

Removal of Arsenic from Water using Manganese Oxides Adsorbents

BY

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THESIS

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**This thesis is dedicated to
my wife, Nasim Azimi
for her love, endless support
and encouragement.**

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Contribution of Authors

Chapter 1 is a literature review and highlights the significance of my research question.

Chapter 2 represents a series of my own unpublished experiments directed at studying the effect of different manganese oxides on arsenic removal from contaminated water.

Chapter 3 represents an accepted manuscript, not published at the time of submission of this dissertation, (Babaeiveli, K., Khodadoust, A.P., Bogdan, D.: *Sorption Of Arsenic (V) Onto Commercial Mn₃O₄: Effect Of pH, Ionic Strength, And Co-existing Ions. Accepted to Journal of Environmental Science and Health, Part A.*) for which I was the primary author and major driver of the research. Dorin Bogdan assisted me in the experiments for isotherm study. My research advisor, Dr. Amid Khodadoust contributed to supervising the experiments and the writing of the manuscript and.

Chapter 4 represents a series of my own unpublished experiments directed at studying the As(III) and As(V) adsorption capability of Mn₂O₃.

Chapter 5 represents a published proceeding (Babaeiveli, K., Khodadoust, A.P.: *Adsorption and Removal of Arsenic from Coal Fly Ash Leachate using Manganese Oxide Sorbent. Proceedings of Air & Waste Management Association's 106th Annual Conference & Exhibition, Chicago, Jun 2013.*) for which I was the primary author and major driver of the research. Chapter 3 represents also a published manuscript (Khodadoust, A.P., Theis, T.L., Murarka, I.P., Naithani, P. and Babaeiveli, K.: *Uptake of arsenic by alkaline soils near alkaline coal fly ash disposal facilities, Environ Monit Assess, 185(12):10339-49, 2013.*) for which I was the last author who played a large role in the statistical analysis of the data along with the first author Dr. Amid Khodadoust and the other authors.

Chapter 6 to 8 represent a series of my own unpublished experiments and modeling directed at developing of an efficient novel sorbent and its arsenic removal efficiency in batch and column systems. I anticipate that this line of research will be continued in the laboratory after I leave and that this work will ultimately be published.

Chapter 9 represents the overall conclusions of this dissertation and includes the future directions of this research.

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SUMMARY

Arsenic is a well known carcinogen which in natural waters poses a problem worldwide. Many countries are affected by high levels of natural and anthropogenic arsenic in surface water and groundwater. In addition to natural sources of arsenic in groundwater, leaching of arsenic from ash in coal fly ash disposal facilities and from chemical landfills is a cause for concern due to possible contamination of groundwater. U.S. EPA has established a maximum contaminant level (MCL) of 10 $\mu\text{g/L}$ of arsenic in drinking water. Therefore, applying effective methods and appropriate materials to selectively remove arsenic from natural waters is required. Technologies that have shown to be effective for removal of arsenic from water include lime softening, precipitation/co-precipitation, membrane processes, ion exchange, and adsorption. Most of these processes usually suffer from one or more drawbacks, scope of application and limitations. However, adsorption has been recognized as a superior method for removal of arsenic owing to its lower cost, flexibility of design, easy handling and high selectivity.

Manganese oxides may be effective oxidizer of As(III), the more toxic species of arsenic, to As(V) in water treatment and in the natural environment, rendering the adsorption of As(III) easier and more effective. A few compounds of manganese have been used in mixed oxides sorbents or as substituted material for enhancement of arsenic sorption from aqueous solutions, but there is little information on arsenic adsorption using pure manganese oxides. In this study, first several manganese oxides with different oxidation states [MnO , Mn_2O_3 , Mn_3O_4 and MnO_2] were tested for the removal of arsenic from water. The study then focused on the arsenic adsorption ability of the two more effective manganese oxides [Mn_2O_3 and Mn_3O_4], where the

SUMMARY (continued)

effect of different parameters such as contact time, pH and co-existing ions on the removal efficiency was investigated. The application of Mn_2O_3 for removal of arsenic from ash leachates containing arsenic was studied. Thereafter, two new manganese oxide coated sands were developed in which the oxidation/adsorption capacity of manganese oxides for removal of arsenic from aqueous solution was complemented by coating the manganese oxides on an inexpensive matrix like sand. The developed sorbents were applied in the batch and continuous flow modes to remove arsenic from water.

Manganese oxides containing Mn^{3+} was able to adsorb more arsenic from water than other manganese oxides containing Mn^{2+} or Mn^{4+} . Manganese (III) oxide (Mn_2O_3) was evaluated as a potential sorbent for removal of both As(III) and As(V) from water. Favorable adsorption of As(III) and As(V) onto Mn_2O_3 was observed; the binding of As(V) onto Mn_2O_3 was stronger than that of As(III), whereas the adsorption capacity of Mn_2O_3 was greater for As(III) than for As(V). Adsorption of As(III) and As(V) followed pseudo-second order kinetics. As(III) adsorption was not affected by pH less than 9, whereas As(V) adsorption at pH 6-9 was within 61-93 percent of maximum As(V) adsorption at pH 2. Surface charge analysis of Mn_2O_3 in separate solutions of As(III) and As(V) indicated that oxidation of As(III) to As(V) may have occurred on the surface of Mn_2O_3 in the pH range of 3-9. The Mn_2O_3 was also tested for As(III) and As(V) removal from two natural groundwaters. The 10 g/L of the sorbent was able to remove greater than 95 percent of arsenic from both groundwaters. Overall, Mn_2O_3 was found to

SUMMARY (continued)

be an effective and viable sorbent for rapid removal of As(III) and As(V) from natural waters with a pH of 6-9. Manganese (III) oxide sorbent was also tested for the adsorption and removal of arsenic from coal fly ash leachate and associated groundwater contaminated.

Two manganese oxide coated sand (MCS) sorbents, 5-hr MCS and 24-hr MCS, were developed as alternative, effective and potentially sustainable sorbents to remove As(V) and As(III) from water. The manganese on the MCS exhibited oxidation states between Mn^{3+} and Mn^{4+} with a predominance of Mn^{3+} . The MCS sorbents showed comparable affinity for adsorption of As(III) as well as As(V). The formation of arsenic inner-sphere complexes was evidenced by zeta potential measurements. The maximum adsorption of arsenic was obtained in the pH range from 3 to 10 suggesting that the MCS can be successfully utilized in water treatment without pre- and post- pH adjustment. Calcium, bicarbonate and sulfate did not inhibit the adsorption of As(III) and As(V) onto MCS sorbents, while phosphate decreased the uptake of arsenic from water. The kinetics experiments were indicative of a rapid arsenic adsorption onto MCS during the first 60 min. The 5-hr and 24-hr MCS sorbents were effective for rapid removal of As(III) and As(V) from natural waters in the pH range of 3-10 in batch systems.

A column study was performed to evaluate the removal of arsenic from water in a continuous flow system using both MCS sorbents. The breakthrough of arsenic occurred after 1,050 min for 24-hr MCS column and 1,440 min for 5-hr MCS column. The point of column exhaustion

SUMMARY (continued)

occurred after 2,600 min and 3,740 min for 24-hr MCS and 5-hr MCS, respectively. For the prediction of breakthrough curves, the Adams–Bohart and Thomas models, were applied. The Adams-Bohart model was used to predict the initial breakthrough of arsenic from the column, while the Thomas model was in good agreement with experimental data and could be used to predict the overall performance of the column and the column exhaustion. For an initial arsenic concentration of 1,070 $\mu\text{g/L}$ and a flow rate of 10 mL/min, the capacity of the MCS sorbents was 166 mg/kg for the 5-hr MCS and 127 mg/kg for the 24-hr MCS.

