes had been found to be able or been used in the removal of organic pollutants. All of these processes or a combination of more than 2 together is able to remove BPA from water. However, each of the technology or processes has its advantages and disadvantages. But all of them have one key element in common, they all produce byproducts during the BPA removal from water. In most of the cases these byproducts estrogenic activity is less than that of BPA alone, but in some cases is higher. Depending on the processes or technology a greater contact time with the BPA would result in the removal of the newly formed byproducts also. For example for the removal of the newly formed byproducts during the ozonation treatment of BPA in water an extra dose of ozone is needed for a complete removal of BPA and all of its byproducts. For the removal of BPA using biodegradation there are byproducts that could not be further reduce unless specific degrading bacteria for the newly formed compound would be present. As a result, the cost of removal would increase with the removal of BPA as new byproducts would form.

No matter what processes would be used; some of the byproducts would be the same, such as hydroquinone, benzoquinone, aliphatic acids, 4-isopropenylphenol, carbon dioxide or phenol. Some of the byproducts are very specific to the process that is used, for example the chlorination of BPA in water leads to the formation of chlorinated BPA molecules. During the normal treatment of wastewater or drinking water some of these byproducts could be produced and bypass the treatment. It was also found that BPA would not be removing 100 % during normal treatment operations. As a result the study and evaluation of these byproducts it is important. In this chapter the formation of different byproducts had been address and the identification of many of them made.

One of the pathways for the productions of byproducts from the degradation of BPA is through the bacterial biodegradation or photooxidation of BPA in the environment. As a result further investigation of the fate of those byproducts is important to better understand the fate of BPA in the environment. The fate of the byproducts during the adsorption with the two magnetites and one hematite was also investigated and presented in Chapter 7. The removal of hydroquinone and benzoquinone which are two of the byproducts found during the removal of BPA was investigated and the results presented in Chapter 7. The results helped to understand the fate of these two byproducts during adsorption.

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CHAPTER VI

STATISTICAL ANALYSIS AND MULTIVARIATE LINEAR REGRESSION

6.1 INTRODUCTION

The data from Chapters 2, 3, and 4 had been also analyzed using Statistical Package for Social Sciences 20 (SPSS) in order to better understand the statistical significant of each individual parameter that had been taking into consideration during the adsorption tests. The statistical analysis of the data helped us to better understand the factors that influence most the adsorption of BPA onto iron oxides adsorbents. The statistical parameters and tests that were taken into consideration were the analysis of variance (ANOVA Test), coefficient of determination (R^2) , significant interval or also known as confidence interval (p or CI), Pearson correlation coefficient, and multivariate linear regression (MLR). The MLR had been previously used to model other adsorption experiments such as sodium dodecyl benzene sulfonate (SDBS) onto polyaniline (PANI) (Ozdemir et al., 2011), and adsorption of cationic dyes from aqueous medium using polyurethane foam (PUF) loaded with sodium dodecylsulfate (SDS) as solid phase (Robaina et al., 2009). The modeling of the data using the MLR enabled us to better understand the effect on the adsorption of individual parameters or the interaction of two and three parameters at the time. The MLR model could help us to optimize the adsorption by finding the optimum concentration of different parameters. MLR had also been used to do analysis on the removal of methylene blue from aqueous solution using gulmohar (Delonix regia) plant leaf powder (Ponnusami et al., 2009), study the optimization of Pb(II) biosorption by Robinia tree leaves (Zolgharnein et al., 2008), found optimization for Hg(II) adsorption onto Fraxinus tree leaves (Zolgharnein and Shahmoradi, 2010), to predict trihalomethanes (THMs) formation during the chlorination of water (Golfinopoulos et al., 1998), to model the ground level ozone

(Ozbay et al., 2011), to find the impact of meteorological factors on ozone concentrations (Kovac, et al., 2009), to optimize a spectrophotometric method for copper determination in sugar cane spirits (Caldas et al., 2011).

The MLR used for the regression has the following mathematical expression in equation 1:

$$Y = \beta_0 + \beta_i X_i + \beta_2 X_2 + \dots + \beta_n X_n + \varepsilon$$
(1)

From equation 1, Y is denoted as the dependent (predicted) variable, β_i (i=0,...,n) are the regression coefficients, X_i are the independent variables (predictors), and ε is the stochastic error of regression. For the study of BPA adsorption onto iron oxides adsorbents the MLR analysis can determine the individual and cumulative effect of several independent variables, such as Time of adsorption, total dissolved solids (TDS), initial BPA concentration (C₀), pH, adsorbent type (AdsType), adsorbent dosage (Dosage), soluble iron (Fe), calcium (Ca), sodium bicarbonate (NaHCO₃), and potassium chloride concentration (KCl), on a dependent variable such as the BPA equilibrium concentration (C_e).

There are at least three different ways to enter the independent variables in the MLR model such as standard (simultaneous), hierarchical (sequential), and stepwise (statistical). No matter which method is chosen, a MLR having the same independent and dependent variables would produce the same MLR model. The stepwise backward regression was chosen for the MLR model determination, because is designed to find the most parsimonious model. The backward stepwise regression is able to find the independent variables that are most useful in predicting the dependent variable. The MLR model starts with all the independent variables and is removed from the MLR model one at the time by checking the statistical significance and removing those they are not significant. As a result all the remaining independent variables to the

MLR model would create a model that would have a significant relationship to the dependent variable. A confidence interval (CI) of 95% or a p value of < 0.05 was considered as being meaningful for the regression. As a result any independent variable in the MLR model would have a significance level lower than 0.05 for the student t test.

6.2 STATISTICAL ANALYSIS FOR CHAPTER 2

The data analyzed statistically from Chapter 2 were the 30 days time study for all three iron oxides adsorbents, two magnetites M1, M2, and one hematite H. The kinetic experiments were done for two separate BPA concentrations of 1.2 mg/L and 10 mg/L, with a solid to aqueous solution ratio of 5g:50mL at 16 rotation per minute (rpm) at 25 ^oC for a period of 1, 3, 7, 10, 14, 21, and 30 days. The data were analyzed in three different parts. During the first part the statistical parameters and MLR regression of each different adsorbent were analyzed for the 30 days time study using both initial BPA concentrations of 1.2 and 10 mg/L. In the second part the data were combined for all the three adsorbents together, and in the last part the interaction between the independent variables were taken into consideration for the MLR model.

For the first part of the statistical analysis, the MLR was composed of the dependent variable C_e and independent variables of Time (days), C_0 , pH and TDS.

For the data that used all the combined adsorbents together M1, M2 and H an additional independent variable as adsorbent type (AdsType) was added. However, the AdsType variable was nominal and not scale since it did not had any mathematical value to it. As a result the AdsType variable was only used to better understand if there could be a significant statistical difference between the three iron oxide adsorbents.

For the MLR model that took into consideration the interactions between the individual independent variables the stepwise regression method was used in order to determine the MLR model. The independent variables used to study the interactions for the MLR model analysis were Time (days), C_0 , pH, TDS, AdsType, Time • C_0 , Time • pH, Time • TDS, Time • AdsType, $C_0 • pH$, $C_0 • TDS$, $C_0 • AdsType$, pH • TDS, pH • AdsType, TDS • AdsType, Time • $C_0 • pH$, Time • $C_0 • pH$, Time • $C_0 • pH$, Time • $C_0 • pH • AdsType$, Time

6.3 STATISTICAL ANALYSIS FOR CHAPTER 3

For Chapter 3 the data used for the statistical analysis and MLR model were the isotherm data for 1 day, 7 days, and both time studies together with the 1 and 7 days for hematite H. The isotherm experiments were done with 1g, 2g, and 5g of hematite H to 50 mL of deionized water (DI) at pH 2 at 16 rpm and 25 ^oC. For the 1g:50mL loading, the BPA aqueous concentrations used were 0.4, 0.8, 1, 2, 4, 6, 8, 10, 12, 15, 17, 20, 25, 33, 40, and 50 parts per million (ppm). For the 2g:50mL loading, the BPA aqueous concentrations used were 0.4, 1, 2, 4, 6, 8, 10, 15, 17, 20, 25, 33, 40, and 50 parts per million (ppm). For the 2g:50mL loading, the BPA aqueous concentrations used were 0.4, 1, 2, 4, 6, 8, 10, 15, 17, 20, 25, 33, 40, 45, 50, 60, 70 and 80 ppm. Finally for the 5g:50mL loading, the BPA aqueous concentrations used were 1, 2, 4, 6, 8, 10, 20, 25, 40, 50, 65, 85, 100, 115, 130, 150, 180 and 200ppm. In the second part of the statistical analysis the interactions between the independent variables were analyzed.

For the first part of the statistical analysis for the 1 day and 7 days isotherm data, the MLR was composed of the dependent variable C_e and independent variables of C_0 , Dosage, and soluble iron concentration (Fe). For all the data combined for both 1 and 7 days isotherms results Time (days) was the additional independent variable added. For the interactions between the

independent variables analysis for the MLR model selection the independent variables used were C_0 , Dosage, Fe, $C_0 \bullet$ Dosage, $C_0 \bullet$ Fe, Dosage \bullet Fe, and $C_0 \bullet$ Dosage \bullet Fe.

6.4 STATISTICAL ANALYSIS FOR CHAPTER 4

For Chapter 4 the data used for the statistical analysis and MLR model were the different hematite H adsorbent dosages at a fix BPA concentration and different pHs. For the adsorbent dosage study the dosages used were 1g, 2g, and 5g of hematite H with the pHs of 2, 2.5, 3, 3.5, 4, 5, 7, and 10 and a initial BPA concentration of 1.2mg/L. The adsorbent dosage study was conducted using an 50 mL aqueous solution of DI water at 16 rpm, 25 ⁰C, and for a period of 1 day. The data used to be analyzed for Chapter 4 in the first part of the analysis were all the dosages 1g, 2g, and 5g of hematite H together with and without the analysis of the independent variables interactions.

The second part of statistical analysis was the study of ionic strength on the adsorption of BPA using hematite H. For the study of ionic strength, two different ions of Calcium (Ca²⁺) and potassium (K⁺) had been investigated. The Ca²⁺ ions were studied using CaCl₂ with the ionic strengths of 0.001, 0.005, 0.05, 0.1 and 0.5M. All the ionic strengths were done using three different BPA concentrations of 1.3, 13, and 130 ppm. The adsorbent dosage used was 5g to 50 mL of aqueous solution at 16 rpm, 25 $^{\circ}$ C, and for a period of 1 day. For the CaCl₂ there were three different cases: case I with just the CaCl₂ present, case II with all the ionic strengths mentioned earlier with the addition of 1mM of sodium bicarbonate (NaHCO₃), and finally case III having all CaCl₂ ionic strengths of 0.005, 0.05, 0.1 and 0.5M. All the ionic strengths were done using KCl with the ionic strengths of 0.001, 0.005, 0.05, 0.1 and 0.5M. All the ionic strengths were done using three

different BPA concentrations of 1.3, 13, and 130 ppm. For both the ions studies the statistical analysis was done first on the independent variables alone and with the interactions between those independent variables in the second part.

For the first part of the statistical analysis, the MLR was composed if the dependent variable C_e and independent variables of pH, Dosage, C_0 , TDS, and Fe.

For the interactions between the independent variables analysis for the MLR model selection for the adsorbent dosage study the independent variables used were pH, Dosage, C_0 , TDS, Fe, pH • Dosage, pH • C_0 , pH • TDS, pH • Fe, Dosage • C_0 , Dosage • TDS, Dosage • Fe, $C_0 • TDS$, $C_0 • Fe$, TDS • Fe, pH • Dosage • C_0 , pH • Dosage • TDS, pH • Dosage • Fe, pH • $C_0 •$ TDS, pH • $C_0 • Fe$, pH • TDS • Fe, Dosage • $C_0 • TDS$, Dosage • $C_0 • Fe$, pH • TDS • Fe, Dosage • $C_0 • TDS$, Dosage • $C_0 • Fe$, Dosage • TDS • Fe, and $C_0 • TDS • Fe$.

The next two MLR models used were for the effect of calcium ions and first the effect of all the independent variables were analyzed followed by the MLR model for the effect of the interactions between the independent variables added to the first model. The independent variables used for the effect of calcium ions were the dependent variable C_e and the independent variables such as pH, C_0 , Ca^{2+} ions concentration (Ca), TDS, Fe, and the presence of bicarbonate (NaHCO₃) in the solution. Because only one bicarbonate concentration of 1 mM was used for the experiments, the bicarbonate independent variable was chosen to be only nominal. As a result the statistical significant of the bicarbonate variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate independent variable is just to determine if the presence of bicarbonate in the solution had a significant role in the adsorption or not.

For the MLR model that added the interactions between the independent variables also to the original MLR model, the total independent variables used for the analysis were pH, C_0 , C_a ,

TDS, NaHCO₃, pH • C₀, pH • Ca, pH • TDS, pH • NaHCO₃, C₀ • Ca, C₀ • TDS, C₀ • NaHCO₃, Ca • TDS, Ca • NaHCO₃, TDS • NaHCO₃, pH • C₀ • Ca, pH • C₀ • TDS, pH • C₀ • NaHCO₃, pH • C₀ • TDS, pH • C₀ • NaHCO₃, pH • C₀ • TDS, pH • C₀ • NaHCO₃, pH • TDS • NaHCO₃, C₀ • Ca • TDS, C₀ • Ca • NaHCO₃, C₀ • TDS • NaHCO₃, and Ca • TDS • NaHCO₃.

The independent variables used for the effect of potassium ions were the dependent variable C_e and the independent variables such as pH, C_0 , TDS, K^+ ions concentration (K), and soluble iron (Fe).

For the MLR model that added the interactions between the independent variables also to the original MLR model, the total independent variables used for the analysis were pH, C₀, TDS, K, Fe , pH • C₀, pH • TDS, pH • K, pH • Fe, C₀ • TDS, C₀ • K, C₀ • Fe, TDS • K, TDS • Fe, K • Fe, pH • C₀ • TDS, pH • C₀ • K, pH • C₀ • Fe, pH • TDS • K, pH • TDS • Fe, pH • K • Fe, C₀ • TDS • K, C₀ • TDS • Fe, C₀ • K • Fe, and TDS • K • Fe.

6.5.1 STATISTICAL ANALYSIS FOR CHAPTER 2

6.5.1.1 STATISTICAL ANALYSIS FOR THE 30 DAYS TIME STUDY FOR HEMATITE H

The ANOVA test, Pearson correlations, and MLR model for the 30 days time study using hematite H at two different initial BPA concentrations can been seen in Table 6.0, 6.1, and 6.2 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.2 we can see a positive correlation between C_e with C_0 and pH, and negative correlation with TDS at a 99% CI having coefficients of 0.994, 0.616, and -0.775, respectively. The highest correlation was between the C_e and C_0 was observed as expected, with a higher initial BPA concentration resulting in a higher equilibrium concentration. The strong correlation between the C_e with pH indicates that the adsorption for hematite H is pH sensitive, with an increase in pH resulting in a decrease in the adsorption and increase in C_0 resulting in an increase in the pH. The TDS had only a positive correlation with Time, which indicates that the TDS would increase as the mixing of the samples would cause to have more dissociation from the hematite H. The negative correlation of TDS with the C_e indicates that a salting effect is taking place resulting a increase in adsorption with the increase in the TDS.

The MLR model had two different independent variables of Time and C_0 . We can see the MLR model in equation 2.

$$C_e = 0.124 - 0.019Time + 0.827C_0 \tag{2}$$

The strongest factor in the MLR model was C_0 , and the independent variable Time had a negative correlation. The increase in Time would lead to a decrease the C_e . The MLR model had a good fit with and a regression coefficient of 0.991.

Table 6.0 Analysis of Variance (ANOVA) for Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days

Source	DF	SS	MS	F	р
Regression	2	598.850	299.425	1902.467	0.000
Residual Error.	39	6.138	0.157		
Total	41	604.988			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.1 Pearson correlation between independent variables for Hematite H with 1.2 and10 ppm initial BPA concentration for time study of 30 days

		Ce	Time	C ₀	pН	TDS
Ce	Pearson Cor.	1	-0.029	0.994**	0.616**	-0.775**
	Sig.		0.856	0.000	0.000	0.000
Time	Pearson Cor.		1	0.018	-0.216	0.367*
	Sig.			0.908	0.170	0.017
C ₀	Pearson Cor.			1	0.625**	-0.750**
	Sig.				0.000	0.000
pН	Pearson Cor.				1	-0.458**
	Sig.					0.002
TDS	Pearson Cor.					1
	Sig.					

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Table 6.2	Final Model	Statistical	Information for	Hematite H	I with 1.2	2 and 10 pp	om initial
BPA conc	entration for	time study	v of 30 days				

Madal	Standardized Coefficients		Standardized	4	Sia	D ²	Std. Error of
wodel	β	Std. Error	Beta (β)	l	51g.	ĸ	the Estimate
Constant	0.124	0.125		0.988	0.329	0.991	0.39107
Time (Days)	-0.019	0.006	-0.047	-2.921	0.006		
C ₀	0.827	0.013	0.995	61.658	0.000		

t = Student t-test, Sig. = Significance Interval.

6.5.1.2 STATISTICAL ANALYSIS FOR THE 30 DAYS TIME STUDY FOR MAGNETITE M1

The ANOVA test, Pearson correlations, and MLR model for the 30 days time study using magnetite M1 at two different initial BPA concentrations can been seen in Table 6.3, 6.4, and 6.5 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.4 we can see a positive correlation between C_e with C_0 , and negative correlation with TDS at a 99% CI having coefficients of 0.956, and -0.667, respectively. The pH of the solution did not seem to influence the adsorption of BPA, since there was no correlation found between C_e and pH. There was a strong negative correlation between Time and pH, which indicated a decrease in the pH with an increase in Time. Just like in the case of hematite H, there was a negative correlation between TDS and C_e , C_0 , and pH.

The MLR model had two different independent variables of Time and C_0 . We can see the MLR model in equation 3.

$$C_e = 0.517 - 0.061Time + 0.601C_0 \tag{2}$$

The strongest factor in the MLR model was C_0 and Time with a negative correlation. The increase in Time would lead to a decrease the C_e , however the decrease would not be very significant at current conditions. The MLR model had a good fit with a R^2 of 0.958.

Table 6.3 Analysis of Variance (ANOVA) for Magnetite M1 with 1.2 and 10 ppm initialBPA concentration for time study of 30 days

Source	DF	SS	MS	\mathbf{F}	р
Regression	2	328.561	164.280	425.785	0.000
Residual Error.	39	15.047	0.386		
Total	41	343.608			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Time C_0 TDS Ce pН Ce 0.956** 0.224 Pearson Cor. 1 -0.187 -0.667** Sig. 0.237 0.000 0.153 0.000 Time Pearson Cor. 1 0.018 -0.715** 0.566** 0.908 Sig. 0.000 0.000 Pearson Cor. $\mathbf{C}_{\mathbf{0}}$ 1 0.105 -0.557** 0.506 0.000 Sig. Pearson Cor. pН 1 -0.504** 0.001 Sig. Pearson Cor. TDS 1 Sig.

 Table 6.4 Pearson correlation between independent variables for Magnetite M1 with 1.2

 and 10 ppm initial BPA concentration for time study of 30 days

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

 Table 6.5 Final Model Statistical Information for Magnetite M1 with 1.2 and 10 ppm

 initial BPA concentration for time study of 30 days

Madal	Standardized Coefficients		Standardized Coefficients	4	Sig	\mathbf{P}^2	Std. Error of
widdei	β	Std. Error	Beta (β)	ι	51g.	ĸ	the Estimate
Constant	0.517	0.196		2.634	0.012	0.958	0.62226
Time (Days)	-0.061	0.010	-0.204	-6.095	0.000		
C ₀	0.601	0.021	0.960	28.645	0.000		

t = Student t-test, Sig. = Significance Interval.

6.5.1.3 STATISTICAL ANALYSIS FOR THE 30 DAYS TIME STUDY FOR MAGNETITE M2

The ANOVA test, Pearson correlations, and MLR model for the 30 days time study using magnetite M2 at two different initial BPA concentrations can been seen in Table 6.6, 6.7, and 6.8 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.7 we can see a positive correlation between C_e with C_0 and pH, and negative correlation with TDS at a 99% CI, having coefficients of 0.996, 0.670, and -0.426, respectively. The highest correlation was between the C_e and C_0 as expected, with a

higher initial BPA concentration leading to a higher equilibrium concentration. The strong correlation between the C_e with pH indicates that the adsorption for magnetite M2 is pH sensitive, with an increase in pH resulting in a decrease in the adsorption and increase in C_0 resulting in an increase in the pH. The TDS did not show significant correlation with Time, which meant that the only dissociation of Fe ions would happened in the first 24 hours and remained constant. The TDS had a negative correlation with the C_e indicating that a salting effect was taking place, like in the case with the other two iron oxides.

The MLR model had the same two independent variables as the other two iron oxides of Time and C_0 . We can see the MLR model in equation 3.

$$C_e = 0.166 - 0.021Time + 0.925C_0 \tag{3}$$

The strongest factor in the MLR model was C_0 and the independent variable Time had a negative correlation. The increase in Time would lead to a decrease the C_e . The MLR model had a good fit with a regression coefficient of 0.995. For all the three iron oxides we can see that the MLR model is almost identical having the same independent variables. As a result the data was also analyzed using all the three different iron oxides adsorbents together. The results are presented in the next section of the results.

Table 6.6 Analysis of Variance (ANOVA)for Magnetite M2 with 1.2 and 10 ppm initialBPA concentration for time study of 30 days

Source	DF	SS	MS	F	р
Regression	2	749.175	374.587	3748.257	0.000
Residual Error.	39	3.898	0.100		
Total	41	753.072			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.7 Pearson correlation between independent variables for Magnetite M2 with 1.2and 10 ppm initial BPA concentration for time study of 30 days

		Ce	Time	C ₀	pН	TDS
Ce	Pearson Cor.	1	-0.028	0.996**	0.670**	-0.426**
	Sig.		0.860	0.000	0.000	0.005
Time	Pearson Cor.		1	0.018	-0.146	0.099
	Sig.			0.908	0.357	0.531
C ₀	Pearson Cor.			1	0.651**	-0.426**
	Sig.				0.000	0.005
pН	Pearson Cor.				1	-0.212
	Sig.					0.177
TDS	Pearson Cor.					1
	Sig.					

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

 Table 6.8 Final Model Statistical Information for Magnetite M2 with 1.2 and 10 ppm

 initial BPA concentration for time study of 30 days

Madal	Standardized Coefficients		Standardized	4	Sig	\mathbf{P}^2	Std. Error of
widdel	β	Std. Error	Beta (β)	ι	51g.	ĸ	the Estimate
Constant	0.166	0.100		1.661	0.105	0.995	0.31302
Time (Days)	-0.021	0.005	-0.046	-4.025	0.000		
C ₀	0.925	0.011	0.997	86.548	0.000		

t = Student t-test, Sig. = Significance Interval.

6.5.1.4 STATISTICAL ANALYSIS FOR THE 30 DAYS TIME STUDY FOR HEMATITE H AND MAGNETITE M1, M2

The ANOVA test, Pearson correlations, and MLR model for the 30 days time study using all the three different iron oxides adsorbents magnetite M1, M2 and hematite H at two different initial BPA concentrations of 1.2 and 10 mg/L can been seen in Table 6.9, 6.10, and 6.11 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000 and that the degrees of freedom increased from 2 to 4. From Table 6.10 we can see a positive correlation between C_e with C_0 and pH at a 99% CI, and negative correlation
with TDS at a 95% CI. The correlation coefficients were 0.948, 0.271, and -0.208 for C_0 , pH, and TDS, respectively. For both the pH and TDS the correlation was weak. The strongest correlation was between the C_e and C_0 as expected, with a higher initial BPA concentration leading to a higher equilibrium concentration. There was also a strong negative correlation between pH and TDS. The decrease in pH would lead to a higher TDS in the solution. Adsorbent type (AdsType) was an additional parameter added to the statistical analysis and had a weak negative correlation with the TDS. This was due to the fact that the iron oxides presence in the solution increased the TDS differently. As we seen from the results before, magnetite M2 for example, had the same TDS for the entire 30 days of the study and had no significant correlation with Time. The weak correlation between the C_e with pH indicates that the adsorption is pH sensitive, with an increase in pH resulting in a decrease in the adsorption. The correlation is only weak because the effect of pH was not observed for all the three different iron oxides adsorbents.

The MLR model had the same four independent variables of Time, C_0 , pH, and TDS. We can see the MLR model in equation 4.

$$C_{e} = -8.215 - 0.028Time + 0.772C_{0} + 1.035pH + 0.003TDS$$
(4)

The strongest factor in the MLR model was C_0 followed by pH, TDS and Time. Time was the only independent variable that had a negative correlation with C_e . The increase in Time would lead to a decrease the C_e . The increase in the pH leads to a decrease in the adsorption. The MLR model had a good fit with and a regression coefficient of 0.959. The linear relationship between the predicted C_e values versus the experimental C_e values can be seen in Figure 6.0. The linear relationship between the predicted and experimental values has a good fit with a coefficient of regression of 0.969.

Source	DF	SS	MS	F	р
Regression	4	1,718.50	429.63	711.53	0.000
Residual Error.	121	73.06	0.604		
Total	125	1,791.56			

 Table 6.9 Analysis of Variance (ANOVA) for Magnetite M1, M2 and Hematite H with 1.2

 and 10 ppm initial BPA concentration for time study of 30 days

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.10Pearson correlation between independent variables for Magnetite M1, M2 andHematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days

		Ce	Time	C ₀	pН	TDS	AdsType
C	Pearson Cor.	1	067	.948**	.271**	208 [*]	063
Ce	Sig.		.453	.000	.002	.019	.482
Time	Pearson Cor.		1	.018	046	.019	.000
TIME	Sig.			.839	.612	.831	1.000
C	Pearson Cor.			1	.049	025	.000
C_0	Sig.				.586	.782	1.000
nЦ	Pearson Cor.				1	930 ***	044
hu						.000	.629
TDS	Pearson Cor.					1	313 **
105	Sig.						.000
A.JTT	Pearson Cor.						1
Aasiype	Sig.						

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Model	Standardized <u>Coefficients Beta (β)</u> β Std. <u>Error.</u>		Standardized - Coefficients Beta (β)	t	Sig.	R ²	Std. Error of the Estimate
Constant	-8.215	1.328		-6.187	.000	0.959	0.77705
Time	028	.007	070	-3.822	.000		
C ₀	.772	.015	.935	50.776	.000		
рН	1.035	.136	.382	7.604	.000		
TDS	.003	.001	.171	3.417	.001		

Table 6.11 Final Model Statistical Information for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days

t = Student t-test, Sig. = Significance Interval,



Figure 6.1 - Predicted and experimental equilibrium BPA concentrations (C_e) for magnetite M1,M2 and hematite H for the 30 days time study

6.5.1.5 STATISTICAL ANALYSIS FOR THE 30 DAYS TIME STUDY FOR HEMATITE H AND MAGNETITE M1, M2 WITH INDEPENDENT VARIABLE INTERACTIONS

The ANOVA test, MLR model, and Pearson correlations for the 30 days time study using all the three different iron oxides adsorbents magnetite M1, M2 and hematite H at two different initial BPA concentrations of 1.2 and 10 mg/L with the independent variables interactions can been seen in Table 6.12, 6.13, and 6.14 respectively. Based on the ANOVA analysis the regression model showed to be significant with p value of 0.000. From Table 6.14 we can see the positive and negative correlations between all the independent variables and the dependent variable. The MLR model had 6 different coefficients and all had significant statistical

correlation with the dependent variable Ce. The strongest correlation it was found to be with the independent variable composed of the interaction between C₀ and pH (C₀ x pH). The weakest correlation between Ce was with the interactions of Time, Co, and TDS (Time x Co x TDS). However, the depended variable Ce had weak to strong correlation with other independent variables that were not added to the MLR model. The independent variables were added to the model such that the total regression coefficient R^2 would increase and the standard error would be the lowest. As a result the independent variable C_0 for example was present in the MLR model when the interactions between the independent variable were not taking into consideration. The independent variable C₀ had the strongest correlation coefficient with C_e with the coefficient 0.948 at a 99% CI. We can see all the individual correlations between the variables in Table 6.14. Due to the large number of different variables only the variables present in the MLR model will only be discussed. The correlation coefficients were all at a significant level at 99% CI and had values of 0.522, 0.986, 0.332, 0.435, 0.761, and 0.535 for Time • C₀, C₀ • pH, Time • C_0 • TDS, Time • C_0 • AdsType, C_0 • pH • AdsType, and C_0 • TDS • AdsType, respectively. The interactions between the C₀ and pH were the strongest coefficient from the MLR model and had a positive correlation with Ce. Ce had also a positive correlation with Time • Co, Co • TDS • AdsType and negative correlation with Time • C_0 • TDS, Time • C_0 • AdsType, and C_0 • pH • AdsType. The presence of interactions could mean that the independent variables may affect the response interactively and not in an independent way, for example the combined effect is greater or less than that expected for the straight addition of the effects (Zolgharnein et al., 2008, Zolgharnein et al., 2010). A positive interaction in the case of Time and C₀ for example indicates that increasing the initial concentration

 C_0 would have a less pronounced effect when the Time of the study would be high. As a result we can conclude that for a long period of time the initial concentration would not have a great effect on the adsorption. The same effect was observed between C_0 and pH, as a result at a high pH

the initial concentration would not have a pronounced effect on the adsorption. This is expected since at high pH the adsorption is not as strong.

The MLR model had the independent variables of Time • C_0 , C_0 • pH, Time • C_0 • TDS, Time • C_0 • AdsType, C_0 • pH • AdsType, and C_0 • TDS • AdsType. We can see the MLR model in equation 5.

$$C_{e} = -0.132 + 0.004 \text{Time} \cdot C_{0} + 0.122C_{0} \cdot pH - 0.000013 \text{ Time} \cdot C_{0} \cdot TDS - 0.001 \text{ Time} \cdot C_{0} \cdot AdsType - 0.007 C_{0} \cdot pH \cdot AdsType - 0.00011 C_{0} \cdot TDS \cdot AdsType$$
(5)

The strongest factor in the MLR model was $C_0 \cdot pH$. The MLR model had a good fit with an a regression coefficient of 0.959. The MLR model was based on 126 different experimental points. Only about 4.1% of the total variance could not be explained by the model. The linear relationship between the predicted C_e values versus the experimental C_e values can been seen in Figure 6.1. The linear relationship between the predicted nd experimental values of C_e had a good fit with a coefficient of regression of 0.993.

Table 6.12 Analysis of Variance (ANOVA) for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions

Source	DF	SS	MS	F	р
Regression	6	1,778.91	296.48	2,787.51	0.000
Residual Error.	119	12.66	0.106		
Total	125	1,791.56			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.13 Final Model Statistical Information for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions

	Standa Coeffi	rdized cients	Standardized		G •	D ²	Std. Error
Model	β	Std. Error	Beta (β)	t	Sig.	K-	of the Estimate
Constant	132	.047		-2.831	.005	0.992	0.33989
Time • C ₀	.004	.002	.102	2.520	.013		
C ₀ • pH	.122	.002	1.082	51.577	.000		
Time • C ₀ • TDS	-1.3E-5	.000	198	-7.456	.000		
Time • C ₀ • AdsType	001	.001	076	-2.618	.010		
C ₀ • pH • AdsType	007	.001	158	-7.127	.000		
C ₀ • TDS • AdsType	-1.1E-4	.000	.170	11.191	.000		

t = Student t-test, Sig. = Significance Interval



Predicted C_e values (mg/L)

Figure 6.2 - Predicted and experimental equilibrium BPA concentrations (Ce) for magnetite M1,M2 and hematite H for the 30 days time study with independent variables interactions

								Time	Time	Time	Time	C ₀	C ₀	C ₀
		Ce	Time	C ₀	pН	TDS	AdsType	•	•	•	•	•	•	•
								C ₀	pН	TDS	AdsType	pН	TDS	AdsType
C	Pear. Cor.	1	067	.948**	.27 1 ^{**}	208*	063	.522**	.016	170	083	.986**	.621**	.749**
Ce	Sig.		.453	.000	.002	.019	.482	.000	.858	.058	.353	.000	.000	.000
Time	Pear. Cor.		1	.018	046	.019	.000	.613**	.945**	.796**	.833**	.009	.025	.015
Time	Sig.			.839	.612	.831	1.000	.000	.000	.000	.000	.923	.784	.865
C	Pear. Cor.			1	.049	025	.000	.641**	.032	.003	.015	.950**	.800**	.836**
C_0	Sig.				.586	.782	1.000	.000	.720	.971	.865	.000	.000	.000
TT	Pear. Cor.				1	930**	044	.009	$.220^{*}$	491 **	058	.294**	406**	.021
рп	Sig.					.000	.629	.923	.013	.000	.520	.001	.000	.815
TDC	Pear. Cor.					1	313**	003	224*	.496**	120	248**	.445**	156
105	Sig.						.000	.974	.012	.000	.181	.005	.000	.082
	Pear. Cor.						1	.000	011	146	.437**	011	149	.430**
AdsType	Sig.							1.000	.900	.103	.000	.902	.095	.000
Time •	Pear. Cor.							1	.595**	.477**	.510**	.601**	.523**	.536**
C ₀	Sig.								.000	.000	.000	.000	.000	.000
Time •	Pear. Cor.								1	.566**	.779**	.087	082	.023
pН	Sig.									.000	.000	.330	.363	.798
Time •	Pear. Cor.									1	.561**	115	.238**	060
TDS	Sig.										.000	.201	.007	.505
Time •	Pear. Cor.										1	.003	044	.203 *
AdsType	Sig.											.970	.622	.023
C ₀ •	Pear. Cor.											1	.586**	.786**
pH	Sig.												.000	.000
C ₀ •	Pear. Cor.												1	.564**
TDS	Sig.													.000
C ₀ •	Pear. Cor.													1
AdsType	Sig.													

Table 6.14 Pearson correlation between independent variables for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

		pH • TDS	pH • AdsTy pe	TDS • AdsType	Time • C₀• pH	Time • C ₀ • TDS	Time • C₀• AdsType	Time • pH • TDS	Time • pH • AdsType	Time • TDS • AdsType	C ₀ • pH • TDS	C ₀ • pH • AdsType	C ₀ • TDS • AdsType	pH • TDS • AdsType
Ce	Pear. Cor.	111	.049	246**	.571**	.332**	.435**	104	016	195*	.820**	.761**	.535**	220*
	Sig.	.215	.588	.005	.000	.000	.000	.247	.860	.029	.000	.000	.000	.013
Time	Pear. Cor.	022	019	.018	.589**	.530**	.544**	.918**	.770***	.754**	.013	.008	.025	019
	Sig.	.803	.833	.838	.000	.000	.000	.000	.000	.000	.881	.928	.778	.836
C ₀	Pear. Cor.	009	.019	023	.622**	.547**	.570**	.018	.027	.003	.917**	.778 ^{**}	.758**	013
	Sig.	.919	.830	.795	.000	.000	.000	.844	.762	.971	.000	.000	.000	.889
pН	Pear. Cor.	666**	.360**	968 **	.172	296**	003	255**	.157	548**	163	.218*	469**	840**
	Sig.	.000	.000	.000	.054	.001	.977	.004	.080	.000	.068	.014	.000	.000
TDS	Pear. Cor.	.892**	665**	.830**	151	.311**	090	.300**	327**	.450**	.251**	345**	.401**	.616**
	Sig.	.000	.000	.000	.091	.000	.319	.001	.000	.000	.005	.000	.000	.000
AdsType	Pear. Cor.	695**	.916**	.270**	006	096	.282**	223*	.459**	.139	222*	.449**	.138	.550**
	Sig.	.000	.000	.002	.951	.287	.001	.012	.000	.121	.013	.000	.125	.000
Time • C ₀	Pear. Cor.	012	.004	001	.966***	.860**	.888***	.566	.486	.453	.586	.494***	.498***	008
	Sig.	.894	.961	.988	.000	.000	.000	.000	.000	.000	.000	.000	.000	.928
Time •	Pear. Cor.	186	.077	235	.638	.391	.524	.782	.806	.503	027	.068	096	227
рН	Sig.	.037	.389	.008	.000	.000	.000	.000	.000	.000	.762	.449	.283	.010
Time •	Pear. Cor.	.393**	333**	.416**	.346**	.653**	.359**	.942**	.354**	.932**	.129	159	.218*	.268**
TDS	Sig.	.000	.000	.000	.000	.000	.000	.000	.000	.000	.149	.075	.014	.002
Time •	Pear. Cor.	321**	.383**	.135	.487**	.375**	.652**	.608**	.962**	.725**	084	.206*	.083	.226*
Austype	Sig.	.000	.000	.133	.000	.000	.000	.000	.000	.000	.348	.021	.354	.011
С ₀ • рН	Pear. Cor.	167	.107	256**	.648**	.392**	.530**	044	.068	128	.790**	.810 **	.522**	215*
	Sig.	.061	.232	.004	.000	.000	.000	.625	.452	.154	.000	.000	.000	.016
$C_0 \bullet TDS$	Pear. Cor.	.407**	303**	.367**	.391**	.692**	.396**	.157	135	$.216^{*}$.946**	.370**	.931**	.273**
	Sig.	.000	.001	.000	.000	.000	.000	.078	.131	.015	.000	.000	.000	.002
C ₀ •	Pear. Cor.	311	.414	.095	.516	.389	.677	081	.225	.063	.611	.966	.730	.224
AdsType	Sig.	.000	.000	.292	.000	.000	.000	.365	.011	.485	.000	.000	.000	.012

Table 6.14 cont. Pearson correlation between independent variables for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions

		pН	pН	TDS	Time	Time	Time	Time	Time	Time	C ₀	C ₀	C ₀	pH
		•	•	•	• C ₀ •	• C ₀ •	• C ₀ •	• pH •	• pH •	• TDS •	• pH •	• pH •	• TDS •	• TDS
		TDS	AdsType	AdsType	pН	TDS	AdsType	TDS	AdsType	AdsType	TDS	AdsType	AdsType	• AdsType
pH • TDS	Pear. Cor.	1	916**	.496**	114	.258**	204*	.288**	474**	$.227^{*}$.302**	459**	.238**	.217*
	Sig.		.000	.000	.203	.003	.022	.001	.000	.010	.001	.000	.007	.015
pH • AdsType	Pear. Cor.		1	136	.065	208*	.265**	310**	.490**	091	275**	.511**	058	.177*
	Sig.			.128	.471	.019	.003	.000	.000	.311	.002	.000	.516	.047
TDS • AdsType	Pear. Cor.			1	155	.260**	.075	.172	062	.536**	.127	087	.488**	.947**
	Sig.			l	.084	.003	.401	.055	.493	.000	.155	.334	.000	.000
Time • C ₀ • pH	Pear. Cor.				1	.707**	.855**	.491**	.516**	.308**	.515**	.528**	.351**	136
	Sig.			l		.000	.000	.000	.000	.000	.000	.000	.000	.128
Time • C ₀ • TDS	Pear. Cor.					1	.693**	.631**	.248**	.610**	.639**	.251**	.647**	.178*
	Sig.	l !	1	l			.000	.000	.005	.000	.000	.005	.000	.046
Time	Pear. Cor.						1	.403**	.643**	.465**	.420**	.649**	.508**	.151
• C ₀ • AdsType	Sig.	l '	1					.000	.000	.000	.000	.000	.000	.091
Time	Pear. Cor.							1	.471**	.817**	.110	137	.104	.040
• pH • TDS	Sig.	l '	1						.000	.000	.219	.126	.246	.657
Time	Pear. Cor.								1	.516**	124	.271**	010	.075
• pH • AdsType	Sig.									.000	.166	.002	.912	.402
Time	Pear. Cor.									1	.078	040	.280**	.463**
• TDS • AdsType	Sig.										.388	.660	.002	.000
C ₄ • pH • TDS	Pear. Cor.										1	.482**	.820**	.048
-0 1	Sig.	'								<u> </u>		.000	.000	.594
C ₀	Pear. Cor.											1	.532**	.075
• pH • AdsType	Sig.	1 I							l l				.000	.403
C ₀	Pear. Cor.												1	.468**
• TDS • AdsType	Sig.													.000
pH	Pear. Cor.													1
• TDS • AdsType	Sig.													