Chapter I

I. RESEARCH BACKGROUND

1. INTRODUCTION

Arsenic is a well known carcinogen, which is considered as one of the world's most hazardous chemicals[1]. Arsenic (atomic number 33) is ubiquitous in the environment and ranks 20th in natural abundance, 14th in the seawater, and 12th in the human body [2]. It is widely distributed in the earth's crust, with a crustal abundance of about 2 mg/kg [3] while higher concentrations are found in finer grained argillaceous sediments and phosphorites[1,4]. Arsenic is a silver-grey brittle crystalline solid. Some physicochemical properties of the arsenic are listed in Table 1[5].

Table 1. Physicochemical properties of Arsenic

| | |
|---------------------------|---------|
| MW | 74.9 |
| Specific gravity | 5.73 |
| Melting point (at 28 atm) | 817 °C |
| Boiling point | 613 °C |
| Vapor pressure(at 372°C) | 1 mm Hg |

Arsenic is mobilized by geochemical reactions, natural weathering reactions, biological activity, volcanic emissions and other anthropogenic activities. Soil erosion and leaching contribute to 612×10^8 and 2380×10^8 g/year of arsenic, respectively, in dissolved and suspended forms in the oceans [6].

1.1. Application, Health effect and Chemistry of Arsenic

1.1.1. Uses of Arsenic

Arsenic is used as an additive in the alloy for manufacturing high-strength structural iron, abrasion-resistant steel, storage batteries, as therapeutic agent in Cancer treatment and as pesticides and preservatives [7, 8].

1.1.2. Health effect and risk assessment of arsenic

Arsenic is a documented human carcinogen. The mechanisms behind arsenic carcinogenesis in humans is not fully understood yet [9]. Non-occupational exposure to arsenic commonly occurs through contaminated food and water [10]. Burning of arsenic contaminated coal for cooking and heating purpose would also lead to exposure to airborne arsenic in non-occupational exposure [11]. The largest contribution to total arsenic exposure is generally through food with daily arsenic intakes in the range of 5-1000 µg. But this exposure has not caught much attention since most of arsenic in food is in the organic form and is considered to be rather non-toxic. However, in some regions like Bengal delta the major contributor to total arsenic intake is arsenic contaminated ground water. In case of Bengal delta, the concentration of arsenic was found to be up to 4000 µg/L [12]. The daily water intake in Bengal delta is also very high (4-6 L [13]) compared to the WHO's assumption of 2 L [10], because of the hot climate and consumption of food items like rice and lentils prepared with ample water[15].

Arsenic in natural waters is a worldwide problem. Many countries are affected by high level of arsenic concentrations in surface and ground water. The largest population at risk among the countries with known groundwater arsenic contamination is in Bangladesh, followed by West Bengal in India [16–20]. Because of different socio-politicoeconomical contexts as well as the unavailability of different treatment technologies, the maximum contaminant level (MCL) of countries differs [21]. The maximum permissible limits for drinking water of some affected countries are listed in Table 2.

Table 2. Maximum permissible limits for drinking water in different countries

| Country | Maximum permissible limits($\mu\text{g/L}$) | References |
|-------------|---|------------|
| India | 10 | [22] |
| Bangladesh | 50 | [23] |
| Taiwan | 10 | [24] |
| Vietnam | 10 | [25] |
| Mexico | 50 | [26] |
| Nepal | 50 | [27] |
| China | 50 | [28] |
| USA | 10 | [29] |
| Argentina | 50 | [30] |
| New Zealand | 10 | [31] |
| Chile | 50 | [32] |

The type of arsenic species, bioavailability, amount of exposure, duration of exposure, genetic conditions, nutritional status, selenium intake, methylation capacity, presence of co-carcinogenic factors like exposure to sunlight and cigarette smoking can effect the toxicity of arsenic [33-36]. Since the pentavalent organic arsenic metabolites [mono methyl arsenic (MMA), dimethyl arsenic acid (DMA)] were the most common forms found in urine samples of exposed humans, the arsenic methylation is considered to be a detoxification path. These forms are readily excreted and less toxic than inorganic arsenic. In general, the toxicity decreases in the order of $\text{AsH}_3 > \text{As(III)} > \text{As(V)} > \text{organic arsenic compounds}$. The lethal dosage of arsenic range from 1.5 mg/kg body weight for As_2O_3 to 500 mg/kg of body weight for DMA [10].

In the study of arsenic species in the environment, as it moves through the environment various processes lead to changes in the chemical form of the arsenic. The processes can be chemical, biological or geological. Exposure to arsenic can occur through food, water and air [10]. Inhalation and ingestion are the primary routes of arsenic entry into the body. Exposure dose is the cumulative exposure by all routes. In the general U.S. population, ingestion of food containing arsenic is basically the main source of arsenic exposure while intake from drinking water ,air and soil is usually much less. The average daily dietary intake of arsenic by adults in the United States has been estimated to be 40 micrograms per day [39]. Most of the arsenic in food occur in the form of organic arsenic and has low toxicity to humans and is rapidly excreted in urine. However, a high level of inorganic arsenic was found in one form of seaweed, hijiki, in recent studies. [40].

The second major route of exposure is water. Arsenic is mainly present as inorganic form in natural waters. Well water contaminated by natural sources such as bedrock containing arsenic has been reported to be the cause of arsenic toxicity throughout the world. Arsenic in drinking-water has attracted much attention since recognition in the 1990s of its wide occurrence in well-water in Bangladesh [41]. Long-term drinking water exposure to arsenic has been linked to the cancer of the kidney, bladder, skin, lung and the cardiovascular and neurological systems [16, 39-41]. Considering arsenic high toxicity and the serious effects of arsenic on human health, World Health Organization as well as USEPA have specified the maximum contaminant level(MCL) of arsenic in drinking water as $10\mu\text{g/L}$ [42,43]. The latency period for development of internal and skin cancers are reported to be 6->40 years and depends on many factors like gender, duration of exposure, exposure level, sunlight and genetic conditions, smoking habits and nutritional status [44,45]. In the United States, arsenic contamination of drinking water is of concern mainly in parts of the west, midwest, and New Hampshire [46].

High concentration of arsenic in soil can be due to either natural or man-made contamination and it may be an ingestion risk, especially for children with pica and mouthing behaviors during play. Arsenic uptake in plants does not appear to reach levels dangerous to human health [47].

Pesticide manufacturing facilities, burning of fossil fuels that contain arsenic, glass manufacturing operations and tobacco smoke are generally the major source of inhaled arsenic [47]. Airborne arsenic in the workplace is generally in the form of arsenic trioxide [48]. Welch et al. [49] reported eight-hour averages of airborne arsenic in a U.S. copper smelter measured during 1943–1965 to be between 6.9 and 20 mg/m^3 . Inhalation of burning material containing arsenic as a wood preservative may cause a severe arsenic toxicity [50].

1.1.3. Arsenic Chemistry

There are two primary forms of arsenic in environment; organic and inorganic. Organic species of arsenic are mainly found in foodstuffs and have the form of mono methyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), and arseno-sugars. The organic arsenic species are generally present in smaller amounts than the inorganic forms. Ligand substitution of oxygen by methyl groups results in various methylated arsenic species [51].

Arsenic may exist in water in different oxidation states (+5, +3, 0,-3) [52] but arsenite [As (III)] and arsenate [As(V)] are two predominant valence states of inorganic arsenic species. Speciation of arsenic is significantly affected by the Eh and pH. As(III) ,the more toxic form, exists as an uncharged species (H_3AsO_3) or anionic species (H_2AsO_3^-) in a moderately reducing environment. Under reducing conditions at pH $< \sim 9.2$, the uncharged H_3AsO_4^0 predominates. As(V) species consist primarily of monovalent (H_2AsO_4^-) or divalent(HAsO_4^{2-}) anions in natural waters [53, 54]. H_2AsO_4^- dominates at low pH (less than about pH 6.9) in oxidizing conditions. At higher pH, HAsO_4^{2-} is dominant. In natural surface waters, As(V) is the dominant species while natural ground waters contain mainly As(III) due to the dominant reducing conditions [55]. Arsenic is uniquely sensitive to mobilization (pH 6.5–8.5) and under both oxidizing and reducing conditions among heavy metalloids [56].

Arsenate is a weak triprotic acid with acid dissociation constants (pK) ranging from 2.20 to 11.53 [57,58]. Reported pK_a values for both arsenous and arsenic acids are given in Table 3.

Table 3. pK_a Values for Arsenous and Arsenic acids[58].

| Compound | pK _{a1} | pK _{a2} | pK _{a3} |
|---------------------------------|------------------|------------------|------------------|
| H ₃ AsO ₃ | 9.22 | 12.13 | 13.40 |
| H ₃ AsO ₄ | 2.20 | 6.97 | 11.53 |

The rate of oxidation of As(III) to As(V) or reduction of As(V) to As(III) depends on many factors like pH, Eh, the presence of micro-organisms, the presence of other oxidizing agents like manganese and Fe, exposure to light and temperature[59-61]. Generally the rate of oxidation of As(III) to As(V) is very low[62] in natural waters, but can proceed measurably in several days in strongly alkaline or acid solutions. The mobility of As is mainly controlled by the presence of metal (hydr) oxides. Since at the pH of natural water As(III) is present as a neutral species and As(V) is present in anionic form, the sorption of As(V) is strongly favoured. Therefore As(III) is more mobile compared to As(V) in neutral to slightly acidic pH range. Arsenic is readily absorbed when ingested in dissolved form (80-90%) or inhaled (30-85%). As(V), whether organic or inorganic, is better absorbed from the gastrointestinal tract compared to As(III). In contrast to inorganic arsenic, neither mono- methyl arsenic nor di-methyl arsenic binds strongly to biological molecules in humans [63].

1.2. Different methods used to remove arsenic from water

Different treatment technologies have been suggested in the literature for the removal of arsenic from water. The final desired concentration of arsenic, associated cost and the feasibility of

monitoring the method efficiency should be considered during choosing a removal method. Investigations have shown that the natural distribution of inorganic arsenic species and the form of the arsenic present in the water (particulate/colloidal or dissolved) can effect the treatment strategy and the removal efficiency [64-66].

The neutral characteristics of arsenite at near neutral pH limit its removal efficiency in water while the anionic characteristics of arsenate promote its removal [67, 68]. Therefore, in case of the presence of arsenite in water, a pre-oxidation step should be provided to oxidize arsenite to arsenate for an efficient arsenic removal. An arsenic treatment method should preferably be effective in removing both arsenite and arsenate species. An appropriate arsenic removal technique should be effective enough to meet the required water quality standards for arsenic. Also, the expected cost of the method including set-up, operation and maintenance should be affordable. Safety, reliability and social acceptance of the method must be considered before developing the method. The applied method is preferred to need minimal energy requirements in addition to simple maintenance and operational requirements. Also, in case of the production of other pollutants like wastewater and toxic sludge as a result of the applied method, their treatment should be addressed.

The arsenic removal technologies can be divided into: Coagulation/filtration, oxidation, membrane technologies, ion exchange methods and adsorption onto surfaces [69, 70]. In addition to these widely used methods, some other methods like microbial processes [71], in-situ immobilization [72] and point of use units [73] have been reported.

1.2.1. Coagulation/filtration

The processes involved in arsenic removal by coagulation are addition of metal salts, sedimentation and filtration. Coagulation is the process by which colloidal impurities is removed from water [74]. Entrapment during coagulation removes the particulate arsenic [75]. Co-precipitation occurs when arsenic forms an insoluble complex with the coagulants like aluminum or ferric chlorides/sulfates or lime. The relevant amorphous ferric hydroxide or aluminum hydroxide is precipitated following the addition of ferric chlorides/sulfates or aluminum, respectively [76,77] while hydrated lime, $\text{Ca}(\text{OH})_2$, or $\text{Mg}(\text{OH})_2$ solids form by addition of lime. The formation of these insoluble products facilitates arsenic subsequent removal from the water by means of sedimentation and filtration processes [78,79].

The advantages of this method are as follow [76-82]:

- Simple in operation
- Simple in maintenance
- Locally available chemicals
- Low capital Costs
- No use of electricity
- Already exists at many treatment plants

Whereas the associated disadvantages are:

- Frequent filter maintenance
- Longer treatment time required

- Care is necessary for dosage of chemicals
- Problems with Sludge disposal
- Procedure is effective only over a narrow pH range and coagulant dosage.
- The presence of competing ions needs to be considered.

1.2.2. Oxidation

The purpose of oxidation is to convert soluble As(III) to As(V), which is followed by precipitation of As(V). Most of the arsenic removal technologies perform better when removing anionic arsenate than uncharged arsenite at neutral pH values. As(V) is adsorbed more easily onto solid surfaces than As(III) and thus, oxidation followed by adsorption is thought to be effective for the removal of As [83,84]. Different oxidizing agents and their removal efficiencies are listed in Table 4. In a recent study, Criscuoli et al. [85] studied the oxidation of As(III) by MnO₂ coated PEEC-WC(polymer) nanostructured capsules and demonstrated that they have a higher efficiency than conventional oxidation methods when the water contains a low concentration of As. All oxidants have their advantages and disadvantages that should be considered when choosing one to be used. For instance, the possibility of producing elevated concentrations of unwanted disinfection by-products with organic matter is one of the problem associated by chlorine [87].

The oxidation treatment process is simple with the low operational cost and it is applicable for large water volume. However, interfering substances decrease the removal efficiency and as

mentioned before for chlorine, the toxic chemicals and carcinogens are produced as by-products.

The additional removal process is usually essential after oxidation treatment.

Table 4. Different oxidizing agents and their removal efficiencies

| Oxidant | Operating pH | Initial Arsenic | Type of Water | Reference |
|---|--------------|-----------------|---------------------|-----------|
| H₂O₂ | 7.5-10.3 | 0.65 µmole/L | Sea and river water | [86] |
| Cl₂O | 6.3-8.3 | 50 µg/L | Synthetic water | [87] |
| MnO₂ coated capsules | 5.7-5.8 | 0.1-1 mg/L | Laboratory water | [85] |
| MnO₄⁻ | 6.3-8.3 | 50 µg/L | Synthetic water | [87] |
| Hypochlorite | 3-8 | 3 mg/L | Laboratory water | [88] |
| Free available chlorine(HOCl OCl⁻) | 7 | 50 µg/L | Real water | [89] |
| O₃ pure air and oxygen | 7.6-8.5 | 64-62 µg/L | Groundwater | [90] |
| UV-C/H₂O₂ and UV-A/TiO₂ | 7 | 500 µg/L | Ultrapure water | [91] |

1.2.3. Membrane Technologies

The principle of a membrane process is that water is allowed to pass through special filter media, which physically retain the impurities, present in the water. Generally four different types of membrane processes, i.e., microfiltration(MF), ultrafiltration(UF), nanofiltration(NF) and reverse osmosis (RO) are used for treatment of As contaminated water.

The selectivity of the membranes increases with increasing driving pressure [92]. The separation by these processes depends on the pore size of the membrane; for MF and UF membranes,

separation is achieved via mechanical sieving while for NF and RO membranes, capillary flow or solution diffusion are responsible for the separation [93,94]

MF membranes are only able to remove particulate form of arsenic from water and the size of the soluble arsenic are small enough to pass through the pores of the MF membrane. UF is another low pressure technique that is considered not favorable for treatment of arsenic contaminated water [95]. NF and RO are high pressure techniques and are able to remove dissolved arsenic from water to an appreciable level provided that the feed water contains a very low amount of suspended solids [96].