Table 6.14 cont. Pearson correlation between independent variables for Magnetite M1, M2 and Hematite H with 1.2 and 10 ppm initial BPA concentration for time study of 30 days with the independent variables interactions

6.5.2.1 STATISTICAL ANALYSIS FOR THE 1 DAY ISOTHERM STUDY FOR HEMATITE H

The ANOVA test, Pearson correlations, and MLR model for the 1 day isotherm time study using hematite H at pH 2.0 with three different adsorbents dosages of 1g, 2g,and 5g at different initial BPA concentrations can been seen in Table 6.15, 6.16, and 6.17 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.16 we can see a positive correlation between Ce with Co, Dosage, and Fe at a 99% CI having coefficients of 0.987, 0.372, and 0.485, respectively. Ce had only a strong correlation with C₀ and mild correlation with Dosage and Fe. The highest correlation was between the C_e and C₀, which was observed as expected, with a higher initial BPA concentration to have a higher equilibrium concentration. The positive mild correlation between Ce with Dosage and Fe was not expected. This could be due to the fact that when the Dosage was increased the C₀ was also increased; as a result the C_e was also higher. This is also confirmed by positive correlation of C_0 with Dosage. When the dosage was increased the C_0 was also increased, as a result there was a moderate correlation between C₀ and Dosage. However, for the MLR model the correlation was negative with both Dosage and Fe as expected. For the Fe the positive correlation with the Ce is related to the increase of the hematite H dosage.

The MLR model had three different independent variables of C_0 , Dosage, and Fe. We can see the MLR model in equation 6.

$$C_e = 8.657 + 0.783C_0 - 2.098Dosage - 3.156Fe$$
(6)

The predominant and strongest factor in the MLR model was C_0 and had a positive correlation with C_e . As expected the increased in the C_0 would result in a higher C_e . There was a negative correlation between the C_e with Dosage and Fe in the MLR model. However, when compared to the C_0 the impact on the regression is not that strong. The MLR model had a good fit with and a regression coefficient of 0.986. From the MLR model we can see that only 1.4% of total variance could not been explained.

Table 6.15 Analysis of Variance (ANOVA) for Hematite H for 1 day isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

Source	DF	SS	MS	F	р
Regression	3	65,775	21,924.95	1,125.88	0.000
Residual Error.	47	915.259	19.474		
Total	50	66,690.13			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.16 Pearson correlation between independent variables for Hematite H for 1 day isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

		Ce	C ₀	Dosage	Fe
Ce	Pearson Cor.	1	0.987**	0.372**	0.485**
	Sig.		0.000	0.007	0.000
C ₀	Pearson Cor.		1	0.468**	-0.425**
	Sig.			0.001	0.002
Dosage	Pearson Cor.			1	0.040
	Sig.				0.781
Fe	Pearson Cor.				1
	Sig.				

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Table 6.17 Final Model Statistical Information for Hematite H for 1 day isotherm studyusing 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

Model	Standardized Coefficients		Standardized Coefficients	t	Sig.	\mathbf{R}^2	Std. Error of the	
	β	Std. Error	Beta (ß)		8		Estimate	
Constant	8.657	3.083		2.808	0.007	0.986	4.41289	
C ₀	0.783	0.017	1.012	45.247	0.000			
Dosage	-2.098	0.428	-0.099	-4.906	0.000			
Fe	-3.156	1.226	-0.051	-2.574	0.013			

t = Student t-test, Sig. = Significance Interval.

6.5.2.2 STATISTICAL ANALYSIS FOR THE 7 DAYS ISOTHERM STUDY FOR HEMATITE H

The ANOVA test, Pearson correlations, and MLR model for the 7 days isotherm time study using hematite H at pH 2.0 with three different adsorbents dosages of 1g, 2g,and 5g at different initial BPA concentrations can been seen in Table 6.18, 6.19, and 6.20 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.19 we can see a positive correlation between C_e with C_0 , Dosage, and Fe at a 99% CI, having coefficients of 0.995, 0.431, and 0.753, respectively. Ce had a strong correlation with C₀. Fe and mild one with Dosage. The highest correlation was between the C_e and C₀ was observed as expected with a higher initial BPA concentration resulting in a higher equilibrium concentration. The same relationship between the Ce with Dosage and Fe as in the case for 1 day was found and was discussed earlier. The only new correlation found for 7 days study was the negative correlation between the Dosage and Fe. This could be explained by the fact that increasing the adsorbent dosage some of the soluble iron would precipitated or get adsorbed back onto the adsorbent. However, for the MLR model the correlation was negative for Dosage as expected. The MLR model had three different independent variables of C₀, Dosage, and Fe. We can see the MLR model in equation 7.

$$C_e = -18.613 + 0.891C_0 - 1.100Dosage + 3.591Fe$$
(7)

The predominant and strongest factor in the MLR model was C_0 and had a positive correlation. As expected, the increased in the C_0 would result in a higher C_e . There was a negative correlation between the C_e with Dosage in the MLR model. The negative correlation in the MLR model between the C_e and Fe was not expected. This could be explained by the fact that the increase in the Dosage will have a negative correlation with the Fe, as a result the increase in the Fe would have a positive correlation with C_e . This was the result due to the negative correlation between Dosage and C_e in the MLR model. However, when compared to the C_0 the impact on the regression is not that strong for Dosage and Fe. The MLR model had a good fit with and a regression coefficient of 0.995. From the MLR model we can see that only 0.5% of total variance could not been explained.

Table 6.18 Analysis of Variance (ANOVA)for Hematite H for 7 days isotherm study using1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

Source	DF	SS	MS	F	р
Regression	3	88,966.5	29,655.52	3,130.26	0.000
Residual Error.	47	454.74	9.474		
Total	50	89,421.29			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.19 Pearson correlation between independent variables for Hematite H for 7 daysisotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

		Ce	C ₀	Dosage	Fe
Ce	Pearson Cor.	1	0.995**	0.431**	0.753**
	Sig.		0.000	0.001	0.000
C ₀	Pearson Cor.		1	0.492**	-0.797**
	Sig.			0.000	0.000
Dosage	Pearson Cor.			1	-0.780**
	Sig.				0.000
Fe	Pearson Cor.				1
	Sig.				

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Model	Unstandardized Coefficients		Standardized	4	Sig	\mathbf{P}^2	Std. Error	
Model	β	Std. Error	Beta (β)	ι	51g.	ĸ	Estimate	
Constant	-18.613	7.879		-2.362	0.022	0.995	3.07796	
C ₀	0.891	0.015	1.067	58.769	0.000			
Dosage	-1.100	0.421	-0.046	-2.612	0.012			
Fe	3.591	1.446	0.063	2.483	0.017			

Table 6.20 Final Model Statistical Information for Hematite H for 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

t = Student t-test, Sig. = Significance Interval.

6.5.2.3 STATISTICAL ANALYSIS FOR THE 1 AND 7 DAYS ISOTHERM STUDY FOR HEMATITE H

The ANOVA test, Pearson correlations, and MLR model for the 1 and 7 days isotherm time study using hematite H at pH 2.0 with three different adsorbents dosages of 1g, 2g, and 5g at different initial BPA concentrations can been seen in Table 6.21, 6.22, and 6.23 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.22 we can see a positive correlation between C_e with C₀, Dosage and Fe at a 99% CI. The new independent variable Time had only a significant correlation with Fe. The Ce had a positive correlation with C₀ and Dosage, and a negative correlation with Fe. For the C_e correlation coefficients were 0.990, 0.403, and -0.277 for C₀, Dosage, and Fe, respectively. For both the Dosage and Fe the correlation was moderate and weak, respectively. The highest correlation was between the Ce and Co as expected, with a higher initial BPA concentration leading to a higher equilibrium concentration. There was also a strong negative correlation between Time and Fe. The increase in Time leaded to a decreased in the Fe. There was also a moderate positive correlation for C₀ with Dosage and negative moderate correlation for C₀ with Fe. This two different correlations can be explained by the fact that the initial BPA concentration was increased when the adsorbent dosage was also increased and as a result at a lower initial

BPA concentration a lower soluble iron concentration would be expected. As a result the weak correlation at 95% CI between the Dosage and Fe was not expected.

The MLR model had four independent variables of Time, C_0 , Dosage, and Fe. We can see the MLR model in equation 8.

$$C_e = 15.65 - 1.394Time + 0.818C_0 - 2.278Dosage - 2.334Fe$$
(8)

The strongest factor in the MLR model was C_0 followed by Time, Dosage and Fe. C_0 was the only independent variable that had a positive correlation with C_e . The increase in C_0 would lead to an increase in the C_e as expected. All the other three parameters Time, Dosage, and Fe had a negative correlation with C_e for the MLR model as expected. The MLR model had a good fit with and a regression coefficient of 0.989. Only 1.1% of total variance could not be explained by the current model. The linear relationship between the predicted C_e values versus the experimental C_e values can be seen in Figure 6.2. The linear relationship between the predicted and experimental values had a good fit with a coefficient of 0.993.

Table 6.21 Analysis of Variance (ANOVA) for Hematite H for 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

Source	DF	SS	MS	\mathbf{F}	р
Regression	7	155,116.4	38,779.1	2,232.13	0.000
Residual Error.	98	1,702.6	13.37		
Total	102	156,818.95			

DF = Degree of Freedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.22 Pearson correlation between independent variables for Hematite H for1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

		C _e	Time	C ₀	Dosage	Fe
Ce	Pearson Cor.	1	067	.990**	.403**	277**
	Sig.		.500	.000	.000	.005
Time	Pearson Cor.		1	025	013	853**
	Sig.			.799	.899	.000
C ₀	Pearson Cor.			1	.480**	310**
	Sig.				.000	.001
Dosage	Pearson Cor.				1	207*
	Sig.					.036
Fe	Pearson Cor.					1
	Sig.					

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Table 6.23 Final Model Statistical Information for Hematite H 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0

Model	Unstandardized Coefficients		Standardized	t	Sig	\mathbf{R}^2	Std. Error
Model	(β)	Std. Error	Beta (β)	•	015.	A	Estimate
Constant	15.65	4.474		3.499	0.001	0.989	4.16811
Time	-1.394	0.328	-0.107	-4.255	0.000		
C ₀	0.818	0.012	1.012	70.53	0.000		
Dosage	-2.278	0.276	-0.100	-8.249	0.000		
Fe	-2.334	0.820	-0.076	-2.846	0.005		

t = Student t-test, Sig. = Significance Interval



Figure 6.3 - Predicted and experimental equilibrium BPA concentrations (C_e) using hematite H for the 1 and 7 days isotherm study

6.5.2.4 STATISTICAL ANALYSIS FOR THE 1 AND 7 DAYS ISOTHERM STUDY FOR HEMATITE H WITH INDEPENDENT VARIABLE INTERACTIONS

The ANOVA test, MLR model, and Pearson correlations for the 1 and 7 days isotherm time study using hematite H at pH 2.0 with three different adsorbents dosages of 1g, 2g, and 5g at different initial BPA concentrations with independent variables interactions can been seen in Table 6.24, 6.25, and 6.26 respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.26 we can see the positive and negative correlations between all the variables. Due to the large number of different variables only the variables present in the MLR model will be discussed. The MLR model had 9 different coefficients out of which 6 independent variables had significant positive statistical correlation with the dependent variable C_e at a 99% CI. Out from the 6 independent variables 5 had strong correlations and one had a moderate correlation with C_e . The correlation coefficients for the 6 independent variables that are part of the MLR model were 0.990, 0.403, 0.648, 0.907, 0.647, and 0.994 for C_0 , Dosage, Time • C_0 , C_0 • Fe, Time • C_0 • Dosage, and C_0 • Dosage • Fe, respectively. Even though there were only positive correlations for the C_e with all the 9 independent variables in the Pearson correlations the MLR model had only 3 independent variables that had a positive correlation with C_e .

The negative correlation of the interactions between Time and C_0 can be explained that at longer periods of time the low initial concentration of BPA would have a less pronounced effect. As a result the high initial BPA concentration would have a more significant effect for longer contact time. The same negative correlation was found for the C_0 and Fe. As a result, at high concentrations of Fe, a high initial BPA concentration would have a significant effect on the C_e . For the positive correlation between Time and Dosage can be explained that for a long period of time only a low dosage would have a significant effect on the adsorption. This was expected since a small dosage of adsorbent given time would be able to absorb more BPA, as a result a high dose of adsorbent for a long period of time would not have a significant effect to the adsorption. This fact has to be quantified since, we know that Dosage is correlated negatively with C_e for the MLR model. The higher the adsorbent dosage the lower the C_e would as expected.

The MLR model had the independent variables of C_0 , Dosage, Time • C_0 , Time • Dosage, C_0 • Fe, Dosage • Fe, Time • C_0 • Dosage, Time • Dosage • Fe, and C_0 • Dosage • Fe. We can see the MLR model in equation 9.

$$C_e = -2.117 + 1.460C_0 - 12.591Dosage - 0.045 \text{ Time} \cdot C_0 + 1.573 \text{ Time} \cdot \text{Dosage} - 0.100 C_0 \cdot \text{Fe} + 2.659 \text{ Dosage} \cdot \text{Fe} - 0.004 \text{ Time} \cdot C_0 \cdot \text{Dosage} - 0.336 \text{ Time} \cdot \text{Dosage} \cdot \text{Fe} - 0.009 C_0 \cdot \text{Dosage} \cdot \text{Fe}$$
(9)

The strongest positive correlation from the MLR model was C_0 , followed with the next strongest correlation with Dosage which was a negative one as we can see from Table 6.28 by comparing the standardized β coefficients. The MLR model had a good fit with and a regression coefficient of 0.995. The MLR model was based on 103 different experimental experiments. Only about 0.7% of the total variance could not be explained by the model. The linear relationship between the predicted C_e values versus the experimental C_e values can be seen in Figure 6.3. The linear relationship between the predicted and experimental values has a good fit with a coefficient of regression of 0.962.

Table 6.24 Analysis of Variance (ANOVA) for Hematite H for 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0 with the independent variables interactions

Source	DF	SS	MS	F	р
Regression	9	156,082.78	17,342.53	2,190.88	0.000
Residual Error.	93	736.17	7.92		
Total	102	156,818.95			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval



Figure 6.4 - Predicted and experimental equilibrium BPA concentrations (C_e) using hematite H for the 1 and 7 days isotherm study with independent variables interactions

Madal	Unstand Coeffi	lardized icients	Standardized	4	Sia	D ²	Std. Error of
With	(β)	Std. Error	Beta (β)	ι	Sig.	K	the Estimate
Constant	-2.117	.790		-2.678	.009	0.995	2.81350
C ₀	1.460	.069	1.805	21.287	.000		
Dosage	-12.59	2.289	555	-5.502	.000		
Time • C ₀	045	.007	299	-6.397	.000		
Time • Dosage	1.573	.348	.477	4.516	.000		
C ₀ • Fe	100	.014	334	-6.974	.000		
Dosage • Fe	2.659	.521	.422	5.105	.000		
Time • C ₀ • Dosage	004	.001	119	-3.261	.002		
Time • Dosage • Fe	336	.082	261	-4.091	.000		
C ₀ • Dosage • Fe	009	.003	147	-3.325	.001		

Table 6.25 Final Model Statistical Information for Hematite H 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0 with the independent variables interactions

t = Student t-test, Sig. = Significance Interval

							T*	T!	T!	C	C	D	Time •	Time	Time •	Co •
		Ce	Time	C	Посаде	Fe	• Co	Dosage	• Fe	CO • Dosage	CO • Fe	Dosage	СО• Догаде	• C0 • Fe	Dosage • Fe	Dosage
Се	Door Cor	1	067	000**	102**	7C 277**	- CU 649**	160	- re 241*	040**	1C 007**	- rc	LUSage	(70 ^{**}	002	• FC 002**
	rear. Cor.	1	007	.990	.405	277	.040	.100	-,241	.940	.907	.141	.047	.070	.002	.005
	Sig.		.500	.000	.000	.005	.000	.107	.014	.000	.000	.155	.000	.000	.985	.000
Time	Pear. Cor.		1	025	013	853	.430	.694	.898	027	284	411	.329	.426	.559	200
C	Sig.			.799	.899	.000	.000	.000	.000	./ 89	.004	.000	.001	.000	.000	.042
C_0	Pear. Cor.			1	.480	510	.097	.247	195	.905	.900	.195	./00	./29	.093	.899
Deserve	Big.				.000	.001	.000	.012	.030	.000	.000	.040	.000	.000	.349	.000
Dosage	Pear. Cor.				1	207	.335	.505	042	.598	.414	.822	.445	.3/4	.570	.592
T -	Sig.					.030	.001	.000	.072	.000	.000	.000	.000	.000	.000	.000
ге	Pear. Cor.					1	534	010	594	308	047	.280	443	494	301	148
	<u></u>						.000	.000	.000	.002	.035	.003	.000	.000	.000	.130
Time • Co	Pear. Cor.						1	.603	.213	.669	.353	079	.962	.950	.351	.385
	Sig.							.000	.030	.000	.000	.430	.000	.000	.000	.000
Time • Dosage	Pear. Cor.							1	.629	.313	008	.124	.630	.615	.887	.124
	Sig.								.000	.001	.935	.213	.000	.000	.000	.212
Time • Fe	Pear. Cor.								1	181	341***	261***	.134	.296**	.697***	264**
	Sig.									.067	.000	.008	.177	.002	.000	.007
Co • Dosage	Pear. Cor.									1	.842**	.301**	.731***	.683**	.168	.927**
	Sig.										.000	.002	.000	.000	.090	.000
Co • Fe	Pear. Cor.										1	.308**	.374**	.464**	028	.934**
	Sig.											.002	.000	.000	.776	.000
Dosage • Fe	Pear. Cor.											1	.040	.011	.339**	.432**
	Sig.												.687	.914	.000	.000
Time • Co •	Pear. Cor.												1	.896**	.389**	.448**
Dosage	Sig.													.000	.000	.000
Time • Co • Fe	Pear. Cor.													1	.462**	.477**
	Sig.														.000	.000
Time • Dosage	Pear. Cor.														1	.099
• Fe	Sig.															.321
Co • Dosage •	Pear. Cor.															1
Fe	Sig.															

Table 6.26 Final Model Statistical Information for Hematite H 1 and 7 days isotherm study using 1g, 2g, and 5g adsorbent dosage to 50 mL aqueous solution at pH 2.0 with the independent variables interactions

6.5.3 STATISTICAL ANALYSIS FOR CHAPTER 3

6.5.3.1 STATISTICAL ANALYSIS FOR 1G, 2G, AND 5G OF HEMATITE H ADSORBENT AT DIFFERENT $\rm PH_{S}$

The ANOVA test, Pearson correlations, and MLR model for the 1 day time study using hematite H at different pHs with three different adsorbents dosages of 1g, 2g, and 5g at different initial BPA concentrations can been seen in Table 6.27, 6.28, and 6.29, respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.29 we can see a positive correlation between C_e with C_0 and Dosage at a 99% CI. The correlation with the C_0 was strong and with the Dosage moderate. For the C_e correlation coefficients were 0.423, and 0.996 for Dosage and C_0 , respectively. From the Person correlations we see the moderate positive correlation between C_e and Dosage as expected due to the fact that the C_0 was increased with an increase in Dosage.

The MLR model had five independent variables of pH, Dosage, C_0 , TDS, and Fe. We can see the MLR model in equation 10.

$$C_e = -2.733 + 0.962pH - 0.653Dosage + 0.901C_0 + 0.003TDS - 3.208Fe$$
(10)

The strongest factor in the MLR model was C_0 followed by Fe, pH, TDS and Dosage. C_0 , pH, and TDS had a positive correlation, while Dosage and Fe had a negative correlation with C_e . The positive correlation for TDS was not expected, however the standardized β coefficients were very small for the MLR model. The positive correlation for pH in the MLR model is due to the fact that the adsorption at low pH is stronger in the presence of hematite H. As a result, a higher pH would lead to higher C_e . The positive correlation with C_0 is also expected since not all the BPA would be absorbed by the hematite H, as a result a higher C_0 would lead to a higher C_e . The negative correlation with Dosage and Fe was expected since higher Dosage would increase the total adsorptions or higher Fe concentration would contributed to the salting effect of the solution, as a result C_e would be less for both cases. The MLR model had a good fit with an a regression coefficient of 0.995. Only 0.5% of total variance could not be explained by the current model. The MLR model was based on 240 different experimental points. The linear relationship between the predicted C_e values versus the experimental C_e values can be seen in Figure 6.4. The linear relationship between the predicted and experimental values had a good fit with a coefficient of regression of 0.995.

Table 6.27 Analysis of Variance (ANOVA) for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L

Source	DF	SS	MS	F	р
Regression	5	467,607.1	153,521.4	9,609.46	0.000
Residual Error.	234	3,738.4	15.97		
Total	239	771,345.52			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.28 Pearson correlation between independent variables for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L

		Ce	pН	Dosage	C ₀	TDS	Fe
C	Pearson Cor.	1	0.047	0.423**	0.996**	-0.093	0.123
Ce	Sig.		0.469	0.000	0.000	0.153	0.058
пЦ	Pearson Cor.		1	0.000	0.000	-0.443**	-0.376**
рп	Sig.			1.000	0.995	0.000	0.00
Deces	Pearson Cor.			1	0.447**	-0.096	0.166**
Dosage	Sig.				0.000	0.137	0.010
C	Pearson Cor.				1	-0.068	0.163*
C_0						0.291	0.012
TDS	Pearson Cor.					1	0.791**
105	Sig.						0.000
Fo	Pearson Cor.						1
ге	Sig.						

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Model	Unstand Coeffi	lardized icients	Standardized	4	Sia	D ²	Std. Error
Model	β	Std. Error	Beta (β)	l	51g.	K	Estimate
Constant	-2.733	.810		-3.375	.001	0.995	3.99701
pН	.962	.115	.043	8.375	.000		
Dosage	653	.172	020	-3.801	.000		
C ₀	.901	.005	1.015	194.604	.000		
TDS	.003	.001	.033	3.854	.000		
Fe	-3.208	.545	049	-5.885	.000		

Table 6.29 Final Model Statistical Information for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L

t = Student t-test, Sig. = Significance Interval



Predicted C_e values (mg/L)

Figure 6.5 - Predicted and experimental equilibrium BPA concentrations (Ce) using 1g, 2g, and 5g of hematite H for at different pHs.

6.5.3.2 STATISTICAL ANALYSIS FOR 1G,2G, AND 5G HEMATITE H ADSORBENT AT DIFFERENT PH_S WITH INDEPENDENT VARIABLE INTERACTIONS

The ANOVA test, MLR model, and Pearson correlations for the 1 day time study using hematite H with independent variables interactions at different pHs with three different adsorbent dosages of 1g, 2g, and 5g at different initial BPA concentrations can been seen in Table 6.30, 6.31, and 6.32, respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. In the Table 6.32 we can see the positive and negative correlations between all the variables. From Table 6.32 we can see a positive correlation between C_e with other 8 different independent variables. The positive regression coefficients between C_e and the independent variables were 0.996, 0.952, 0.282, 0.836, 0.382, 0.359, 0.740, and 0.230 for C₀, Dosage • C₀, C₀ • TDS, pH • Dosage • C₀, pH • Dosage • Fe, pH • C₀ • TDS, pH • C₀ • Fe, and C₀ • TDS • Fe, respectively. Due to the large number of different variables, only the variables present in the MLR model will be discussed. The MLR model had 12 different coefficients out of which the 8 independent variables presented earlier had significant positive statistical correlations with the dependent variables presented earlier had significant positive statistical had strong correlations and the other 4 had moderate correlations with C_e.

Even though there were only positive correlations for the C_e from all the 12 independent variables in the Pearson correlations the MLR model had only 7 independent variables that had a positive correlation with C_e . As in the previous models the first and strongest correlation parameter from the MLR model was C_0 which had a very strong positive correlation with C_e as expected and explained earlier in the previous models. The negative effect of Fe to the C_e is expected, because of the salting effect in the solution which increases the adsorption. The negative correlation of the interactions between Dosage and C_0 can be explained that for very high initial concentrations of BPA a higher dosage of adsorbent is needed in order to have a significant effect on the adsorption. The other two positive interactions between C_0 with TDS and TDS with Fe can be explained that for high concentrations of TDS in order to make a significant effect on the adsorption the C_0 and Fe have to be low, otherwise the effect of the interactions of the other two independent variables is minimal.

The MLR model had the independent variables of C_0 , Fe, Dosage • C_0 , C_0 • TDS, TDS • Fe, pH • Dosage • C_0 , pH • Dosage • TDS, pH • Dosage • Fe, pH • C_0 • TDS, pH • C_0 • Fe, Dosage • TDS • Fe, and C_0 • TDS • Fe. We can see the MLR model in equation 11.

$$C_{e} = 0.363 + 1.002C_{0} - 12.145Fe - 0.037 \text{ Dosage} \cdot \text{Fe} + 0.001 C_{0} \cdot TDS + 0.006 TDS \cdot \text{Fe} + 0.002 \text{ pH} \cdot \text{Dosage} \cdot C_{0} - 0.001 \text{ pH} \cdot \text{Dosage} \cdot \text{TDS} + 0.376 \text{ pH} \cdot \text{Dosage} \cdot Fe - 0.000212pH \cdot C_{0} \cdot TDS + 0.022 pH \cdot C_{0} \cdot Fe + 0.001 \text{ Dosage} \cdot TDS \cdot De - 0.0000616 C_{0} \cdot TDS \cdot Fe$$
(11)

The MLR model had a good fit with a regression coefficient of 0.998. The MLR model was based on 240 different experimental points. Only about 0.2% of the total variance could not be explained by the model. The linear relationship between the predicted C_e values versus the experimental C_e values can be seen in Figure 6.5. The linear relationship between the predicted and experimental values had a good fit with a coefficient of regression of 0.997.

Table 6.30 Analysis of Variance (ANOVA) for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions

Source	DF	SS	MS	F	р	
Regression	12	769,579.16	64,131.59	8,241.74	0.000	
Residual Error.	227	1,766.36	7.781			
Total	239	771,345.52				

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Model	Unstanda Coeffic	ardized cients	Standardized	4	Sig	\mathbf{R}^2	Std. Error of
Model	β	Std. Error.	Beta (β)	ι	Sig.	K	the Estimate
Constant	.363	.435		.833	.406	0.998	2.78950
C ₀	1.002	.014	1.128	73.520	.000		
Fe	-12.145	2.233	185	-5.438	.000		
Dosage • C_0	037	.003	211	-11.195	.000		
$C_0 \bullet TDS$.001	.000	.380	3.099	.002		
TDS • Fe	.006	.001	.145	4.758	.000		
pH • Dosage • C ₀	.002	.001	.068	2.490	.013		
pH • Dosage • TDS	001	.000	068	-3.026	.003		
pH • Dosage • Fe	.376	.074	.052	5.078	.000		
$\mathbf{pH} \bullet \mathbf{C}_0 \bullet \mathbf{TDS}$	-2.12E-4	.000	321	-3.357	.001		
$\mathbf{pH} \bullet \mathbf{C}_0 \bullet \mathbf{Fe}$.022	.007	.090	3.059	.002		
Dosage • TDS • Fe	.001	.000	.057	1.994	.047		
$C_0 \bullet TDS \bullet Fe$	-6.16E-5	.000	144	-3.195	.002		

Table 6.31 Final Model Statistical Information for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions

t = Student t-test, Sig. = Significance Interval



Figure 6.6 - Predicted and experimental equilibrium BPA concentrations (C_e) using 1g, 2g, and 5g of hematite H for at different pHs with independent variables interactions.

		C.	нa	Dosage	Co	TDS	Fe	pH•	pH•	pH•	pH•	Dosage	Dosage	Dosage
			F		- 0			Dosage	C ₀	TDS	F'e	• C ₀	• TDS	• Fe
C	Pear. Cor.	1	.047	.423	.996	093	.123	.331	.853	085	.264	.952	.001	.243
∪e	Sig.		.469	.000	.000	.153	.058	.000	.000	.187	.000	.000	.991	.000
U	Pear. Cor.		1	.000	.000	443**	376**	.618**	.357**	414**	.004	.000	359**	284**
рп	Sig.			1.000	.995	.000	.000	.000	.000	.000	.953	.999	.000	.000
Deserve	Pear. Cor.			1	.447**	096	.166**	.691**	.367**	091	.369**	.576**	.171**	.441**
Dosage	Sig.				.000	.137	.010	.000	.000	.161	.000	.000	.008	.000
	Pear. Cor.				1	068	.163*	.309**	.821**	063	.282**	.965**	.034	.293**
C ₀	Sig.					.291	.012	.000	.000	.329	.000	.000	.603	.000
	Pear. Cor.					1	.791**	301**	180**	.997**	.598**	080	.801**	.463**
TDS	Sig.						.000	.000	.005	.000	.000	.216	.000	.000
E	Pear. Cor.						1	116	028	.777**	.868**	.164*	.658**	.833**
re	Sig.							.072	.661	.000	.000	.011	.000	.000
u b	Pear. Cor.							1	.549**	266**	.331**	.398**	156*	.064
pH • Dosage	Sig.								.000	.000	.000	.000	.016	.324
	Pear. Cor.								1	154 [*]	.255**	.792**	106	.069
р Н • С ₀	Sig.									.017	.000	.000	.101	.285
	Pear. Cor.									1	.605**	074	.795**	.452**
pH • TDS	Sig.										.000	.250	.000	.000
- U - F-	Pear. Cor.										1	.289**	.508**	.755**
рн•ге	Sig.											.000	.000	.000
	Pear. Cor.											1	.056	.339**
Dosage • C_0	Sig.												.390	.000
	Pear. Cor.												1	.648**
Dosage •TDS	Sig.													.000
Decese A Fe	Pear. Cor.													1
Dosage • Fe	Sig.													

Table 6.32 Pearson correlation between independent variables for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

		C ₀ •	C ₀ •	TDS •	pH•	pH•	pH•	pH•	pH•	pH•	Dosage	Dosage	Dosage •	$C_0 \bullet TDS$
		TDS	Fe	Fe	Dosage	• TDS	Dosage • Fe		C₀• Fe	IDS• Fe	• C_0 • TDS	• C ₀ • Fe	IDS•Fe	• re
	Pear, Cor,	.282**	.496**	- 034	.836**	031	.382**	.359**	.740**	- 031	.304**	.500**	052	.230**
C _e	Sig.	.000	.000	.597	.000	.633	.000	.000	.000	.633	.000	.000	.420	.000
Ĭ	Pear. Cor.	230**	204**	372**	.278**	311**	.084	185**	.026	368**	167**	170**	317**	199 ^{**}
pН	Sig.	.000	.001	.000	.000	.000	.194	.004	.693	.000	.010	.008	.000	.002
_	Pear. Cor.	.078	.281**	072	.486**	.224**	.680**	.113	.402**	068	.159*	.335**	.131*	.073
Dosage	Sig.	.226	.000	.268	.000	.000	.000	.080	.000	.298	.014	.000	.043	.263
C	Pear. Cor.	.313**	.540**	011	.815**	.062	.407**	.386**	.757**	008	.337**	.545**	.085	.260**
\mathbb{C}_0	Sig.	.000	.000	.865	.000	.341	.000	.000	.000	.904	.000	.000	.191	.000
TDC	Pear. Cor.	.528**	.292**	.965 **	150 [*]	.787**	.253**	.508**	.157*	.965**	.385**	.190**	.792**	.505**
TDS Sig.	Sig.	.000	.000	.000	.020	.000	.000	.000	.015	.000	.000	.003	.000	.000
Pear.	Pear. Cor.	.532**	.688**	.834**	.007	.648**	.643**	.517**	.535**	.834**	.419**	.604**	.702**	.530**
re	Sig.	.000	.000	.000	.914	.000	.000	.000	.000	.000	.000	.000	.000	.000
U D	Pear. Cor.	108	.018	250**	.606**	070	.573**	040	.312**	243**	041	.064	15 4 [*]	099
pH • Dosage	Sig.	.095	.776	.000	.000	.283	.000	.540	.000	.000	.523	.325	.017	.125
~	Pear. Cor.	.056	.252**	135 *	.965**	048	.369**	.167**	.661**	130 *	.090	.266**	081	.026
pН•С ₀	Sig.	.386	.000	.036	.000	.455	.000	.010	.000	.045	.167	.000	.211	.693
	Pear. Cor.	.526**	.284**	.953**	124	.787**	.264**	.511**	.166*	.954**	.382**	.183**	.782**	.498**
рн•тр5	Sig.	.000	.000	.000	.055	.000	.000	.000	.010	.000	.000	.005	.000	.000
нь	Pear. Cor.	.432**	.624**	.662**	.274**	.537**	.830**	.452**	.641**	.666**	.348**	.555**	.557**	.435**
рн • ге	Sig.	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
	Pear. Cor.	.282**	.535**	026	.844**	.090	.477**	.354**	.753**	023	.339**	.569**	.096	.239**
Dosage • C_0	Sig.	.000	.000	.686	.000	.163	.000	.000	.000	.723	.000	.000	.138	.000
Dana an aTDC	Pear. Cor.	.609**	.399**	.767**	067	.995**	.446**	.592**	.268**	.767**	.589**	.366**	.966**	.601**
Dosage •1D5	Sig.	.000	.000	.000	.301	.000	.000	.000	.000	.000	.000	.000	.000	.000
	Pear. Cor.	.505**	.823**	.496**	.127	.649**	.844**	.498**	.680**	.497**	.515**	.823**	.671**	.513**
Dosage • Fe	Sig.	.000	.000	.000	.050	.000	.000	.000	.000	.000	.000	.000	.000	.000

Table 6.32 cont. Pearson correlation between independent variables for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions

		C ₀ •	C ₀ •	TDS •	pH•	pH•	pH•	р Н•	pH•	pH•	Dosage	Dosage	Dosage	
		TDS	Fe	Fe	Dosage	Dosage	Dosage	C ₀ • TDS	$C_0 \bullet$	TDS • Fo	• C ₀ • TDS	• C ₀ •	• TDS •	TDS •
	Pear Cor	1	741**	612**	066	- 1D3 - 606**	364**	992**	588**	613 ^{**}	951 ^{**}	675 ^{**}	747 ^{**}	987 ^{**}
$C_0 \cdot TDS$	Sig.		.000	.000	.305	.000	.000	.000	.000	.000	.000	.000	.000	.000
	Pear. Cor.		1	.388**	.275**	.399**	.686**	.748**	.882**	.388**	.734**	.977**	.524**	.742**
C ₀ • Fe	Sig.			.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
	Pear. Cor.			1	112	.750***	.303**	.589**	.249**	1.000**	.467**	.274**	.814**	.609**
TDS • Fe	Sig.				.084	.000	.000	.000	.000	.000	.000	.000	.000	.000
и в	Pear. Cor.				1	004	.437**	.176**	.676**	106	.109	.303**	051	.036
$pH \bullet Dosage \bullet C_0$	Sig.					.956	.000	.006	.000	.102	.093	.000	.435	.580
	Pear. Cor.					1	.495**	.598**	.300**	.751**	.590**	.368**	.956**	.594**
pH • Dosage • TDS	Sig.						.000	.000	.000	.000	.000	.000	.000	.000
II. DE.	Pear. Cor.						1	.398**	.738**	.308**	.395**	.701**	.470**	.373**
pri • Dosage • re	Sig.							.000	.000	.000	.000	.000	.000	.000
DHAC ATDS	Pear. Cor.							1	.649**	.591**	.945**	.684**	.726**	.97 1 ^{**}
	Sig.								.000	.000	.000	.000	.000	.000
nH o C o Fo	Pear. Cor.								1	.253**	.597**	.870***	.374**	.580**
	Sig.									.000	.000	.000	.000	.000
	Pear. Cor.									1	.468**	.274**	.814**	.609**
pr•1D5•re	Sig.										.000	.000	.000	.000
	Pear. Cor.										1	.730**	.725**	.951**
Dosage • C_0 • 1DS	Sig.											.000	.000	.000
	Pear. Cor.											1	.481**	.680**
Dosage • C_0 • Fe	Sig.												.000	.000
	Pear. Cor.												1	.756**
Dosage • 1D5 • Fe	Sig.													.000
	Pear. Cor.													1
$C_0 \bullet TDS \bullet Fe$	Sig.													

Table 6.32 cont. Pearson correlation between independent variables for Hematite H using 1g, 2g, and 5g adsorbent dosage to 50 mL at different pHs with a BPA initial concentration of 1.2 mg/L with the independent variables interactions

6.5.3.3 STATISTICAL ANALYSIS FOR HEMATITE H ADSORBENT IN THE PRECENSE OF CALCIUM IONS

The ANOVA test, Pearson correlations, and MLR model for the 1 day time study using 5g of hematite H at different initial BPA concentrations of 1.3, 13, and 130 mg/L with different Calcium ions concentrations can been seen in Table 6.33, 6.34, and 6.35, respectively. Based on the ANOVA analysis the regression model showed to be significant with p a value of 0.000. From Table 6.34 we can see a positive correlation between C_e with C_0 at a 99% CI. The correlation with the C_0 was strong with the coefficient correlation of 0.986. There was also a weak and strong correlation at 99% CI between pH with TDS and NaHCO₃, respectively. The correlation between pH with TDS and NaHCO₃ were 0.264 and 0.507, respectively. The strong correlation between pH and NaHCO₃ was expected since there was a buffering effect in the presence of bicarbonate ions. There was also a negative moderate correlation between Calcium and TDS at a 99% CI with a correlation coefficient of -0.339.

The MLR model had three independent variables of pH, C_0 , and Ca. We can see the MLR model in equation 12.

$$C_e = -12.285 + 2.148pH + 0.775C_0 - 0.00023Ca$$
(12)

The strongest factor in the MLR model was C_0 followed by Fe, pH, and Ca. C_0 and pH had a positive correlation, while Ca had a negative correlation with C_e . The positive correlation for C_0 was expected, since a higher initial concentration would lead to a higher equilibrium concentration. The positive correlation with the pH is also expected, because the low pH had a positive effect on the total adsorption. The negative correlation between C_e and Ca was also expected since the increase in the ionic strength due in particular to the salting effect in the solution and neutralization of adsorbent dosage would increase the total absorbance of BPA onto hematite H. As a result the increase in the Ca would result in a decrease in C_e . The MLR model had a good fit with and a regression coefficient of 0.985. Only 1.5% of total variance could not be explained by the current model. The MLR model was based on 114 different experimental points. The linear relationship between the predicted C_e values versus the experimental C_e values can been seen in Figure 6.6. The linear relationship between the predicted and experimental values had a good fit with a coefficient of regression of 0.988.