The advantages of the membrane technologies can be summarized as:

- High removal efficiency for As(V) from water along with other contaminants
- Good purification and no toxic solid waste are produced

Whereas the associated disadvantages are:

- High electrical energy needs to run the models
- Pretreatment steps are often required
- Efficiency is very low with high concentration arsenic contaminated water
- Removal efficiency is very low for As(III)
- High operation and capital cost

1.2.4 Ion exchange:

The principle of ion exchange is that arsenic is adsorbed on to anion-exchange resins in exchange of the anionic charged functional group of the resin, thus a low concentration of As(V) is produced in effluents[93]. Arsenic removal using strong base anion exchange resins has been

investigated in various studies [96-99]. Since arsenite usually exists as a neutral molecule and is not exchanged, oxidation of As(III) to As(V) is an important pretreatment step for ion exchange processes[100]. The resin bed is usually flushed with HCl before passing arsenic contaminated water to implant Cl^- on the surface of the resin, which is later easily exchanged with As. This results an effluent with a great amount of Cl^- and additional secondary treatment is needed to improve the quality. The removal efficiency of ion exchange method does not depend on the pH and concentration of the influent. There are usually interferences from other anions. The removal of As(III) in ion exchange is not possible without prior oxidation. Also, the large volume of toxic brine is normally produced during regeneration of resins.

1.3. Adsorption of arsenic

Adsorption has been recognized as a superior method for arsenic treatment. Various adsorbents like mineral oxides, activated carbons, biological materials, or polymer resins, have been used for the adsorption of arsenic [101,102]. Comparative evaluation of different adsorbents for arsenic removal are presented in Table 5.

1.3.1. Industrial by-products/wastes

Mohan et al. [103] investigated the capability of biochar by-products from fast wood/bark pyrolysis as adsorbents for the removal of the As^{3+} , Cd^{2+} and Pb^{2+} from water. Oak bark, pine bark, oak wood, and pine wood chars were obtained from fast pyrolysis at 400 and 450°C in an auger-fed reactor and characterized. Experiments were conducted to determine the optimum pH for As(III) uptake by various chars and activated carbons . Pine wood char, oak wood char, and

pine bark char behaved in a similar fashion. In each case, the removal increased when the pH increased from 2.0 to 4.0. A further pH increase from 4.0 to 5.0, decreased adsorption and at pH >5.0, the adsorption was almost negligible. The maximum arsenic adsorption was obtained over a pH range of 3–4. The As(III) removal followed the order: pine wood char (1.20 µg/g) < oak wood char (5.85 µg/g) < oak bark char (12.1 µg/g) < pine bark char (12.15 µg/g). They proposed that by-product chars from bio-oil production might be used as plentiful inexpensive adsorbents for arsenic remediation.

Altundogan et al.[104] explored Red mud, which is a waste product from bauxite processing , as an alternate adsorbent for arsenic. The tests showed that the alkaline aqueous medium (pH 9.5) favored the removal of As(III), whereas the pH range from 1.1 to 3.2 was effective for As(V) removal. The process of arsenic adsorption obeyed the Langmuir's model. It was found that the adsorption of As(III) was exothermic, whereas As(V) adsorption was endothermic. The effect of red mud dosage on the removal of arsenic was also studied. It was observed that the final arsenic concentration can be reduced below the regulation limits by increasing the adsorbent dosage. In general, the red mud adsorbed As(V) effectively more than the As(III). About a 100 g/L red mud dosage was found to be required for a final arsenic concentration below the regulation values of potable waters for As(V) while more was needed to adequately remove As(III).

Zhang and Itoh [105] synthesized an adsorbent for aqueous arsenic removal by loading iron(III) oxide onto melted municipal solid waste incinerator slag. The loading was accomplished via chemical processes and thermal coating technique. Loading of iron oxide on the slag increased the surface area of iron(III) oxide-loaded melted slag (IOLMS) by 68% compared to FeOOH, which attributed to the porous structure formation in IOLMS during the synthesis process.

The adsorbent was found to be effective for both arsenate and arsenite removal with the removal capabilities for As(V) and As(III) as 2.5 and 3 times of those of FeOOH, respectively. They also showed that the leaching of hazardous elements such as Se, Cd, Cr(VI), Pb and As from the adsorbent at a pH range of 2.5–12.5 was below the standard limits. They suggested their iron oxide-loaded slag adsorbent as an applicable industrial sorbent for wastewater treatment.

1.3.2. Synthetic activated carbons

Various types of activated carbons were synthesized and used for the removal of arsenic from water/wastewater [106-108]. Mondal et al. [109] investigated the removal of arsenic from a simulated contaminated ground water by the adsorption onto Fe³⁺ impregnated granular activated carbon (GAC-Fe) in presence of Fe²⁺, Fe³⁺, and Mn²⁺. The effects of shaking time, pH, and temperature on the percentage removal of total arsenic, As(III), As(V), Fe²⁺, Fe³⁺, and Mn was discussed. The shaking time for optimum removal of arsenic species was found to be 8 h for GAC-Fe and 12 h for GAC, respectively. The reason for the larger difference between the adsorption of As(III) and As(V) in granular activated carbon (GAC) versus the GAC-Fe was explained as: with time As(III) is converted to As(V), which is then adsorbed onto the surface of GAC or GAC-Fe. The greater peak area at λ value of 860 cm⁻¹ than that at λ value of 780 cm⁻¹ in the FTIR spectra of GAC-Fe(AA) was considered as an indicative of the partial conversion of As(III) to As(V). The addition of bands at the wave number of 825 and 860 cm⁻¹ in the spectrum of GAC-Fe(AA) was shown to be an indicative of the adsorption of As(V) onto the GAC-Fe.

The results also showed that the total arsenic removal was less affected by the change in pH within the pH range of 2–11. Maximum removal of As(V) and As(III) was observed in the pH range of 5–7 and 9–11, respectively, for both the adsorbents.

1.3.3. Commercial activated carbons

Commercial activated carbons have been extensively used for As(III) and As(V) adsorption from water[110-112]. Eguez and Cho [113] studied adsorption of As(III) and As(V) on activated charcoal versus pH and temperature. The As(V) showed a maximum adsorption at pH 2.35 over the pH range of 0.86–6.33 while the removal efficiency of As(III) was found to be constant at pH 0.16–3.5. Activated charcoal adsorbed 2.5 wt.% As(V) and 1.2 wt.% As(III) (based on the weight of carbon) at an equilibrium concentration of 2.2×10^{-2} M of both As(III) and As(V).

1.3.4. Soils, Sands and Clay minerals

Manning and Goldberg [114] studied the adsorption of As(III) and As(V) on three arid-zone soils from California(Wasco, Fallbrook, and Wyo) at different pH, arsenic concentration and ionic strength. The chromatographic speciation of As(III)/(V) in their study showed that the three soils contained low levels of background As(V). Oxidation of As(III) to As(V) was not detected below pH 8 in soil suspensions during 16-h adsorption experiments while As(III) oxidation was detected at higher adjusted pH. The soil with the highest citrate-dithionite extractable Fe and %clay showed the highest affinity for As(III) and As(V) and displayed adsorption behavior

similar to pure ferric oxide. Adsorption isotherms indicated that As(V) species were adsorbed more strongly than As(III) under most conditions.

A study investigated the removal of arsenic from water by the iron oxide-coated sand (IOCS) [115]. Batch studies were conducted in the study using IOCS with natural water containing 325 µg/L arsenic, and the removal of approximately 90% was achieved. The adsorption capacity of the IOCS for arsenic was estimated as 18.3 µg/g. The experimental data fitted well with Langmuir, Freundlich, and BET, indicating a favorable adsorption by IOCS.