Table 6.33 Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at differentBPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions

Source	DF	SS	MS	F	р
Regression	3	240,030.07	80,010.02	2,334.63	0.000
Residual Error.	110	3,769.80	34.27		
Total	113	243,799.87			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.34 Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions

		Ce	pН	C ₀	Ca	TDS	NaHCO ₃
Ce	Pearson Cor.	1	.071	.986**	058	.023	.041
	Sig.		.455	.000	.543	.807	.666
11	Pearson Cor.		1	034	120	.264**	.507**
рп	Sig.			.718	.203	.005	.000
C	Pearson Cor.			1	005	017	009
C_0	Sig.				.955	.859	.922
Ca	Pearson Cor.				1	339**	.022
Ca						.000	.820
TDS	Pearson Cor.					1	138
105	Sig.						.145
N ₂ HCO ₂	Pearson Cor.						1
	Sig.						

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Madal	Unstanda Coeffic	ardized cients	Standardized	4	Sig.	R ²	Std. Error of
Model	β	Std. Error	Beta (β)	L			the Estimate
Constant	-12.285	1.701		-7.221	.000	0.985	5.85414
pН	2.148	.258	.100	8.337	.000		
C ₀	.775	.009	.989	83.372	.000		
Ca	-2.3E-4	.000	040	-3.377	.001		

Table 6.35 Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions

t = Student t-test, Sig. = Significance Interval.



Figure 6.7 - Predicted and experimental equilibrium BPA concentrations (C_e) for hematite H in the presence of Calcium ions

6.5.3.4 STATISTICAL ANALYSIS FOR HEMATITE H ADSORBENT IN THE PRECENSE OF CALCIUM IONS WITH INDEPENDENT VARIABLE INTERACTIONS

The ANOVA test, MLR model, and Pearson correlations for the 1 day time study using 5g of hematite H with independent variables interactions at different initial BPA concentrations of 1.3, 13, and 130 mg/L with different Calcium ions concentrations can been seen in Table 6.36, 6.37, and 6.38, respectively. Based on the ANOVA analysis the regression model showed to be significant with p value of 0.000. In the Table 6.38 we can see the positive and negative correlations between all the variables. There is a positive correlation between Ce with other 9 different independent variables out of the total 12 from the MLR model. The positive regression coefficients between Ce and the independent variables were 0.986, 0.935, 0.449, 0.369, 0.462, 0.371, 0.281, 0.296 and 0.279 for C₀, pH • C₀, C₀ • Ca, C₀ • TDS, pH • C₀ • Ca, pH • C₀ • TDS, $C_0 \bullet Ca \bullet TDS$, $C_0 \bullet Ca \bullet NaHCO_3$, and $C_0 \bullet TDS \bullet NaHCO_3$ respectively. Due to the large number of different variables only the variables present in the MLR model will be discussed. The MLR model had 12 different coefficients out of which the 9 independent variables presented earlier had the significant positive statistical correlations with the dependent variable Ce at a 99% CI. Out from the 9 independent variables 2 had strong correlations and the other 7 had moderate correlations with Ce.

Even though there were only positive correlations for the C_e from all the 12 independent variables in the Pearson correlations, the MLR model had only 7 independent variables that had a positive correlation with C_e . As in the previous models the first and strongest correlation parameter from the MLR model was C_0 , which had a very strong positive correlation with C_e as expected and explained earlier in the previous models. There was also a positive correlation with pH, pH • C_0 , pH • TDS, and C_0 • TDS, which can be explained as follows. The positive correlation with pH is expected since hematite H adsorbs better at low pH. The positive

correlation with the interaction of variables pH and C_0 (pH • C_0) is also expected since there was a positive correlation with both individual independent variables. The interactions coefficient pH • C_0 can be explained that at a high pH the C_0 has to be low in order to have strong effect on the adsorption. The high C₀ would only have a marginal effect on the C_e at a high pH due to the fact that the adsorption potential is already reduced due to the high pH. For the independent coefficient $C_0 \bullet TDS$ could be explained that at high TDS the initial concentration C_0 should be low in order to have a significant effect on the adsorption. At high C₀ the effect of TDS at high concentration is only marginal. The negative regression with TDS is expected since the salting effect on the aqueous solution is expected to improve the adsorption. The negative correlation with $C_0 \bullet Ca$ can also be explained by looking to the previous MLR model that did not take the interactions between the impendent variables, where we see a negative correlation between Ce and Ca. As a result in the current model even though the correlation was not significant with the Ca it was still negative as expected, thus a higher Ca concentration would lead to a lower Ce. Due to the fact that C_0 has a positive correlation with C_e the negative correlation between $C_0 \bullet Ca$ with C_e can be explained by the fact that at high concentrations of Ca the C₀ has to be low in order to have a significant effect on the adsorption. As a result the effect of Ca on the adsorption would be minimal if the C_0 would be high.

The MLR model had the independent variables of pH, C_0 , TDS, pH • C_0 , pH • TDS, C_0 • Ca, C_0 • TDS, pH • C_0 • Ca, pH • C_0 • TDS, C_0 • Ca • TDS, C_0 • Ca • NaHCO₃, and C_0 • TDS • NaHCO₃. We can see the MLR model in equation 13.

 $C_e = -4.417 + 0.443 \text{pH} + 0.679C_0 - 0.097 \text{ TDS} + 0.0196 \text{ } pH \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS - 0.0143 \text{ } \text{pH} \bullet TDS - 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS - 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{pH} \bullet C_0 + 0.0143 \text{ } \text{pH} \bullet TDS + 0.0196 \text{ } \text{p$ $0.0000131 C_0 \bullet Ca + 0.0017 C_0 \bullet TDS + 0.0000019 pH \bullet C_0 \bullet Ca - 0.000207 pH \bullet C_0 \bullet$ NaHCO₃ (13)

The MLR model had a good fit with a regression coefficient of 0.998. The MLR model was based on 114 different experimental points. Only about 0.2% of the total variance could not be explained by the model. The linear relationship between the predicted C_e values versus the experimental Ce values can be seen in Figure 6.7. The linear relationship between the predicted and experimental values had a good fit with a coefficient of regression of 0.998.

Table 6.36 Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interactions

Source	DF	SS	MS	F	р
Regression	12	243,314.75	20,276.23	4,221.42	0.000
Residual Error.	101	485.12	4.803		
Total	113	243,799.87			





Figure 6.8 - Predicted and experimental equilibrium BPA concentrations (C_{e}) for hematite H in the presence of Calcium ions with independent variables interactions.
	Unstand Coeffi	ardized cients	Standardized		a.	\mathbf{D}^2	Std. Error
Model	β	Std. Error	Beta (β)	t	S1g.	K-	of the Estimate
Constant	-4.42E+00	8.17E-01		-5.403	.000	0.998	2.19162
рН	4.33E-01	1.45E-01	.020	2.979	.004		
C ₀	6.79E-01	1.35E-02	.867	50.246	.000		
TDS	-9.71E-02	4.13E-02	371	-2.353	.021		
рН • C ₀	1.96E-02	2.40E-03	.152	8.150	.000		
pH•TDS	1.43E-02	6.03E-03	.372	2.377	.019		
$C_0 \bullet Ca$	-1.31E-05	1.02E-06	207	-12.757	.000		
$C_0 \bullet TDS$	1.70E-03	5.61E-04	.490	3.039	.003		
pH • C_0 • Ca	1.94E-06	2.03E-07	.171	9.543	.000		
pH•C ₀ •TDS	-2.07E-04	7.86E-05	389	-2.629	.010		
$C_0 \cdot C_a \cdot TDS$	-1.42E-06	5.36E-07	080	-2.640	.010		
$C_0 \cdot Ca \cdot$	-1.94E-06	6.62E-07	019	-2.931	.004		
NaHCO3 C0 • TDS • NaHCO3	3.84E-04	9.44E-05	.029	4.066	.000		

Table 6.37 Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interactions

t = Student t-test, Sig. = Significance Interval.

		Ce	рН	C ₀	Ca	TDS	NaHCO ₃	pH• Co	pH• Ca	pH• TDS	pH ∙ NaHCO₂	C ₀ • Ca	C ₀ • TDS	C ₀ • NaHCO ₂
	Pear. Cor.	1	.071	.986**	058	.023	.041	.935**	018	.015	.042	.449**	.369**	.515**
C _e	Sig.		.455	.000	.543	.807	.666	.000	.852	.877	.656	.000	.000	.000
	Pear. Cor.		1	034	120	.264**	.507**	.275**	.163	.286**	.510**	063	.140	.285**
рн	Sig.			.718	.203	.005	.000	.003	.083	.002	.000	.507	.136	.002
C	Pear. Cor.			1	005	017	009	.885**	004	028	010	.521**	.320**	.461**
C_0	Sig.				.955	.859	.922	.000	.969	.771	.919	.000	.001	.000
Ca	Pear. Cor.				1	339**	.022	029	.893 **	339**	001	.548**	215 *	.022
Ca	Sig.					.000	.820	.756	.000	.000	.989	.000	.022	.814
TDS	Pear. Cor.					1	138	.053	305***	.998**	128	184	.577**	079
105	Sig.						.145	.577	.001	.000	.176	.050	.000	.401
NaHCO ₂	Pear. Cor.						1	.147	.182	120	.999**	.019	086	.564**
Tuireo,	Sig.							.118	.053	.204	.000	.842	.364	.000
nH•Co	Pear. Cor.							1	.055	.050	.148	.429**	.387**	.623**
pri co	Sig.								.561	.595	.117	.000	.000	.000
nH • Ca	Pear. Cor.								1	305	.155	.490**	193 [*]	.114
рн•Са	Sig.									.001	.100	.000	.039	.225
	Pear. Cor.									1	109	184	.556**	070
pH•TDS	Sig.										.248	.050	.000	.461
pH •	Pear. Cor.										1	.006	080	.562**
NaHCO ₃	Sig.											.949	.400	.000
	Pear. Cor.											1	112	.280**
	Sig.												.236	.003
C . TDC	Pear. Cor.												1	.033
	Sig.													.731
C ₀ •	Pear. Cor.													1
NaHCO ₃	Sig.													

Table 6.38 Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interactions

				TDS •	рН • С ₀ •	рН• С ₀ •	рН • С₀ •	рН • С ₀ •	рН • С ₀ •	pH• TDS•	$\begin{array}{c} \mathbf{C}_{0} \bullet \\ \mathbf{Ca} \bullet \end{array}$	C ₀ • Ca•	$\begin{array}{c} C_0 \bullet \\ TDS \bullet \end{array}$	Ca• TDS•
		105	Nanco ₃	Nanco ₃	Ca	TDS	NaHCO ₃	TDS	NaHCO ₃	NaHCO ₃	TDS	NaHCO ₃	NaHCO ₃	NaHCO ₃
C	Pear. Cor.	001	.010	.043	.462**	.371**	.516**	010	.010	.043	.281**	.296**	.279**	.059
C _e	Sig.	.995	.917	.649	.000	.000	.000	.918	.915	.650	.002	.001	.003	.536
ոՍ	Pear. Cor.	.175	.237*	.277**	.093	.161	.287**	.191*	.240*	.277**	.087	.143	.172	.276**
pm	Sig.	.062	.011	.003	.324	.087	.002	.042	.010	.003	.360	.130	.068	.003
C ₀	Pear. Cor.	024	.005	009	.485**	.318**	.461**	035	.005	009	.250**	.294**	.211*	.004
	Sig.	.797	.958	.925	.000	.001	.000	.715	.958	.923	.007	.002	.025	.964
Ca	Pear. Cor.	256**	.470***	232*	.500**	215*	.009	251**	.468**	232*	169	.291**	144	231 [*]
Ca	Sig.	.006	.000	.013	.000	.022	.923	.007	.000	.013	.072	.002	.126	.013
TDS	Pear. Cor.	.967**	168	.147	170	.579**	074	.967**	170	.147	.576**	102	.091	.147
100	Sig.	.000	.073	.119	.071	.000	.434	.000	.070	.119	.000	.281	.334	.119
NaHCO	Pear. Cor.	194*	.569**	.431**	.108	071	.564**	186*	.575**	.431***	126	.344**	.268**	.430***
Tune 03	Sig.	.038	.000	.000	.251	.450	.000	.048	.000	.000	.182	.000	.004	.000
nH•C	Pear. Cor.	.018	.080	.074	.509***	.400**	.624**	.013	.081	.074	.285**	.372**	.312**	.091
pii C0	Sig.	.853	.396	.432	.000	.000	.000	.887	.390	.433	.002	.000	.001	.338
- II - Ca	Pear. Cor.	230*	.642**	209*	.561**	194*	.099	225*	.640**	209*	152	.396**	130	209*
рп•Са	Sig.	.014	.000	.025	.000	.039	.295	.016	.000	.025	.106	.000	.168	.026
nH•	Pear. Cor.	.959**	168	.176	169	.560**	064	.961**	170	.176	.550**	101	.109	.176
TDS	Sig.	.000	.074	.061	.072	.000	.500	.000	.071	.061	.000	.283	.247	.061
pН•	Pear. Cor.	192*	.534**	.468**	.093	064	.564**	184	.541**	.468**	124	.323**	.291**	.468**
NaHCO ₃	Sig.	.041	.000	.000	.325	.496	.000	.051	.000	.000	.188	.000	.002	.000
	Pear. Cor.	139	.271**	125	.920**	112	.262**	136	.269**	125	088	.553**	077	125
	Sig.	.140	.004	.184	.000	.234	.005	.149	.004	.184	.354	.000	.415	.185
C ATDS	Pear. Cor.	.524**	106	.095	102	.998**	.041	.504**	107	.094	.965**	064	.218*	.104
$C_0 \cdot IDS$	Sig.	.000	.260	.317	.278	.000	.665	.000	.255	.318	.000	.499	.020	.270
C ₀ •	Pear. Cor.	109	.336**	.236*	.389**	.052	.999**	104	.339**	.235*	052	.628**	.463**	.255**
NaHCO ₃	Sig.	.249	.000	.012	.000	.581	.000	.270	.000	.012	.580	.000	.000	.006

Table 6.38 cont. Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interactions

		Ca• TDS	Ca• NaHCO3	TDS • NaHCO ₃	pH ∙ C₀ ∙ Ca	рН• С0• TDS	pH • C₀ • NaHCO₃	рН• С₀• TDS	рН • С₀ • NaHCO3	pH • TDS • NaHCO₃	C ₀ • Ca• TDS	C₀ • Ca • NaHCO₃	C₀ • TDS • NaHCO₃	Ca• TDS• NaHCO₃
a	Pear. Cor.	1	128	043	128	.520**	108	.999***	130	043	.564**	077	025	043
Ca • TDS	Sig.		.174	.648	.174	.000	.254	.000	.170	.648	.000	.413	.791	.649
Ca •	Pear. Cor.		1	111	.373**	106	.316**	125	1.000^{**}	111	084	.615***	069	111
NaHCO ₃	Sig.			.240	.000	.261	.001	.184	.000	.240	.371	.000	.467	.241
TDS •	Pear. Cor.			1	116	.120	.257**	035	112	1.000^{**}	024	067	.622**	.999**
NaHCO ₃	Sig.				.220	.205	.006	.710	.236	.000	.796	.479	.000	.000
pН•С₀•	Pear. Cor.				1	103	.368**	125	.372**	116	080	.696**	071	116
Ca	Sig.					.277	.000	.184	.000	.220	.398	.000	.453	.221
$\mathbf{pH} \bullet \mathbf{C}_0 \bullet$	Pear. Cor.					1	.062	.502	107	.119	.952	064	.256	.131
TDS	Sig.						.513	.000	.255	.206	.000	.500	.006	.166
$\mathbf{pH} \bullet \mathbf{C}_0 \bullet$	Pear. Cor.						1	103	.320	.256	050	.599	.495	.277
NaHCO ₃	Sig.							.276	.001	.006	.594	.000	.000	.003
$\mathbf{pH} \bullet \mathbf{C}_0 \bullet$	Pear. Cor.							1	127	035	.542	076	020	035
TDS	Sig.								.179	.710	.000	.423	.834	.711
$pH \bullet C_0 \bullet$	Pear. Cor.								1	112	085	.614	069	112
NaHCO ₃	Sig.									.236	.366	.000	.463	.237
pH•TDS•	Pear. Cor.									1	024	067	.621**	.999**
NaHCO ₃	Sig.										.796	.479	.000	.000
$C_0 \bullet Ca \bullet$	Pear. Cor.										1	051	.021	022
TDS	Sig.											.590	.822	.815
$C_0 \bullet Ca \bullet$	Pear. Cor.											1	040	067
NaHCO ₃	Sig.												.670	.480
$C_0 \bullet TDS \bullet$	Pear. Cor.												1	.659**
NaHCO ₃	Sig.													.000
Ca • TDS •	Pear. Cor.													1
NaHCO ₃	Sig.													

Table 6.38 cont. Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Calcium ions with the independent variables interaction

The ANOVA test, Pearson correlations, and MLR model for the 1 day time study using 5g of hematite H at different initial BPA concentrations of 1.3, 13, and 130 mg/L with different potassium ions concentrations can been seen in Table 6.39, 6.40, and 6.41, respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. From Table 6.40 we can see a positive correlation between C_e with C_0 at a 99% CI. The correlation with the C_0 was strong with the coefficient correlation of 0.999. There were also strong correlations at 99% CI for TDS with KCl and Fe, and between KCl with Fe. The correlation coefficients between TDS with KCl and Fe were 1.00 and 0.929, respectively. The strong correlation between TDS and KCl was expected, since the potassium chloride would dissociate in the aqueous solution. The same is true for the correlation between the TDS and Fe , since increasing the concentration of Fe at a low pH would dissociate more as a result increasing the TDS of the solution.

The MLR model had three independent variables of pH, C_0 , and TDS. We can see the MLR model in equation 14.

$$C_e = -95.433 + 13.532pH + 0.900C_0 - 0.0000636TDS$$
(14)

The strongest factor in the MLR model was C_0 followed by pH and TDS. C_0 and pH had a positive correlation, while TDS had a negative correlation with C_e . The positive correlation for C_0 was expected, since a higher initial concentration would lead to a higher equilibrium concentration. The positive correlation with the pH is also expected, because the low pH had a positive effect on the total adsorption. The negative correlation with TDS was also expected since the increase in the TDS would lead to the salting effect in the solution as a result increased

the total absorbance of BPA onto hematite H. The increase in the TDS would result in a decrease in C_e . The MLR model had a good fit with and a regression coefficient of 0.999. Only 0.1% of total variance could not be explained by the current model. The MLR model was based on 45 different experimental points. The linear relationship between the predicted C_e values versus the experimental C_e values can be seen in Figure 6.8. The linear relationship between the predicted and experimental values had a good fit with a coefficient of regression of 0.997.

Table 6.39 Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at differentBPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions

Source	DF	SS	MS	F	р
Regression	3	127,325.07	42,441.69	13,985.89	0.000
Residual Error.	41	124.42	3.04		
Total	44	127,449.48			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.40 Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions

		Ce	pН	C ₀	TDS	KCl	Fe
C	Pearson Cor.	1	022	.999 **	009	013	113
Ce	Sig.		.884	.000	.956	.931	.459
ъЦ	Pearson Cor.		1	039	.080	.068	.154
рп	Sig.			.799	.603	.658	.312
C	Pearson Cor.			1	.007	.002	100
C_0	Sig.				.963	.988	.512
TDS	Pearson Cor.				1	1.000**	.929**
105						.000	.000
KCI	Pearson Cor.					1	.930 **
KU	Sig.						.000
Fo	Pearson Cor.						1
ге	Sig.						

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

Table 6.41 Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions

Model	Unstandard lel <u>Coefficier</u> β ant -95,433		Standardized	4	Sig	\mathbf{P}^2	Std. Error
Model	β	Std. Error	Beta (β)	ι	Sig.	K	Estimate
Constant	-95.433	25.752		-3.706	.001	0.999	1.74201
рН	13.532	3.654	.018	3.704	.001		
C ₀	.900	.004	1.000	204.780	.000		
TDS	-6.363E-5	.000	017	-3.476	.001		

t = Student t-test, Sig. = Significance Interval.



Figure 6.9 - Predicted and experimental equilibrium BPA concentrations (C_e) for hematite H in the presence of Potassium ions

6.5.3.6 STATISTICAL ANALYSIS FOR HEMATITE H ADSORBENT IN THE PRECENSE OF POTASSIUM IONS WITH INDEPENDENT VARIABLE INTERACTIONS

The ANOVA test, MLR model, and Pearson correlations for the 1 day time study using 5g of hematite H with independent variables interactions at different initial BPA concentrations of 1.3, 13, and 130 mg/L with different potassium ions concentrations can been seen in Table 6.42, 6.43, and 6.44, respectively. Based on the ANOVA analysis the regression model showed to be significant with a p value of 0.000. In the Table 6.43 we can see the positive and negative correlations between all the variables. There was a positive correlation between Ce with all of the 6 different independent variables from the MLR model. The positive regression coefficients between C_e and the independent variables were 0.999, 0.999, 0.444, 0.452, 0.415, and 0.336 for pH • C₀, pH • C₀ • Fe, C₀ • TDS • Fe, pH • C₀ • KCl, C₀ • TDS, and C₀ respectively. Due to the large number of different variables only the variables present in the MLR model will be discussed. The MLR model had 6 different coefficients out of which 5 independent variables presented earlier had positive statistical correlations with the dependent variable C_e at a 99% CI and one of them at 95% CI. The independent variable $C_0 \cdot TDS \cdot Fe$ had a statistical correlation with C_e at 95% CI. Out from the 6 independent variables 5 had strong correlations and one a moderate correlation with C_e.

Even though there were only positive correlations for the C_e with all the 6 independent variables in the Pearson correlations, the MLR model had only 4 independent variables that had a positive correlation with C_e . The strongest correlation parameter from the MLR model with C_e was $C_0 \cdot$ TDS. The positive correlation of $C_0 \cdot$ TDS could be explained that at high TDS the C_0 had to be low in order to have a significant effect on the adsorption. A high C_0 with a high TDS would have only a marginal effect on the adsorption. This was due to the fact that C_0 had a strong positive correlation with C_e , as a result a higher C_0 would lead to a higher C_e . There was also a positive correlation with pH • C_0 and $C_0 • TDS • Fe$, which can be explained as follows. The positive correlation with pH • C_0 is expected, because at high pH the adsorption would not be as strong. As a result at a high pH a high C_0 would not have a significant effect on the adsorption anymore because the high pH is already making the adsorption weak. However, at a low C_0 the high pH would have a lot more significant effect on the adsorption, because the effect of the high pH would be able to affect the adsorption more.

The MLR model had the independent variables of pH • C₀, pH • C₀ • Fe, C₀ • TDS • Fe, pH • C₀ • KCl, C₀ • TDS, and C₀. We can see the MLR model in equation 15.

$$C_e = -0.447 + 0.059 \, pH \bullet C_0 - 0.085 \, pH \bullet C_0 \bullet Fe + 0.0000144 \, C_0 \bullet TDS \bullet Fe - 0.449 \, pH \bullet C_0 \bullet KCl + 0.0000404 \, C_0 \bullet TDS + 0.514C_0$$
(15)

The MLR model had a good fit with a regression coefficient of 1.00. The MLR model was based on 45 different experimental points. The total variance could be explained by the model. The linear relationship between the predicted C_e values versus the experimental C_e values can be seen in Figure 6.9. The linear relationship between the predicted and experimental values had a good fit with a coefficient of regression of 0.997.

Table 6.42 Analysis of Variance (ANOVA) for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction

Source	DF	SS	MS	F	р
Regression	6	127,417.63	21,236.27	25,331.93	0.000
Residual Error.	38	31.86	0.838		
Total	44	127,449.48			

DF = Degree of Freeedom, SS = Sum of Square, MS = Mean Square, F = F-test, and p the significant interval

Table 6.43 Final Model Statistical Information for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction

Model	Unstanda Coeffic	rdized ients	Standardized	f	Sia	\mathbf{R}^2	Std. Error
	β	Std. Error	Beta (β)	t	oig.	K	Estimate
Constant	-0.447	.125		-3.566	.001	1.000	0.91
pН•С ₀	0.059	.017	0.464	3.499	.001		
pH • C ₀ • Fe	-0.085	.011	-0.143	-7.967	.000		
C ₀ • TDS • Fe	1.44E-5	.000	0.132	6.475	.000		
pH • C ₀ • KCl	-0.449	.061	-0.984	-7.325	.000		
$C_0 \bullet TDS$	4.04E-5 .000		0.956	7.064	.000		
C ₀	0.514	.121	0.571	4.264	.000		

t = Student t-test, Sig. = Significance Interval.



Figure 6.10 - Predicted and experimental equilibrium BPA concentrations (C_e) for hematite H in the presence of Potassium ions with independent variables interactions

		Ce	рН	C ₀	TDS	KCl	Fe	pH•C ₀	pH• TDS	pH• KCl	рН• Fe	C ₀ • TDS	C ₀ • KCl	C ₀ •Fe
C	Pear. Cor.	1	022	.999**	009	013	113	.999**	010	014	113	.444**	.454**	.415**
Ce	Sig.		.884	.000	.956	.931	.459	.000	.950	.925	.459	.002	.002	.005
лH	Pear. Cor.		1	039	.080	.068	.154	024	.083	.072	.156	023	036	.066
pm	Sig.			.799	.603	.658	.312	.877	.586	.639	.305	.880	.813	.668
C	Pear. Cor.			1	.007	.002	100	1.000^{**}	.006	.001	100	.465**	.476**	.436**
C0	Sig.				.963	.988	.512	.000	.969	.993	.512	.001	.001	.003
TDS	Pear. Cor.				1	1.000**	.929**	.007	1.000**	1.000**	.929**	.572**	.569**	.595**
100	Sig.					.000	.000	.964	.000	.000	.000	.000	.000	.000
KCI	Pear. Cor.					1	.930**	.002	1.000**	1.000**	.929**	.563**	.561**	.586**
	Sig.						.000	.989	.000	.000	.000	.000	.000	.000
Fe	Pear. Cor.						1	099	.930	.931	1.000	.395	.391	.470
	Sig.							.516	.000	.000	.000	.007	.008	.001
pH•Co	Pear. Cor.							1	.006	.001	099	.465	.475	.438
pii 00	Sig.								.969	.994	.516	.001	.001	.003
"HATDS	Pear. Cor.								1	1.000	.930	.571	.568	.595
pn•1D5	Sig.									.000	.000	.000	.000	.000
	Pear. Cor.									1	.930**	.562**	.560**	.586**
рн•ксі	Sig.										.000	.000	.000	.000
nH • Fe	Pear. Cor.										1	.394**	.391**	.469**
pii it	Sig.											.007	.008	.001
C ₀ • TDS	Pear. Cor.											1	1.000^{**}	.972**
	Sig.												.000	.000
	Pear. Cor.												1	.970 **
	Sig.													.000
	Pear. Cor.													1
$C_0 \bullet Fe$	Sig.													

Table 6.44 Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction

** Correlation is significant at 0.01 level (2-tailed), * Correlation is significant at 0.05 level (1-tailed)

		TDS .	TDS .	KCL	pH•	pH•	pH•	pH •	pH•	pH •	C ₀ •	C ₀ •	C ₀ •	TDS •
		KCI	TDS -	Fo	C ₀ •	$C_0 \bullet$	C ₀ •	TDS •	TDS •	KCl•	TDS •	TDS •	KCl•	KCl•
		KCI	re	re	TDS	KCl	Fe	KCl	Fe	Fe	KCl	Fe	Fe	Fe
C	Pear. Cor.	006	073	077	.442**	.452**	.415**	006	074	077	.364*	.336*	.336*	068
C _e	Sig.	.971	.632	.614	.002	.002	.005	.969	.631	.613	.014	.024	.024	.657
nН	Pear. Cor.	.167	.186	.186	019	032	.069	.169	.187	.187	.073	.090	.090	.192
pm	Sig.	.272	.220	.222	.902	.837	.653	.268	.218	.219	.633	.556	.559	.206
C ₀	Pear. Cor.	.008	062	066	.463**	.474**	.436**	.007	062	066	.383**	.356*	.356*	057
	Sig.	.960	.687	.668	.001	.001	.003	.962	.686	.666	.009	.017	.016	.712
TDS	Pear. Cor.	.990**	.936**	.935**	.572**	.570**	.596**	.990**	.936**	.935**	.590**	.620**	.621**	.934**
105	Sig.	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
KCI	Pear. Cor.	.987**	.935**	.934**	.564**	.561**	.587**	.987**	.935**	.934**	.580**	.611**	.612**	.932**
KCI	Sig.	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
Fe	Pear. Cor.	.928**	.990 **	.990**	.396**	.393**	.470**	.929**	.990 **	.990**	.426**	.492**	.494**	.987**
rt	Sig.	.000	.000	.000	.007	.008	.001	.000	.000	.000	.004	.001	.001	.000
nH•C.	Pear. Cor.	.009	061	065	.463**	.473**	.437**	.009	061	065	.384**	.358*	.358*	055
pii C ₀	Sig.	.953	.693	.673	.001	.001	.003	.955	.691	.672	.009	.016	.016	.718
nH • TDS	Pear. Cor.	.990 **	.937**	.936**	.572**	.569**	.595**	.990**	.937**	.935**	.590**	.620**	.621**	.935**
pii · ibb	Sig.	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
nH • KCl	Pear. Cor.	.988**	.936**	.935**	.563**	.561**	.586**	.988**	.935**	.934**	.580**	.611**	.612**	.933**
piivikei	Sig.	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
pH • Fe	Pear. Cor.	.928**	.990**	.991**	.395**	.392**	.469**	.928**	.990***	.991**	.426**	.491**	.493**	.987 **
*	Sig.	.000	.000	.000	.007	.008	.001	.000	.000	.000	.004	.001	.001	.000
C. TDS	Pear. Cor.	.566**	.420 **	.413 **	1.000^{**}	1.000^{**}	.972 **	.566**	.419 **	.412**	.988 **	.969 **	.969 **	.421**
	Sig.	.000	.004	.005	.000	.000	.000	.000	.004	.005	.000	.000	.000	.004
C. • KCl	Pear. Cor.	.562**	.417**	.410 **	1.000^{**}	1.000^{**}	.970**	.561**	.416**	.409**	.985**	.965**	.965**	.417**
	Sig.	.000	.004	.005	.000	.000	.000	.000	.004	.005	.000	.000	.000	.004
C. Fc	Pear. Cor.	.599**	.487 ^{**}	.481 ^{**}	.972**	.970 ^{**}	1.000^{**}	.599**	.486**	.480 ^{**}	.976**	.991 **	.991**	.488**
C ₀ · re	Sig.	.000	.001	.001	.000	.000	.000	.000	.001	.001	.000	.000	.000	.001

Table 6.44 cont. Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction

		TDS	TDS	KCL	pH •	pH •	pH •	pH •	pH•	pH •	C ₀ •	C ₀ •	C ₀ •	TDS •
					C ₀ •	$C_0 \bullet$	C ₀ •	TDS •	TDS •	KCl •	TDS •	TDS •	KCl•	KCl•
		KU	ге	ге	TDS	KCl	Fe	KCl	Fe	Fe	KCl	Fe	Fe	Fe
TDS • VCI	Pear. Cor.	1	.947**	.945**	.567**	.563**	.600**	1.000**	.946**	.945**	.596**	.628**	.628**	.947**
1D5 • KCI	Sig.		.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000
TDS • Fo	Pear. Cor.		1	1.000**	.421**	.418**	.488**	.947**	1.000**	1.000^{**}	.451**	.514**	.516**	1.000**
105 • Fe	Sig.			.000	.004	.004	.001	.000	.000	.000	.002	.000	.000	.000
KCl • Fo	Pear. Cor.			1	.414**	.411**	.481**	.946**	1.000^{**}	1.000^{**}	.444**	.508**	.509**	1.000**
KCI · FC	Sig.				.005	.005	.001	.000	.000	.000	.002	.000	.000	.000
рН • С ₀ •	Pear. Cor.				1	1.000^{**}	.972**	.567**	.420***	.413***	.989**	.969**	.969**	.422**
TDS	Sig.					.000	.000	.000	.004	.005	.000	.000	.000	.004
$pH \bullet C_0 \bullet$	Pear. Cor.					1	.970**	.562**	.417**	.410***	.985**	.966**	.966**	.418**
KCl	Sig.						.000	.000	.004	.005	.000	.000	.000	.004
nH • C. • Fo	Pear. Cor.						1	.600**	.487***	.480**	.977**	.991**	.991**	.489**
	Sig.							.000	.001	.001	.000	.000	.000	.001
pH • TDS •	Pear. Cor.							1	.947**	.945**	.596**	.627**	.628**	.948**
KCl	Sig.								.000	.000	.000	.000	.000	.000
pH • TDS •	Pear. Cor.								1	1.000^{**}	.450**	.513**	.515**	1.000**
Fe	Sig.									.000	.002	.000	.000	.000
	Pear. Cor.									1	.443**	.507**	.509**	1.000**
pH•KCI•Fe	Sig.										.002	.000	.000	.000
$C_0 \bullet TDS \bullet$	Pear. Cor.										1	.985**	.984**	.452**
KCl	Sig.											.000	.000	.002
C . TDC . Fe	Pear. Cor.											1	1.000**	.515**
$C_0 \cdot IDS \cdot Fe$	Sig.												.000	.000
	Pear. Cor.												1	.517**
$C_0 \bullet KCI \bullet Fe$	Sig.													.000
TDS • KCl •	Pear. Cor.													1
Fe	Sig.													

Table 6.44 cont. Pearson correlation between independent variables for Hematite H using 5g to 50 mL at different BPA initial concentration of 1.3, 13, and 130 mg/L in the presence of Potassium ions with the independent variables interaction

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CHAPTER VII

REMOVAL OF HYDROQUINONE FROM WATER USING IRON OXIDES ADSORBENTS

7.1 INTRODUCTION

Phenolic compounds such as hydroquinone (HQ) have been introduced to the environment through many industrial sources. HQ it is widely used in the production of rubber, pharmaceutical, and food industry. HQ has been also used as a reducing agent in the photographic industry and as a depigmenting agent for the dermatologic preparation for skin blemishes treatment (Meng, et al. 2004). About 33% of its use is in the photographic industry that includes the black and white photographic film, hospital x-ray films, and lithography (UNEP, 2007). For the stabilization of monomers it is used as intermediate about 25%. For the chemical conversion to stabilizers such as motor oils, fuels, paints, varnishes and for antioxidants in industrial fats and oils it is used about 12%. For the manufacture of rubber HQ is used as an intermediate for the synthesis of antioxidants and antiozonants about 25% (UNEP, 2007).

HQ may be released in the environment through the degradation of other phenolic compounds such as BPA or phenol. In Chapter 5 we identified HQ as a byproduct of BPA degradation in the environment through natural or anthropogenic processes. As in the case of BPA, microbial activity is capable of degrading phenol to HQ by *Mycobacterium* sp. B-394 (Yoshida et al., 1990). The aquatic toxicity of HQ is the most critical due to the reported side effects at low concentration of 0.05 to 0.355 mg/L in the aqueous medium to fresh water fish, Daphnia, and algae. The US EPA had reported a predicted no effect concentration (PNEC) at 1 μ g/L for fresh water and 8 μ g/L for salt water species. Due to the limited information on aquatic toxicity of HQ the United Nations Environment Programme (UNEP) had derived an PNEC of 0.44 μ g/L. Based on the evaluation of 66,000 users and 16,000 processors of hydroquinone in the

USA only few had been found to have higher discharge value above the PNEC level. Based on the Probabilistic Dilution Model (PDM 3) program only 0.5 days per year had been found to have a discharge higher than the concern concentration of $1\mu g/L$ and 3 days per year for the 0.44 $\mu g/L$. The discharge estimated concentration had to be $180\mu g/L$ in order to be above the level of concern. As a result the concerned for the aquatic system would be only to a site specific condition. The toxicity for mammals has been associated only at high doses of HQ and found to be strain and species specific and minimized to humans due to reduced exposure. The only concern of HQ to humans had been identified from misuse of dermal HQ-containing skin products.

Based on the calculated Fugacity Level I about 99.6 % of HQ would distribute itself in water followed with 0.21 % in air, 0.06 % in sediment, and finally 0.01 % in soil (UNEP, 2007). The distribution of HQ and BQ in the environment is controlled by physical chemical properties, which can be seen in Tables 7.0 and 7.1 for HQ and BQ, respectively. Also the chemical structure of HQ and BQ can be seen in Figure 7.0 and 7.1, respectively.

Physicochemical properties of Hydroquinone		Reference
Case Number	123-31-9	UNEP, 2007
Formula	$C_6H_6O_2$	UNEP, 2007
Molecular Weight g mol ⁻¹	110.11	Alfa Aesar MSDS, 2012
Density	1.341 g/cm^3	UNEP, 2007
Melting point	169 ⁰ C	UNEP, 2007
Boiling point	286 ⁰ C	UNEP, 2007
Vapor Pressure @25 ⁰ C	2.34 x 10-3 Pa	UNEP, 2007
Aqueous solubility $(25^{\circ}C)$	70 g/L	Alfa Aesar MSDS, 2012
log K _{OW} Calculated	0.50-0.61	UNEP, 2007
pK_{a1} and pK_{a2}	10.1and 11.66	LaKind and Stone, 1989

Table 7.0 Physicochemical properties of Hydroquinone (HQ).

Physicochemical properties of Benzoquinone		Reference
Case Number	106-51-4	NIOSH, 2010
Formula	$C_6H_4O_2$	NIOSH, 2010
Molecular Weight g mol ⁻¹	108.09	NIOSH, 2010
Density	1.32 g/cm^3	NIOSH, 2010
Melting point	240 ⁰ F	NIOSH, 2010
Boiling point	180 ⁰ C	Alfa Aesar MSDS, 2011
Vapor Pressure @25 ⁰ C	0.1 mm Hg	NIOSH, 2010
Aqueous solubility (25°C)	1.5 %	Fisher Scientific MSDS, 2009
$\log K_{\rm OW}$	0.20	NIOSH, 2010

Table 7.1 Physicochemical properties of Benzoquinone (BQ).