Doušová et al. [116] used three samples of clay minerals (natural metakaoline, natural clinoptilolite-rich tuff, and synthetic zeolite) in both untreated and Fe-treated forms for arsenate adsorption from model aqueous solution. The minerals were exposed to concentrated solution of Fe(II). Within this process the mineral surface was laden with Fe(III)oxi(hydroxides) whose high affinity for the As(V) adsorption is well known. The results showed that the sorption removal efficiency(%ε) of Fe(II)treated sorbents increased significantly versus the untreated material. The efficiency of arsenic sorption on all FeII-treated aluminosilicates MTF_e, CLFe_e, and SZFe_e was found to be almost to maximum (>99%).

Aluminum-loaded Shirasu-zeolite P₁(Al-SZP₁) has been developed for adsorption and removal of As(V) from aqueous solution [117]. Al-SZP₁ was prepared by treating a P₁ type Shirasu-zeolite (SZP₁) with aluminum sulfate solution. Shirasu is of volcanic origin and is located in southern Kyushu area of Japan in large quantities, and SZP₁ is easily synthesized by one-step reaction from Shirasu. Al-SZP₁ was found effective to the adsorption of not only As(V), but also phosphate and fluoride ions. The addition of arsenite, chloride, nitrate, sulfate, chromate, and

acetate ions was found to be not effective on the As(V) adsorption, while the coexisting phosphate showed negative effect on the removal efficiency of arsenic. Continuous operation was demonstrated in a column packed with Al-SZP₁. The feasibility of this technique to practical utilization was also assessed by adsorption/desorption multiple cycles with in situ desorption/regeneration operation.

1.3.5. Biosorbents

Arsenic removal from groundwater by pretreated waste tea fungal biomass was investigated. [118] The tea fungus is a waste produced during black tea fermentation. Autoclaved tea fungal mat and autoclaving followed by FeCl₃ pretreated tea fungal mat were exploited for removal of Fe(II), As(III) and As(V) from ground water sample collected from Kolkata, West Bengal, India. The biosorption rate increased with the increase in adsorbent dosage and contact time. Autoclaved and FeCl₃ pretreated fungal mats removed 100% of Fe(II) and As(III) after 30 min contact time while a removal percent of 77 was obtained for As(V) after 90 min contact time.

1.3.6. Oxides

Singh and Pant [119-122] used activated alumina(AA) and iron oxide-impregnated AA to remove arsenite from water. They also investigated the effect of pH, contact time and adsorbent dose on the arsenic removal efficiency. The results showed that As(III) removal was strongly pH dependent. The adsorption process of As(III) on AA and impregnated activated alumina were found to be exothermic and endothermic, respectively. The experimental data were fitted well by Freundlich and Langmuir adsorption isotherms. The adsorption capacity of iron oxide

impregnated AA (12 mg/g) was much higher than AA (7.6 mg/g). The column studies were also performed and the parameters necessary for the design of fixed-bed reactors were evaluated in the study.

Pena et al.[123] investigated the adsorption of As(V) and As(III) by nanocrystalline titanium dioxide. Two different solutions, TiO₂ suspensions prepared in a 0.04M NaCl solution and a solution containing the competing anions like phosphate, silicate, and carbonate, were prepared and used for batch adsorption. The TiO₂ showed maximum removal for As(III) at pH of about 7.5 in the water with the coexisting ions while the effective pH for As(V) removal was found to be at pH 8. In a neutral pH range, the presence of the competing anions had a moderate effect on the adsorption capacities of the TiO₂ for As(III) and As(V). The higher adsorption capacity of the TiO₂ for As(V) and As(III) versus the fumed TiO₂ (Degussa P25) and granular ferric oxide was observed in the study. They basically proposed the nanocrystalline TiO₂ as an effective adsorbent for As(V) and As(III). The effect of light irradiation and dissolved oxygen on the photocatalytic oxidation of As(III) in TiO₂ suspensions was also studied in the study by conducting five different experimental systems for As(III) removal tests : (1) air and light system(air–light), where the suspension was open to the air and under room light (natural and florescent light); (2) air–dark system, where the reactor was wrapped with aluminum foil and oxygen in the air was dissolved in the suspension; (3) N₂–dark system, which was obtained by purging the suspension with high purity nitrogen gas in the dark; (4) air–sunlight system, where the suspension in a 1-L glass beaker was mixed directly under the sunlight outside of the laboratory and (5) N₂–light system. The result of the study showed that arsenic removal by TiO₂ took place rapidly in all systems except the air–light system. The longer time was needed for nanocrystalline TiO₂ versus

P25 to reach adsorption equilibrium which was explained by the different structure of nanocrystalline TiO_2 versus P25. P25 was made of nonporous TiO_2 particles and the nanocrystalline TiO_2 was composed of aggregated particles with high porosity. Hence, it was expected that longer time was needed to reach adsorption equilibrium in porous adsorbent. The adsorption kinetics of As(III) in the sunlight system was found to be similar to that of As(V). Also, the results indicated that the nanocrystalline TiO_2 had a much higher adsorption capacity than P25 which was attributed to much higher specific surface area of the nanocrystalline TiO_2 than that of P25. Formation of soluble As(V) species in mentioned five different systems were also studied. The soluble As(III) was observed to be completely oxidized to As(V) in the air–sunlight system within 25 min. In the air–light system, soluble As(III) was slowly oxidized to As(V) due to the presence of very low intensity of UV light in the roomlight. Soluble As(III) was found to be completely converted to As(V) in about 24 h. The formation of small amounts of As(V) in the anoxic suspensions like N_2 –light and N_2 –dark systems was related to the presence of minor amounts of oxygen adsorbed on TiO_2 , which were not removed by purging with nitrogen gas.

Iron oxides, oxyhydroxides and hydroxides have been widely used for removing As(III) and As(V) from water [64,124,125]. Raven et al. [126] studied arsenite and arsenate adsorption on Ferrihydrite. The adsorption behavior of arsenite and arsenate on ferrihydrite, under carefully controlled conditions was compared in that study regarding adsorption isotherms, adsorption kinetics, and the effect of pH on removal efficiency. Maximum adsorption of approximately 0.60 (0.58) and 0.25 (0.16) $\text{mol}_{\text{As}} \text{mol}_{\text{Fe}}^{-1}$ were achieved for arsenite and arsenate, respectively, at pH 4.6 (pH 9.2). At the highest initial arsenic concentration of 13.3 $\text{mol}_{\text{As}} \text{kg}^{-1}$ ferrihydrite, a distinct adsorption maximum was observed for arsenite adsorption at approximately pH 9.0, which

corresponds closely to the first pKa (9.2) of H_3AsO_3^0 , whereas there was a continuous drop in arsenate adsorption with increasing pH from 3 to 11. In general, the adsorption reactions were found to be relatively fast, with the reactions almost completed within the first few hours. At low arsenic concentrations and low pH, arsenate adsorption was faster than arsenite while arsenite reacted faster than arsenate with the ferrihydrite at high arsenic concentrations.