Figure 7.0 – Hydroquinone



Figure 7.1 – Benzoquinone

The HQ use in agriculture had been promoted by few researches due to its ability to promote increase crop yield when applied with urea nitrogen fertilizer (Xiaoyan et al., 1993). When a concentration of 533.3 ng/g of HQ was added to the soil, only 0.25% was absorbed as HQ in the rice plant and 58% was degraded in the soil (Xiaoyan et al., 1993). The biodegradation of HQ has found to be readily biodegradable, which means that about 80% or more will be biodegraded in 28 days. In the past decade more research had been conducted for the detection and removal of HQ from aqueous medium. Based on the current research, it was found that HQ could be a possible byproduct of BPA through advanced oxidation processes (AOPs) such as indirect photolysis with H₂O₂ (Neamtu and Frimmel 2006), indirect photolysis with Fenton's reagent (Katsumata et al., 2004), indirect photolysis with natural humic substances (Zhan et al., 2006), photocatalysis with TiO2 suspension (Fukahori et al., 2003, Horikoshi et al., 2004), ozonation (Gultekin and Ince, 2007), and electrochemical oxidation generated Fenton's reagent (Gozmen et al., 2003). As a result the remediation or degradation of HQ had been studied by anaerobic degradation (Latkar et al., 2003), electrochemical oxidation (Nasr et al., 2005), oxidation by a nonheme iron(IV)-oxo species (Nehru et al., 2008), oxidation in the presence of iron oxide (Shin et al., 2005), abiotic degradation and mineralization through catalytic oxidation in the presence of birnessite(δ -MnO₂) (Chien et al., 2009), oxidation in the presence of H₂O₂ catalyzed by transitional metal ions (Meng et al., 2004), anodic oxidation (Kobayashi et al., 1994), oxidation by acrylic resins catalyzed by Cu(II) ions (Jakubiak et al., 2005), oxidation by aqueous suspensions of manganese(IV) dioxide (MnO_{1.97}) and cobalt(III) oxide (CoOOH) (Stone and Ulrich, 1989), electrocatalytic oxidation by order mesoporous carbon (Hou et al., 2008), adsorption on Pd(111) (Kim et al 2006), adsorption by activated carbon (Mohamed et al., 2006), adsorption by organically modified bentonites (Yildiz et al., 2005), and adsorption by hematite

(Stack et al., 2004a; 2004b). The detection of HQ by various techniques had been done with high performance liquid chromatography (HPLC), voltammetry, gas chromatography-mass spectrometry (GC-MS), UV-vis spectrometry (Sirajuddin et al., 2007), and magnetic surface modified core-shell (Fe₃O₄-SIO₄) biosensor (Zhang et al., 2007).

The oxidation of HQ leads to the formation of p-benzoquinone (BQ) through different processes such as biodegradation or reaction with different minerals or oxidative chemicals. The formation of BQ was observed during the current adsorption studies done with two different magnetites such as M1 and M2. Magnetite M2 had the highest BQ production and the results will be discussed in the results and conclusions sections of the Chapter 7. The HQ is thermodynamically less stable than the quinones (Qs) at neutral pH. HQ is slowly oxidized to BQ in buffered aqueous solution via a semiquinone (SQ) radical (Soucek et al., 2000). The SQ radical is unstable intermediate for enzymatic and spontaneous quinone interconversions (O'Brein, 1991). The Cu(II) mediated oxidation of HQ to BQ can produce DNA damage in bacteria and happens according to Figure 7.2.



Figure 7.2 Conversion of HQ to BQ with Cu(II) mediation. (Sirajuddin et al., 2007)

Sirajuddin et al., 2007 found that the oxidation of HQ (1µg/mL) in the presence of oxygen gas (O₂) occurs and only SQ is formed. However, Li et al., 1996 and Zhang et al., 1994 found that HQ undergoes auto oxidation to SQ radical and further to BQ under air saturated buffered solution. After the addition of potassium permanganate KMnO₄ at a concentration higher than 1 µM both HQ and SQ are further transformed completely to BQ. In the presence of 0.1 to 0.5 µM KMnO₄ the concentration of both SQ and BQ increases with a decrease in the HQ. The species responsible for the oxidation of HQ to BQ happens due to the presence of permanganate Mn(VII) which is reduced to a lower state according to Figure 7.3.



Figure 7.3 Proposed mechanisms for conversion of HQ into SQ and BQ. (Sirajuddin et al., 2007)

Stone and Ulrich, 1989 also found that BQ is produced during the reductive dissolution of Mn(IV) dioxide and Co(III) oxide particles by HQ. The presence of hematite nano particles produced in the laboratory had found to react with HQ leading to the production of BQ with further reduction until the formation of carbon oxide (CO), carbon dioxide (CO₂), and water (H₂O) (Shin et al., 2005). The BET surface area of the hematite was 140 m²/g and the particle size between 6 to 20 nm and after the reaction the BET surface area was reduced to zero and the particle size 4 to 35 nm. The degradation of HQ in the presence of hematite is seen in Figure 7.4.



Figure 7.4 Degradation of HQ in the presence of hematite. (Shin et al., 2005)

The interaction between HQ and different iron oxides had been investigated previously since 1988, when the adsorption of HQ to the iron oxide surface was explained and followed electron transfer leading to the formation of SQ radical and the reduction of iron (Kung and McBride, 1988, 1989). The SQ radical then undergoes desorption with reduced iron dissolution. The steps are repeated after which the SQ radical is further transformed to BQ with a further iron reduction. The proposed stoichiometric reaction between HQ and hematite is seen in equation 1 (Kung and McBride, 1988, 1988).

$$\alpha - Fe_2O_{3(s)} + HQ + 4H^+ \to 2Fe_{(aq)}^{2+} + BQ + 3H_2O$$
(1)

Stack et al., 2004a studied the adsorption and reaction of HQ with a hematite having a BET surface area of $1.52 \text{ m}^2/\text{g}$ (Stack et al., 2004a; 2004b). The pathway proposed had been an reversible oxidation of HQ (QH₂) through a SQ radical (QH) to BQ (Q) by the loss of two electrons and two protons, which could happen through four different pathways depending on the order of proton and electron loss. The pH has a strong effect on the oxidation of HQ to BQ, which occurs more rapidly under alkaline conditions (Sirajuddin et al., 2007). We can see the proposed pathway of oxidation in Figure 7.5. The top pathway from Figure 7.5 for pHs lower than 5.0 happens with the electron loss first followed by the proton loss and repeated twice. For the bottom pathway from Figure 7.5 for the pHs greater than 5.0 happens with the loss of proton

followed with the loss of electron and repeated twice. All of these pathways can occur as long as SQ is produced.



Figure 7.5 Pathways for oxidation of HQ through SQ to BQ. Oxidation proceeds via the top pathway for pHs < 5, and the bottom pathway for pH > 5 (Stack et al., 2004a)

7.2 ADSORPTION OF HYDROQUINONE

The adsorption of HQ to hematite (Stack et al., 2004a), activated carbon (Mohamed et al., 2006), and organically modified bentonites (Yildiz et al., 2005). The non-activated carbon (CZ) was obtained in the laboratory by carbonizing sawdust at 875K in nitrogen atmosphere. The carbon adsorbent was than activated using sulfuric acid H_2SO_4 with four different ratios of acid

to sawdust (w/w) of 3:1, 4:1, 5:1, and 6:1 and denoted CSI, CSII, CSIII, and CSIV, respectively. The BET surface were were 43, 115, 152, 182, and 210 m2/g for CZ, CSI, CSII, CSIII, and CSIV, respectively. The experiments were conducted by the shaking of 0.25 g of the carbon adsorbent with 50 mL of the aqueous solution at different concentrations at 298 K, for a period of 48h to reach the equilibrium. We can see the adsorption isotherm of HQ on the five different carbon adsorbents on Figure 7.6 (Mohamed et al., 2006).



Figure 7.6 Adsorption isotherms of hydroquinone on the carbonized product (CZ) and sulfuric acid-activated carbons at 298 K. (Mohamed et al., 2006)

From Figure 7.6 we can see that the BET surface area is not the only important factor that influences the adsorption of HQ onto the carbon adsorbent. The non-activated CZ performed better than three activated carbons that had higher BET surface areas. As a result the surface area of the carbon adsorbent plays a significant role on the adsorption. From the FTIR spectra there was no clear connection made for CZ and CSIV.

The adsorption of HQ was done on two different organically modified bentonites (organobentonites) called ODTMA-B and HDTMA-B, which were synthesized using octadecyltrimethyle ammonium bromide (ODTMAB) and hexadecyltrimethyle ammonium bromide (HDTMAB) (Yildiz et al., 2005). The ODTMA-B and HDTMA-B had the BET surface area of 28.92, and 35.68 m²/g, respectively. The total organic carbon content for ODTMA-B and HDTMA-B was 24.28 and 19.88%, respectively. The experiments used 0.2g of adsorbent in a 250 mL of Erlenmeyer flask in a 50 mL aqueous solution with initial concentrations of HQ of 10 to 600mg/L was shaken at 150rpm for a period of 18h at two different temperatures of 298 K and 313 K. The influence of pH was also investigated for the pH of 3.0, 6.0, and 11.0. The sorption of HQ on both of the organobentonites can been seen in Figure 7.7.



Figure 7.7 Sorption of hydroquinone by ODTMA-B and HDTMA-B at various pH (dotted: ODTMA-B, line: HDTMA-B). (Yildiz et al., 2005)

From the Langmuir isotherms we can see the maximum adsorption capacities q_m (mg/g) found for the HDTMA-B 22.52, 17.89, and 8.29 for pH 3.0, 6.0, and 11.0, respectively. For the

ODTMA-B the maximum adsorption capacities q_m were 20.50, 14.22, and 5.40 for pH 3.0, 6.0, and 11.0, respectively. As a result an increase in the adsorption capacities was observed with a decrease in the pH. There was also an increase in the adsorption with an increase in temperature for both adsorbents.

For the adsorption of HQ onto the hematite H there could be two different pathways one through a bridging oxygen and the other by π -backbonding complex, which can be seen in Figure 7.8 a and b. The hematite structure is composed of coexisting domains that have Fe- and O-termination (Eggleston et al., 2003).



Figure 7.8 Illustration o conceivable adsorption behaviors on hematite. Iron atoms are dark grey, oxygen is white, carbon is black, and protons are light gray. a) Chemisorption via bridging oxygen. b) Chemisorption via a π -backbonding complex. (Stack et al., 2004a)

At a neutral pH of 7.0 it was found that HQ can absorb onto the hematite through bridging oxygen (Kung and McBride, 1988). For the adsorption to take place first HQ has to lose one of its protons which are very unlikely under acidic conditions. The loss of proton could happen through reverse oxidation for a pH under 5.0 as seen in Figure 7.5. Strong π -backbonding complex have found to form with metals that have electrons on the d⁶ shells. Iron (III) had an d⁵ electronic structure which is not expected to create an π -backbonding complex with HQ, however the iron (II) has a d⁶ electronic structure and is more likely to form π -backbonding complex with HQ. Stack et al., 2004a found that HQ and BQ were able to adsorb onto the hematite surface at packing density of 1.1 HQ/nm². The ferrous iron was also found for not being retained on the surface of hematite, as a result is was concluded that the metal detachment would not be a liming step. As mentioned earlier the adsorption of HQ to the hematite on the iron surface site is followed by electron transfer reaction, which leads to the initial formation of SQ. Then through repeated steps of adsorption and desorption of HQ and SQ the formation of BQ takes place plus the dissolution of ferrous iron.

7.3 RESEARCH OBJECTIVE

The objective of the research presented in Chapter 7 was to evaluate the adsorption of HQ and BQ onto two different magnetites M1 and M2. The magnetites were the same used for the removal of BPA. HQ and BQ are byproducts of BPA through different processes as mentioned earlier in this chapter; as a result their fate in the presence of the adsorbent is important. During this research the adsorption of HQ and BQ as a function of time was investigated and the possible reaction with the magnetite. Based on the literature review the adsorption and reaction with the two iron oxides M1 and M2 is expected. The extraction of HQ and BQ from the adsorbents was also investigated using different solvents and time periods. The extraction is very important step for the calculation of mass balance, which helps us to better understand the fate of the adsorbate HQ and BQ.

7.4 MATERIALS AND METHODS

7.4.1 CHEMICALS

All the chemicals used for these experiments are presented in Table 7.2.

Table 7.2 Chemicals

Chemical	Specification	Source
Methyl tert-butyl ether	HPLC grade	Fisher Chemicals, Fairlawn, NJ
(MTBE)		
Acetone	Certified ACS	Fisher Chemicals, Fairlawn, NJ
2-Propanol	Certified ACS	Fisher Chemicals, Fairlawn, NJ
6N Hydrochloric Acid (HCl)	ACS Reagent grade	RICCA Chemical Company,
		Arlington, TX
1,4-Benzoquinone	\geq 98 % , Reagent Grade	Sigma-Aldrich, St.Louis, MO
Hydroquinone	\geq 99% , Reagent Plus	Sigma-Aldrich, St.Louis, MO
Magnetite (M1) Fe ₃ O ₄ ,	Laboratory Grade	Fisher Chemicals, Fairlawn, NJ
Magnetite (M2) Fe ₃ O ₄ ,	325 Mesh Powder	Alfa Aesar, Ward Hill, MA

7.4.2 TIME STUDY

The time studies were done with two adsorbents (M1 and M2) and a solid to solution ratio of 5g:50mL. The experiments were dividing in two major parts with the first part of the study being an initial 7 days study done under oxic and anoxic conditions. Under oxic conditions it is more favorable for the HQ to degrade to BQ. The experiments were carried on with deionized water (DI) in a 125 mL serum bottle. A control blank system with no adsorbent was also used. The purpose of the blank was to determine if any HQ transferred from the water phase to the air phase or if there was any major adsorption to the glass walls of the serum bottle. After the addition of water, the serum bottles were capped with butyl rubber septa and crimped with aluminum seals for the oxic system. For the anoxic system after the addition of adsorbent the serum bottles with the aqueous solution were placed in the controlled atmospheric chamber for the removal of oxygen from the head space. The head space of the serum bottles was replaced

with nitrogen (N₂). The serum bottles were than shaken and placed in a rotating tumbler at 16 rotation per minute (rpm) in the dark for the purpose of mixing at 25 0 C. The experiments were carried out initially for a period of 1, 3, 7 days for the oxic and anoxic system. After the first part of the experiments were over it was determined that the anoxic system is more suitable, since there was less degradation of HQ and BQ. A longer time study was performed with both magnetites for a period of 1, 3, 5, 7, 10, 14, 19, 22, 26 and 30 days. All the points of the data were done in triplicates and a standard deviation error was obtained for each point from the data. The total dissolved solids (TDS), pH, soluble iron concentration, alkalinity, and chemical oxygen demand (COD) was monitored for both the oxic and anoxic systems. In addition for the anoxic system the oxidation reduction potential (ORP) was also analyzed. For both time study experiments 1day extraction was performed using acetone to monitor the mass balance. The data were fitted using the assumption that follows a completely mixed batch reactor (CMBR) as a results the equations for zero, first and second order were obtained and are presented in equations 1, 2, and 3, respectively (Crittenden, 2005).

$$C = C_0 - kt \qquad 1$$

$$C = C_0 e^{-tk} \qquad 2$$

$$\frac{1}{C} = \frac{1}{C_0} + kt \qquad 3$$

where, C is the equilibrium HQ and BQ concentration (μ mol/L), C₀ is the initial HQ and BQ concentration (μ mol/L), t is the time of adsorption (days), and k is the adsorption rate constant having different units, depending on the order of the equation, with units of mole/L•s, s⁻¹ and L/ mole•s for zero, first and second order, respectively. To obtain a linear relationship the zero order was ploted as C vs time, first order as ln(C) vs time, and second order as 1/C vs time. For

all the graphs the slope was equal to k. The data were analyzed using Statistical Package for the Social Sciences (SPSS) and correlations parameters such as coefficient of determination R^2 and statistical significance value p were obtained.

7.4.3 EXTRACTIONS STUDY

Based on the results obtained from the time studies of 7 and 30 days and the literature the reaction between the HQ and BQ with the adsorbents was expected to take place. Based on the 1 day acetone extraction performed on both of the adsorbents there was a loss in the total HQ and BQ in the system from the possible reaction with the iron oxides. To better investigate this, there were a series of different adsorption, performed on the two adsorbents. In the first part of the experiments the extraction of HQ and BQ was done using DI water at pH 2.0 followed by a second day extraction with acetone. In the second part seven different extraction experiments cases, Case A to G, were done on magnetite M2 only, since it was the adsorbent that performed the best. For five of the seven cases the extraction was performed for a period of 3 days. For case A the extraction was done with DI water at pH 1 first, followed with extraction of acetone, for case B the acetone extraction was first followed by the extraction with DI water at pH 1.0 and for the cases D to G there was a three day extraction done with acetone, DI water at pH 7.0, 4.5, and 2.0 for case D, E, F, and G, respectively.

7.4.4 ADSORBENT DOSAGE STUDY

The last sets of experiments were done with the purpose of investigating the effect of adsorbent dosage on the adsorption. Three different cases were performed with two oxic and one anoxic condition. For the oxic conditions there was a test done at initial HQ concentration of 110.11 µmol/L with 0.5 and 5g of adsorbent to 50 mL of solution. For the second set of

experiments there was 0.5g, 1.5g, and 5g of adsorbent to 150 mL of aqueous solution at a initial HQ concentration of 11.01 μ mol/L. Finally the last sets of experiments were done using 1g and 5g of adsorbent to 150 mL of solution under anoxic conditions.

There was other experiments done to investigate the effect of ionic strength and different solvents such as isopropanol (2-Propanol) and MTBE were investigated for the extraction of HQ and BQ from the adsorbents. The results of these experiments will be briefly discussed in the results section.

7.4.5 CONTROL ATMOSPHERE CHAMBER

The control atmosphere chamber was used for the setup of anoxic studies and for the analysis of ORD and pH. The control atmosphere chamber was used in order to replace the head space in the serum bottles for the anoxic systems with nitrogen gas (N_2). The samples were subject to vacuuming and purging using nitrogen gas by applying 12 cycles. After the purging was complete the samples were then sealed with butyl rubber septa and crimped with aluminum seals.

For the ORD and pH analysis for the anoxic samples, the serum bottles were place in the control atmospheric chamber and 10 cycles of vacuuming and purging with nitrogen gas was performed, after which the aluminum seals were removed. After the ORP and pH analysis the rest of analysis were performed outside the control atmospheric chamber.

7.4.5.1 ROUTINE ANALYSIS

The serum bottles were removed from the rotating tumbler, and then a 50 mL of the sample was transferred into 50mL Teflon centrifuge tube and centrifuge for 10 minutes at 7100 rpm using an Eppendroft centrifuge 5810R. The solution was then transferred in two different

vials. Approximately 15mL of the solution was transferred into a 20 mL glass vial; another 7 mL was transferred in another 20 mL vial, and the rest in a 50 mL glass vial. The 20 mL vial with the 7 mL solution was acidified with 3 drops of HNO₃ acid for soluble iron analysis. The 20 mL vial with 15 mL solution was used for the measurement of total dissolved solids and pH for the oxic system, and the rest of the solution from 50 mL vial were used for the HQ, BQ, and alkalinity analysis.

7.4.5.2 TDS, pH, and ALKALINITY ANALYSIS

The analysis of total dissolve solids (TDS) was done using Orion conductivity meter model 150 with an Orion conductivity cell 013005D and the pH analysis was performed using Thermo Orion ph/mV/temperature meter 720 using an Orion comb. pH probe model 915600 from the 20mL vial for both oxic and anoxic system. The instrument was calibrated for the pH using Fisher Scientific pH standards of 4, 7, and 10. The calibration of TDS was done using Fisher Scientific TDS standards with a conductivity of 1413 μ s and 12.9 ms from Fisher Scientific. The alkalinity was performed by titration using a 0.02 H₂SO₄ titration solution.

7.4.5.3 SOLUBLE IRON ANALYSIS

The analysis of soluble iron was performed using flame atomic adsorption spectrometry (FAAS). A 6-point calibration curves used the standard Fe concentrations of 0.5, 1, 2, 3, 4, and 5 mg/L were freshly prepared for each day of injection in a DI water aqueous solution of 2% HNO₃.

7.4.5.4 LIQUID -LIQUID EXTRACTION (LLE)

The sample was diluted in a volumetric flask of 25mL or higher. Exactly 10 mL of samples were transferred from the 40 mL vial or from the diluted sample in the volumetric flask

into a 15mL glass test tube. After the water sample was transferred in the glass test tube, 20 μ L of 2,4,6-tribromophenol (TBP) from a stock solution of 1,000 ppm prepared in acetone was added using a 250 μ L syringe. After adding one drop of concentrated hydrochloric acid (HCl) into the test tube, the test tube was then closed and shaken gently twice. After the shaking of test tubes, 2 mL of methyl *tert*-butyl ether (MTBE) was added. The test tube was then shaken for 30 seconds vigorously and then followed by a 2 minutes and 30 seconds of slow and constant mixing. After separation of the two phases, 1 mL of the MTBE from the top phase was pipetted using an Eppendorf pipette into a 2 mL gas chromatography (GC) vial.

7.4.5.5 HQ and BQ ANALYSIS

The MTBE sample from the LLE step was stored in the 2 mL GC vial was analyzed on a Agilent Model 6890 GC. The GC was equipped with a flame ionization detector (FID). The injection was done using an auto sampler by direct injection of 1.0 μ L of MTBE sample at an inlet temperature of 250 °C, while the detector temperature was maintained at 300 °C. For the separation of HQ, BQ, and TBP, a DB-5 (J&W) widebore capillary GC column with dimensions of 30m x 320 μ m x 0.25 μ m was used. The oven temperature in the beginning was set at 60 °C and hold at that temperature for 2 minutes. The temperature was then ramped from to 180 °C at 18 °C /min and held at 180 °C for 1 minute. Helium was the carrier gas with a flow rate of 6.0mL/min at an inlet pressure of 25psi. The other gasses used were dry grade air, hydrogen (H₂), and the makeup gas nitrogen (N₂). The flow of the air was 400 mL/min, nitrogen flow was 10 mL/min, and the hydrogen flow of 35 mL/min. The total program run was for 9.67 minutes.

The individual HQ and BQ samples were identified by the retention time from the HQ and BQ standard calibration that were prepared directly in MTBE. The HQ and BQ calibration

was done using an internal standard calibration with the HQ and BQ concentrations of 0.1, 0.2, 0.5, and 1 mg/L. TBP was used as an internal standard with a concentration of 2 mg/L.

For the analysis of HQ and BQ from the acetone and water extracts different procedures were followed. For the water extracts the procedure was the same as for the water samples. The acetone extracts were injected using an HQ and BQ internal standard calibration with the HQ and BQ concentrations of 0.2, 0.4, 0.8, and 1 ppm. TBP was used as an internal standard with a concentration of 10 ppm. The acetone extracts and calibration samples were diluted in a volumetric flask in acetone and transferred into 2 mL gas chromatography (GC) vials. All the sample points of the data were done in triplicates and HQ standard deviation was obtained for each sample.

7.5 RESULTS AND DISCUSSION

The initial experiments were divided in two different parts, one for oxic system and the other one for anoxic system. The results for the oxic system showed a total decrease of about 59%, and 66% for magnetite M1 and M2, respectively. There was a total loss of 6.6 % in the blank system after 7 days. We can see the total concentration of HQ, BQ, and HQ plus BQ in Figure 7.9 (a) through (c). The water and acetone distribution for both magnetite M1 and M2 can be found in Figure 7.10. We can see from Figure 7.10 that there is a loss in the total mass of HQ and BQ for 1day, 3days, and 7 days for both magnetites believed to be due to the reaction with the adsorbent. The tabulated values of water concentrations and acetone extracts of HQ, BQ and HQ plus BQ could be seen in Tables 7.3 and 7.4 for magnetite M1 and M2, respectively. We can see the fitting for zero, first, and second order for total HQ and BQ for magnetite M1 and M2 in Figure 7.11 and 7.12, respectively. Based on the coefficient of determination R² and significant

interval p, we can see that for both magnetite M1 and M2 the adsorption followed second order kinetics. All the linear regression parameters along with the coefficient of determination R^2 and significant interval p could be found in Table 7.5 for both magnetite M1 and M2.

The pH, TDS, alkalinity, and soluble iron are presented in Table 7.6, 7.7, 7.8, and 7.9, respectively. The initial pH of the solution was about 6.6 and remained constant for the blank system to about 6.7. For magnetite M1 the pH decreased to about 4.2 and for M2 it increased to about 7.1. The TDS for the initial solution and blank remained the same to 1mg/L, however for magnetite M1 it increased to about 685 mg/L and for M2 to about 38 mg/L. Because of the low pH for magnetite M1 alkalinity could not be calculated. For magnetite M2 there was an increase in alkalinity from 2.67 mg/L to 7.33 mg/L as CaCO₃ after 7 days. The soluble iron increased significantly only for Magnetite M1 as expected due to the low pH to about 41 at 7days.



Figure 7.9 Total concentration as a function of time for the oxic study: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Hydroquinone (HQ), b) Benzoquinone (BQ), and c) HQ+BQ



Figure 7.10 Total concentration partition for the oxic study as a function of time: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) 1 Day, b) 3 Days, and c) 7 Days


Figure 7.11 Total HQ+BQ as a function of time for the oxic study for Magnetite M1: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order



Figure 7.12 Total HQ+BQ as a function of time for the oxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order

Sample	DL	Magnetite (M1)							
	Blank HO+BO	Solution			Acetone Extracts				
	11Q12Q	HQ	BQ	HQ+BQ	HQ	BQ	HQ+BQ		
0 Days	90.49	78.56	11.94	90.49					
1 Day	92.51	45.50	19.24	64.74	2.18	0.83	3.01		
3 Days	98.67	38.23	14.99	53.22	2.09	0.74	2.83		
7 Days	84.55	19.53	15.08	34.61	1.36	0.93	2.28		

Table 7.3 Total HQ+BQ concentration (µmol/L) as function of time for oxic system for magnetite (M1):

Table 7.4 Total HQ+BQ concentration (µmol/L) as function of time for oxic system for magnetite (M2):

c				Magne	etite (M2)		
Sample	Blank HO+BO	Solution			Acetone Extracts		
		HQ	BQ	HQ+BQ	HQ	BQ	HQ+BQ
0 Days	90.49	78.56	11.94	90.49			
1 Day	92.51	10.89	45.43	56.32	1.99	0.74	2.74
3 Days	98.67	9.45	36.17	45.62	1.82	0.74	2.56
7 Days	84.55	6.45	23.31	29.76	0.27	1.11	1.38

Table 7.5 Total BPA concentration linear regression parameters for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Sorbent	Equation	$\mathbf{y} = \mathbf{z}$	ax +b	\mathbf{P}^2	n
Sorbent	Fit	а	b	K	Р
Magnetite (M1)	Zero Order	-6.838	81.61	0.892	0.056
Magnetite (M1)	First Order	-0.119	4.416	0.962	0.019
Magnetite (M1)	Second Order	0.002	0.012	0.990	0.005
Magnetite (M2)	Zero Order	-7.228	77.074	0.801	0.105
Magnetite (M2)	First Order	-0.137	4.351	0.917	0.042
Magnetite (M2)	Second Order	0.012	0.003	0.980	0.010

Before		After									
Blank	Timo	Blank		Magnet	Magnetite (M1)		Magnetite (M2)				
pН	1 11110	pН	Stdv	pН	Stdv	pН	Stdv				
6.612	1Day	6.709	0.137	4.319	0.033	7.103	0.009				
6.624	3Days	6.728	0.123	4.190	0.024	7.116	0.014				
6.542	7 Days	6.428	0.045	4.198	0.006	7.077	0.076				

Table 7.6 Solution pH values for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Table 7.7 Solution TDS (mg/L) values for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution

Before		After									
Blank	Timo	Bla	nk	Magnetite (M1)		Magnetite (M2)					
TDS	1 mie	TDS	Stdv	TDS	Stdv	TDS	Stdv				
1	1Day	1.000	0.000	670.667	1.155	37.333	0.577				
1	3Days	1.000	0.000	689.333	2.517	38.667	0.577				
1	7 Days	1.000	0.000	689.667	4.509	37.667	0.577				

Table 7.8 Alkalinity for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Before		After								
Blank	Time	Bla	nk	Magnetite (M2)						
Alk	1 mie	Alk	Stdv	Alk	Stdv					
2.67	1Day	2.67	0.00	5.333	0.667					
2.67	3Days	2.67	0.00	7.222	0.192					
2.67	7 Days	2.67	0.00	7.333	0.000					

Table 7.9 Solution soluble iron (Fe mg/L) for the oxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution

Before		After								
Blank	Time	Magneti	ite (M2)							
Fe	Time	Fe	Stdv	Fe	Stdv					
0.000	1Day	30.123	0.174	0.030	0.000					
0.000	3Days	36.333	1.392	0.040	0.000					
0.000	7 Days	40.993	0.813	0.037	0.006					

For the anoxic system there was a total decrease for HQ and BQ of about 52%, 72% for magnetite M1 and M2, respectively. There was no loss in the blank system after 7 days. We can see the total concentration of HQ, BQ, and HQ plus BQ in Figure 7.13 (a) through (c). The total water and acetone distribution for both magnetite M1 and M2 can be found in Figure 7.14. We can see from Figure 7.14 that there is a loss in the total mass of HQ and BQ for 1day, 3days, and 7 days for both magnetites, which was believed to be due to the reaction with the adsorbent. The tabulated values of water concentrations and acetone extracts of HQ, BQ and HQ plus BQ could be seen in Tables 7.11 and 7.12 for magnetite M1 and M2, respectively. The fitting for zero, first, and second order for total HQ plus BQ for magnetite M1 and M2 are presented in Figures 7.15 and 7.16, respectively. Based on the coefficient of determination R^2 and significant interval p we can see that for both magnetite M1 and M2 the adsorption followed better a second order kinetics. All the linear regression parameters along with the coefficient of determination R^2 and significant interval p could be found in Table 7.10 for both magnetite M1 and M2. For the anoxic system the total oxygen demand (COD) was also analyzed for magnetite M2. The COD could not be established for aqueous solution that was used in the contact with magnetite M1, because of the high TDS values of the aqueous solution. The total COD as a function of time can be seen in Figure 7.17, where we can see there was a 75 % decrease in the total COD. From Figure 7.18 we can see that the removal of total COD from the aqueous solution follows better a first order kinetic model.

The pH, TDS, alkalinity, soluble iron, and oxidation reduction potential (ORP) are presented in Table 7.13, 7.14, 7.15, 7.16, and 7.17 respectively. The initial pH of the solution was about 6.6 and increased for the blank system to about 7.3. For magnetite M1 the pH decreased to about 4.3 and for M2 it increased to about 7.0. The TDS for the initial solution and

blank remained the same to 1mg/L, however for magnetite M1 it increased to about 700 mg/L and for M2 to about 38 mg/L. Because of the low pH for magnetite M1 alkalinity could not be calculated. For magnetite M2 there was an increase in alkalinity from 2.67 mg/L to 7.33 mg/L as CaCO₃ after 7 days. The soluble iron increased significantly only for Magnetite M1 as expected due to the low pH to about 35 mg/L and only to 0.04 mg/L for M2. The ORP of the blank solution was on average of -245mV and for the magnetite system the ORP was on average -310mV and -305mV for M1 and M2, respectively.



Figure 7.13 Total concentration as a function of time for the anoxic study: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Hydroquinone (HQ), b) Benzoquinone (BQ), and c) HQ+BQ



Figure 7.14 Total concentration partition for the anoxic study as a function of time: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) 1 Day, b) 3 Days, and c) 7 Days



Figure 7.15 Total HQ+BQ as a function of time for the anoxic study for Magnetite M1: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order



Figure 7.16 Total HQ+BQ as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order

Sorbent	Equation	$\mathbf{y} = \mathbf{a}$	ax +b	\mathbf{P}^2	n
Sorbent	Fit	а	b	K	þ
Magnetite (M1)	Zero Order	-6.202	87.429	0.827	0.090
Magnetite (M1)	First Order	-0.093	4.475	0.906	0.048
Magnetite (M1)	Second Order	0.001	0.011	0.955	0.022
Magnetite (M2)	Zero Order	-8.804	85.692	0.876	0.064
Magnetite (M2)	First Order	-0.168	4.485	0.963	0.018
Magnetite (M2)	Second Order	0.004	0.010	0.968	0.016

Table 7.10 Total BPA concentration linear regression parameters for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution



Figure 7.17 Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution



Figure 7.18 Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order

				Magn	etite (M1)			
Sample	Blank HO+BO	Solution			Acetone Extracts			
		HQ	BQ	HQ+BQ	HQ	BQ	HQ+BQ	
0 Days	97.98	79.27	18.71	97.98				
1 Day	109.2	52.67	14.89	67.57	2.99	0.93	3.92	
3 Days	102.2	47.04	15.08	62.12	1.82	1.02	2.83	
7 Days	98.10	34.69	9.99	44.68	0.99	0.65	1.65	

Table 7.11 Total HQ+BQ concentration (µmol/L) as function of time for anoxic system for magnetite (M1):

Table 7.12 Total HQ+BQ concentration (µmol/L) as function of time for anoxic system for magnetite (M2):

c				Magne	etite (M2)		
Sample	Blank HO+BO	Solution			Acetone Extracts		
	1.4.2.4	HQ	BQ	HQ+BQ	HQ	BQ	HQ+BQ
0 Days	97.98	79.27	18.71	97.98			
1 Day	109.2	12.72	49.77	62.49	1.91	0.74	2.65
3 Days	102.2	11.81	41.35	53.16	1.36	1.02	2.38
7 Days	98.10	5.36	20.45	25.80	1.00	0.65	1.65

Table 7.13 Solution pH values for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Before		After									
Blank	Timo	Blank		Magnetite (M1)		Magnetite (M2)					
pН	1 1110	pН	Stdv	pН	Stdv	pН	Stdv				
6.638	1Day	7.908	0.129	4.333	0.024	6.801	0.210				
6.628	3Days	7.303	0.056	4.317	0.042	7.071	0.271				
6.612	7 Days	7.416	0.028	4.324	0.105	7.150	0.031				

Before		After									
Blank	Timo	Blank		Magneti	te (M1)	Magnetite (M2)					
TDS	1 mie	TDS	Stdv	TDS	Stdv	TDS	Stdv				
1	1Day	1.000	0.000	682.000	3.000	37.333	0.577				
1	3Days	1.000	0.000	705.667	4.041	37.333	0.577				
1	7 Days	1.000	0.000	715.000	5.000	38.000	1.000				

Table 7.14 Solution TDS values for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Table 7.15 Solution soluble iron (Fe) for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution

Before			After		
Blank	Timo	Magneti	te (M1)	Magnetite (M2)	
Fe	11110	Fe	Stdv	Fe	Stdv
0.000	1Day	27.757	0.996	0.033	0.006
0.000	3Days	32.380	0.276	0.043	0.006
0.000	7 Days	35.367	0.095	0.040	0.000

Table 7.16 Alkalinity (mg/L as CaCO₃) for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution

Before	After							
Blank	Time	Bla	nk	Magnet	Magnetite (M2)			
Alk	Time	Alk	Stdv	Alk	Stdv			
2.67	1Day	2.67	0.00	7.376	0.075			
2.67	3Days	2.67	0.00	7.376	0.075			
2.67	7 Days	2.67	0.00	7.333	0.000			

Table 7.17 Solution ORP (mV) values for the anoxic 7 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution

Timo	Blank		Magneti	ite (M1)	Magnetite (M2)	
Time	ORP	Stdv	ORP	Stdv	ORP	Stdv
1Day	-222.66	8.327	-324.00	9.179	-280.60	2.55
3Days	-254.33	15.04	-306.67	16.653	-305.33	12.50
7 Days	-248.67	18.77	-293.93	2.639	-310.27	7.40

For the 30 days time study the anoxic system was chosen due to the no loss after 7 days in the blank system from the previous anoxic study. We can see in Figure 7.19 (a) through (c) the removal of HQ, BQ, and HQ+BQ as a function of time for both M1 and M2. Magnetite M1 was able to remove the total HQ and BQ at 68, 86, 97, and 100 % after 19, 22, 26, and 30 days, respectively. M2 performed better than M2 being able to remove the total HQ and BQ at 75, 83, 88, 99.5, 99.9, and 100% after 7, 10, 14, 19, 22, and 26 days, respectively. After a period of 30 days there was only 5.8% loss in the total HQ+BQ. For the blank system there was a formation of about 18µmol/L of BO and remained constant for the rest of experiments with a small decrease to about 13µmol/L. For the M1 system, the BQ remained constant at 18 µmol/L, with a slow decrease to about $11 \mu mol/L$ and a sudden drop to $3 \mu mol/L$ at 22 days, and total removal at 26 days. For the HQ the drop in the first day was to about 54 µmol/L from original concentration of 78 µmol/L, followed with a slow decrease until 30 days, with complete removal for the M1. For M2 there was a sudden drop of 84 % from 78 µmol/L to 13 µmol/L, and followed with a slow decrease until complete removal after 26 days. BQ had an increase of 150 % from an 18 µmol/L to 47 µmol/L in the first day for M2 system. The removal of BQ was than faster than that of HQ with a complete removal at 22 days. The total water and acetone distribution for both magnetite M1 and M2 can be found in Figure 7.20 (a) through (i). From Figure 7.20 we can see a loss in the total mass of HQ and BQ for the period of all 30 days for both magnetites, which is believed to be due to the reaction with the adsorbent surface. The tabulated values of water concentrations and acetone extracts of HQ, BQ and HQ + BQ could be seen in Tables 7.19 and 7.20 for magnetite M1 and M2, respectively.

The total COD was also analyzed just for magnetite M2, because of the high TDS for the aqueous solution with magnetite M1. The total COD as a function of time can be seen in Figure

7.21, where we can see there was a 90% decrease in the total COD after 30 days. About 89% of total COD was removed at 19 days at the time when 99.5% of total HQ and BQ had been removed. The fitting for zero, first, and second order for total HQ plus BQ for magnetite M1 and M2 are presented in Figures 7.22 and 7.23, respectively. Based on the coefficient of determination R^2 and significant interval p we can see that for both magnetite M1 and M2 the adsorption followed better a second order kinetic model. All the linear regression parameters along with the coefficient of determination R^2 and significant interval R^2 and significant interval p could be found in Table 7.18 for both magnetite M1 and M2. From Figure 7.24 we can see that the removal of total COD from the aqueous solution follows better a second order kinetic model.

The pH, TDS, alkalinity, soluble iron, and oxidation reduction potential (ORP) are presented in Table 7.21, 7.22, 7.23, 7.24, and 7.25 respectively. The initial pH of the solution varied between 5.8 to 6.5 and increased for the blank system to about 6.0 to 6.8. For magnetite M1 the pH decreased to about 4.2 and for M2 it increased to about 7.9 after 30 days. The TDS for the initial solution and blank remained the same to 1mg/L, however, for magnetite M1 it increased to about 700 mg/L and for M2 to about 240 mg/L after 30 days. For the M1 the TDS remained the same for the 30days and for magnetite M2 it increased from 39 mg/L to 138 mg/L at 5 days and remained constant to about 240 after 19 days. The soluble iron increased significantly only for Magnetite M1 as expected due to the low pH to about 42 mg/L after 30 days, with a slow increase from 27 mg/L after first day. The soluble iron for M2 was zero for most of the days. Because of the low pH for magnetite M1 alkalinity could not be calculated. For magnetite M2 there was an increase in alkalinity from 2.67mg/L to 8.0mg/L as CaCO₃ after 30 days. The ORP of the blank solution was on average of -246mV and for the magnetite systems the ORP was on average -329mV and -299mV for M1 and M2, respectively.



Figure 7.19 Total concentration as a function of time for the anoxic study: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Hydroquinone (HQ), b) Benzoquinone (BQ), and c) HQ+BQ



Figure 7.20 Total concentration partition for the anoxic study as a function of time: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) 1 Day, b) 3 Days, and c) 5 Days



Figure 7.20 cont. Total concentration partition for the anoxic study as a function of time: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution d) 7 Days, e) 10 Days, and f) 14 Days



Figure 7.20 cont. Total concentration partition for the anoxic study as a function of time: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution g) 19 Days, h) 22 Days, and i) 26 Days



Figure 7.20 cont. Total concentration partition for the anoxic study as a function of time: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution j) 30 Days



Figure 7.21 Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution



Figure 7.22 Total HQ+BQ as a function of time for the anoxic study for Magnetite M1: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order



Figure 7.23 Total HQ+BQ as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order



Figure 7.24 Total COD as a function of time for the anoxic study for Magnetite M2: $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution a) Zero order, b) First order, and c) Second order

Sorbont	Equation	$\mathbf{y} = \mathbf{z}$	ax +b	P ²	n
Sorbent	Fit	а	b	K	þ
Magnetite (M1)	Zero Order	-2.763	79.093	0.847	0.001
Magnetite (M1)	First Order	-0.051	4.369	0.944	0.000
Magnetite (M1)	Second Order	0.001	0.011	0.959	0.000
Magnetite (M2)	Zero Order	-5.245	71.097	0.784	0.008
Magnetite (M2)	First Order	-0.148	4.332	0.969	0.000
Magnetite (M2)	Second Order	0.006	0.007	0.977	0.000

Table 7.18 Total BPA concentration linear regression parameters for the anoxic 30 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Table 7.19 Total HQ+BQ concentration (µmol/L) as function of time for anoxic system for magnetite (M1):

~ •		Magnetite (M1)							
Sample	Blank HO+BO	Solution			Ac	Acetone Extracts			
	Πų÷bų	HQ	BQ HQ-		HQ	BQ	HQ+BQ		
0 Days	96.1	77.85	18.22	96.07					
1Day	101.8	54.31	17.01	71.32	1.36	0.55	1.91		
3Days	94.4	49.08	16.18	65.26	2.55	1.06	3.61		
5Days	93.8	46.66	13.29	59.95	0.78	0.29	1.08		
7Days	94.4	40.75	13.52	54.26	0.66	0.26	0.92		
10 Days	91.1	36.82	13.55	50.36	0.53	0.02	0.55		
14 Days	97.7	28.97	12.75	41.72	0.24	0.18	0.42		
19 Days	92.9	19.57	11.19	30.76	0.00	0.00	0.00		
22 Days	90.4	10.59	3.01	13.61	0.00	0.00	0.00		
26 Days	92.1	2.98	0.00	2.98	0.00	0.00	0.00		
30 Days	90.4	0.00	0.00	0.00	0.00	0.00	0.00		

		Magnetite (M2)							
Sample	Blank HO+BO	Solution			Ac	Acetone Extracts			
	шұтрұ	HQ	BQ	HQ+BQ	HQ	BQ	HQ+BQ		
0 Days	96.1	77.85	18.22	96.07					
1Day	101.8	12.87	47.34	60.21	2.44	0.87	3.31		
3Days	94.4	9.73	37.81	47.54	2.33	0.96	3.29		
5Days	93.8	7.52	37.81	45.34	0.23	0.23	0.46		
7Days	94.4	5.22	18.57	23.78	0.14	0.22	0.36		
10 Days	91.1	3.61	12.69	16.31	0.02	0.20	0.22		
14 Days	97.7	3.17	7.77	41.72	0.03	0.15	0.18		
19 Days	82.9	0.22	0.28	0.50	0.00	0.00	0.00		
22 Days	90.4	0.03	0.00	0.03	0.00	0.00	0.00		
26 Days	92.1	0.00	0.00	0.00	0.00	0.00	0.00		
30 Days	90.4	0.00	0.00	0.00	0.00	0.00	0.00		

Table 7.20 Total HQ+BQ concentration (µmol/L) as function of time for anoxic system for magnetite (M2):

Table 7.21 Solution pH values for the 30 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Before		After							
Blank	Timo	Bla	nk	Magnet	ite (M1)	Magnet	Magnetite (M2)		
pН	Time	pН	Stdv	pН	Stdv	pН	Stdv		
6.523	1Day	6.648	0.242	4.371	0.050	7.187	0.229		
6.180	3Days	6.708	0.102	4.298	0.004	7.470	0.102		
6.523	5Days	6.831	0.209	4.386	0.073	7.317	0.129		
5.862	7Days	6.555	0.201	4.285	0.024	7.390	0.105		
5.879	10 Days	6.597	0.165	4.279	0.018	7.465	0.093		
6.423	14 Days	6.605	0.301	4.255	0.014	7.697	0.108		
6.342	19 Days	6.383	0.193	4.285	0.013	7.843	0.066		
6.179	22 Days	6.314	0.013	4.194	0.013	7.824	0.049		
5.967	26 Days	6.070	0.128	4.272	0.092	7.923	0.052		
6.214	30 Days	6.142	0.147	4.202	0.014	7.903	0.051		

Before		After								
Blank	Timo	Bla	nk	Magnet	ite (M1)	Magnet	Magnetite (M2)			
TDS	Time	TDS	Stdv	TDS	Stdv	TDS	Stdv			
1	1Day	1.0	0.0	692.3	4.0	38.7	0.6			
1	3Days	1.0	0.0	688.7	3.1	39.0	0.0			
1	5Days	1.0	0.0	699.8	7.3	138.3	5.5			
1	7Days	1.0	0.0	692.2	6.0	134.0	8.3			
1	10 Days	1.0	0.0	694.7	5.1	139.2	8.8			
1	14 Days	1.0	0.0	718.7	2.8	132.8	1.5			
1	19 Days	1.0	0.0	698.3	3.5	250.3	1.5			
1	22 Days	1.0	0.0	695.3	9.1	244.7	3.2			
1	26 Days	1.0	0.0	702.7	12.7	248.0	2.0			
1	30 Days	1.0	0.0	703.3	6.1	242.7	4.0			

Table 7.22 Solution TDS values for the 30 days time study, $C_0 = 1.2 \text{ mg/L}$, 5g sorbent: 50mL solution

Table 7.23 Solution soluble iron (Fe) for the anoxic 30 days time study, $C_{0(HQ)} = 110.11 \mu mol/L$, 5g sorbent : 50mL solution

Before			After			
Blank	Time	Magneti	te (M1)	Magnetite (M2)		
Fe	1 11110	Fe	Stdv	Fe	Stdv	
0.00	1Day	27.01	0.58	0.00	0.00	
0.00	3Days	33.24	2.12	0.00	0.00	
0.00	5Days	37.28	2.91	0.01	0.01	
0.00	7Days	39.70	0.51	0.00	0.00	
0.00	10 Days	39.18	1.11	0.01	0.01	
0.00	14 Days	41.34	0.97	0.00	0.01	
0.00	19 Days	41.56	0.76	0.00	0.00	
0.00	22 Days	41.86	0.79	0.00	0.01	
0.00	26 Days	42.20	0.62	0.00	0.00	
0.00	30 Days	42.75	1.53	0.00	0.00	

Before			After		
Blank	Time	Bla	nnk	Magnet	tite (M2)
Alk	1 mie	Alk	Stdv	Alk	Stdv
2.67	1Day	2.67	0.00	6.00	0.00
2.67	3Days	2.67	0.00	7.11	0.38
2.67	5Days	2.67	0.00	7.56	0.38
2.67	7Days	2.89	0.38	6.67	0.67
2.67	10 Days	2.67	0.00	7.78	0.38
2.67	14 Days	2.89	0.38	8.00	0.00
2.67	19 Days	2.67	0.00	8.22	0.39
2.67	22 Days	2.67	0.00	8.00	0.39
2.67	26 Days	2.67	0.00	8.67	0.67
2.67	30 Days	2.67	0.00	8.00	0.67

Table 7.24 Alkalinity for the anoxic 30 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Table 7.25 Solution ORP values for the anoxic 30 days time study, $C_{0(HQ)} = 110.11 \ \mu mol/L$, 5g sorbent : 50mL solution

Timo	Blank		Magneti	te (M1)	Magnetite (M2)	
Ime	ORP	Stdv	ORP	Stdv	ORP	Stdv
1Day	-261.0	16.1	-315.3	4.0	-337.7	6.8
3Days	-264.3	12.9	-333.3	10.2	-316.3	9.5
5Days	-291.6	12.4	-345.4	13.3	-280.7	27.3
7Days	-248.0	11.6	-348.7	9.3	-287.8	5.9
10 Days	-254.5	12.3	-340.5	8.4	-297.2	31.9
14 Days	-270.2	13.9	-331.9	15.7	-296.5	13.9
19 Days	-256.2	13.3	-330.3	10.0	-302.0	1.1
22 Days	-267.2	28.4	-308.4	2.0	-283.2	18.2
26 Days	-213.9	10.0	-323.7	12.9	-302.4	9.8
30 Days	-241.8	26.1	-318.1	21.4	-295.6	9.2

The extraction study was done in order to determine if the HQ and BQ could be further extracted. In order to determine if the loss in mass for HQ and BQ first an anoxic test was conducted using the initial HQ concentration of $110.11 \mu mol/L$ for a 5g to 50 mL solution ratio was used. The extraction was done for both magnetites M1 and M2 using in the first day DI

water with pH 2.0 and in the second day acetone. We can see the tabulated values for both M1 and M2 in Table 7.26. The extraction of HQ and BQ was also tried with isopropanol (2-propanol) and Methyl tert-butyl ether (MTBE), but the extraction was not successful. Based on the initial results we determine that M2 is a more suitable adsorbent to do further analysis. From Table 7.26 we can see that the extraction from M2 was higher with 3.32 µmol/L compare to that of M1 of 1.89 µmol/L.

For magnetite M2 seven different cases were done and denoted as Case A through G. In Table 7.27 we can see the water and extraction values for HQ, BQ, HQ+BQ for cases A through C. For cases A and B a two day extraction was done using DI water at pH 1.0 and acetone. For case A the extraction with acetone was done in the second day of extraction, and for case B was done in the first day of the extraction. We can see that for both cases the extraction was close to $3.10 \mu mol/L$. For case C three days extraction was performed using DI water at pH 1.0. In the first day the extraction was the same as cases A and B, for the second day was slightly better and for the third day it decreased to only 0.19 $\mu mol/L$ with a total extraction of 3.39 $\mu mol/L$ for 3 days.

Table 7.26 Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic system with $C_{0(HQ)} = 110.11 \ \mu$ mol/L and 50mL solution :

Blank				Water	Day 1 Extract	Day 2 Extract
HQ	85.85	Adsorbent		Sample	Water pH 2.0	Acetone
BQ	12.54		HQ	45.69	0.52	0.27
HQ+BQ	98.39	Magnetite (M1)	BQ	20.56	0.77	0.30
			HQ+BQ	66.25	1.29	0.57
			HQ	12.55	0.70	0.28
		Magnetite (M2)	BQ	47.98	2.07	0.24
			HQ+BQ	60.53	2.77	0.52

Blank		Case		Water Sample	Day 1 Extract	Day 2 Extract	Day 3 Extract
HQ	85.85				Water pH 1.0	Acetone	None
BQ	12.54	Case A	HQ	10.65	1.28	0.28	
HQ+BQ	98.39		BQ	42.79	0.55	0.22	
			HQ+BQ	53.43	2.38	0.50	
					Acetone	Water pH 1.0	None
		Case B	HQ	10.72	0.51	0.31	
			BQ	41.20	2.10	0.24	
			HQ+BQ	51.92	2.61	0.55	
					Water	Water	Water
					pH 1.0	pH 1.0	pH 1.0
		Case C	HQ	10.79	0.48	0.47	0.10
			BQ	40.62	2.01	0.24	0.09
			HQ+BQ	51.41	2.49	0.71	0.19

Table 7.27 Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic systems (Case A-C) with C_{0(HQ)} = 110.11 μ mol/L and 50mL solution for Magnetite (M2):

The extraction for cases D through G was done using acetone and DI water at three different pHs for a period of 3 days and the data are presented in Table 7.28 for the QH, BQ, and HQ+BQ. In Table 7.29 we can see the pH and TDS for cases D through G. From Table 7.28 we can see that the extraction with DI water at pH 4.5 had the lowest removal with 2.92 µmol/L and the highest removal was the one with acetone of 3.50 µmol/L. Based on these results we may concluded that most of the HQ and BQ that could be extracted, had been removed and there was no more HQ and BQ on the adsorbent. As a result the difference in mass loss can be attributed to the reaction of HQ and BQ with the iron oxides M1 and M2. The pH for the water samples and the extracts for both the DI water extracts with pH of 7.0 and 4.5 reached a equilibrium about 7.0 at the third day of extraction with the highest pH of 7.6 for the DI extract. The pH for the DI water extract of pH 2.0 remained constant between 2.073 and 2.16. The TDS for the DI water

extracts was significantly higher for the acidic DI water extract with pH 2.0. The TDS increased from first day from the value of 1,530 mg/L to 2,213 mg/L after 3 days.

Table 7.28 Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic systems (Case D-G) with $C_{0(HQ)} = 110.11 \ \mu$ mol/L and 50mL solution for Magnetite (M2):

Blank		Case		Water Sample	Day 1 Extract	Day 2 Extract	Day 3 Extract
HQ	90.77				Acetone	Acetone	Acetone
BQ	23.05	Case D	HQ	10.80	0.77	0.18	0.08
HQ+BQ	113.82		BQ	40.37	2.05	0.36	0.05
			HQ+BQ	51.17	1.12	0.55	0.13
					DI Water pH 7.0	DI Water pH 7.0	DI Water pH 7.0
		Case E	HQ	9.59	0.44	0.26	0.23
			BQ	38.19	1.74	0.18	0.18
			HQ+BQ	47.78	2.17	0.44	0.41
					Water pH 4.5	Water pH 4.5	Water pH 4.5
		Case F	HQ	9.75	0.41	0.20	0.23
			BQ	39.52	1.79	0.14	0.14
			HQ+BQ	49.27	2.20	0.34	0.38
					Water pH 2.0	Water pH 2.0	Water pH 2.0
		Case G	HQ	9.11	0.43	0.52	0.13
			BQ	38.55	1.96	0.14	0.14
			HQ+BQ	47.66	2.39	0.66	0.27

Bla	ank	Case		Water Sample	Day 1 Extract	Day 2 Extract	Day 3 Extract
pН	6.301	0 1			Acetone	Acetone	Acetone
TDS	1.0	Case 1	pН	7.033 ± 0.108			
			TDS	38.33 ± 0.58			
		Case 2			DI Water pH 7.0	DI Water pH 7.0	DI Water pH 7.0
		Cuse 2	pН	7.214±0.022	7.633±0.011	7.193±0.116	6.944±0.093
			TDS	38.67 ± 0.58	7.0 ± 0.0	3.33 ± 0.58	2.0±0.0
		~			Water pH 4.5	Water pH 4.5	Water pH 4.5
		Case 3	pН	7.323 ± 0.022	7.456 ± 0.047	6.605±0.169	6.931±0.057
			TDS	38.33±0.58	8.0 ± 0.0	4.67 ± 0.58	4.0 ± 0.0
		Casa A			Water pH 2.0	Water pH 2.0	Water pH 2.0
			pН	7.315±0.014	2.160±0.004	2.073±0.007	2.091±0.003
			TDS	39.67±1.53	1530±17.32	2090±10.0	2213±5.7

Table 7.29 Total pH and TDS for anoxic systems (Case 1-4) with $C_{0(HQ)} = 110.11 \ \mu mol/L$ and 50mL solution for Magnetite (M2):

The adsorbent dosage was also analyzed using three different experiments; first two experiments were done using initial HQ concentration of 110.11µmol/L. One experiment was done using oxic system with adsorbent dosage of 0.5g and 5g to 50 mL presented in Figure 7.25 and one anoxic system with adsorbent dosage of 1g and 5g to 150mL presented in Figure 7.26. The pH and TDS for the oxic system is presented in Table 7.30 and for the anoxic system in Table 7.31. There was no significant difference in the removal of HQ and BQ at oxic or anoxic conditions for a period of 1 day. The volume of the sample was increase to 150 mL to see if the surface of the adsorbent gets saturated and reaches the capacity. From Figure 7.25 we can see that the removal by M1 for the oxic system with 50 mL of solution had a removal of 24% and 33% for 0.5g and 5g, respectively. Using M2 the removal was 33% and 37% for 0.5g and 5g, respectively. From Table 7.30 we can see that the pH for the M1 using 0.5g was slightly higher

to 4.6 from 4.3 for 5g and for M2 the pH was only slightly higher for 5g with an pH of 6.99 compare for the 0.5g, which had the pH of 6.7. As a conclusion the small difference in the pH is not believe to had any effect on the total adsorption.

For the anoxic system with aqueous solution of 150mL we can see from Figure 7.26 that the removal for M1was 14 % for 1g and 18.8% for 5g and for M2 was 26.6% for 1g and 32.3% for 5g. Based on these two different experiments we can conclude that there was less adsorption due to the extra HQ and BQ from the higher volume of aqueous solution. There was an decrease in the adsorption for 5g of M1 with 14.2% and for M2 with 4.7%. As a result we can see that M1 had the highest drop in the adsorption due to the increase in the total HQ and BQ molar mass. From Table 7.31 we can see that the pH of the solution did not show significant change from the 50ml aqueous solution. As a result the slight change in the pH cannot be responsible for the drop in the adsorption. The lower TDS values in the anoxic system were expected since there was more aqueous solution volume.

The last part of the experiments was an oxic system for an initial concentration of HQ of 11.01µmol/L with an adsorbent to aqueous solution ratio of 0.5g, 1.5g, and 5g to 150 mL. We can see the total HQ+BQ percentage removal as a function of different adsorbent dosages in Figure 7.27, the tabulated values of HQ, BQ and HQ+BQ in Table 7.32, and the pH and TDS for both magnetite solutions in Table 7.33. For magnetite M1 the percentage removed after 24hours was 24%, 33%, and 51% for 0.5g, 1.5g, and 5g, respectively. The increase in the adsorption with the increase in the adsorbent mass was expected. However, for magnetite M2 we see there was 19%, 16.5%, and 14.8% for 0.5g, 1.5g, and 5g, respectively. The reason that this happened is believe to be partially because of the high BQ production in the first day, which had been

observed to other systems; as a result an increase in the adsorbent would generate an increase in the BQ. Another reason that could be the way that magnetite M2 mixes in the solution, it was observed that M2 has a very small suspension time in the solution as a result would settle a lot faster. The addition of extra adsorbent would not help very much for the short run, but would make a difference in the long run. Magnetite M1 dissolves and stays suspended in the solution longer than M2, which we can see from the TDS values tabulated in Table 7.33.



Figure 7.25 Total HQ+BQ % removal as a function of adsorbent for oxic study for: $C_{0(HQ)} = 110.11 \mu mol/L$, 50mL solution a) Magnetite (M1), and b) Magnetite (M2)

Blank			Adsorbent	Dosage		
рН	6.205			5g	0.5 g	
TDS	1.00	pН	Magnetite (M1)	4.298 ± 0.037	4.591 ± 0.018	
		•	Magnetite (M2)	6.998 ± 0.134	6.725 ± 0.096	
		TDS	Magnetite (M1)	706.0 ± 6.24	91.33 ± 0.58	
			Magnetite (M2)	39 ± 0.0	5.0 ± 0.0	

Table 7.30 Total pH and TDS for oxic system with $C_{0(HQ)}$ = 110.11 µmol/L and 50mL solution:



 $\label{eq:Figure 7.26 Total HQ+BQ \% removal as a function of adsorbent for anoxic study for: $C_{0(HQ)} = 110.11 \ \mu mol/L, 150 mL solution$$ a) Magnetite (M1), and $$ b) Magnetite (M2)$}$

Blank Dosage Adsorbent 5.935 pН 5 g 1 g Magnetite (M1) 4.315 ± 0.023 4.673 ± 0.040 TDS 1.00 pН 7.081 ± 0.050 6.609 ± 0.064 Magnetite (M2) Magnetite (M1) 263.0 ± 1.73 66.33 ± 3.79 TDS 14.33 ± 0.58 3.33 ± 0.58 Magnetite (M2) 60 Total HQ+BQ % Removal 50 40 30 20 10 a) 0 -0⁵⁹ , ⁵⁹ 69 25 Total HQ+BQ % Removal 20 15 10 5 b) 0 0.50 , ⁵⁹ 69

Table 7.31 Total pH and TDS for an oxic system with $C_{0(HQ)} = 110.11 \ \mu mol/L$ and 150mL solution:
Blank			Adsorbent		Dosage	
pН	6.115			5 g	1.5 g	0.5 g
TDS	0.00	pН	Magnetite (M1)	4.417 ± 0.007	4.577 ± 0.026	4.862 ± 0.035
		•	Magnetite (M2)	7.056 ± 0.117	7.064 ± 0.126	6.603 ± 0.142
		TDS	Magnetite (M1)	262.0 ± 2.65	89.67 ± 0.58	33.67 ± 0.58
			Magnetite (M2)	14.0 ± 0	5.00 ± 0	2.67 ± 0.58

Table 7.32 Total pH and TDS for oxic system with $C_{0(HQ)} = 11.1 \ \mu mol/L$ and 150mL solution:

Table 7.33 Total HQ, BQ, and HQ+BQ concentration (μ mol/L) for anoxic system with $C_{0(HQ)} = 110.11 \ \mu$ mol/L and 150mL solution :

Blank		Adsorbent			Dosage	
HQ	8.24	nuson bent		5 g	1.5 g	0.5 g
BQ	1.24		HQ	3.17 ± 0.11	3.93 ± 0.13	4.46 ± 0.21
HQ+BQ	9.48	Magnetite (M1)	BQ	1.45 ± 0.08	2.40 ± 0.11	2.78 ± 0.21
			HQ+BQ	4.62 ± 0.19	6.32 ± 0.24	7.24 ± 0.42
			HQ	1.40 ± 0.05	1.35 ± 0.01	1.22 ± 0.04
		Magnetite (M2)	BQ	7.47 ± 0.15	7.35 ± 0.22	7.19 ± 0.29
			HQ+BQ	8.88 ± 0.20	8.70 ± 0.23	8.41 ± 0.33

7.6 CONCLUSIONS

From our study it was found that HQ had been able to be removed efficiently with both magnetites M1 and M2. The main difference between the two magnetites was the pH of the solution and TDS, with magnetite M1 increasing the TDS of the solution to about 700 mg/L and reducing the pH from original 6.6 to about 4.3 after one day. Even though the removal of HQ under acidic conditions had been found to be more favorable using some adsorbents, magnetite M2 was able to remove more efficiently than magnetite M1 at a higher pH of 7.4 to 7.9.

The main part of the study was the time study done for a period of 30 days under anoxic condition with an adsorbent ratio of 5g to 50 mL of aqueous solution. Magnetite M2 reacted with

the HQ from the first day, which leads to the formation of BQ. In contrast the magnetite M1 did not lead to any BQ formation other than the original that was found in the blank, which was believe to be due to natural oxidation of HQ. The anoxic system seemed to be more suitable for long time study due to possible lost in the total HQ+BQ in the blank system.

The removal of both HQ and BQ was completely removed after 19 days for M2 and 30 days for M1. Both magnetites followed a second order kinetic model better than the zero order and first order models. The significance level for both magnetites M1 and M2 as a function of time for the anoxic 30 days study had a significance interval p=0.000 and a coefficient of determination R^2 of 0.959 and 0.977 for M1 and M2, respectively. As a result it was found that time had a strong relationship to the equilibrium concentration of HQ+BQ. This set of data was also validated with the analysis of the COD, which also followed a second order kinetic model. The total COD decreased from an initial concentration of 18.45mg/L to 1.87mg/L for M2. The COD for M1 could not be calculated because of the high TDS of the solution, which interfered with our readings of COD.

For the acidic conditions there was some soluble iron (Fe) present to a concentration of about 43 mg/L after 30 days for magnetite M1. For magnetite M2 there was no soluble iron present due to the high pH of the solution. The alkalinity could only be calculated for magnetite M2, because of the low pH for the magnetite M1. The alkalinity increased from the blank system from 2.67 mg/L to about 8.0 mg/L as CaCO₃ for the solution with magnetite M2. The oxidation reduction potential (ORP) was slightly lower for the magnetite M1 with an average of -329mV and for magnetite M2 with an average of -299mV. The average ORP of the bank for the 30 day study was about -246mV.

From the mass balance calculations it was concluded that there was possible reaction with the surface of both magnetites, which explained the loss in the total HQ+BQ. When the total concentration of HQ+BQ from the water solution had been removed the extraction was also zero. To verify this, there were different extraction experiments done in order to establish if more HQ+BQ could have been remained on the adsorbent and had not been extracting through our routine extraction of one day with acetone. After taking in consideration several DI water solutions at different pHs and two other solvents such as MTBE and 2-Propanol, it was found that our extraction of one day with acetone was removing most of the HQ and BQ adsorbed. There was only a small fraction of HQ and BQ that could had been removed with further extractions. However, acetone was found to be the best extraction solution.

The increase in the adsorbent prove to help the extraction for the long run, however for 1 day study at a low concentration of only 10.11 μ mol/L magnetite M2 performed slightly better with an adsorbent dosage of 0.5g compare to that of 1.5g and 5g. This was believed to be the result of the BQ production by M2 in the first day of the adsorption.

When a ionic strength of 0.5mM and 1mM aqueous solution of sodium bicarbonate (NaHO₃) was used there could be no analysis of the solution done due to the fact that HQ and BQ could not be found. The ionic strength of the solution probably made the HQ and BQ from the solution to precipitate.

In conclusion both magnetites had been able to successfully remove HQ and BQ from the solution.

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CHAPTER VIII

RISK ASSESSMENT OF BISPHENOL A (BPA) EXPOSURE

8.1 INTRODUCTION

The production of Bisphenol A (BPA) is mostly used for the production of plastics throughout the world, and is also known as 2,2-bis(4'-hydroxyphenoyl) propane, 4,4' isopropyllidenediphenol, and 2,2'-bis(4-hydroxyphenyl) propane (Huang et al., 2012). It is also used in unsaturated polyester-styrene resins, flame retardants, food and drink packaging, and as antioxidants in plastics (Barnabe et al., 2009). BPA is not a strong estrogenic compound having a estrogenic activity of four orders of magnitude lower than that of 17 β -estridol (Barnabe et al., 2009). However, BPA can still manage to do harm in the environment and is a potential health risk for humans even at low concentrations (Crain et al., 2007). During an proposed ranking system done for pharmaceuticals, personal care products and endocrine-disrupting chemicals or EOCs, out of 100 chemicals the overall priority for BPA was second place and 17 β -estridol came only in place seventeen for the overall score (Kumar and Xagoraraki, 2010). It was also reported that BPA has some anti-androgenetic activity (Birkett and Lester, 2003).

The capacity production of BPA had increased over the years with US being the highest producer (Huang et al., 2012). The total production capacity of BPA in 2007 was estimated to be about 4.7×10^6 tonnes, with US accounting for about 23.9 % of that total production. The Asia-Pacific region had 43.5 % of the global total output in 2007. Since 2001 China had increased the volume consumption of BPA from 106,000 tonnes to 570,000 tonnes in 2007 (Huang et al., 2012). The use of Bisphenol A to manufacture different products it had been speculated that human exposure could reach high levels.

Since 1930 BPA has been suspected to be hazardous to humans via estrogenic activity, and has recently been designated as an endocrine disrupter compound (EDC). Like natural estrogens, these estrogenic chemicals can bind to the estrogen receptor and regulate the activity of estrogen responsive genes. Therefore, such effects have raised concern that prolonged exposure to environmentally relevant concentrations of these chemicals could result in reproductive toxicity. Endocrine disruptors include (a) natural compounds such as steroid hormones naturally secreted by humans and animals and (b) anthropogenic compounds such as synthetic hormones or agricultural and industrial chemicals (pesticides, bisphenol A, phthalates plasticizers, etc.). The presence of these EDCs is supposed to cause the feminization of male fish observed in several countries over the past 20 years (Jobling et al., 1998, Larsson et al., 1999). Also the blood levels of BPA in humans had been statistically associated with the cause of different human diseases such as ovarian dysfunction, recurrent miscarriage, and endometrial hyperplasia.

BPA is widely produced and found in the environment all over the world from Europe to Japan (Environmental Agency of Japan, 1997, Yamamoto et al., 2001). BPA had been found in the environment in surface waters, atmosphere, dust, soil, sediment, landfill leachate or sewage influents and effluents (Crain et al., 2007; Barnabe et al., 2009; Snyder et al., 2003; Staples et al., 1998; Fromme et al., 2002; Kim et al., 2007; Kang et al., 2006; Cousins et al., 2002; Fu and Kawamura, 2010). It is important to understand the fate of BPA in the environment to understand the possible exposure to BPA from the environment. The pollution of the aquatic medium was found to be very important in the fate of the BPA in the environment due to its chemical physical properties. If the emission of BPA is done in water medium at steady state conditions about 95 % of the total emission would remain in the water and not transfer to other medium as soil or air (Cousins et al., 2002). As a result due to the current pollution with BPA in the environment it is expect that most of the pollution to be present in water where it was initially

released through different sources. BPA is not considering as a persistent pollutant, because of its residence time is close to about 7 days in most of the environmental medium. However, as mentioned earlier, environmental adverse effects due to BPA had already been found in the environment, even though it was found that BPA could be biodegraded or metabolized by many organisms such as bacteria, fungi, planktons, plants, and animals (Kang et al., 2006).

Because of the toxic effect at low levels of BPA studies started to be conducted to obtain levels of different exposure pathways that are a possible intake exposures for humans. BPA could be ingested trough inhalation of air, ingestion of water, dust and different foods. Several treatment processes for BPA in water have been examined, using chemical (Sajiki et al., 2002), biological (Staples et al., 1998), photochemical (Ohko et al., 2001), electrochemical processes (Boscoletto et al., 1994; Tanaka et al., 1999; Tanaka et al., 2002), and as well as adsorption to different sorbents (Asada et al., 2004; Nakanishi et al., 2002; Tsai et al., 2006a; 2006b; Pan et al., 2008; Toledo et al., 2005; Zeng et al., 2006; Dong et al., 2010; Shareef et al., 2006; Li et al., 2007, 2008; Li et al., 2009; Xu et al., 2008; Sun et al., 2005; Cao et al., 2009b). However, some of the exposure pathways are hard to treat or cannot be treated, for example the ingestion from the migration from baby bottles, infant formula, dietary intake, dust, breastfed milk, and inhalation of air. As a result, these pathways are very important to analyze and found the potential adverse effect from the intake of BPA. Some low levels of BPA could bypass the treatment process in the drinking and waste water treatment facilities. The daily intake of BPA through all these exposure pathways would be investigated in the current chapter.

8.2 STUDY OBJECTIVES

As mention earlier the exposure through different food ingestions of BPA is a very likely possibility. Also these exposures could be critical to a more sensitive sub population such as

children and infants. In the current chapter of risk assessment a multi pathway BPA exposure for infants up to 50 years old was conducted. The exposure of infants is very important, because their immune system had not been fully developed and they have a low body mass, as a result have a higher risk as a subpopulation. One such study to estimate the risk due to exposure of BPA of infants was done in Singapore (Wong et al., 2005). The study compared the estimated daily intake over the body weight to the allowable reference dose of 0.05 mg/Kg bw/day. But the study only took into consideration the migration of BPA from baby bottles to the aqueous food solution. The report found no health risk in this study and was limited taking into consideration only one pathway food ingestion. Several other studies had been done and evaluated the intake of BPA by humans (European Commission, 2002; Kamrin, 2004; Degen and Bolt, 2000; Bolt et al., 2001; Volkel et al., 2008; Miyamoto and Kotake, 2006; Geens et al., 2010; Lakind and Naiman, 2011). During the current risk assessment chapter the exposure to BPA from atmosphere, dietary intake, and dust ingestion using different case scenarios would be evaluated. As a result the risk assessment would give us a better estimate for the daily intake and total risk over the period of 50 years.

8.3 METHODS

8.3.1 HAZARD IDENTIFICATION

The BPA exposure levels were obtained from research literature. Concentrations for infant formula were obtained from a total of four papers with a total of 147 sample points (Kuo and Ding, 2004; Ackerman et al., 2010; Biles et al., 1997; Cao et al., 2008a). The concentration for the human milk was obtained from four papers with a total of 28 sample points (Otaka et al., 2003; Sun et al., 2004; Nam et al., 2010; Ye et al., 2006). The migration concentration of BPA from baby bottle to food solution was obtained from three studies with a total of 37 sample

points. For the concentration of BPA in bottle water was obtained from three papers with a total of 45 sample points (Wong et al., 2005, Sun et al., 2000, Nam et al., 2010). The concentration in milk was obtained from three papers with a total of 16 points (Maragou et al., 2006, Hadjmohammadi and Saeidi, 2010, Casajuana and Lacorte, 2004). The concentration for the drinking water from bottle water was obtained from five papers with a total of 66 points (Cao et al., 2008b; Biles et al., 1997; Wu et al., 2010; Li et al., 2010; Health Canada, 2009).

The concentrations for solid foods used for infants, children, and adults were found in the following papers. The concentration for the vegetables was obtained from fifteen papers with a total of 195 points (Schecter et al., 2010; Noonan et al., 2011; Goodson et al., 2002, Thomson et al., 2005; Grumetto et al., 2008; Yoshida et al., 2001; Geens et al., 2010; Rastkari et al., 2011; Cao et al., 2010a; Lim et al., 2009; Braunrath et al., 2005; Sajiki et al., 2007; Imanaka et al., 2001; Brotons et al., 1995).

The concentration for meats was obtained from eight papers with a total of 41 points (Schecter et al., 2010; Goodson et al., 2002, Thomson et al., 2005; Geens et al., 2010; Lim et al., 2009; Sajiki et al., 2007; Imanaka et al., 2001).

The concentration for fish was obtained from fifteen papers with a total of 117 points (Schecter et al., 2010; Noonan et al., 2011; Yonekubo et al., 2008; Goodson et al., 2002, Thomson et al., 2005; Basheer et al., 2004; Geens et al., 2010; Buket et al., 2011; Rastkari et al., 2011; Cao et al., 2010a; Lim et al., 2009; Braunrath et al., 2005; Munguia-Lopez et al., 2005; Sajiki et al., 2007; Imanaka et al., 2001).

The concentration for fruits was obtained from five papers with a total of 21 points (Noonan et al., 2011; Geens et al., 2010; Lim et al., 2009; Braunrath et al., 2005; Imanaka et al., 2001).

The concentration for pasta was obtained from three papers with a total of 14 points (Noonan et al., 2011; Geens et al., 2010; Cao et al., 2010a).

The concentrations for liquid foods used for infants, children, and adults were found in the following papers. The concentration for the soup was obtained from eight papers with a total of 52 points (Schecter et al., 2010; Noonan et al., 2011; Goodson et al., 2002, Thomson et al., 2005; Geens et al., 2010; Cao et al., 2009c; Braunrath et al., 2005; Sajiki et al., 2007).

The concentration for the coffee was obtained from five papers with a total of 42 points (Schecter et al., 2010; Lim et al., 2009; Kawamura et al., 198; Horie et al., 1999, Sajiki et al., 2007).

The concentration for the fruit juice was obtained from four papers with a total of 14 points (Schecter et al., 2010; Noonan et al., 2011; Geens et al., 2010; Lim et al., 2009).

The concentration for the tea was obtained from four papers with a total of 26 points (Geens et al., 2010; Kawamura et al., 1998; Horie et al., 1999, Lim et al., 2009).

The concentration for the soft drinks was obtained from six papers with a total of 85 points (Geens et al., 2010; Cao et al., 2009b; Cao et al., 2010b; Cunha et al., 2011, Lim et al., 2009; Braunrath et al., 2005).

The concentration for drinking water obtained from bottle water was the same presented earlier for infants.

The concentrations for indoor and outdoor air and dust used for infants, children, and adults were found in the following papers. The concentration for the outdoor air was obtained from seven papers with a total of 72 points (Wilson et al., 2001; Wilson et al., 2007; Berkner et al., 2005; Matsumoto et al., 2005; Wilson et al., 2003; Fu and Kawamura, 2010; Rudel et al., 2003).

The concentration for the indoor air was obtained from three papers with a total of 13 points (Wilson et al., 2001; Wilson et al., 2007; Wilson et al., 2003).

The concentration for the dust was obtained from six papers with a total of 19 points (Volkel et al., 2008; Wilson et al., 2001; Geens et al., 2009; Wilson et al., 2007; Wilson et al., 2003; Rudel et al., 2003).

The concentrations from infant formula, migration from baby bottle, milk, and human milk that were reported as none detect were taken equal to the concentration of half the level of detection. For rest of the concentrations the none detect were not used. Using ProUCL software the data distribution was obtained for all the data sets. Depending on the distribution normal, gamma or lognormal the 95th percentile upper confidence limit above the means (95%UCLM) was obtained. For the data that did not follow any of the three distributions, a non-parametric UCL was used and the recommended value was used. If a higher UCL was used. The detailed data selection is presented in section 2.3 under the exposure assessment.

In Table 8.1 we can see in tabulated form all the concentrations used for each type of route exposure with the number of observations found in literature and the recommended UCL by the ProUCL software.

Type of food	Route of exposure	Number of observations	Recommended UCL for CTE and RME ^a
	Vegetables	195	8.16E-02
	Meat	41	1.12E-01
Solid (µg/g)	Fish	117	1.55E-01
	Fruits	21	1.55E-02
	Pasta	14	4.06E-02
	Infant formula	147	1.98E-02
Liquid food	Human Milk	27	6.49E-04
(μg/mL)	Migration from Baby Bottle	9	1.29E-01

Table 8.1 Concentrations used for both CTE and RME calculations for the EDI.

	Milk	CTE = 12 $RME = 4$	CTE = 6.42E-03 RME = 7.01E-01
	Drinking Water (Bottled Water)	66	3.03E-03
	Coffee	42	7.89E-02
	Fruit Juice	14	6.71E-02
	Tea	26	3.48E-02
	Soft Drinks	85	6.26E-03
	Soup	52	3.55E-02
$Aim(ug/m^3)$	Outdoor Air	72	1.96E-02
Air (µg/m)	Indoor Air	13	7.24E-02
Dust (µg/mg)	Indoor Dust	19	7.22E-03

^aThe concentrations values are for both CTE and RME calculations unless otherwise specified.

8.3.2 TOXICITY ASSESSMENT

In order to evaluate the non-carcinogenic effect of BPA the Reference Dosage (RfD) was obtained from Environmental Protection Agency (EPA) website, where they have listed a safe level for children and adults of 50 µg/Kg-body weight/day (USEPA, 1993). The value was obtained from animal studies and was extrapolated to humans using a modifying factor of 1 and a uncertainty factor of 1000. The uncertainty factor was calculated as follows: 10 for uncertainty in the extrapolation of dose levels for animals to humans, 10 for uncertainty in the threshold for sensitive humans, and 10 for uncertainty in the effects of duration on toxicity when extrapolating for subchronic to chronic exposure. However, since 1993 when the last revision of the BPA RfD was done, many research papers showed adverse health effects at levels much lower to the current EPA standard. Adverse health effects at dose as low as 0.025µg/kg/day had been reported. Thus when calculations were done different RfD were compared in order to understand a possible implication if the reduction of RfD will occur in the future. Outside US for example the European Commission Scientific Committee on Food proposed a temporary total daily intake of 10µg/kg/day (Schecter et al., 2010). Whillhite et al., 2008 derived on NOAEL for oral RfD of 16 µg/Kg/day from which a total allowable concentration (TAC) for drinking water was calculated as 100 µg/L.