Table 5. Comparative evaluation of different adsorbents for arsenic removal

| Adsorbent | Type of water | pH | Concentration /range | Surface area(m ² /g) | Model used to calculate adsorption capacity | Capacity (mg/g) | | Refer ence |
|---|--|---|---|------------------------------------|--|-----------------|-------|---------------|
| | | | | | | As(III) | As(V) | |
| Iron oxide coated sand | Drinking | 7.6 | 100 ug/L | 10.6 | Langmuir | 0.041 | 0.043 | [127] |
| Ferrihydrite (FH) | Natural (dose 0.02– 0.09 g/100 mL); 5 h | - | 325 ug/L | 141 | Langmuir | - | 0.25 | [115] |
| Al ₂ O ₃ /Fe(OH) ₃ | Drinking (63.3 g in 50 ML; 100 g in 80 ML) | 8.2–8.9 | 0.05 mg/L | - | Breakthrough capacity | - | 0.09 | [128] |
| Basic yttrium carbonate | Drinking | 9.8–10.5 for As(III) and 7.5– 9.0 for As(V) | 5.0–0.20 mmol/L for As(III) and 10– 60 mmol/L for As(V) | 28.6 | Langmuir | 305.8 | 352.6 | [129] |
| Waste Fe(III)/Cr(III) | Aqueous solution (dose 500 mg/50 ML; 5 h) | 4 | 20–100 mg/L | - | Langmuir | - | 11.02 | [130] |
| Activated carbon | Aqueous solution | 6.4–7.5 | 157–737 for As(V) and 193– 992 for As(III) | 43.4 | - | 29.9 | 30.48 | [131] |
| Bauxsol | Water (dose: 5 g/L) | 4.5 | 0.80–32.00Mm | - | Langmuir | - | 1.081 | [132] |
| Red mud (RRM) | Water (dose: 20 g/L) | 7.25 for As(III); 3.50 for As(V) | 33.37–400.4 umol/L | - | Langmuir | 0.663 | 0.514 | [133] |

| | | | | | | | | |
|---------------------------------|--------------------------|-----------------------------------|---|---------|------------|-------|-------|-------|
| Activated alumina | Drinking water | 7.6 | 1 mg/L | 370 | Langmuir | 0.18 | - | [134] |
| Zr resin | Drinking water | 8.0 for As(III); 4.5 for As(V) | 0–5 mmol/L | - | Langmuir | 79.42 | 53.94 | [135] |
| TiO ₂ (Degussa P25) | Drinking water | 4 | <0.0015M 55 | - | - | 3.45 | 4.65 | [136] |
| HFO | Drinking water | 9 | 0–60 mg/L | 200 | - | 28 | 7 | [137] |
| Goethite | Drinking water | 9 | 0–60 mg/L | 39 | - | 22 | 4 | [138] |
| TiO ₂ | Ground water | 7 | 0.4–80 mg/L | 251 | Langmuir | 32.4 | 41 | [138] |
| Methylated biomass | Surface and ground water | 6.5 | 0.5–2.5Mm | 6.5 | - | - | 3.75 | [139] |
| Granular ferric hydroxide (GFH) | Surface and ground water | 7 | - | 226–252 | Freundlich | - | 0.004 | [140] |
| Gibbsite | Wastewater | 5.5 | 10–1000 mg/L | 13.5 | Langmuir | 3.3 | 4.6 | [141] |
| Activated alumina grains | Drinking water | 7 for As(III) and 5.2 for As(V) | 0.79–4.90 mg/L for As(III) and 2.85–11.5 mg/L for As(V) | 116–118 | Langmuir | 3.48 | 15.9 | [142] |
| Alumina | Drinking water | 6.5 | 0.133–1.33 mmol/L | 768 | Langmuir | - | 8.99 | [143] |

| | | | | | | | | |
|-----------------------------------|---------------------|---|----------------|-------|------------|--------|-------|-------|
| Nanoscale zero-valent iron (NZVI) | Ground water | 7 | - | 37.2 | Langmuir | 2.47 | - | [144] |
| Portland cement | Drinking water | 4–5 | 0.2 mg/L | 15.38 | Langmuir | - | 3.98 | [145] |
| Iron oxide coated cement (IOCC) | Drinking water | ~7 | 0.5–10.0 mg/L | - | Langmuir | - | 6.43 | [146] |
| Shirasu-zeolite(SZP1) | Drinking water | 3:10 | 1.3 Mm | 15.6 | Freundlich | - | 65.93 | [117] |
| Penicillium purpurogenum | - | 5 | 10–750 mg/L | - | Langmuir | 35.6 | - | [147] |
| Feldspar | Water/wastewater | 4.2 | 133.49 umol/L | 10.25 | Langmuir | - | 0.18 | [148] |
| Windsor soil | Soil | 5–6 | 5–100 mg/L | - | Langmuir | - | 0.55 | [149] |
| Olivier soil | Soil | 5–6 | 5–100 mg/L | - | Langmuir | - | 0.42 | [149] |
| Iron hydroxide coated alumina | Drinking water | 6.62–6.74 for As(III) 7.15–7.2 for AS(V) | 0.1–1.8 mmol/L | - | Langmuir | 7.64 | 36.64 | [150] |
| Granular activated carbone(GAC) | Drinking/wastewater | 7 | 1 mg/L | 1.065 | - | 0.09 | 4.5 | [151] |
| Pine wood char | Drinking water | 3.5 | 10–100 Ug/L | 2.73 | Langmuir | 0.0012 | - | [152] |

2. RESEARCH OBJECTIVES

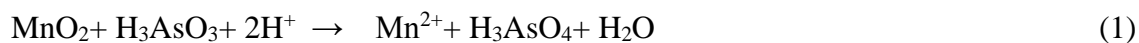
Adsorption has been recognized as a superior method for removal of arsenic from water because of its lower cost, flexibility and simplicity of design, high efficiency, easy handling and high selectivity. MnO_2 is an effective oxidizer of the more toxic species of arsenic [As(III)] to As(V) in water treatment and in the natural environment, making the sorption process more effective [54,153-155]. Manning et al. [155] have suggested that birnessite(MnO_2) materials used at near neutral pH in drinking water treatment and environmental remediation may play a beneficial role as both an efficient oxidant of As(III) and a sorbent for As(V). A low cost ferruginous manganese ore (FMO) with the major mineral phases of pyrolusite and goethite was studied for the removal of arsenic from groundwater [156]. The results showed that FMO can adsorb both As(III) and As(V) without any pre-treatment in the pH range of 2–8 with the maximum adsorbed arsenic(III) of 0.53 mg/g at pH of 6.3 and the maximum adsorbed arsenic(V) of 15.38 mg/g at a pH of 6.5 . The adsorption of arsenate has also been studied by natural manganese oxides by monocomponent column experiments [157]. The maximum arsenate adsorption of 2.23 $\mu\text{mol/g}$ was obtained from a solution of 0.67 mM sodium arsenate (50 mg/L arsenic) and 1mM sodium chloride at pH 7.9.

Thirunavukkarasu et al. [158] applied manganese “greensand” in column studies to examine the removal of arsenic in drinking water. They indicated that manganese greensand was found to be efficient in decreasing As(III) to a level below 25 $\mu\text{g/L}$. The addition of iron enhanced arsenic removal in filtration studies where in the case of Fe:As(III) ratio of 20:1, the maximum solid phase concentration was estimated at 22.3 $\mu\text{g/g}$ based on the weight of manganese greensand and it was estimated at 2.5 $\mu\text{g/g}$ for Fe:As(III) ratio of 7:1. The performance of manganese oxide-coated-

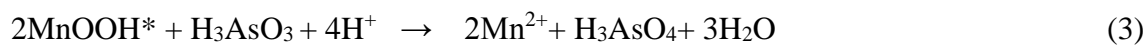
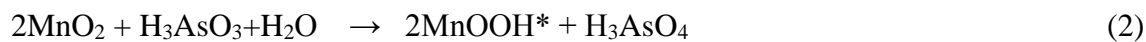
alumina (MOCA) in removing As(III) and its interaction with As(III) in drinking water was studied and compared to activated alumina[159]. The sorption process was found to be pH dependent and the optimum removal was observed between pH of 4 and 7.5. The predicted maximum As(III) sorption capacity of 29.15 mg/g was obtained from the Langmuir model at $\text{pH}=7 \pm 0.2$ which was higher than that of activated alumina (19.63 mg/g) . A MnO_2 -loaded polystyrene resin(R- MnO_2) has been demonstrated as a strong solid sorbent for arsenic retention where the R- MnO_2 maximal capacities were 0.7 and 0.3 mmol/g towards As(III) and As(V), respectively[160]. Deschamps et al. [161] investigated the arsenic adsorption onto some soils enriched with Mn and Fe. They have claimed that the presence of naturally occurring Mn oxides promotes the effective oxidation of As (III) to As(V). Also, the Mn minerals in their study showed a significant uptake of both the As (III) and As(V).