For most of the studies there was no carcinogenic effect recorded for the BPA; however for few studies some cancerous tumors had been detected (Durando et al., 2007, Murray et al., 2007, Ho et al., 2006). The Federal Drug Administration (FDA) in 2010 had announced that has some concern about the potential health effects for infants and children. The National Toxicology Program (NTP) in 2008 expressed some concerns about the neurological effect of the BPA could have in infants and children at current exposure levels. However, the FDA during the Bush administration maintained that the BPA in food and beverages are safe. The FDA showed support for actions such as replacing the BPA in infant formula cans and also minimizing the concentration in other food can linings (Erickson, 2010). We can see some of the health effects observed at different BPA daily exposure rates done in laboratory on mouse and rats in Table 8.2. Richter et al., 2007 presented 105 studies in detailed that found adverse health effect in animal studies in laboratories at a BPA concentration level lower that the current recommended EPA safe dose. In 94 government studies out of 104 there was significant health effects found at the doses of BPA < 50 mg/Kg/day, however out of 11 different industry funded studies none found such adverse health effects (vom Saal and Hughes, 2005).

Average Daily Intake μg/Kg/Day	Adverse Health Effects	Reference
0.0001	Alterations in cell signaling pathways	Wozniak et al., 2005
0.002	Influence the development of the central dopaminergic system in the limbic area.	Mizuo et al., 2004
0.02	Increased the mRNA expression of receptors Embryonic brain and gonad AhR expression, RARα	Nishizawa et al., 2005b Nishizawa et al., 2005a
0.025	Persistent changes to breast tissue, predispose cells to hormones Permanent changes to genital tract Reduced/loss of expected sexual dimorphism Mammary gland morphogenesis, terminal end bud density	Munoz et al., 2005 Markey et al., 2005 Rubin et al., 2006 Munoz et al., 2005
0.2	Decreased antioxidant enzymes Decreased in sperm motility and sperm counts	Chitra et al., 2003a Chitra et al., 2003b
0.25	Altered development of fetal mammary glands	Vanderberg et al., 2007

Table 8.2 Adverse Health effects in rats and mouse laboratory studies in the presence of BPA under recommended EPA safe dose limit of 50,000 µg/Kg-BW/day

	Delay in lumen formation	Vanderberg et al., 2007
	Reduced/loss of expected sexual dimorphism	Rubin et al., 2006
	Mammary gland morphogenesis, terminal end bud density	Munoz et al., 2005
0.5	Enhanced reward effect and hyperlocomotion in response to morphine	Mizuo et al., 2004
1	Long-term adverse reproductive and carcinogenic effects	Newbold et al., 2004
	Decreased plasma testosterone in males	Akingbemi et al., 2004
	Increased prostate weight	Nagel et al., 1997
	Increased aggression	Kawai et al., 2003
	Increased prostate weight	Nagel et al., 1997
	Decreased in sperm motility and sperm counts	Chitra et al., 2003
2	Reduction in sperm production	Vom Saal et al., 1998
Z	Changes in ER α , ER β immoactivity in dorsal raphe nucleus	Kawai et al., 2007
	Motor hyperactivity	Masuo et al., 2004a
	Embryonic brain and gonad AhR expression, RARa	Nishizawa et al., 2005a
	Enhanced reward effect and hyperlocomotion in response to morphine	Mizuo et al., 2004
	Alterations in the expression of behavior modifications at the CNS level.	Razzoli et al., 2005
	Placental nuclear receptor gene expression	Imanishi et al., 2003
	Weight gain and early onset of puberty	Howdeshell et al., 1999
2.4	Signs of early puberty, increased anogenital distance	Honma et al., 2002
	Decline in testicular testosterone	Akingbemi et al., 2004
2.5	Altered immune function	Sawai et al., 2003
2.5	Predisposes breast cells to cancer	Murray et al., 2007
3	Hyperactivity	Ishido et al., 2004
5	Reduction in body weight	Al-Hiyasat et al., 2004
	Increase in prostate duct volume	Timms et al., 2005
10	Decreased maternal behavior	Palanza et al., 2002
10	Amphetamine-induced conditioned place reference	Laviola et al., 2005
	Precancerous prostatic lesions	Ho et al., 2006
14	Significant disruption of chromosomes alignment during meiosis	Hunt et al., 2003
15	Forced swimming behavioral tests	Fujimoto et al., 2006
	Earlier vaginal opening	Honma et al., 2002
	Increased prostate weight	Nagel et al., 1997
	Decreased in sperm motility and sperm counts	Chitra et al., 2003a
	Reduction in sperm production	Sakaue et al., 2001
	Reduction in sperm production	vom Saal et al., 1998
20	Increased aggression	Kawai et al., 2003
20	Motor hyperactivity	Masuo et al., 2004b
	Disruption of normal neocortical development in its early stage	Iton et al., 2008
	Usordeny arranged cerebral conex and abnormal fiber projections	Nakamura et al., 2007
	Inspectactivity	Nakamura et al., 2012
	Alterations in the expression of behavior modifications at the CNS level	Razzoli et al. 2005
	Disruption of chromosomes	Susiario et al. 2007
	Changes in brain: increased in FR-8 mRNA	Ramos et al 2003
	Reduction in body weight	Al-Hivasat et al 2004
	Significant increases in the weights of the uterus	Al-Hiyasat et al 2004
25	Increased in embryos mortality	Al-Hiyasat et al., 2004
	Effect the development of mammary gland	Markey et al., 2001
	Increased ERB mRNA expression	Ramos et al., 2003
	Development of mammary tumors (Cancer)	Durando et al., 2007
	Hyperactivity	Ishido et al., 2004
20	Altered immune function	Yoshino et al., 2003
30	Altered immune function	Yoshino et al., 2004
	Behavioral changes	Kubo et al., 2003

	Changes in brain: increased in ER-α	Aloisi et al., 2001
	Increased in Aggression	Farabollini et al., 2002
	Masculization of female behavior	Dessì et al., 2002
	Altered reactivity of fear-provoking or painful stimuli	Aloisi et al., 2002
	Alteration of sensorial mechanisms underlying behavior	Della Seta et al., 2005
40	Increased activity rate	Adriani et al., 2003
	Hypothalamic ERa	Ceccarelli et al., 2007
	Impair of cornu ammonis (CA1) pyramidal cell dendritic spine synapse	MacLusky et al. 2005
	density (PSSD)	
	Decreased serum testosterone	Della Seta et al., 2006
	Socio-sexual behaviors	Porrini et al., 2005
42	Significant disruption of chromosomes alignment during meiosis	Hunt et al., 2003
50	Increase in prostate	Gupta, 2000
72	Significant disruption of chromosomes alignment during meiosis	Hunt et al., 2003
	Reduction in body weight	Al-Hiyasat et al., 2004
	Significant increases in the weights of the uterus	Al-Hiyasat et al., 2004
100	Increase in the relative weight of ovaries	Al-Hiyasat et al., 2004
	Altered reactivity of fear-provoking stimuli	Negishi et al., 2004
	Permanent change in the central nervous system	Kubo et al., 2003
200	Earlier vaginal opening	Nikaido et al., 2000
250	Effect the development of mammary gland	Markey et al., 2001
400	Changes in brain: increase in progesterone receptor mRNA levels	Funabashi et al., 2003
400	Changes in brain somatostatin receptors	Facciolo et al., 2002

In October 2008, the FDA acknowledges that the scientific research had been inconclusive to establish a pose risk at the current established level of 5 mg/Kg-BW/day. During that announcement FDA failed to disclosed the conflict of interest by the FDA's BPA Subcommittee Chair, Martin Philbert, which benefited a \$15 million grant from Dow Chemical Company for the University of Michigan Risk Science Center, which he founded and codirects (Erler and Novak, 2010). A 6 month review done by Canada of 150 research studies came to the conclusions contrary to that of FDA, and was the first country to declare BPA as a health hazard and is in the process to ban it from their products.

8.3.3 EXPOSURE ASSESSMENT

For the exposure assessment for infants in the beginning 3 different case scenarios were done. First major category was the central tendency exposure (CTE) or also known as average exposure (AVE). For the second category of analysis was the reasonable maximum exposure (RME) was calculated. This helped us to see if there is a imminent health risk or possible only in the most extreme cases. The case scenarios were distributed as follows: Case 1 was a infant fed with infant formula for 12 months, and the preparation of infant formula was assumed to be done with water using a 1:1 dilution (Wong et al., 2005); Case 2 was a infant fed for 12 months using infant formula but diluted using a 1:1 dilution ration using milk; Case 3 was a infant fed for 12 months using human milk (breast fed). For the first two cases the migration from baby bottle of BPA was also taking into consideration. For all the three cases the ingestion of water was also taken into consideration. However, due to the high BPA concentration that migrated from the bottles it was removed from the third case. The risk assessment for the first three case scenarios 1 through 3 was done in order to understand which pathway of ingestion poses the highest risk especially in the first 6 months from birth. Based on these three cases it was decided to further investigate Case 1 and 3 without the migration of BPA from baby bottles, and were denoted as Case A and C.

In the second part of the study additional routes of exposure such as inhalation of indoor air, and ingestion of dust, meats, fruits, fish, vegetables, soup, tea, fruit juice and soda was also taking into consideration and was noted as Case 4. From all the additional routes of exposure only the inhalation of indoor air was taking into account since birth, the rest only after the infant was 6 months old. Four different case scenarios were compared as Case A through D for further analysis. Case B and D were chosen as the most likely routes of exposure for infants from birth to 12 months. Case B was taking into consideration an infant fed with infant formula food and Case D was an infant that was breast fed, with both cases having taken into consideration all the addition routes of exposure mentioned earlier such as inhalation of indoor air, and ingestion of dust, meats, fruits, fish, vegetables, soup, tea, fruit juice and soda. Finally in our final risk assessment the time period was done for 50 years. The risk assessment was divided into four different categories as infants (0-1 year), children (1-6 years and 6-11 years), teenagers (11-21 years), and adults (21-50 years). There were also two different case scenarios as Case E and F, for the infants fed with infant formula, and breast fed, respectively. For both cases E and F the additional routes of exposure for children, teens, and adults were inhalation of outdoor air, ingestion of pasta and coffee.

All the concentrations used for the risk assessment was done using statistical software ProUCL version 4 obtained from USEPA website. For all the concentrations used the value recommended by ProUCL was used, which were composed of six different recommendations. The recommendations were 95% UCL, 97.5% UCL, and 99% UCL Chebyshev for the nonparametric distribution and 95% UCL for normal, gamma, and lognormal distribution data sets. The recommended concentration by ProUCL was use for both CTE and RME exposure unless otherwise specified. For the infant formula, human milk, baby bottle migration, drinking water, and milk (only for CTE) the recommended values were 97.5% UCL Chebyshev, 95% UCL normal distribution, 95% UCL gamma distribution, 99% UCL Chebyshev, and 95% UCL log normal distribution, respectively. The milk concentration used for the RME was the mean of the higher range of values obtained from only one study. For the coffee, fruit juice, tea, soft drink the recommended values were 95% UCL gamma distribution, 99% UCL Chebyshev, 95% UCL gamma distribution, and 97.5% UCL Chebyshev, respectively. For the vegetables, meat, fish, soup, fruits, and pasta the recommended values were 97.5% UCL Chebyshev, 95% UCL gamma distribution, 95% UCL log normal distribution, 95% UCL gamma distribution, 95% UCL gamma distribution, and 95% UCL normal distribution, respectively. Finally for outdoor air, indoor air,

and dust the recommended values were 95% UCL Chebyshev, 95% UCL gamma distribution, and 95% UCL gamma distribution, respectively.

8.3.3.1 MODEL SETUP

The models were determined using the Risk Assessment Guidance for Superfund (USEPA, 1989), but were modified to fit my particular pathway of ingestion to determine the estimated daily intake (EDI). Also the input variables were obtained from the Child-Specific Exposure Factors Handbook (CSEFH) from EPA (USEPA CSEFH, 2008) and used for model formulation for infants. The Exposure Factors Handbook (USEPA EFH, 2011) was used for infants, children, teens, and adults. The model for the infant formula ingestion and average daily intake is given below in equation1:

$$EDI (\mu g/kg-d) = [Cs * (IR/BW) * EF * ED] / AT$$
(1)
Where,

Cs - Conc. in Infant Formula (µg/mL, Recommended ProUCL - UCL)

IR / BW - Infant Formula rate (mL / Kg-day) (half of Table 15.1 values, because the other half was for the water or milk depending on the scenario) (USEPA CSEFH, 2008)

EF - Exposure Frequency (Average of 30 days per month)

- **ED** Exposure Duration (Months)
- AT Averaging time (AT = ED but converted in days)

It is important to mention that for all the cases the total risk was calculated using four different stages 0-1 month, 1-3 months, 3-6 months, and 6-12 months. The division was good to take different intervals, because the mass of the infants changes rapidly during the first 12

months. Also the recommended mean and 95th percentile for the RME and mean numbers were used for the CTE.

For the ingestion of milk the ingestion parameters were the same as for infant formula. For the migration from baby bottle the full numbers from Table 15.1 from CSEFH was used, because that was the total food coming in contact with the bottle. For the consumption of water alone the same model was used, but the IR/BW parameter was obtained from Table ES-1, Chapter 3 Recommendations (USEPA EFH, 2011). Equation 1 was used for the consumption of water for the children, teens and adults risk assessment.

For the ingestion of fruits, vegetables, fish, meats, and pasta Equation 1 was used for the calculations of EDI, however the concentrations used were in μ g/g and the IR/BW used had the units of g/Kg-day and were taken from Table ES-1, Chapter 9 (for both fruits and vegetables), Chapter 10, Chapter 11 Recommendations, and Table12.26, respectively (USEPA EFH, 2011). For the infants the EF, ED, were used as in Equation 1. For 1 to 50 years the EF and ED used were in the units of days/year and years, respectively.

For the ingestion of soup, tea, coffee, soft drink, and fruit juice the Equation 2 was used for the calculations of EDI and the model is given below:

 $EDI (\mu g/kg-d) = [C_L * (IR) * EF * ED] / AT * BW$ (2) Where,

 C_L - Conc. in Liquid Food (µg/mL, Recommended ProUCL - UCL)

- **IR** Water intake (mL/day)
- **EF** Exposure Frequency (365 days per year)

ED - Exposure Duration (Years)

AT - Averaging time (AT = ED but converted in days)

BW - Body Weight (Kg) (Table ES-1, Chapter 8 Recommendations) (USEPA EFH, 2011)

For infants the Equation 2 had the units from Equation 1 for the EF and ED. For infants' soup, tea, soft drinks, and fruit juice was taken into consideration.

For the ages 1 to 50 years the ingestion rate of soup Table 3.52 was used for the CTE calculations and Table 3.50 for RME calculations (USEPA EFH, 2011). For infants the ingestion of soup mean value from Table 3.52 was used for the CTE calculations and the mean value plus the standard deviation for RME calculations.

IR for tea for infants was obtained from Table 3.63 and the same value of 0.5 ml/day was used for both CTE and RME calculations. For the ages 1 to 50 years for the ingestion rate of tea Table 3.63 was sued for CTE calculations and Table 3.50 was used for RME calculations (USEPA EFH, 2011).

The IR of fruit juice for infants was obtained from Table 3.63 and Table 3.73 for CTE and RME calculations, respectively. For the ages 1 to 50 years for the ingestion rate of fruit juice Table 3.63 was used for CTE calculations and Table 3.50 was used for RME calculations (USEPA EFH, 2011).

The IR or coffee was only used for ages 1 to 50 years and Table 3.63 and Table 3.50 was used for the calculations for CTE and RME, respectively (USEPA EFH, 2011).

The IR of soft drinks for infants was obtained from Table 3.73 and the value for 6 months was used for CTE calculations and the value for 12 months was used for the RME calculations. For the ages 1 to 6 years the CTE calculations used IR from Table 3.68 and the mean value from Table 3.73. For the RME calculations Table 3.73 was used by taking the mean calculations plus

the standard error. For the ages 6 to 11 years the CTE calculations used IR from Table 3.68 and for the RME calculations from Table 3.69. Finally for the 11 to 21 years and 21 to 50 years the mean value was used for the CTE and 95th percentile for the RME calculations (USEPA EFH, 2011).

For the inhalation of indoor and outdoor air the Equation 3 was used for the calculations of EDI and the model is given below:

$EDI (\mu g/kg-d) = [C_A * (IR) *ET * EF * ED] / AT * BW$ (3) Where,

 C_A - Conc. in Air ($\mu g/m^3$, Recommended ProUCL - UCL)

IR - Inhalation rate (m³/hour) (Table ES-1, Chapter 6 Recommendations) (USEPA EFH, 2011)

ET - Exposure Time (hours/day) (Table ES-1, Chapter 16 Recommendations) (USEPA EFH, 2011)

EF - Exposure Frequency (365 days per year)

ED - Exposure Duration (Years)

AT - Averaging time (AT = ED but converted in days)

BW - Body Weight (Kg) (Table ES-1, Chapter 8 Recommendations) (USEPA EFH, 2011)

The IR of indoor and outdoor air was obtained from Table ES-1, Chapter 6 for CTE and RME calculations. The ET values were obtained from Table ES-1, Chapter 16 for both CTE and RME calculations. The outdoor ET value was calculated based on the indoor time (USEPA EFH, 2011).

The dust ingestion is the last ingestion route used, the Equation 4 was used for the calculations of EDI and the model is given below:

$$EDI (\mu g/kg-d) = [C_d * (IR) * EF * ED] / AT * BW$$
(4)

Where,

 C_L - Conc. in Dust (µg/mg, Recommended ProUCL - UCL)

IR - Dust Ingestion (mg/day) (Table ES-1, Chapter 5 Recommendations) (USEPA EFH, 2011)

EF - Exposure Frequency (365 days per year)

ED - Exposure Duration (Years)

AT - Averaging time (AT = ED but converted in days)

BW - Body Weight (Kg) (Table ES-1, Chapter 8 Recommendations) (USEPA EFH, 2011)

8.3.4 RISK CHARACTERIZATION

For the evaluation of non-cancer risk calculating for the all exposure routes Hazard Quotient (HQ) was calculated using the following formula:

HQ = EDI / RfD

Where,

RfD – Reference dose (μ g/kg-d) depending on the case scenario.

The Hazard Index (HI) was calculated using the sum of all hazard quotients. If the HI >1,

it implies that an adverse health affect is possible to occur depending on the value of HI.

8.4 RESULTS AND DISCUSSION

The total expected daily intake (EDI) calculated for Case 1 can be seen in Table 8.3 and 8.4 for CTE and RME, respectively. From both tables we can see that the most critical age period is the first month due to the low body weight (BW) of the baby. During the first month the baby has the highest EDI with small decrease as he grows. Even though the baby consumes more food as he grows the increase in BW is higher resulting in a lower EDI. We can also observe that the highest ingestion of BPA occurs from the migration from baby bottles. The exposure hazard quotient (HQ) calculations for Case 1 using the CTE rates were calculated using subchronic RfD of 50, 10, and 2 μ g/kg-day and can been seen in Table 8.5 through 8.7, respectively. The

calculations using the RME rates can been seen in Table 8.8 though 8.10 for the subchronic RfD of 50, 10, and 2 μ g/kg-day, respectively. Due to the fact that BPA could migrate from baby bottles, there was a health effect risk for babies even using the subchronic RfD of 50 μ g/kg-day. The second highest exposure route is the ingestion from the infant formula. The total HQ for 12 months was 1.380, 6.899, and 34.497 using CTE rates for 50, 10, and 2 μ g/kg-day RfD, respectively. For the RME the exposure risk were 1.988, 9.938, and 49.690 for 50, 10, and 2 μ g/kg-day RfD, respectively. Using CTE rates there was an expected adverse effect from infant formula exposure only if the RfD was chosen at 2 μ g/kg-day. We can see the CTE and RME exposure calculations for Case 1 in Figure 8.1 using all the three RfDs. The percentage of each pathway can been found for both CTE and RME calculations in Table 8.11.

Douto of Exposure	Estimated Daily Intake (µg/Kg-bw-day) of Bisphenol A by various age groups					
Koute of Exposure	0-1 Months	1-3 Montha	3-6 Martha	6-12 Months		
	Months	WIONUNS	Months	Months		
Ingestion of Infant Formula	1.484	1.385	1.088	0.821		
Ingestion of Water preparing food	0.227	0.212	0.167	0.126		
Ingestion of Water	0.415	0.361	0.242	0.161		
Ingestion from Migration from Baby Bottle	19.350	18.060	14.190	10.707		
Total	21.476	20.017	15.687	11.814		

Table 8.3 CTE estimated daily intake (µg/kg-bw-day) calculations for Case 1

Table 8.4 RME estimated daily intake (µg/kg-bw-day) calculations for Case 1

Pouto of Exposuro	Estimated Daily Intake (μg/Kg-bw-day) of Bisphenol A by various age groups					
Route of Exposure	0-1	1-3	3-6	6-12		
	Months	Months	Months	Months		
Ingestion of Infant Formula	2.176	1.879	1.484	1.286		
Ingestion of Water preparing food	0.333	0.288	0.227	0.197		
Ingestion of Water	0.721	0.864	0.524	0.391		
Ingestion from Migration from Baby Bottle	28.380	24.510	19.350	16.770		
Total	31.611	27.541	21.585	18.644		

Pouto of Evnoguno	HQ of				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Infant Formula	0.030	0.028	0.022	0.016	
Ingestion of Water preparing food	0.005	0.004	0.003	0.003	
Ingestion of Water	0.008	0.007	0.005	0.003	
Ingestion from Migration from Baby Bottle	0.387	0.361	0.284	0.214	1-12 Months
Total	0.430	0.400	0.314	0.236	1.380

Table 8.5 CTE exposure risk calculations for Case 1 using Subchronic R_fD of 50 µg/kg-day

Table 8.6 CTE exposure risk calculations for Case 1 using Subchronic R_fD of 10 µg/kg-day

	HQ of				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Infant Formula	0.148	0.138	0.109	0.082	
Ingestion of Water preparing food	0.023	0.021	0.017	0.013	
Ingestion of Water	0.042	0.036	0.024	0.016	
Ingestion from Migration from Baby Bottle	1.935	1.806	1.419	1.071	0-12 Months
Total	2.148	2.002	1.569	1.181	6.899

Table 8.7 CTE exposure risk calculations for Case 1 using Subchronic R_fD of 2 μ g/kg-day

Pouto of Exposure	HQ of				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Infant Formula	0.742	0.692	0.544	0.410	
Ingestion of Water preparing food	0.114	0.106	0.083	0.063	
Ingestion of Water	0.208	0.180	0.121	0.080	
Ingestion from Migration from Baby Bottle	9.675	9.030	7.095	5.354	1-12 Months
Total	10.738	10.009	7.844	5.907	34.497

Pouto of Evnoguno	HQ of]				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Infant Formula	0.044	0.038	0.030	0.026	
Ingestion of Water preparing food	0.007	0.006	0.005	0.004	
Ingestion of Water	0.014	0.017	0.010	0.008	
Ingestion from Migration from Baby Bottle	0.568	0.490	0.387	0.335	1-12 Months
Total	0.632	0.551	0.432	0.373	1.988

Table 8.8 RME exposure risk calculations for Case 1 using Subchronic R_fD of 50 µg/kg-day

Table 8.9 RME exposure risk calculations for Case 1 using Subchronic R_fD of 10 µg/kg-day

	HQ of				
B oute of Evnosure		gro	ups		
Route of Exposure	0-1	1-3	3-6	6-12	
	Months	Months	Months	Months	
Ingestion of Infant Formula	0.218	0.188	0.148	0.129	
Ingestion of Water preparing food	0.033	0.029	0.023	0.020	
Ingestion of Water	0.072	0.086	0.052	0.039	
Ingestion from Migration from Baby	2.838	2.451	1.935	1.677	1-12
Bottle					Months
Total	3.161	2.754	2.159	1.864	9.938

Table 8.10 RME exposure risk calculations for Case 1 using Subchronic R_fD of 2 µg/kg-day

Boute of Evnoguna	HQ of				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Infant Formula	1.088	0.940	0.742	0.643	
Ingestion of Water preparing food	0.167	0.144	0.114	0.099	
Ingestion of Water	0.361	0.432	0.262	0.195	
Ingestion from Migration from Baby Bottle	14.190	12.255	9.675	8.385	1-12 Months
Total	15.805	13.770	10.793	9.322	49.690



Figure 8.1 - CTE and RME exposure risk calculations for Case 1 using Subchronic R_fD of 50,10, and 2 μ g/kg-day

	Ingestion from							
Chemical of Concern R _f D 50 μg/kg-day	Infant Formula	Water preparing the food	Water Alone	Migration from Baby Bottle	Total			
		CTE	Calculatio	ons				
Cumulative BPA Risk	0.096	0.015	0.024	1.246	1.380			
Percent Contribution of Each Pathway	6.92	1.06	1.71	90.31	100			
RME Calculations								
Cumulative BPA Risk	0.136	0.021	0.050	1.780	1.988			
Percent Contribution of Each Pathway	6.867	1.052	2.516	89.565	100			

Table 8.11 CTE and RME exposure risk calculations for Case 1 and the percentage contribution of each pathway using Subchronic R_fD of 50 µg/kg-day

The total expected daily intake (EDI) calculated for Case 2 can be seen in Table 8.12 and 8.13 for CTE and RME, respectively. From both tables we can see that the most critical age period is the first month due to the low body weight (BW) of the baby as in the Case 1. Again the highest exposure risk comes from the migration from baby bottles. The exposure hazard quotient (HQ) calculations for Case 2 using the CTE and RME rates were calculated using subchronic RfD of 50 and can been seen in Table 8.14 and 8.15. The second highest exposure route is the ingestion from the infant formula. We can see the CTE and RME exposure calculations for Case 2 in Figure 8.2. Using the CTE calculations the infant formula was the second highest exposure route after the migration from the baby bottles, and for the RME calculations the milk that was used to prepare the infant formula. The total HQ for 12 months was above 1 for both CTE and RME calculations the milk and migration from bay bottle both had an possible adverse health effect alone using the 50 µg/kg-day. The percentage of each pathway can been found for both CTE and RME calculations in Table 8.16. We can see that for the CTE calculations the migration from baby bottle posses

the highest risk with 89 % of the total exposure risk followed by the infant formula with 6.8 %. For the RME calculations the milk used for the food preparation had the highest percentage of 71.1 % followed by migration from the baby bottle with 26.1 %.

Table 8.12 CTE estimated daily intake (µg/kg-day) calculations for Case 2

Doute of Exposure	Estimated Daily Intake (µg/Kg-bw-day) of Bisphenol A by various age groups					
Koute of Exposure	0-1	1-3	3-6	6-12		
	Months	Months	Months	Months		
Ingestion of Infant Formula	1.484	1.385	1.088	0.821		
Ingestion of Milk preparing food	0.481	0.449	0.353	0.266		
Ingestion of Water	0.415	0.361	0.242	0.161		
Ingestion from Migration from Baby Bottle	19.350	18.060	14.190	10.707		
Total	21.730	20.254	15.873	11.955		

Table 8.13 RME estimated daily intake (µg/kg-day) calculations for Case 2

Pouto of Exposure	Estimated Daily Intake (µg/Kg-bw-day) of Bisphenol A by various age groups					
Route of Exposure	0-1	1-3	3-6	6-12		
	Months	Months	Months	Months		
Ingestion of Infant Formula	2.176	1.879	1.484	1.286		
Ingestion of Milk preparing food	77.138	66.619	52.594	45.581		
Ingestion of Water	0.721	0.864	0.221	0.391		
Ingestion from Migration from Baby Bottle	28.380	24.510	19.350	16.770		
Total	108.415	93.872	73.649	64.028		

	HQ of						
Douto of Exposure		groups					
Route of Exposure	0-1	1-3	3-6	6-12			
	Months	Months	Months	Months			
Ingestion of Infant Formula	0.030	0.028	0.022	0.016			
Ingestion of Milk preparing food	0.010	0.009	0.007	0.005			
Ingestion of Water	0.008	0.007	0.005	0.003			
Ingestion from Migration from Baby	0 387	0 361	0 284	0.214	1-12		
Bottle	0.307	0.387	0.301	0.204	0.214	Months	
Total	0.435	0.405	0.317	0.239	1.396		

Table 8.14 CTE exposure risk calculations for Case 2 using Subchronic R_fD of 50 $\mu g/kg$ day

Table 8.15 RME exposure risk calculations for Case 2 using Subchronic $R_{\rm f}D$ of 50 $\mu g/kg$ day

D / 02	HQ of				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Infant Formula	0.044	0.038	0.030	0.026	
Ingestion of Milk preparing food	1.543	1.332	1.052	0.912	
Ingestion of Water	0.014	0.017	0.004	0.008	
Ingestion from Migration from Baby Bottle	0.568	0.490	0.387	0.335	1-12 Months
Total	2.168	1.877	1.473	1.281	6.799



Figure 8.2 - CTE and RME exposure risk calculations for Case 2 using Subchronic R_fD of 50 $\mu g/kg\text{-}day$

	Ingestion from						
Chemical of Concern R_fD 50 μg/kg-day	Infant Formula	Milk preparing the food	Water Alone	Migration from Baby Bottle	Total		
CTE Calculations							
Cumulative BPA Risk	0.096	0.031	0.024	1.246	1.396		
Percent Contribution of Each Pathway	6.842	2.219	1.689	89.250	100		
		RMI	E Calculation	ons			

Table 8.16 CTE and RME exposure risk calculations for Case 2 and the percentage contribution of each pathway using Subchronic R_fD of 50 μ g/kg-day

Cumulative BPA Risk	0.136	4.839	0.044	1.780	6.799
Percent Contribution of	2 007	71 164	0.646	26 182	100
Each Pathway	2.007	/1.104	0.040	20.162	100

The total expected daily intakes (EDI) were calculated for Case 3 and can be seen in Table 8.17 and 8.18 for CTE and RME, respectively. In the Case 3 only the CTE rates had the most critical age period was the first month due to the low body weight (BW) of the baby. During the first month the baby had the highest EDI with small decrease as he grows. For the RME case the months 1 to 3 are the most critical followed by the first month, 6 to 1 months, and finally 3 to 6 months. This is due to the fact that the increase in drinking water sometimes is greater than the increase in the BW as a result leading to a higher EDI. For the CTE the opposite is true just like in Case 1 and 2, even though the baby consumes more food as he grows the increase in BW is higher resulting in a lower EDI. We can also observe that the highest ingestion of BPA occurs from the drinking water. The exposure hazard quotient (HQ) calculations for Case 3 using the CTE rates were calculated using subchronic RfD of 50, 10, and 2 μ g/kg-day and can been seen in Tables 8.19 through 8.21, respectively. The calculations using the RME rates can been seen in Tables 8.22 though 8.24 for the subchronic RfD of 50, 10, and 2 μ g/kg-day, respectively. The total HQ for 12 months is 0.027, 0.134, and 0.668 using CTE rate for 50, 10,

and 2 μ g/kg-day RfD, respectively. For the RME the exposure risk were 0.048, 0.242, and 2.421 for 50, 10, and 2 μ g/kg-day RfD, respectively. As a result we can see that the only health risk can be found at 2 μ g/kg-day RfD using RME rates, and more than 90 % of that risk is due to the drinking water. We can see the CTE and RME exposure calculations for Case 3 in Figure 8.3 using all the three RfDs. The percentage of each pathway can been found for both CTE and RME calculations in Table 8.25.

Table 8.17 CTE estimated intake (µg/kg-day) calculations for Case 3

B outo of Exposuro	Estimated Daily Intake (µg/Kg-bw-day) of Bisphenol A by various age groups					
Route of Exposure	0-1	1-3	3-6	6-12		
	Months	Months	Months	Months		
Ingestion of Human Milk	0.049	0.045	0.036	0.027		
Ingestion of Water	0.415	0.361	0.242	0.161		
Total	0.464	0.406	0.278	0.188		

Table 8.18 RME estimated intake (μ g/kg-day) calculations for Case 3

Boute of Exposure	Estimated Daily Intake (µg/Kg-bw-day) of Bisphenol A by various age groups					
Koute of Exposure	0-1	1-3	3-6	6-12		
	Months	Months	Months	Months		
Ingestion of Human Milk	0.071	0.062	0.049	0.042		
Ingestion of Water	0.721	0.864	0.221	0.391		
Total	0.793	0.925	0.270	0.433		

Table 8.19 CTE exposure risk for Case 3 using Subchronic R_fD of 50 µg/kg-day

Douto of Europuno	HQ of Bisphenol A by various age groups				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Human Milk	0.001	0.001	0.001	0.001	
Ingestion of Water	0.008	0.007	0.005	0.003	1-12 Months
Total	0.009	0.008	0.006	0.004	0.027

Doute of Europupe	HQ of Bisphenol A by various age groups				
Koute of Exposure	0-1	1-3	3-6	6-12	
	Months	Months	Months	Months	
Ingestion of Human Milk	0.005	0.005	0.004	0.003	
Ingestion of Water	0.042	0.036	0.024	0.016	1-12 Months
Total	0.046	0.041	0.028	0.019	0.134

Table 8.20 CTE exposure risk for Case 3 using Subchronic R_fD of 10 µg/kg-day

Table 8.21 CTE exposure risk for Case 3 using Subchronic R_fD of 2 μ g/kg-day

Douto of Exposure	HQ of Bis				
Koute of Exposure	0-1	1-3	3-6	6-12	
	Months	Months	Months	Months	
Ingestion of Human Milk	0.024	0.023	0.018	0.013	
Ingestion of Water	0.208	0.180	0.121	0.080	1-12 Months
Total	0.232	0.203	0.139	0.094	0.668

Table 8.22 RME exposure risk for Case 3 using Subchronic $R_{\rm f}D$ of 50 $\mu g/kg\text{-}day$

Doute of Functions	HQ of Bisphenol A by various age groups				
Route of Exposure	0-1	1-3	3-6	6-12	
	Months	Months	Months	Months	
Ingestion of Human Milk	0.001	0.001	0.001	0.001	
Ingestion of Water	0.014	0.017	0.004	0.008	1-12 Months
Total	0.016	0.019	0.005	0.009	0.048

Table 8.23 RME exposure risk for Case 3 using Subchronic R_fD of 10 μ g/kg-day

Doute of Function	HQ of Bisphenol A by various age groups				
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Ingestion of Human Milk	0.007	0.006	0.005	0.004	
Ingestion of Water	0.072	0.086	0.022	0.039	1-12 Months
Total	0.079	0.093	0.027	0.043	0.242

	HQ of Bisphenol A by various age groups				
Route of Exposure	0-1	1-3	3-6	6-12	
	Months	Months	Months	Months	
Ingestion of Human Milk	0.071	0.062	0.049	0.042	
Ingestion of Water alone	0.721	0.864	0.221	0.391	1-12 Months
Total	0.793	0.925	0.270	0.433	2.421

Table 8.24 RME exposure risk for Case 3 using Subchronic R_fD of 2 µg/kg-day

Table 8.25 CTE and RME exposure risk calculations for Case 3 and the percentage contribution of each pathway using Subchronic R_fD of 50 $\mu g/kg$ -day

Chemical of Concern	Ingestion from			
R _f D 50 μg/kg-day	Human Milk	Human Milk Water Alone		
	CTH	E Calculations		
Cumulative BPA Risk	0.078	0.590	0.668	
Percent Contribution of Each Pathway	11.73	88.27	100	
	RME Calculations			
Cumulative BPA Risk	0.112	1.099	1.211	
Percent Contribution of Each Pathway	9.25	90.75	100	

Table 8.26 CTE and RME exposure risk calculations using Subchronic RfD of 50 μ g/kg-day and estimated daily intake for Case 1, 2, and 3.

Case	Chemical Tendency (CTE)	Exposure	Reasonable Maximum Expos (RME)		
	ADI (µg/kg-day)	HQ	ADI (µg/kg-day)	HQ	
Case 1	17.249	1.380	24.845	1.988	
Case 2	17.453	1.396	84.991	6.799	
Case 3	0.334	0.027	0.605	0.048	


Figure 8.3 - CTE and RME exposure risk calculations for Case 3 using Subchronic R_fD of 50,10, and 2 $\mu g/kg\text{-}day$

We can see both the CTE and RME exposure risk calculated using 50 μ g/kg-day RfD and EDI for Case 1, 2, and 3 in Table 8.26. We can see that the most critical for both CTE and RME is Case 2 followed by Cases 1 and 3.

For the Case 4 additional possible exposure routes had been investigated. The ingestion for different liquid drinks, solid foods and dust only was taken into consideration after 6 months. We can see the CTE and RME EDI for Case 4 in Table 8.27 and 8.28, respectively. The CTE and RME exposure risk calculations for Case 4 can be found in Table 8.29 and 8.30, respectively. Also the exposure risk using 50 μ g/kg-day RfD with the percentage of each exposure routes for CTE and RME and can been seen in Table 8.31 and 8.32, respectively. For the CTE rates the ingestion of vegetables was the most critical followed by the indoor air inhalation, dust, and fruit juice posing the highest exposure risks. For the RME rates the highest ingestion rate was through the vegetables followed by indoor air, vegetables, fruits, dust, and meats.

Route of Exposure	Estimated Daily Intake (µg/Kg-bw per day) of Bisphenol A by various age groups					
Koute of Exposure	0-1	1-3	3-6	6-12		
	Months	Months	Months	Months		
Inhalation from Indoor Air	0.071	0.253	0.297	0.391		
Ingestion from Dust				0.217		
Ingestion from Meats				0.039		
Ingestion from Fruits				0.096		
Ingestion of Fish				0.201		
Ingestion of Vegetables				1.051		
Ingestion of Soup				0.041		
Ingestion of Tea				0.040		
Ingestion of Fruit Juice				0.131		
Ingestion of Soda				0.004		
Total	0.071	0.253	0.297	2.212		

Table 8.27 CTE estimated daily intake (µg/kg-day) calculations for Case 4

Pouto of Exposure	Estimated Daily Intake (µg/Kg-bw per day) of Bisphenol A by various age groups					
Koute of Exposure	0-1	1-3	3-6	6-12		
	Months	Months	Months	Months		
Inhalation from Indoor Air	0.139	0.420	0.442	0.579		
Ingestion from Dust				0.217		
Ingestion from Meats				0.119		
Ingestion from Fruits				0.248		
Ingestion of Fish				0.045		
Ingestion of Vegetables				0.281		
Ingestion of Soup				0.074		
Ingestion of Tea				0.002		
Ingestion of Fruit Juice				0.799		
Ingestion of Soda				0.006		
Total	0.139	0.420	0.442	2.369		

Table 8.28 RME estimated daily intake ($\mu g/kg$ -day) calculations for Case 4

Table 8.29 CTE exposure risk for Case 4 using Subchronic $R_f D$ of 50 μ g/kg-day

	HQ of B	isphenol A by	y various ag	e groups	
Route of Exposure	0-1 Months	1-3 Months	3-6 Months	6-12 Months	
Inhalation from Indoor Air	1.41E-03	5.07E-03	5.94E-03	7.82E-03	
Ingestion from Dust				4.33E-03	
Ingestion from Meats				7.74E-04	
Ingestion from Fruits				1.92E-03	
Ingestion of Fish				4.02E-03	
Ingestion of Vegetables				2.10E-02	
Ingestion of Soup				8.26E-04	
Ingestion of Tea				8.09E-04	
Ingestion of Fruit Juice				2.63E-03	
Ingestion of Soda				8.65E-05	1- Mo
Total	1.41E-03	5.07E-03	5.94E-03	4.42E-02	0.0

Doute of Euroguno	HQ of B	y various ag	e groups		
Koute of Exposure	0-1	1-3	3-6	6-12	
	Months	Months	Months	Months	
Inhalation from Indoor Air	2.78E-03	8.40E-03	8.83E-03	1.16E-02	
Ingestion from Dust				4.33E-03	
Ingestion from Meats				2.37E-03	
Ingestion from Fruits				4.96E-03	
Ingestion of Fish				8.99E-04	
Ingestion of Vegetables				5.61E-03	
Ingestion of Soup				1.50E-03	
Ingestion of Tea				4.01E-05	
Ingestion of Fruit Juice				1.60E-02	
Ingestion of Soda				$1.30E_{-}0.0$	1-12
ingestion of Soua				1.501-04	Months
Total	2.78E-03	8.40E-03	8.83E-03	4.74E-02	0.067

Table 8.30 RME exposure risk for Case 4 using Subchronic RfD of 50 µg/kg-day

Table 8.31 CTE exposure risk for Case 4 and the percentage contribution of each pathway using Subchronic R_fD of 50 $\mu g/kg$ -day

Route of exposure for CTE	Cumulative BPA Risk	Percent Contribution of Each Pathway
Inhalation from Indoor Air	0.020	35.71
Ingestion from Dust	0.004	7.65
Ingestion from Meats	0.001	1.37
Ingestion from Fruits	0.002	3.39
Ingestion of Fish	0.004	7.10
Ingestion of Vegetables	0.021	37.12
Ingestion of Soup	0.001	1.46
Ingestion of Tea	0.001	1.43
Ingestion of Fruit Juice	0.003	4.63
Ingestion of Soda	0.00009	0.15
Total	0.093	100

Route of exposure for RME	Cumulative BPA Risk	Percent Contribution of Each Pathway
Inhalation from Indoor Air	0.032	27.28
Ingestion from Dust	0.004	7.65
Ingestion from Meats	0.002	4.19
Ingestion from Fruits	0.005	8.76
Ingestion of Fish	0.001	1.59
Ingestion of Vegetables	0.006	9.90
Ingestion of Soup	0.056	2.60
Ingestion of Tea	0.00004	0.07
Ingestion of Fruit Juice	0.016	28.21
Ingestion of Soda	0.00013	0.23
Total	0.122	100

Table 8.32 RME exposure risk calculations for Case 4 and the percentage contribution of each pathway using Subchronic $R_f D$ of 50 $\mu g/kg$ -day

Based on the results from Cases 1 through 4 four different cases were further analyzed and denoted as Case A through D. Case A used the same exposure routes as Case 1 without the migration from baby bottle, and case C was the same as Case 3 and used for comparison purposes. Case B added the new exposure routes from Case 4 to Case A, and Case D was the combination between Case C and Case 4. Case B and D are the final two models used to evaluate the exposure to BPA by infants for 1 to 12 months old. We can see the exposure risk calculations for Cases A through D using subchronic RfD 50, 10, and $2\mu g/kg$ -day, and the percentage of each exposure route for CTE and RME in Table 8.33 and 8.34, respectively. In Figure 8.4 and 8.5 we can see the CTE and RME exposure risk calculations for Case B and D, respectively.

For Case A we can that the ingestion of BPA from infant formula is the highest, and for the CTE rates at RfD of 2 μ g/kg-day infant formula alone posed an health risk having an HQ of 2.388. For Case B we can see that the highest exposure route was the drinking water ingestion. For Case D the ingestion of drinking water became the highest exposure route. For both Cases B and D there was only an exposure risk at an RfD of 2 μ g/kg-day. The ingestion of drinking water using the CTE rates was 20 % and 28 % for Case B and D, respectively. For the RME rates Case B showed a possible health risk even at an RfD of 10 μ g/kg-day. Case D had a possible health risk for both CTE and RME rates at an RfD of 2 μ g/kg-day. For both cases B and D the drinking water at an RfD of 2 μ g/kg-day had an HQ value above 1.

As mentioned earlier, the drinking water was assumed to come from bottle water due to the fact that many people are using only bottled water as the only drinking water source. The UCL concentration from bottle water was highest as a result it was used to be in the safe side and have a more conservative value. The UCL water concentration was $3.031 \times 10^{-3} \, \mu g/mL$ for the bottle water. The concentration for the drinking water from water treatment plants or wells was obtained from four papers with a total of 10 points (Kleywegt et al, 2011; Ignatius et al., 2010; Holger at al., 2001; Chen et al., 2006). The recommended UCL was found using ProUCL was 5.16 x10⁻⁴ μ g/mL. For example for Case D at an RfD of 2 μ g/kg-day, if the ingestion of drinking water was assumed to come from a water treatment plant or a well, the total HQ dropped from 0.590 to 0.10 and 1.099 to 0.187 for CTE and RME, respectively. The percentage of exposure route decreased from 28 % to 6.29 % and 38 % to 9.43 % for CTE and RME, respectively. As expected the total HQ dropped also from 2.084 to 1.595 and 2.895 to 1.984 for CTE and RME, respectively. As a result there is still a possible health risk using an RfD of 2 µg/kg-day, but the ingestion of drinking water is not as significant as for the case of bottled water. Based on these results two final cases were used for the risk assessment for 0 to 50 years. Case B and D were used as part of the longer study to create Case E and F for the infant formula baby fed and human milk baby fed, respectively.

		Rfl	D =	RfI) =	Rf	D =	
		50 μg/l	kg-day	10 µg/l	kg-day	2 μg/k	kg-day	% of
		HQ	Total HQ	HQ	Total HQ	HQ	Total HQ	each pathway
Casa	Ingestion of Infant Formula	0.096		0.478		2.388		71.42
	Ingestion of Water preparing food	0.015	0.134	0.073	0.669	0.366	2.866	10.94
A	Ingestion of Water	0.024		0.118		0.112		17.63
	Ingestion of Infant Formula	0.096		0.478		2.388		50.18
	Ingestion of Water preparing food	0.015		0.073		0.366		7.69
	Ingestion of Water alone	0.024		0.118		0.112		12.38
	Inhalation from Indoor Air	0.20		0.101		0.506		10.62
	Ingestion from Dust	0.004		0.022		0.108		2.27
Casa	Ingestion from Meats	0.001		0.004		0.019		0.41
	Ingestion from Fruits	0.002	0.191	0.010	0.952	0.048	4.760	1.01
D	Ingestion of Fish	0.004		0.020		0.100		2.11
	Ingestion of Vegetables	0.021		0.105		0.526		11.04
	Ingestion of Soup	0.001		0.004		0.021		0.43
	Ingestion of Tea	0.001		0.004		0.020		0.42
	Ingestion of Fruit Juice	0.003		0.013		0.066		1.38
	Ingestion of Soda	9E-05		4E-04		0.002		0.05
Case	Ingestion from Human Milk	0.003	0.027	0.016	0.124	0.078	0 669	11.73
С	Ingestion of Water	0.024	0.027	0.118	0.134	0.590	0.008	88.27
	Ingestion from Human Milk	0.003		0.016		0.078		3.76
	Ingestion of Water	0.024		0.118		0.590		28.29
	Inhalation from Indoor Air	0.20		0.101		0.506		24.27
	Ingestion from Dust	0.004		0.022		0.108		5.20
	Ingestion from Meats	0.001		0.004		0.019		0.93
Case	Ingestion from Fruits	0.002	0.083	0.010	0.417	0.048	2 084	2.31
D	Ingestion of Fish	0.004	0.085	0.020	0.417	0.100	2.064	4.82
	Ingestion of Vegetables	0.021		0.105		0.526		25.22
	Ingestion of Soup	0.001		0.004		0.021		0.99
	Ingestion of Tea	0.001		0.004		0.020		0.97
	Ingestion of Fruit Juice	0.003		0.013		0.066		3.15
	Ingestion of Soda	9E-05		4E-04		0.002		0.10

Table 8.33 CTE exposure risk calculations using Subchronic R_fD of 50, 10, and 2 μ g/kg-day for Case A, B, C, and D with the percentage contribution of each pathway for 1 year.

		Rf	D =	Rf	D =	Rf	D =	
		50 μg /	kg-day	10 μg /	kg-day	2 μg/k	kg-day	% of
		HQ	Total HQ	HQ	Total HQ	HQ	Total HQ	each pathway
Casa	Ingestion of Infant Formula	0.136		0.682		3.412		65.80
	Ingestion of Water preparing food	0.021	0.207	0.105	1.037	0.523	5.185	10.08
A	Ingestion of Water	0.050		0.350		1.250		24.11
	Ingestion of Infant Formula	0.136		0.682		3.412		49.65
	Ingestion of Water preparing food	0.021		0.105		0.523		7.64
	Ingestion of Water alone	0.050		0.250		1.250		18.19
	Inhalation from Indoor Air	0.032		0.158		0.789		11.49
	Ingestion from Dust	0.004		0.022		0.108		1.58
Casa	Ingestion from Meats	0.002		0.012		0.059		0.86
	Ingestion from Fruits	0.004	0.275	0.025	1.374	0.124	6.870	1.80
D	Ingestion of Fish	0.009		0.004		0.022		0.33
	Ingestion of Vegetables	0.005		0.028		0.140		2.04
	Ingestion of Soup	0.001		0.007		0.037		0.54
	Ingestion of Tea	4E-05		2E-04		0.001		0.01
	Ingestion of Fruit Juice	0.016		0.079		0.399		5.81
	Ingestion of Soda	1E-04		6E-04		0.003		0.05
Case	Ingestion from Human Milk	0.004	0.049	0.022	0.242	0.112	1 211	9.25
С	Ingestion of Water	0.044	0.048	0.220	0.242	1.099	1.211	90.75
	Ingestion from Human Milk	0.004		0.022		0.112		3.87
	Ingestion of Water	0.044		0.220		1.099		37.95
	Inhalation from Indoor Air	0.032		0.158		0.789		27.28
	Ingestion from Dust	0.004		0.022		0.108		3.74
	Ingestion from Meats	0.002		0.012		0.059		2.05
Case	Ingestion from Fruits	0.005	0.116	0.025	0.570	0.124	2 805	4.28
D	Ingestion of Fish	8E-04	0.110	0.005	0.379	0.022	2.893	0.78
	Ingestion of Vegetables	0.006		0.028		0.140		4.84
	Ingestion of Soup	0.001		0.007		0.037		1.27
	Ingestion of Tea	4E-05		2E-04		0.001		0.03
	Ingestion of Fruit Juice	0.016		0.080		0.400		13.80
	Ingestion of Soda	1E-04		6E-04		0.003		0.11

Table 8.34 RME exposure risk calculations using Subchronic R_fD of 50, 10, and 2 μ g/kg-day for Case A,B,C, and D with the percentage contribution of each pathway for 1 year.



Figure 8.4 - CTE and RME exposure risk calculations for Case B using Subchronic R_fD of 50,10, and 2 μ g/kg-day.



Figure 8.5 - CTE and RME exposure risk calculations for Case D using Subchronic R_fD of 50,10, and 2 μ g/kg-day.

Case E was the risk assessment for which the infants were assumed to be fed only infant formula. The risk evaluation was done for a total of 50 years. The total EDI for Case E for both CTE and RME can be seen in Table 8.35 and Figure 8.6. We can see that the highest EDI can be found for 0 to 1 year and steadily decreased with an increase in age. From Figure 8.7 we can see the percentage of EDI for each age group for both CTE and RME rates. For the CTE rates for the infant age 0 to 1 year the percentage of EDI was 64 % and 50 % for CTE and RME, respectively. This was expected, because the most critical age period is the first year, due to the low BW of the baby. The exposure HQ calculations for Case E using the CTE and RME rates were calculated using subchronic RfD of 50, 10, and 2 μ g/kg-day and can been seen in Table 8.36, 8.37, and 8.37, respectively. We can see that for both CTE and RME the total HQ is above 1 at an RfD of 10 and 2 μ g/kg-day. The 0 to 1 year is the most critical age period as expected from the EDI with the highest HQ of 0.952, 4.760 for CTE rates at an RfD of 10 μ g/kg-day and 1.374, 6.870 for RME rates at an RfD of 2 μ g/kg-day. We can see the total HQ by age group in Figure 8.9.

From Figure 8.8 we can see that the infant formula exposure route has the highest contribution to the total HQ. For the CTE calculations several other exposure routes that contribute highly to the total HQ from the highest to lowest are infant formula, vegetables, drinking water, meats, indoor air, fruit juice, and fish which had the exposure route percentages of 32.11, 15.17, 14.25, 8.27, 7.27, 5.53, and 5.42 %, respectively. For the RME the routes that contributed highest to the total HQ from the highest to lowest were infant formula, drinking water, vegetables, fruit juice, meats and inside air which had the exposure route percentages of 24.90, 15.00, 11.95, 11.33, 10.58, 6.46, and 6.28 %, respectively. We can see all the percentages for all the exposure routes for both CTE and RME calculations in Table 8.39 and Figure 8.10.

		CTE F	Estimated Da	aily Intake	
Route of Exposure	0-1	1-6	6-11	11-21	21-50
	Year	Years	Years	Years	Years
Ingestion of Infant Formula	4.777				
Inhalation of Indoor Air	1.012	0.033	0.017	0.011	0.009
Inhalation of Outdoor Air		0.003	0.003	0.002	0.001
Ingestion of Dust	0.217	0.030	0.014	0.007	0.003
Ingestion of Vegetables	1.051	0.512	0.302	0.188	0.204
Ingestion of Meats	0.039	0.452	0.314	0.224	0.202
Ingestion of Fish	0.201	0.232	0.170	0.102	0.100
Ingestion of Fruits	0.096	0.108	0.039	0.017	0.017
Ingestion of Pasta		0.125	0.083	0.057	0.046
Ingestion of Soup	0.041	0.107	0.040	0.020	0.020
Ingestion of Water	1.911	0.075	0.052	0.033	0.048
Ingestion of Tea	0.040	0.031	0.046	0.049	0.062
Ingestion of Coffee		0.005	0.004	0.020	0.328
Ingestion of Soda	0.004	0.033	0.035	0.017	0.014
Ingestion of Fruit Juice	0.131	0.331	0.211	0.100	0.050
Total	9.520	2.075	1.329	0.847	1.104
		RME 1	Estimated Da	aily Intake	
Route of Exposure	0-1	1-6	6-11	11-21	21-50
	Year	Years	Years	Years	Years
Ingestion of Infant Formula	6.824				
Inhalation of Indoor Air	1.580	0.064	0.033	0.024	0.019
Inhalation of Outdoor Air		0.001	0.001	0.001	0.00004
Ingestion of Dust					
8	0.217	0.049	0.014	0.007	0.003
Ingestion of Vegetables	0.217 0.281	0.049 1.214	0.014 0.849	0.007 0.449	0.003 0.482
Ingestion of Vegetables Ingestion of Meats	0.217 0.281 0.119	0.049 1.214 1.076	0.014 0.849 0.717	0.007 0.449 0.527	$0.003 \\ 0.482 \\ 0.460$
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish	0.217 0.281 0.119 0.045	0.049 1.214 1.076 0.691	0.014 0.849 0.717 0.448	0.007 0.449 0.527 0.263	0.003 0.482 0.460 0.325
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits	0.217 0.281 0.119 0.045 0.248	0.049 1.214 1.076 0.691 0.299	0.014 0.849 0.717 0.448 0.143	0.007 0.449 0.527 0.263 0.059	0.003 0.482 0.460 0.325 0.059
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta	0.217 0.281 0.119 0.045 0.248	0.049 1.214 1.076 0.691 0.299 0.215	0.014 0.849 0.717 0.448 0.143 0.154	0.007 0.449 0.527 0.263 0.059 0.085	$\begin{array}{c} 0.003 \\ 0.482 \\ 0.460 \\ 0.325 \\ 0.059 \\ 0.085 \end{array}$
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup	0.217 0.281 0.119 0.045 0.248 0.074	0.049 1.214 1.076 0.691 0.299 0.215 0.146	$\begin{array}{c} 0.014\\ 0.849\\ 0.717\\ 0.448\\ 0.143\\ 0.154\\ 0.078\\ \end{array}$	$\begin{array}{c} 0.007 \\ 0.449 \\ 0.527 \\ 0.263 \\ 0.059 \\ 0.085 \\ 0.033 \end{array}$	$\begin{array}{c} 0.003 \\ 0.482 \\ 0.460 \\ 0.325 \\ 0.059 \\ 0.085 \\ 0.036 \end{array}$
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water	0.217 0.281 0.119 0.045 0.248 0.074 3.546	0.049 1.214 1.076 0.691 0.299 0.215 0.146 0.191	$\begin{array}{c} 0.014\\ 0.849\\ 0.717\\ 0.448\\ 0.143\\ 0.154\\ 0.078\\ 0.142\\ \end{array}$	$\begin{array}{c} 0.007 \\ 0.449 \\ 0.527 \\ 0.263 \\ 0.059 \\ 0.085 \\ 0.033 \\ 0.102 \end{array}$	$\begin{array}{c} 0.003 \\ 0.482 \\ 0.460 \\ 0.325 \\ 0.059 \\ 0.085 \\ 0.036 \\ 0.127 \end{array}$
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea	0.217 0.281 0.119 0.045 0.248 0.074 3.546 0.002	0.049 1.214 1.076 0.691 0.299 0.215 0.146 0.191 0.024	$\begin{array}{c} 0.014\\ 0.849\\ 0.717\\ 0.448\\ 0.143\\ 0.154\\ 0.078\\ 0.142\\ 0.055\end{array}$	$\begin{array}{c} 0.007\\ 0.449\\ 0.527\\ 0.263\\ 0.059\\ 0.085\\ 0.033\\ 0.102\\ 0.114\\ \end{array}$	$\begin{array}{c} 0.003\\ 0.482\\ 0.460\\ 0.325\\ 0.059\\ 0.085\\ 0.036\\ 0.127\\ 0.135\end{array}$
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea Ingestion of Coffee	0.217 0.281 0.119 0.045 0.248 0.074 3.546 0.002 	$\begin{array}{c} 0.049\\ 1.214\\ 1.076\\ 0.691\\ 0.299\\ 0.215\\ 0.146\\ 0.191\\ 0.024\\ 0.054\end{array}$	$\begin{array}{c} 0.014\\ 0.849\\ 0.717\\ 0.448\\ 0.143\\ 0.154\\ 0.078\\ 0.142\\ 0.055\\ 0.149\\ \end{array}$	$\begin{array}{c} 0.007\\ 0.449\\ 0.527\\ 0.263\\ 0.059\\ 0.085\\ 0.033\\ 0.102\\ 0.114\\ 0.455\end{array}$	$\begin{array}{c} 0.003 \\ 0.482 \\ 0.460 \\ 0.325 \\ 0.059 \\ 0.085 \\ 0.036 \\ 0.127 \\ 0.135 \\ 0.493 \end{array}$
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea Ingestion of Coffee Ingestion of Soda	0.217 0.281 0.119 0.045 0.248 0.074 3.546 0.002 0.006	$\begin{array}{c} 0.049\\ 1.214\\ 1.076\\ 0.691\\ 0.299\\ 0.215\\ 0.146\\ 0.191\\ 0.024\\ 0.054\\ 0.065\end{array}$	$\begin{array}{c} 0.014\\ 0.849\\ 0.717\\ 0.448\\ 0.143\\ 0.154\\ 0.078\\ 0.142\\ 0.055\\ 0.149\\ 0.038\\ \end{array}$	$\begin{array}{c} 0.007\\ 0.449\\ 0.527\\ 0.263\\ 0.059\\ 0.085\\ 0.033\\ 0.102\\ 0.114\\ 0.455\\ 0.058\\ \end{array}$	$\begin{array}{c} 0.003\\ 0.482\\ 0.460\\ 0.325\\ 0.059\\ 0.085\\ 0.036\\ 0.127\\ 0.135\\ 0.493\\ 0.046\end{array}$
Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Fruit Juice	0.217 0.281 0.119 0.045 0.248 0.074 3.546 0.002 0.006 0.799	$\begin{array}{c} 0.049\\ 1.214\\ 1.076\\ 0.691\\ 0.299\\ 0.215\\ 0.146\\ 0.191\\ 0.024\\ 0.054\\ 0.065\\ 1.263\end{array}$	$\begin{array}{c} 0.014\\ 0.849\\ 0.717\\ 0.448\\ 0.143\\ 0.154\\ 0.078\\ 0.142\\ 0.055\\ 0.142\\ 0.055\\ 0.149\\ 0.038\\ 0.717\end{array}$	$\begin{array}{c} 0.007\\ 0.449\\ 0.527\\ 0.263\\ 0.059\\ 0.085\\ 0.033\\ 0.102\\ 0.114\\ 0.455\\ 0.058\\ 0.209\end{array}$	$\begin{array}{c} 0.003\\ 0.482\\ 0.460\\ 0.325\\ 0.059\\ 0.085\\ 0.036\\ 0.127\\ 0.135\\ 0.493\\ 0.046\\ 0.117\end{array}$

Table 8.35 CTE and RME estimated daily intake ($\mu g/kg$ -day) calculations for Case E



Figure 8.6 - CTE and RME estimated daily intake for Case E for different age groups.



Figure 8.7 - CTE and RME EDI percentage for different age groups for Case E.

CTE **Route of Exposure** 0-1 1-6 6-11 11-21 21-50 Year Years Years Years Years 9.6E-02 ____ ____ ____ ____ **Ingestion of Infant Formula Inhalation of Indoor Air** 2.0E-02 6.5E-04 3.4E-04 2.1E-04 1.9E-04 **Inhalation of Outdoor Air** ____ 6.5E-05 5.6E-05 3.9E-05 2.7E-05 4.3E-03 5.9E-04 2.7E-04 **Ingestion of Dust** 1.3E-04 5.4E-05 **Ingestion of Vegetables** 4.1E-03 2.1E-02 1.0E-02 6.0E-03 3.8E-03 **Ingestion of Meats** 7.7E-04 9.0E-03 6.3E-03 4.5E-03 4.0E-03 **Ingestion of Fish** 4.0E-03 4.6E-03 3.4E-03 2.0E-03 2.0E-03 1.9E-03 2.2E-03 7.8E-04 3.4E-04 3.4E-04 **Ingestion of Fruits Ingestion of Pasta** 2.5E-03 1.7E-03 1.1E-03 9.1E-04 3.9E-04 **Ingestion of Soup** 8.3E-04 2.1E-03 8.1E-04 4.1E-04 **Ingestion of Water** 3.8E-02 1.5E-03 1.0E-03 6.7E-04 9.7E-04 **Ingestion of Tea** 8.1E-04 6.3E-04 9.2E-04 9.9E-04 1.2E-03 **Ingestion of Coffee** 9.5E-05 7.4E-05 4.1E-04 6.6E-03 ____ 8.6E-05 7.0E-04 2.7E-04 **Ingestion of Soda** 6.5E-04 3.4E-04 0-50 **Ingestion of Fruit Juice** 2.6E-03 6.6E-03 4.2E-03 2.0E-03 1.0E-03 Years Total 0.190 0.041 0.027 0.017 0.022 0.297 RME **Route of Exposure** 0-1 1-6 6-11 11-21 21-50 Year Years Years Years Years **Ingestion of Infant Formula** 1.4E-01 ____ ____ ____ ____ **Inhalation of Indoor Air** 3.2E-02 1.3E-03 6.7E-04 4.7E-04 3.8E-04 **Inhalation of Outdoor Air** 1.2E-05 2.3E-05 8.7E-07 ____ 1.4E-05 **Ingestion of Dust** 4.3E-03 9.9E-04 2.7E-04 1.3E-04 5.4E-05 **Ingestion of Vegetables** 5.6E-03 2.4E-02 1.7E-02 9.0E-03 9.6E-03 1.4E-02 **Ingestion of Meats** 2.4E-03 2.2E-02 1.1E-02 9.2E-03 9.0E-04 **Ingestion of Fish** 1.4E-02 9.0E-03 5.3E-03 6.5E-03 **Ingestion of Fruits** 5.0E-03 6.0E-03 2.9E-03 1.2E-03 1.2E-03 **Ingestion of Pasta** 4.3E-03 3.1E-03 1.7E-03 1.7E-03 ____ **Ingestion of Soup** 2.9E-03 1.6E-03 6.6E-04 7.1E-04 1.5E-03 **Ingestion of Water** 7.1E-02 3.8E-03 2.8E-03 2.0E-03 2.5E-03 **Ingestion of Tea** 4.0E-05 4.8E-04 1.1E-03 2.3E-03 2.7E-03 9.9E-03 **Ingestion of Coffee** ____ 1.1E-03 3.0E-03 9.1E-03 **Ingestion of Soda** 1.3E-04 1.3E-03 7.5E-04 1.2E-03 9.2E-04 0-50 **Ingestion of Fruit Juice** 1.6E-02 2.5E-02 1.4E-02 4.2E-03 2.3E-03 Years Total 0.548 0.275 0.107 0.071 0.048 0.048

Table 8.36 CTE and RME exposure risk calculations for Case E using Subchronic R_fD of 50 $\mu g/kg\text{-}day$

CTE **Route of Exposure** 0-1 1-6 6-11 11-21 21-50 Year Years Years Years Years 4.8E-01 ____ ____ ____ ____ **Ingestion of Infant Formula Inhalation of Indoor Air** 1.0E-01 3.3E-03 1.7E-03 1.1E-03 9.5E-04 **Inhalation of Outdoor Air** ____ 3.3E-04 2.8E-04 1.9E-04 1.3E-04 2.2E-02 6.7E-04 2.7E-04 **Ingestion of Dust** 3.0E-03 1.4E-03 5.1E-02 **Ingestion of Vegetables** 1.1E-01 3.0E-02 1.9E-02 2.0E-02 **Ingestion of Meats** 3.9E-03 4.5E-02 3.1E-02 2.2E-02 2.0E-02 **Ingestion of Fish** 2.0E-02 2.3E-02 1.7E-02 1.0E-02 1.0E-02 1.1E-02 3.9E-03 1.7E-03 1.7E-03 **Ingestion of Fruits** 9.6E-03 **Ingestion of Pasta** 1.2E-02 8.3E-03 5.7E-03 4.6E-03 ____ **Ingestion of Soup** 4.1E-03 1.1E-02 4.0E-03 2.0E-03 2.0E-03 **Ingestion of Water** 1.9E-01 7.5E-03 5.2E-03 3.3E-03 4.8E-03 **Ingestion of Tea** 4.0E-03 3.1E-03 4.6E-03 4.9E-03 6.2E-03 **Ingestion of Coffee** 4.7E-04 3.7E-04 2.0E-03 3.3E-02 ____ 4.3E-04 3.3E-03 **Ingestion of Soda** 3.5E-03 1.7E-03 1.4E-03 0-50 **Ingestion of Fruit Juice** 1.3E-02 3.3E-02 2.1E-02 1.0E-02 5.0E-03 Years Total 0.952 0.207 0.133 0.085 0.110 1.487 RME **Route of Exposure** 0-1 1-6 6-11 11-21 21-50 Year Years Years Years Years **Ingestion of Infant Formula** 6.8E-01 ____ ____ ____ ____ **Inhalation of Indoor Air** 1.6E-01 6.4E-03 3.3E-03 2.4E-03 1.9E-03 **Inhalation of Outdoor Air** 1.2E-04 4.3E-06 ____ 6.0E-05 6.8E-05 **Ingestion of Dust** 2.2E-02 4.9E-03 1.4E-03 6.7E-04 2.7E-04 **Ingestion of Vegetables** 2.8E-02 1.2E-01 8.5E-02 4.5E-02 4.8E-02 **Ingestion of Meats** 1.2E-02 1.1E-01 7.2E-02 5.3E-02 4.6E-02 **Ingestion of Fish** 4.5E-03 6.9E-02 4.5E-02 2.6E-02 3.2E-02 **Ingestion of Fruits** 2.5E-02 3.0E-02 1.4E-02 5.9E-03 5.9E-03 **Ingestion of Pasta** 2.1E-02 1.5E-02 8.5E-03 8.5E-03 ____ **Ingestion of Soup** 7.4E-03 1.5E-02 7.8E-03 3.3E-03 3.6E-03 **Ingestion of Water** 3.5E-01 1.9E-02 1.4E-02 1.0E-02 1.3E-02 **Ingestion of Tea** 2.0E-04 2.4E-03 5.5E-03 1.3E-02 1.1E-02 **Ingestion of Coffee** ____ 5.4E-03 1.5E-02 4.5E-02 4.9E-02 **Ingestion of Soda** 6.5E-04 6.5E-03 3.8E-03 5.8E-03 4.6E-03 0-50 **Ingestion of Fruit Juice** 8.0E-02 1.3E-01 7.2E-02 2.1E-02 1.2E-02 Years Total 2.740 1.374 0.535 0.354 0.238 0.239

Table 8.37 CTE and RME exposure risk calculations for Case E using Subchronic R_fD of 10 $\mu g/kg\text{-}day$

			CTE			
Route of Exposure	0-1	1-6	6-11	11-21	21-50	
_	Year	Years	Years	Years	Years	
Ingestion of Infant Formula	2.4E+00					
Inhalation of Indoor Air	5.1E-01	1.6E-02	8.5E-03	5.3E-03	4.7E-03	
Inhalation of Outdoor Air		1.6E-03	1.4E-03	9.7E-04	6.6E-04	
Ingestion of Dust	1.1E-01	1.5E-02	6.8E-03	3.4E-03	1.4E-03	
Ingestion of Vegetables	5.3E-01	2.6E-01	1.5E-01	9.4E-02	1.0E-01	
Ingestion of Meats	1.9E-02	2.3E-01	1.6E-01	1.1E-01	1.0E-01	
Ingestion of Fish	1.0E-01	1.2E-01	8.5E-02	5.1E-02	5.0E-02	
Ingestion of Fruits	4.8E-02	5.4E-02	1.9E-02	8.5E-03	8.5E-03	
Ingestion of Pasta		6.2E-02	4.1E-02	2.8E-02	2.3E-02	
Ingestion of Soup	2.1E-02	5.3E-02	2.0E-02	1.0E-02	9.9E-03	
Ingestion of Water	9.6E-01	3.7E-02	2.6E-02	1.7E-02	2.4E-02	
Ingestion of Tea	2.0E-02	1.6E-02	2.3E-02	2.5E-02	3.1E-02	
Ingestion of Coffee		2.4E-03	1.9E-03	1.0E-02	1.6E-01	
Ingestion of Soda	2.2E-03	1.6E-02	1.8E-02	8.5E-03	6.8E-03	
Ingestion of Fruit Juice	6.6E-02	1.7E-01	1.1E-01	5.0E-02	2.5E-02	0-50 Years
Total	4.760	1 037	0 664	0 423	0 552	7 437
1000		1.057	0.004	0.745	0.554	7.457
		1.057	RME	0.425	0.552	7.437
Route of Exposure	0-1	1.037	RME 6-11	11-21	21-50	7.437
Route of Exposure	0-1 Year	1-6 Years	RME 6-11 Years	11-21 Years	21-50 Years	7.457
Route of Exposure Ingestion of Infant Formula	0-1 Year 3.4E+00	1-6 Years	RME 6-11 Years	11-21 Years	21-50 Years	7.457
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air	0-1 Year 3.4E+00 7.9E-01	1-6 Years 3.2E-02	0.004 RME 6-11 Years 1.7E-02	11-21 Years 1.2E-02	21-50 Years 9.6E-03	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air	0-1 Year 3.4E+00 7.9E-01	1-6 Years 3.2E-02 3.0E-04	0.004 RME 6-11 Years 1.7E-02 5.8E-04	11-21 Years 1.2E-02 3.4E-04	21-50 Years 9.6E-03 2.2E-05	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust	0-1 Year 3.4E+00 7.9E-01 1.1E-01	1.037 1-6 Years 3.2E-02 3.0E-04 2.5E-02	0.004 RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03	11-21 Years 1.2E-02 3.4E-04 3.4E-03	21-50 Years 9.6E-03 2.2E-05 1.4E-03	1.451
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01	0.004 RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01	0.004 RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01	0.004 RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01	1.657 1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01	0.004 RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01	0.004 RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.5E-02	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 3.9E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Keats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.5E-02 1.8E+00	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 3.9E-02 7.1E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02	1.401
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Fasta Ingestion of Soup Ingestion of Water Ingestion of Tea	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.5E-02 1.8E+00 1.0E-03	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 2.7E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.7E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Tea Ingestion of Coffee	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.5E-02 1.8E+00 1.0E-03 	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02 2.7E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 7.4E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02 2.3E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.7E-02 2.5E-01	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Coffee Ingestion of Soda	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.5E-02 1.8E+00 1.0E-03 3.2E-03	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02 2.7E-02 3.2E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 7.4E-02 1.9E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02 2.3E-01 2.9E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.4E-02 6.7E-02 2.5E-01 2.3E-01 2.3E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Soup Ingestion of Vater Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Fruit Juice	0-1 Year 3.4E+00 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.5E-02 1.8E+00 1.0E-03 3.2E-03 4.0E-01	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02 2.7E-02 3.2E-02 6.3E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 7.4E-02 1.9E-02 3.6E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02 2.3E-01 2.9E-02 1.0E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.4E-02 6.7E-02 2.5E-01 2.3E-01 2.3E-02 5.9E-02	0-50

Table 8.38 CTE and RME exposure risk calculations for Case E using Subchronic $R_{\rm f}D$ of 2 $\mu g/kg\text{-}day$



Figure 8.8 - Case E CTE and RME exposure risk calculations for each pathway of exposure using Subchronic R_fD of 50,10, and 2 μ g/kg-day.



Figure 8.9 - Case E CTE and RME exposure risk calculations for each age group using Subchronic $R_f D$ of 50,10, and 2 $\mu g/kg$ -day.

	(СТЕ	R	ME
Route of exposure	Cumulative BPA Risk	Percent Contribution of Each Pathway	Cumulative BPA Risk	Percent Contribution of Each Pathway
Ingestion of Infant Formula	9.6E-02	32.11	1.4E-01	24.90
Inhalation of Indoor Air	2.2E-02	7.27	3.4E-02	6.28
Inhalation of Outdoor Air	1.9E-04	0.06	5.0E-05	0.01
Ingestion of Dust	5.4E-03	1.81	5.8E-03	1.06
Ingestion of Vegetables	4.5E-02	15.17	6.5E-02	11.95
Ingestion of Meats	2.5E-02	8.27	5.8E-02	10.58
Ingestion of Fish	1.6E-02	5.42	3.5E-02	6.46
Ingestion of Fruits	5.5E-03	1.86	1.6E-02	2.95
Ingestion of Pasta	6.2E-03	2.08	1.1E-02	1.97
Ingestion of Soup	4.6E-03	1.53	7.3E-03	1.34
Ingestion of Water	4.2E-02	14.25	8.2E-02	15.00
Ingestion of Tea	4.6E-03	1.54	6.6E-03	1.20
Ingestion of Coffee	7.1E-03	2.40	2.3E-02	4.20
Ingestion of Soda	2.1E-03	0.69	4.2E-03	0.78
Ingestion of Fruit Juice	1.6E-02	5.53	6.2E-02	11.33
Total	0.297	100	0.548	100

Table 8.39 Case E CTE and RME exposure risk calculations and the percentage contribution of each pathway using Subchronic R_fD of 50 $\mu g/kg$ -day



Figure 8.10 - Case E CTE and RME exposure risk percentage for each exposure pathway.

Case F was the risk assessment for which the infants were assumed to be fed only human milk (breast fed). The risk evaluation was done for a total of 50 years. The total EDI for Case F for both CTE and RME can be seen in Table 8.40 and Figure 8.11. We can see that the highest EDI can be found for 0 to 1 year and steadily decreased with an increase in age. However, for the RME calculations the decreased was not as fast and there was only small difference from 0 to 1 year to 1 to 6 years. From Figure 8.12 we can see the percentage of EDI for each age group for both CTE and RME rates. For the CTE rates for the infant age 0 to 1 year the percentage of EDI was 43.7 % and 29.8 % for CTE and RME, respectively. This was expected because the most critical age period is the first year, due to the low BW of the baby. For the CTE calculations the percentage of EDI for 1 to 6, 6 to 11, 11 to 21, and 21 to 50 years were 21.8, 13.9, 8.9, and 11.6 %, respectively. For the RME calculations the percentage of EDI for 1 to 6, 6 to 11, 11 to 21, and 21 to 50 years were 27.5, 18.2, 12.25, and 12.26 %, respectively. The exposure HQ calculations for Case F using the CTE and RME rates were calculated using subchronic RfD of 50, 10, and 2 μ g/kg-day and can been seen in Table 8.41, 8.42, and 8.43, respectively. We can see that for the CTE rates the total HQ was above 1 only at an RfD of 2µg/kg-day. For the RME rates the total HQ was above 1 at an RfD of 10 and $2 \mu g/kg$ -day.

The 0 to 1 year is the most critical age period as expected from the EDI with the highest HQ of 0.220, 0.579 for CTE rates at an RfD of 10 μ g/kg-day and 2.084, 4.106 for RME rates at an RfD of 2 μ g/kg-day. We can see the total HQ by age group in Figure 8.14. From Figure 8.14 we can see that the vegetables exposure route has the highest contribution to the total HQ. For the CTE calculations several other exposure routes that contribute highly to the total HQ from the highest to lowest are vegetables, drinking water, meats, indoor air, fruit juice, and fish which had the exposure route percentages of 23.7, 14.6, 12.9, 11.3, 8.6, and 8.5 %, respectively. For the

RME the routes that contributed highest to the total HQ from the highest to lowest were vegetables, fruit juice, meats, drinking water, fish, indoor air, and coffee which had the exposure route percentages of 16.8, 15.9, 14.9, 14.2, 9.1, 8.8 and 5.9 %, respectively. We can see all the percentage for all the exposure routes for both CTE and RME calculations in Table 8.44 and Figure 8.15.