Wu et al.[162] showed that using a manganese sand carrier instead of a quartz sand carrier for arsenic adsorption to iron-oxide-coated sand can improve the adsorption capacity of the sorbent. The maximum adsorption capacities of As(III) and As(V) by iron-oxide-coated manganese sand (IOCMS) were obtained as 2.216 mg/g and 5.452 mg/g, respectively which were nearly 3 and 10 times higher than those by iron-oxide-coated quartz sand (IOCQS) , respectively. Deschamps et al. [163] demonstrated the high adsorption capacity of Fe and Mn enriched samples as sorbent in batch and column experiments for removing As(III) and As(V) from water. At pH 3.0, the maximum uptake of 8.5 mg/g and 14.7 mg/g were obtained for As(V) and for As(III)-treated materials, respectively. The oxidation of As(III) to As(V) of both adsorbed and dissolved arsenic-species were promoted by Mn-minerals. Column experiments with the sorbent for an initial

arsenic-concentration of 100 µg/L showed a very efficient elimination of As(III). Zhang et al.[164] developed a novel Fe–Mn binary oxide adsorbent from low cost materials which could completely oxidize As(III) to As(V) and was effective for both As(V) and As(III) removal, especially the As(III). The maximum adsorption capacities of As(V) and As(III) were found to be 0.93 mmol/g and 1.77 mmol/g, respectively in a 200 mg/L arsenic suspension at pH 5.0. A Mn-substituted iron oxyhydroxide (MIOH) has been used as sorbent for the adsorption of As(III) and As(V) from water[165]. The maximum uptake of As(III) and As(V) onto MIOH was found to be 4.58 and 5.72 mg/g, respectively. The high removal rate of As(III) was related to the probable oxidation of As(III) by manganous oxyhydroxide to the easily removable As(V) ions. Manganese oxides may oxidize reduced species such as As(III). For MnO₂, the oxidation of As(III) by manganese oxide is associated with the reductive dissolution of the MnO₂ surface and results in the release of both As(V) and Mn(II) to solution at low pH [166]. The net stoichiometry of the reaction is

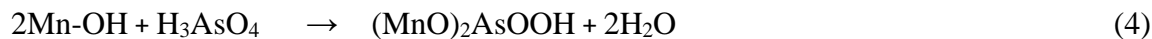


This reaction can proceed by a two step pathway, involving the reduction of Mn(IV) to Mn(III) as follow[167]:



where MnOOH* is a Mn(III) intermediate reaction product.

An additional reaction could include the adsorption of As(V) by the MnO₂ surface



where Mn-OH represents a reactive hydroxyl group on the MnO₂ surface and (MnO)₂ AsOOH represents the As(V) surface complex.

Manganese oxide has been mostly used in combination with other sorbents for removal of arsenic from aqueous solutions but there is no study on arsenic adsorption using different types of bearing manganese oxides. Therefore, first the manganese oxides with different oxidation states were tested for arsenic removal in this study. Adding the mineral oxides to small volumes of water has been identified by USEPA as a feasible process to remove arsenic from water [167]. Then the application of manganese oxides for removal of arsenic from ash leachates containing arsenic was investigated. A new manganese oxide coated sand was developed and applied in the batch and column system to remove arsenic from water. The general research objectives are presented as follow:

2.1. Batch experiments using several manganese oxides compounds

The batch study for the removal of arsenic was studied with different manganese oxides compounds. The experiments was conducted with dry sorbent suspension of different concentrations. Each solid sorbent was immersed in 50 mL of As(V) or As(III) solution. A certain volume of the stock solution was subsequently diluted for a desired level of As(V) or As(III) solutions during the experiment. Different solutions including DI solution, real groundwater solution, 2.5 mM and 5.5 mM sodium bicarbonate were used as target solutions. The last two solutions were prepared by adding 1 mM calcium chloride(CaCl₂) and 0.5 mM sodium

sulfate(Na_2SO_4) to each of these solutions to synthesize a more realistic solution considering the effect of other co-existing ions. The concentration of arsenic was analyzed with graphite furnace atomic absorption spectroscopy (GFAAS) with Zeeman background correction. The uptake of arsenic on the sorbents was determined as:

$$q = \frac{(C_0 - C_e)}{m} \times A \quad (5)$$

where C_0 and C_e are the initial and equilibrium concentration of arsenic in the solution(mg/L), q is the adsorbed arsenic (mg/kg), m is the adsorbent dosage(kg) and A is the solution volume(L). The removal percent (%) was calculated using the following equation:

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (6)$$

2.2. Surface Charge analysis of the manganese oxides

In order to observe the surface charges of the manganese oxides suspensions and understand the interactions at solid/solution interfaces, the zeta potential values was measured in DI solutions. The zeta potential of all manganese oxides was measured by a Zeta-meter system 3.0(Zeta meter Inc,VA). A suspension of 100 mg/L of the sorbent was prepared. The pH of the samples was adjusted from 3 to 12 using 0.1 M HCl and 0.1 M NaOH solutions. The effect of different initial arsenic concentration on the surface charge of the sorbent as also studied.

2.3. Effect of pH and coexisting ions on the adsorption of arsenic

Arsenic speciation is pH dependent and pH can play an effective role on the adsorption of arsenic species. The pH dependence of As(V) adsorption has been indicated for other sorbents[168]. To determine the optimum pH for adsorption of arsenic onto manganese oxides, the uptake of arsenic as a function of pH was studied. In the experiments for the effect of pH on arsenic adsorption, the pH of the 1 mg/L arsenic in DI water was adjusted to 2-10 using 0.1 M HCl and 0.1 M NaOH solutions.

The presence of other ions, such as sulfate, bicarbonate, phosphate and calcium which are usually present in natural water may affect the removal efficiency of arsenic in water. In order to find the effect of ionic strength and the effect of individual co-existing ions on the adsorption of arsenic onto manganese oxide, different concentrations of three anions (bicarbonate , sulfate and phosphate) and one cation (calcium) was selected to evaluate the uptake of arsenic as function of individual ions added to DI water. A 50 mL volume of each solution with an initial arsenic concentration of 1 mg/L was mixed with optimum dosage of the sorbent, and the analysis was performed similar to the batch adsorption tests.

2.4. Adsorption capacity of sorbent: adsorption isotherm experiments

The equilibrium isotherms can provide essential physiochemical data for evaluating the applicability of the adsorption process [169]. The abilities of four common isotherms, Langmuir,

Freundlich, Temkin, and Dubinin–Radushkevich (D-R) was investigated to model the arsenate adsorption equilibrium data at 25 °C using an initial arsenate concentration of 1 mg/L. The correlation coefficient was used to select the best –fit isotherm model.