		СТ	E Estimated	Intake	
Route of Exposure	0-1	1-6	6-11	11-21	21-50
	Year	Years	Years	Years	Years
Ingestion of Human Milk	0.157				
Inhalation of Indoor Air	1.012	0.033	0.017	0.011	0.009
Inhalation of Outdoor Air		0.003	0.003	0.002	0.001
Ingestion of Dust	0.217	0.030	0.014	0.007	0.003
Ingestion of Vegetables	1.051	0.512	0.302	0.188	0.204
Ingestion of Meats	0.039	0.452	0.314	0.224	0.202
Ingestion of Fish	0.201	0.232	0.170	0.102	0.100
Ingestion of Fruits	0.096	0.108	0.039	0.017	0.017
Ingestion of Pasta		0.125	0.083	0.057	0.046
Ingestion of Soup	0.041	0.107	0.040	0.020	0.020
Ingestion of Water	1.179	0.075	0.052	0.033	0.048
Ingestion of Tea	0.040	0.031	0.046	0.049	0.062
Ingestion of Coffee		0.005	0.004	0.020	0.328
Ingestion of Soda	0.004	0.033	0.035	0.017	0.014
Ingestion of Fruit Juice	0.131	0.331	0.211	0.100	0.050
Total	4.168	2.075	1.329	0.847	1.104
	RME Estimated Intake				
		RM	E Estimated	l Intake	
Route of Exposure	0-1	RM 1-6	E Estimated 6-11	l Intake 11-21	21-50
Route of Exposure	0-1 Year	RM 1-6 Years	E Estimated 6-11 Years	l Intake 11-21 Years	21-50 Years
Route of Exposure Ingestion of Human Milk	0-1 Year 0.224	RM 1-6 Years	E Estimated 6-11 Years	l Intake 11-21 Years	21-50 Years
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air	0-1 Year 0.224 1.580	RM 1-6 Years 0.064	E Estimated 6-11 Years 0.033	I Intake 11-21 Years 0.024	21-50 Years 0.019
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air	0-1 Year 0.224 1.580 	RM 1-6 Years 0.064 0.001	E Estimated 6-11 Years 0.033 0.001	I Intake 11-21 Years 0.024 0.001	21-50 Years 0.019 0.00004
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust	0-1 Year 0.224 1.580 0.217	RM 1-6 Years 0.064 0.001 0.049	E Estimated 6-11 Years 0.033 0.001 0.014	l Intake 11-21 Years 0.024 0.001 0.007	21-50 Years 0.019 0.00004 0.003
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables	0-1 Year 0.224 1.580 0.217 0.281	RM 1-6 Years 0.064 0.001 0.049 1.214	E Estimated 6-11 Years 0.033 0.001 0.014 0.849	Intake 11-21 Years 0.024 0.001 0.007 0.449	21-50 Years 0.019 0.00004 0.003 0.482
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats	0-1 Year 0.224 1.580 0.217 0.281 0.119	RM 1-6 Years 0.064 0.001 0.049 1.214 1.076	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527	21-50 Years 0.019 0.00004 0.003 0.482 0.460
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045	RM 1-6 Years 0.064 0.001 0.049 1.214 1.076 0.691	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248	RM1-6Years0.0640.0010.0491.2141.0760.6910.299	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248 	RM1-6Years0.0640.0010.0491.2141.0760.6910.2990.215	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143 0.154	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059 0.085	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059 0.085
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248 0.074	RM 1-6 Years 0.064 0.001 0.049 1.214 1.076 0.691 0.299 0.215 0.146	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143 0.154 0.078	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059 0.085 0.033	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059 0.085 0.036
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248 0.074 2.197	RM 1-6 Years 0.064 0.001 0.049 1.214 1.076 0.691 0.299 0.215 0.146 0.191	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143 0.154 0.078 0.142	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059 0.085 0.033 0.102	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059 0.085 0.036 0.127
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248 0.074 2.197 0.002	RM 1-6 Years 0.064 0.001 0.049 1.214 1.076 0.691 0.299 0.215 0.146 0.191 0.024	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143 0.154 0.078 0.142 0.055	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059 0.085 0.033 0.102 0.114	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059 0.085 0.036 0.127 0.135
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea Ingestion of Coffee	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248 0.074 2.197 0.002 	RM1-6Years0.0640.0010.0491.2141.0760.6910.2990.2150.1460.1910.0240.054	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143 0.154 0.078 0.142 0.055 0.149	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059 0.085 0.033 0.102 0.114 0.455	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059 0.085 0.036 0.127 0.135 0.493
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Coffee Ingestion of Soda	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248 0.074 2.197 0.002 0.006	RM 1-6 Years 0.064 0.001 0.049 1.214 1.076 0.691 0.299 0.215 0.146 0.191 0.024 0.054 0.065	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143 0.154 0.078 0.142 0.055 0.149 0.038	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059 0.085 0.033 0.102 0.114 0.455 0.058	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059 0.085 0.036 0.127 0.135 0.493 0.046
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Soup Ingestion of Vater Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Fruit Juice	0-1 Year 0.224 1.580 0.217 0.281 0.119 0.045 0.248 0.074 2.197 0.002 0.006 0.799	RM1-6Years0.0640.0010.0491.2141.0760.6910.2990.2150.1460.1910.0240.0540.0651.263	E Estimated 6-11 Years 0.033 0.001 0.014 0.849 0.717 0.448 0.143 0.154 0.078 0.142 0.078 0.142 0.055 0.149 0.038 0.717	Intake 11-21 Years 0.024 0.001 0.007 0.449 0.527 0.263 0.059 0.085 0.033 0.102 0.114 0.455 0.058 0.209	21-50 Years 0.019 0.00004 0.003 0.482 0.460 0.325 0.059 0.085 0.036 0.127 0.135 0.493 0.046 0.117

Table 8.40 CTE and RME estimated daily intake ($\mu g/kg\mbox{-}day$) calculations for Case F



Figure 8.11 - CTE and RME estimated daily intake for Case F for different age groups.



Figure 8.12 - Case F CTE and RME EDI percentage for different age groups for Case F.

	СТЕ					
Route of Exposure	0-1	1-6	6-11	11-21	21-50	
_	Year	Years	Years	Years	Years	
Ingestion of Human Milk	3.1E-03					
Inhalation of Indoor Air	2.0E-02	6.5E-04	3.4E-04	2.1E-04	1.9E-04	
Inhalation of Outdoor Air		6.5E-05	5.6E-05	3.9E-05	2.7E-05	
Ingestion of Dust	4.3E-03	5.9E-04	2.7E-04	1.3E-04	5.4E-05	
Ingestion of Vegetables	2.1E-02	1.0E-02	6.0E-03	3.8E-03	4.1E-03	
Ingestion of Meats	7.7E-04	9.0E-03	6.3E-03	4.5E-03	4.0E-03	
Ingestion of Fish	4.0E-03	4.6E-03	3.4E-03	2.0E-03	2.0E-03	
Ingestion of Fruits	1.9E-03	2.2E-03	7.8E-04	3.4E-04	3.4E-04	
Ingestion of Pasta		2.5E-03	1.7E-03	1.1E-03	9.1E-04	
Ingestion of Soup	8.3E-04	2.1E-03	8.1E-04	4.1E-04	3.9E-04	
Ingestion of Water	2.4E-02	1.5E-03	1.0E-03	6.7E-04	9.7E-04	
Ingestion of Tea	8.1E-04	6.3E-04	9.2E-04	9.9E-04	1.2E-03	
Ingestion of Coffee		9.5E-05	7.4E-05	4.1E-04	6.6E-03	
Ingestion of Soda	8.6E-05	6.5E-04	7.0E-04	3.4E-04	2.7E-04	
Ingestion of Fruit Juice	2 6E-03	6 6E-03	4 2E-03	2 0E-03	1 0E-03	0-50
ingestion of Fruit Suice	2.01-03	0.01-05	H.2L -03	2.01-05	1.0L-03	Years
Total	0.083	0.041	0.027	0.017	0.022	0.190
		L	RME	L		
Route of Exposure	0-1	1-6	RME 6-11	11-21	21-50	
Route of Exposure	0-1 Year	1-6 Years	RME 6-11 Years	11-21 Years	21-50 Years	
Route of Exposure Ingestion of Human Milk	0-1 Year 4.5E-03	1-6 Years 	RME 6-11 Years	11-21 Years	21-50 Years	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air	0-1 Year 4.5E-03 3.2E-02	1-6 Years 1.3E-03	RME 6-11 Years 6.7E-04	11-21 Years 4.7E-04	21-50 Years 3.8E-04	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air	0-1 Year 4.5E-03 3.2E-02 	1-6 Years 1.3E-03 1.2E-05	RME 6-11 Years 6.7E-04 2.3E-05	11-21 Years 4.7E-04 1.4E-05	21-50 Years 3.8E-04 8.7E-07	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust	0-1 Year 4.5E-03 3.2E-02 4.3E-03	1-6 Years 1.3E-03 1.2E-05 9.9E-04	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04	11-21 Years 4.7E-04 1.4E-05 1.3E-04	21-50 Years 3.8E-04 8.7E-07 5.4E-05	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.2E-03 1.7E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 1.5E-03	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03 2.9E-03	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03 1.6E-03	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.7E-03 6.6E-04	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03 7.1E-04	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 1.5E-03 4.4E-02	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03 2.9E-03 3.8E-03	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03 1.6E-03 2.8E-03	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.7E-03 6.6E-04 2.0E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03 7.1E-04 2.5E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 1.5E-03 4.4E-02 4.0E-05	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03 2.9E-03 3.8E-03 4.8E-04	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03 1.6E-03 2.8E-03 1.1E-03	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.7E-03 6.6E-04 2.0E-03 2.3E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03 7.1E-04 2.5E-03 2.7E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Vater Ingestion of Tea Ingestion of Coffee	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 1.5E-03 4.4E-02 4.0E-05 	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03 2.9E-03 3.8E-03 4.8E-04 1.1E-03	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03 1.6E-03 2.8E-03 1.1E-03 3.0E-03	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.7E-03 6.6E-04 2.0E-03 2.3E-03 9.1E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03 7.1E-04 2.5E-03 2.7E-03 9.9E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Fish Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Vater Ingestion of Tea Ingestion of Coffee Ingestion of Soda	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 1.5E-03 4.4E-02 4.0E-05 1.3E-04	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03 2.9E-03 3.8E-03 4.8E-04 1.1E-03 1.3E-03	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03 1.6E-03 2.8E-03 1.1E-03 3.0E-03 7.5E-04	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.7E-03 6.6E-04 2.0E-03 2.3E-03 9.1E-03 1.2E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03 7.1E-04 2.5E-03 2.7E-03 9.9E-03 9.2E-04	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Coffee Ingestion of Soda	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 1.5E-03 4.4E-02 4.0E-05 1.3E-04	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03 2.9E-03 3.8E-03 4.8E-04 1.1E-03 1.3E-03 2.5E-02	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03 1.6E-03 2.8E-03 1.1E-03 3.0E-03 7.5E-04 1	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.7E-03 6.6E-04 2.0E-03 2.3E-03 9.1E-03 1.2E-03 4.2E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03 7.1E-04 2.5E-03 9.9E-03 9.2E-04 2.3E-03	0-50
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Soup Ingestion of Soup Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Fruit Juice	0-1 Year 4.5E-03 3.2E-02 4.3E-03 5.6E-03 2.4E-03 9.0E-04 5.0E-03 1.5E-03 4.4E-02 4.0E-05 1.3E-04 1.6E-02	1-6 Years 1.3E-03 1.2E-05 9.9E-04 2.4E-02 2.2E-02 1.4E-02 6.0E-03 4.3E-03 2.9E-03 3.8E-03 4.8E-04 1.1E-03 1.3E-03 2.5E-02	RME 6-11 Years 6.7E-04 2.3E-05 2.7E-04 1.7E-02 1.4E-02 9.0E-03 2.9E-03 3.1E-03 1.6E-03 2.8E-03 1.1E-03 3.0E-03 7.5E-04 1.4E-02	11-21 Years 4.7E-04 1.4E-05 1.3E-04 9.0E-03 1.1E-02 5.3E-03 1.2E-03 1.7E-03 6.6E-04 2.0E-03 2.3E-03 9.1E-03 1.2E-03 4.2E-03	21-50 Years 3.8E-04 8.7E-07 5.4E-05 9.6E-03 9.2E-03 6.5E-03 1.2E-03 1.7E-03 7.1E-04 2.5E-03 2.7E-03 9.9E-03 9.2E-04 2.3E-03	0-50 Years

Table 8.41 CTE and RME exposure risk calculations for Case F using Subchronic $R_{\rm f}D$ of 50 $\mu g/kg\text{-}day$

	СТЕ					
Route of Exposure	0-1	1-6	6-11	11-21	21-50	
	Year	Years	Years	Years	Years	
Ingestion of Human Milk	1.6E-02					
Inhalation of Indoor Air	2.0E-02	3.3E-03	1.7E-03	1.1E-03	9.5E-04	
Inhalation of Outdoor Air		3.3E-04	2.8E-04	1.9E-04	1.3E-04	
Ingestion of Dust	4.3E-03	3.0E-03	1.4E-03	6.7E-04	2.7E-04	
Ingestion of Vegetables	2.1E-02	5.1E-02	3.0E-02	1.9E-02	2.0E-02	
Ingestion of Meats	3.9E-03	4.5E-02	3.1E-02	2.2E-02	2.0E-02	
Ingestion of Fish	4.0E-03	2.3E-02	1.7E-02	1.0E-02	1.0E-02	
Ingestion of Fruits	1.9E-03	1.1E-02	3.9E-03	1.7E-03	1.7E-03	
Ingestion of Pasta		1.2E-02	8.3E-03	5.7E-03	4.6E-03	
Ingestion of Soup	4.1E-03	1.1E-02	4.0E-03	2.0E-03	2.0E-03	
Ingestion of Water	1.2E-01	7.5E-03	5.2E-03	3.3E-03	4.8E-03	
Ingestion of Tea	8.1E-04	3.1E-03	4.6E-03	4.9E-03	6.2E-03	
Ingestion of Coffee		4.7E-04	3.7E-04	2.0E-03	3.3E-02	
Ingestion of Soda	8.6E-05	3.3E-03	3.5E-03	1.7E-03	1.4E-03	
Ingestion of Fruit Juice		3 3E-02	2 1E-02	1.0F-02	5 0E-03	0-50
ingestion of Fruit Suice	2.6E-03	5.51 02	2.112 02	1.0L-02	J.0L-03	Years
Total	0.220	0.207	0.133	0.085	0.110	0.756
			RME			
Route of Exposure	0-1	1-6	RME 6-11	11-21	21-50	
Route of Exposure	0-1 Year	1-6 Years	RME 6-11 Years	11-21 Years	21-50 Years	
Route of Exposure Ingestion of Human Milk	0-1 Year 2.2E-02	1-6 Years	RME 6-11 Years	11-21 Years	21-50 Years	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air	0-1 Year 2.2E-02 1.6E-01	1-6 Years 6.4E-03	RME 6-11 Years 3.3E-03	11-21 Years 2.4E-03	21-50 Years 1.9E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air	0-1 Year 2.2E-02 1.6E-01	1-6 Years 6.4E-03 6.0E-05	RME 6-11 Years 3.3E-03 1.2E-04	11-21 Years 2.4E-03 6.8E-05	21-50 Years 1.9E-03 4.3E-06	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust	0-1 Year 2.2E-02 1.6E-01 2.2E-02	1-6 Years 6.4E-03 6.0E-05 4.9E-03	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03	11-21 Years 2.4E-03 6.8E-05 6.7E-04	21-50 Years 1.9E-03 4.3E-06 2.7E-04	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03 8.5E-03	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 7.4E-03	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02 1.5E-02	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02 7.8E-03	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03 8.5E-03 3.3E-03	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03 3.6E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 7.4E-03 2.2E-01	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02 1.5E-02 1.9E-02	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02 7.8E-03 1.4E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03 8.5E-03 3.3E-03 1.0E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03 3.6E-03 1.3E-02	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 7.4E-03 2.2E-01 2.0E-04	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02 1.5E-02 1.9E-02 2.4E-03	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02 7.8E-03 1.4E-02 5.5E-03	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03 8.5E-03 3.3E-03 1.0E-02 1.1E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03 3.6E-03 1.3E-02 1.3E-02	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Veater Ingestion of Tea Ingestion of Coffee	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 7.4E-03 2.2E-01 2.0E-04 	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02 1.5E-02 1.9E-02 2.4E-03 5.4E-03	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02 7.8E-03 1.4E-02 5.5E-03 1.5E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03 8.5E-03 3.3E-03 1.0E-02 1.1E-02 4.5E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03 3.6E-03 1.3E-02 1.3E-02 4.9E-02	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Tea Ingestion of Coffee Ingestion of Soda	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 7.4E-03 2.2E-01 2.0E-04 6.5E-04	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02 1.5E-02 1.9E-02 2.4E-03 5.4E-03 6.5E-03	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02 7.8E-03 1.4E-02 3.5E-03 1.5E-02 3.8E-03	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03 8.5E-03 3.3E-03 1.0E-02 1.1E-02 4.5E-02 5.8E-03	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03 3.6E-03 1.3E-02 1.3E-02 4.9E-02 4.6E-03	
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Fruit Juice	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 7.4E-03 2.2E-01 2.0E-04 6.5E-04	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02 1.5E-02 1.9E-02 2.4E-03 5.4E-03 6.5E-03 1.3E-01	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02 7.8E-03 1.4E-02 5.5E-03 1.5E-02 3.8E-03 7.2E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 5.9E-03 8.5E-03 3.3E-03 1.0E-02 1.1E-02 4.5E-02 5.8E-03 2.1E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03 3.6E-03 1.3E-02 1.3E-02 4.9E-02 4.6E-03 1.2E-02	0-50
Route of Exposure Ingestion of Human Milk Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Fruit Juice	0-1 Year 2.2E-02 1.6E-01 2.2E-02 2.8E-02 1.2E-02 4.5E-03 2.5E-02 7.4E-03 2.2E-01 2.0E-04 6.5E-04 8.0E-02	1-6 Years 6.4E-03 6.0E-05 4.9E-03 1.2E-01 1.1E-01 6.9E-02 3.0E-02 2.1E-02 1.5E-02 1.9E-02 2.4E-03 5.4E-03 6.5E-03 1.3E-01	RME 6-11 Years 3.3E-03 1.2E-04 1.4E-03 8.5E-02 7.2E-02 4.5E-02 1.4E-02 1.5E-02 7.8E-03 1.5E-02 3.8E-03 7.2E-02	11-21 Years 2.4E-03 6.8E-05 6.7E-04 4.5E-02 5.3E-02 2.6E-02 5.9E-03 8.5E-03 3.3E-03 1.0E-02 1.1E-02 4.5E-02 5.8E-03 2.1E-02	21-50 Years 1.9E-03 4.3E-06 2.7E-04 4.8E-02 4.6E-02 3.2E-02 5.9E-03 8.5E-03 3.6E-03 1.3E-02 4.9E-02 4.6E-03 1.2E-02	0-50 Years

Table 8.42 CTE and RME exposure risk calculations for Case F using Subchronic $R_{\rm f}D$ of 10 $\mu g/kg\text{-}day$

	СТЕ					
Route of Exposure	0-1	1-6	6-11	11-21	21-50	
	Year	Years	Years	Years	Years	
Ingestion of Human Milk	7.8E-02					
Inhalation of Indoor Air	5.1E-01	1.6E-02	8.5E-03	5.3E-03	4.7E-03	
Inhalation of Outdoor Air		1.6E-03	1.4E-03	9.7E-04	6.6E-04	
Ingestion of Dust	1.1E-01	1.5E-02	6.8E-03	3.4E-03	1.4E-03	
Ingestion of Vegetables	5.3E-01	2.6E-01	1.5E-01	9.4E-02	1.0E-01	
Ingestion of Meats	1.9E-02	2.3E-01	1.6E-01	1.1E-01	1.0E-01	
Ingestion of Fish	1.0E-01	1.2E-01	8.5E-02	5.1E-02	5.0E-02	
Ingestion of Fruits	4.8E-02	5.4E-02	1.9E-02	8.5E-03	8.5E-03	
Ingestion of Pasta		6.2E-02	4.1E-02	2.8E-02	2.3E-02	
Ingestion of Soup	2.1E-02	5.3E-02	2.0E-02	1.0E-02	9.9E-03	
Ingestion of Water	5.9E-01	3.7E-02	2.6E-02	1.7E-02	2.4E-02	
Ingestion of Tea	2.0E-02	1.6E-02	2.3E-02	2.5E-02	3.1E-02	
Ingestion of Coffee		2.4E-03	1.9E-03	1.0E-02	1.6E-01	
Ingestion of Soda	2.2E-03	1.6E-02	1.8E-02	8.5E-03	6.8E-03	
Ingestion of Fruit Juice	6.6E-02	1.7E-01	1.1E-01	5.0E-02	2.5E-02	0-50
ingestion of Fruit Suice	0.01 01	11/2 01	1112 01	0.01 01	2.012 02	Years
Total	2.084	1.037	0.664	0.423	0.552	4.761
			RME			
Route of Exposure	0-1	1-6	RME 6-11	11-21	21-50	
Route of Exposure	0-1 Year	1-6 Years	RME 6-11 Years	11-21 Years	21-50 Years	
Route of Exposure Ingestion of Infant Formula	0-1 Year 2.2E-01	1-6 Years 	RME 6-11 Years	11-21 Years	21-50 Years	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air	0-1 Year 2.2E-01 7.9E-01	1-6 Years 3.2E-02	RME 6-11 Years 1.7E-02	11-21 Years 1.2E-02	21-50 Years 9.6E-03	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air	0-1 Year 2.2E-01 7.9E-01 	1-6 Years 3.2E-02 3.0E-04	RME 6-11 Years 1.7E-02 5.8E-04	11-21 Years 1.2E-02 3.4E-04	21-50 Years 9.6E-03 2.2E-05	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust	0-1 Year 2.2E-01 7.9E-01 1.1E-01	1-6 Years 3.2E-02 3.0E-04 2.5E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03	11-21 Years 1.2E-02 3.4E-04 3.4E-03	21-50 Years 9.6E-03 2.2E-05 1.4E-03	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01	11-21 Years 1.2E-02 3.4E-02 3.4E-03 2.2E-01 2.6E-01 1.3E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Weats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.7E-02	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Dust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.7E-02 2.2E+00	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Water Ingestion of Tea	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.7E-02 2.2E+00 1.0E-03	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 2.7E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.7E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fasta Ingestion of Soup Ingestion of Vater Ingestion of Tea Ingestion of Coffee	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.7E-02 2.2E+00 1.0E-03 	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02 2.7E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 7.4E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02 2.3E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.7E-02 2.5E-01	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Dust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Vegetables Ingestion of Soup Ingestion of Tea Ingestion of Coffee Ingestion of Soda	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.7E-02 2.2E+00 1.0E-03 3.2E-03	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02 2.7E-02 3.2E-02	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 7.4E-02 1.9E-02	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02 2.3E-01 2.9E-02	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.4E-02 6.7E-02 2.5E-01 2.3E-02	
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fruits Ingestion of Fruits Ingestion of Pasta Ingestion of Soup Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Soda	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.7E-02 2.2E+00 1.0E-03 3.2E-03 4.0E-01	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02 2.7E-02 3.2E-02 6.3E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 7.4E-02 1.9E-02 3.6E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02 2.3E-01 2.9E-02 1.0E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.7E-02 2.5E-01 2.3E-02 5.9E-02	0-50
Route of Exposure Ingestion of Infant Formula Inhalation of Indoor Air Inhalation of Outdoor Air Ingestion of Oust Ingestion of Vegetables Ingestion of Vegetables Ingestion of Meats Ingestion of Fish Ingestion of Fruits Ingestion of Fasta Ingestion of Pasta Ingestion of Soup Ingestion of Vater Ingestion of Tea Ingestion of Coffee Ingestion of Soda Ingestion of Fruit Juice	0-1 Year 2.2E-01 7.9E-01 1.1E-01 1.4E-01 5.9E-02 2.2E-02 1.2E-01 3.7E-02 2.2E+00 1.0E-03 3.2E-03 4.0E-01	1-6 Years 3.2E-02 3.0E-04 2.5E-02 6.1E-01 5.4E-01 3.5E-01 1.5E-01 1.1E-01 7.3E-02 9.5E-02 1.2E-02 2.7E-02 3.2E-02 6.3E-01	RME 6-11 Years 1.7E-02 5.8E-04 6.8E-03 4.2E-01 3.6E-01 2.2E-01 7.1E-02 7.7E-02 3.9E-02 7.1E-02 7.4E-02 1.9E-02 3.6E-01	11-21 Years 1.2E-02 3.4E-04 3.4E-03 2.2E-01 2.6E-01 1.3E-01 2.9E-02 4.3E-02 1.7E-02 5.1E-02 5.7E-02 2.3E-01 2.9E-02 1.0E-01	21-50 Years 9.6E-03 2.2E-05 1.4E-03 2.4E-01 2.3E-01 1.6E-01 2.9E-02 4.3E-02 1.8E-02 6.4E-02 6.7E-02 2.5E-01 2.3E-01 2.3E-02 5.9E-02	0-50 Years

Table 8.43 CTE and RME exposure risk calculations for Case F using Subchronic R_fD of 2 $\mu g/kg\text{-}day$



Figure 8.13 - Case F CTE and RME exposure risk calculations for each pathway of exposure using Subchronic RfD of 50,10, and $2 \mu g/kg$ -day.

Figure 8.14 - Case F CTE and RME exposure risk calculations for each age group using Subchronic RfD of 50,10, and 2 µg/kg-day.

	C	СТЕ	RME		
Route of exposure	Cumulative BPA Risk	Percent Contribution of Each Pathway	Cumulative BPA Risk	Percent Contribution of Each Pathway	
Ingestion of Human Milk	3.1E-03	1.65	4.5E-03	1.15	
Inhalation of Indoor Air	2.2E-02	11.35	3.4E-02	8.84	
Inhalation of Outdoor Air	1.9E-04	0.10	5.0E-05	0.01	
Ingestion of Dust	5.4E-03	2.83	5.8E-03	1.49	
Ingestion of Vegetables	4.5E-02	23.70	6.5E-02	16.83	
Ingestion of Meats	2.5E-02	12.92	5.8E-02	14.90	
Ingestion of Fish	1.6E-02	8.46	3.5E-02	9.11	
Ingestion of Fruits	5.5E-03	2.91	1.6E-02	4.15	
Ingestion of Pasta	6.2E-03	3.26	1.1E-02	2.77	
Ingestion of Soup	4.6E-03	2.40	7.3E-03	1.88	
Ingestion of Water	2.8E-02	14.57	5.5E-02	14.19	
Ingestion of Tea	4.6E-03	2.40	6.6E-03	1.69	
Ingestion of Coffee	7.1E-03	3.74	2.3E-02	5.92	
Ingestion of Soda	2.1E-03	1.08	4.2E-03	1.09	
Ingestion of Fruit Juice	1.6E-02	8.64	6.2E-02	15.97	
Total	0.190	100	0.389	100	

Table 8.44 Case F CTE and RME exposure risk calculations and the percentage contribution of each pathway using Subchronic R_fD of 50 $\mu g/kg$ -day

Figure 8.15 - Case F CTE and RME exposure risk percentage for each exposure pathway.

8.5 CONCLUSIONS

For Case 1 we can see that at the current EPA RfD of 50 μ g/kg-day there was a possible adverse health effect for both CTE and RME rates with HQ of 1.380 and 6.899, respectively. The main exposure route was the migration from the baby bottle, which could be a limitation to the study due to the increase availability of BPA free baby bottles for purchase. Another important exposure route is the infant formula, which had an HQ above 1 at an RfD of 2 μ g/kg-day. Even though the RfD of 2 μ g/kg-day is way below the EPA RfD there are plenty of studies that identified adverse health effects in animals at this levels as seen in Table 8.2.

For Case 2 the migration of baby bottle again was the dominant exposure route for the CTE rates and for the RME rates the ingestion from the milk preparing the food was the dominant exposure route. There were adverse health effects at both CTE and RME rates for the EPA RfD of 50 μ g/kg-day. For the RME rates there was an HQ above one only from the ingestion of milk preparing the food. However, there was a limitation in the study, because the levels used for the RME from Figure 8.2 and Table 8.15 were very regional from Iran goat milk. As a result is not a concentration that could be representative for the whole world and not even for Iran itself probably due to the limited number of concentration points.

Case 3 which looked only at two exposure routes, which is the ingestion of human milk through breast feeding and drinking water. At an RfD of 2 μ g/kg-day at RME rates there was an possible adverse health effect, with the ingestion of water having 90.75 % of the total HQ.

For the other cases where baby bottles are taking in considerations is also important to note that the migration of BPA in some studies were found using extreme conditions, which are not representative of actual feeding procedures as a result being a limited factor. Also there is a wide range of values for the BPA migration due to different manufacturing process. Thus a consumer could easily purchase brand that has no BPA residue or being a BPA free plastic bottle as mentioned earlier. The further investigation of health risk for the infants the migration of BPA from bay bottle as a result was removed along with the ingestion of milk preparing the food. Two different cases were obtained, where the infant formula and human milk was taking into consideration as the food ingestion for the first 6 months.

The ingestion of infant formula it was found to pose a higher health effect on the infant than the ingestion of human milk. When all the other exposure routes were taken into consideration we can see that the ingestion of vegetables and the inhalation of indoor air are the ones that had the highest contribution to the total HQ. For the Case B at the CTE rates only at RfD of 2 μ g/kg-day there was a possible health risk observed and for the RME rates there was an adverse health risk observed for both 10 and 2 μ g/kg-day. For Case D there was adverse health effects observed only at an RfD of 2 μ g/kg-day for both CTE and RME rates. Case D had the highest exposure route as the drinking water ingestion and for the RME rates it had on HQ above 1 at an RfD of 2 μ g/kg-day.

Due to the fact that the infant age is critical due to the low BW of the infant two major cases were investigated for the 50 years risk assessment, one study assumed the consumption of infant formula and the other the consumption of human milk only for the first 6 months. We can see from Case E and F that most critical period age time is the first year from birth. For Case E the infant formula had the highest contribution to the HQ. For both cases Case E and F vegetables, drinking water, meats, indoor air, and fruit juice were the highest exposure routes. The drinking water ingestion was one of the most significant exposure routes being in the third place for the Case E with CTE rates being very close to the ingestion of vegetables, which was

second place for the RME rates also. For the Case F using the CTE rates the drinking water was second place being very close to meats and indoor air, and for the RME rates the drinking water was in fourth place very close to vegetables, fruit juice, and meats.

The drinking water has found to be a potential hazard to the human health. It is important to pay attention to the new research which has found adverse health effects at concentrations a lot smaller than the current EPA RfD of 50 µg/kg-day. The source of different foods can be easily controlled because most of BPA concentration is found from the canned foods. As a result by not eating canned foods the EDI can be lowered significantly. Even in this study risk assessment the ingestion from the EPA exposure handbook and the child specific hand book did not specifically mentioned that the ingestion of different foods as meats and vegetables for example are found to be canned consumed. As a result some of the ingestion rates of some foods and liquids that were taken into consideration of being from canned or different containers could be from other sources. As a result this could be a limitation to the current study. The ingestion of water is harder to control, because the presence of BPA in the water systems and plastic bottles. Due to lower cost of plastic production using BPA the bottle water industry had not implemented the non use of BPA on their bottled water products. As a result it is important to obtain more data points of BPA concentrations from different ingestion routes especially for infants. Since more and more research has found adverse health effects at environmental levels it is recommended to remove the BPA if possible from drinking water sources, especially from industrial waste effluents in order to don't reach the environment.

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CHAPTER IX

CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

This study investigated the removal of bisphenol A (BPA) from water using different iron oxide adsorbents. The iron oxides used in the study were two magnetites (M1 and M2) and one hematite (H). The removal of BPA using iron oxides adsorbents is an environmentally friendly process that can take advantage of the regeneration of the iron oxide adsorbents using a blast furnace. Even though other organic adsorbents such as activated carbon are capable of removing BPA at higher rates or equilibrium adsorption capacities, the price of such organic adsorbents are still relatively high and not all of the adsorbents perform well. The removal of BPA by other processes or technologies has been shown to be inefficient due to the large number of different intermediates produced during the degradation of BPA.

From the risk assessment study it was found that exposure to BPA through ingestion of drinking water could alone pose a hazardous health effect at environmentally relevant concentrations for an oral subchronic reference dose (RfD) of 2 μ g/kg-day. Even though the current U.S. EPA RfD is set at 50 μ g/kg-day and the European Union (EU) has set an oral RfD of 10 μ g/kg-day, research has shown adverse health effects at an RfD of 2 μ g/kg-day. Additional exposure routes such as air inhalation, different liquid and solid foods, and dust ingestion made the exposure to BPA a possible adverse health effect at the EU RfD of 10 μ g/kg-day when risk assessment was calculated for a period of 50 years. At reasonable maximum exposure (RME) levels, there was an adverse health effect found at one year after birth at EU RfD of 10 μ g/kg-day. The ingestion of BPA from different liquid and solid foods could be avoided, however the ingestion of BPA from drinking water cannot be avoided if the BPA is

present in the treated drinking water and in bottled water products. Therefore, the removal of BPA from water is important.

The adsorption of BPA onto hematite H and two different magnetites (M1 and M2) was investigated. The effect of pH on adsorption was investigated, showing that hematite H was able to remove more BPA at lower pH values. The removal of BPA at an initial concentration of 1.2 mg/L was about 95 percent at an acidic pH of 2.0. As a result, further experiments were performed to evaluate the removal of BPA using hematite H at acidic conditions. The maximum adsorption capacities were found to range from 253 to 302 mg/kg and from 337 to 396 mg/kg after 2 and 7 days, respectively. The effect of solution ionic strength on adsorption was investigated. The effect of calcium (Ca^{2+}) and potassium (K^{+}) ions were evaluated at ionic strengths of 1, 5, 50, 100 and 500 mM. The effect of Ca^{2+} ions was also evaluated in the presence of 1 mM sodium bicarbonate (NaHCO₃). From the experiments performed with calcium at different initial BPA concentrations of 1.3, 13 and 130 mg/L, it was found that there no effect on the adsorption of BPA at acidic conditions at concentration of 1.3 and 13 mg/L with a slight increase in the adsorption at 100 and 500 mM concentrations of calcium. There was a positive effect on adsorption due to calcium with and without bicarbonate with an increase in the adsorption with increasing ionic strength. The effect of potassium was not as strong as the effect of calcium, due to the lower positive valence of potassium ions as compared to calcium ions.

The removal of BPA from water using all three iron oxides was statistically analyzed using multivariate linear regression (MLR) models. The MLR models were obtained using up to three interactions between the different independent variables that affected the adsorption. The experimental equilibrium concentrations (C_e) were compared to the predicted C_e values obtained with the MLR models, where high correlations were obtained between the two sets of C_e values.

The MLR models could be used to understand the independent variables which had the strongest effect on adsorption, and to engineer a better treatment system for removal of BPA from water.

Hydroquinone (HQ) and benzoquinone (BQ) are two intermediates of BPA degradation which occur either naturally in the environment or in engineered processes for treatment of BPA, where BQ is a product of HQ oxidation. Therefore, the removal of HQ and BQ from water using the two magnetite adsorbents (M1 and M2) were examined. At an initial concentration of 110 µmol/L, HQ was completely removed along with BQ (produced from HQ) after 30 days and 19 days by magnetite M1 and magnetite M2, respectively. The removal of HQ and BQ followed second order kinetics for both adsorbents M1 and M2.

9.2 RECOMMENDATIONS

The aqueous samples should also be analyzed with gas chromatography – mass spectrometry (GC-MS) or with liquid chromatography – mass spectrometry (LC-MS) in order to determine possible organic byproducts that could occur during the adsorption of BPA onto the iron oxide adsorbents. At acidic conditions, the adsorption of BPA to hematite H showed that there was a loss in the total mass balance of BPA, which could be an indication of a surface interaction with the BPA. These interactions may have led to a formation of byproducts. The analysis of those byproducts is recommended in order to understand the complete behavior of BPA in aqueous solutions and the impact on the adsorption of BPA.

This research studied the removal of BPA from water through adsorption of BPA onto iron oxide adsorbents, especially adsorption onto hematite H at acidic conditions. Further study on the removal of BPA should be conducted using continuous flow column experiments. The results from the column flow experiments can be used for the design of pilot scale systems and field-scale technologies for the removal of BPA from water.

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632

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Curriculum Vitae

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EDUCATION

Bachelor of Science in Civil EngineeringMinor in MathematicsCum Laude and with College HonorsUniversity of Illinois at Chicago, Chicago, ILOverall GPA 3.50/4.0

EXPERIENCE

Graduate Teaching Assistant - University of Illinois at Chicago

• Held Teaching Assistant hours to assist students with homework. In charge of lab preparation for the lab sections of the course "environmental engineering".

Graduate Research Assistant - University of Illinois at Chicago January 2008 – May 2011

Ph.D. Project: Removal of Bisphenol A from Water using Iron Oxide Adsorbents.

- Investigated the removal of Bisphenol A (BPA) and arsenic from water using various adsorbents.
- Evaluated the enhanced anaerobic biodegradation of Polychlorinated Biphenyls (PCBs) using periodic amendment of iron for the remediation of PCB contaminated sediments.

• Designed a water treatment plant and various stages of the treatment train to meet the current water quality standards.

- Developed various wastewater treatment options as part of the design of a wastewater treatment plant.
- Modeled and analyzed different sediment capping materials for the containment of heavy metal contaminants.
- Studied the performance and slope stability of a municipal landfill by analyzing the water balance using the Hydrologic Evaluation of Landfill Performance (HELP) software.
- Evaluated different sustainable parameters for soil and groundwater remediation technologies using Sustainable Remediation Tool (SRT).

Technical Skills

- Gas Chromatography (µECD/FID/TCD), Ion Chromatography, Anaerobic/Controlled Atmospheric Chamber, Flame Atomic Absorption Spectroscopy, Graphite Furnace Atomic Absorption Spectroscopy, Elemental Analysis of soils and sediments, Zeta potential meter.
- Extraction of organic contaminants from soils and sediments using Soxhlet extraction and batch solvent extraction.

Extraction of heavy metals from soils and sediments using acid digestion

Relevant Course Work

Physical Chemical Principles in Environmental Systems; Water Treatment Design, Advanced Water Treatment; Wastewater Treatment Design; Lake and Watershed Management; Engineering Hydrology, Hydraulic Design; Environmental Microbiology; Water Chemistry, Environmental Organic Chemistry; Computational Methods in Geo-Environmental Engineering; Design of Landfills and Impoundments; Environmental Remediation Engineering; Principles of Nanotechnology; Pollution Prevention Engineering; Risk Assessment.

Software Packages

• Surface water hydrology: WinTR-55, WinTR-20, HY-8, HEC-HMS; Groundwater hydrology: MODFLOW; Sustainable Remediation: SRT; Office and Marketing: MS Office, Adobe Indesign; Landfill Design: HELP Model; Statistics: SPSS.

PUBLICATIONS AND PRESENTATIONS

- Khodadoust, A. P., Babaeivelni, K., Bogdan, D., "Removal of Arsenic from Water using Manganese Oxide Adsorbents," University of Illinois Water Research Forum, Chicago, Illinois, April 2012.
- Godinez, I.G., Darnault, C., Khodadoust, A.P., Bogdan, D., "Aggregation Transport and Deposition Kinetics of Titanium Dioxide Nanoparticles," University of Illinois Water Research Forum, Chicago, Illinois, April 2012.
- Khodadoust, A. P., Varadhan, A. S., Bogdan, D., Brenner, R. C., "Enhanced Anaerobic Biodegradation of PCBs in Contaminated Sediments using Periodic Amendments of Iron," Proceedings of the Fifth International Conference on Remediation of Contaminated Sediments, Jacksonville, Florida, February 2009.

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