Langmuir isotherm assumes that adsorption occurs on a structurally homogenous surface, that is, all the adsorption sites are equivalent and adsorbed molecules do not interact. It can model the monolayer coverage of the adsorption surface and the adsorption that occurs through the same mechanism. The Langmuir isotherm is commonly expressed as the following equation [170]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where q_e is the amount of arsenic(V) adsorbed per unit weight of adsorbent (mg/kg), q_m is maximum arsenic(V) adsorbed (mg/kg) corresponding to complete coverage of available sites, K_L is Langmuir constant related the free energy or net enthalpy of adsorption and C_e is the concentration of adsorbate in solution at equilibrium (mg/L). The linear form of Langmuir model is as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (8)$$

The Freundlich isotherm model has been employed for interpreting both multilayer sorption and sorption on heterogeneous surfaces [171]. Freundlich model assumes a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites. This empirical equation can be represented as :

$$q_e = K_F C_e^{1/n} \quad (9)$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/kg), C_e is the concentration of adsorbate in solution at equilibrium (mg/L), K_F is the Freundlich constant indicating the adsorption capacity and $1/n$ is a constant that shows the adsorption intensity or strength. $1/n$ values less than one shows good adsorption intensity. The linearized form of the Freundlich is represented by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (10)$$

Temkin isotherm [172] assumes that the decrease in the heat of adsorption is linear rather than logarithmic, as entailed in the Freundlich equation; also it assumes the distribution of binding energies is uniform up to some maximum binding energy. It is also applicable for heterogeneous surface and can be represented as:

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \quad (11)$$

and linearized as:

$$q_e = \left(\frac{RT}{b}\right) \ln(A) + \left(\frac{RT}{b}\right) \ln(C_e) \quad (12)$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/kg) and C_e is the concentration of adsorbate in solution at equilibrium (mg/L). A (L/g) is the equilibrium binding constant corresponding to the maximum binding energy and determines the Temkin adsorption potential, b (J/mol) is related to the heat of adsorption and T and R are the temperature (K) and gas constant (8.314 J/mol.K), respectively.

In order to evaluate the nature of the sorption, the adsorption equilibrium data will be also fitted with Dubinin–Radushkevich (D-R) adsorption equation. This model envisages the process mechanisms and determines the mean free energy of the sorption which is defined as the free energy change for removing a molecule from its location in the sorption space to an infinite distance in solution from the sorption surface [173]. D-R adsorption isotherm can be expressed as:

$$q_e = q_m \exp(-K_{DR} \varepsilon^2) \quad (13)$$

where q_e is the amount of the adsorbate adsorbed per unit weight of adsorbent (mg/kg), ε (Polanyi potential) is $RT \ln(1 + 1/C_e)$, C_e is the equilibrium concentration of adsorbate in aqueous solution (mg/L), q_m is the adsorption capacity (mg/kg), K_{DR} is a constant related to adsorption energy ($\text{mol}^2 \cdot \text{kJ}^2$)⁻¹, and R and T are the gas constant and temperature (K), respectively. The linearized form of the D-R equation is expressed as follow:

$$\ln q_e = \ln q_m - K_{DR} E^2 \quad (14)$$

The type of adsorption such as physisorption or chemisorption can be determined by calculating the mean free energy (E) in the system using the following equation: [174]:

$$E = \frac{1}{\sqrt{2K_{DR}}} \quad (15)$$

where R , T , and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. If the magnitude of E is less than 8 kJ/mol the sorption process is of physical sorption; if E is in the range of 8 to 16 kJ /mol the sorption is supposed to proceed via chemisorptions.

2.5. Adsorption kinetics - dynamic modeling

In order to find the effect of contact time on the adsorption of arsenic onto manganese oxide, batch adsorption tests was carried out at several time intervals using an initial arsenic concentration of 1 mg/L in the 2.5 mM HCO_3^- solution with 20 g/L of manganese oxide. In order to understand the dynamics of the adsorption process and evaluate the performance of the sorbent with time, the experimental adsorption data was analyzed by application of three different models, Lagergren pseudo-first order model [175], pseudo-second order model [176] and intra-particle diffusion model. The pseudo-first order model and the pseudo second-second order method can be written as Eq.16 and Eq.17, respectively:

$$\frac{dq}{dt} = k_1 \times (q_e - q_t) \quad (16)$$

$$\frac{dq}{dt} = k_2 \times (q_e - q_t)^2 \quad (17)$$

where q_e and q_t are the adsorption capacities(mg/kg) at equilibrium and at time t , respectively. k_1 is the adsorption rate constant(min^{-1}) of pseudo-first order adsorption and k_2 is the adsorption rate constant($\text{g.mg}^{-1}.\text{min}^{-1}$) of pseudo-second order adsorption. The linearized forms of the Lagergren pseudo-first order and pseudo-second order equations are given in Eq.18 and Eq.19 , respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (18)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2} \right) \left(\frac{1}{q_e^2} \right) + \frac{t}{q_e} \quad (19)$$

The theoretical equilibrium sorption capacity, q_e calculated, and the rate constant k_1 can be obtained from the intercept and slope of a linear plot of $\ln(q_e - q_t)$ against t , respectively. k_2 can be obtained from the intercept of a linear plot of t/q_t against t .

The three main steps occurring in the adsorption process of arsenic onto manganese oxides are:

1. Transport of adsorbate molecules from bulk solution to the external surface of the sorbent by diffusion through the boundary layer (film diffusion).
2. Diffusion of the adsorbate from the external surface into the pores of the adsorbent (pore diffusion)
3. Adsorption of the adsorbate on the active sites on the internal surface of the pores.

Determining the rate limiting step is very important to understand the adsorption mechanism of arsenate adsorption onto the manganese oxides. The last step (step 3) is very rapid and usually does not represent the rate-limiting step in the uptake of arsenic [122]. Hence, either of pore diffusion or film diffusion or a combination of both may be the rate controlling steps. The experimental data can be modeled by intraparticle diffusion equation (Fick's 2nd law (Eq. 20)) to determine the sole existence of intraparticle diffusion in the adsorption process as rate controlling step [177]:

$$q_t = k_{id}t^{1/2} + c \quad (20)$$

where q_t (mg/kg) is the adsorption capacities(mg/kg) at time t (min) , k_{id} (mg.kg⁻¹.min^{-1/2}) is the rate constant of intraparticle diffusion and C represents the boundary layer effect . The greater is the value of C , greater is the thickness of boundary layer [178]. For q_t versus $t^{1/2}$, the straight line

passing through the origin($C=0$) indicates that the intraparticle diffusion model is the main rate determining step for the adsorption process [179]. The value of k_{id} and C can be determined from the slope and intercept of the plot of q_t versus $t^{1/2}$, respectively.

2.6. Sorbent Reusing

The sorbent can be a cost effective sorbent if the sorbent can be reused in multiple cycles of operation. The adsorption capacity of the sorbent was tested by exposing the same mass of sorbent (1 g) to the solution (1 mg/L arsenic) in several consecutive cycles of adsorption. The percent uptake of arsenic by manganese oxide from the solution for each adsorption cycle was determined.

2.7. Removal of arsenic from coal fly ash leachate by manganese oxides

Coal fly ash in coal-fired electric power plants is one of the largest industrial waste streams in the United States. Based on American Coal Ash Association data base, in 2010, 67.7 million short tons of fly ash were generated by coal-fired power plants in US, accounting for 52.0% of the total coal combustion products (CCPs) [180]. Fly ash contains a broad array of trace elements in concentrations greater than 50 mg/kg, many of which are of environmental concern [181]. The phase transformations of the mineral matter in coal during high temperature combustion may make the trace elements in the original coal matrix susceptible to leaching [182]. Some elements contained in fly ash are likely to be released from the storage/disposal/application site when ash comes in contact with water [181]. Leaching of these trace elements can potentially pose health

hazards to humans when they transfer into the groundwater and reach to the domestic area. Thus special attention is to be needed to control and manage these toxic as leached from fly ash.

Arsenic is enriched on fly ash particles as a consequence of the condensation of volatile arsenic species onto the surfaces of the particles. There is concern that leaching of this arsenic will result in contamination of aquatic disposal sites. Because of its reactivity and mobility, As can cycle extensively throughout the abiotic and biotic components of the aquatic and terrestrial systems. The main concern is that pollution from the ash leaches out and contaminates nearby groundwater that is used for drinking. Therefore, applying effective methods and appropriate materials to selectively adsorb the excess amount of arsenic from ash leachate is required. The adsorption and removal of arsenic from coal fly ash leachate and associated groundwater contaminated with arsenic was studied by crystalline manganese oxides as sorbent.

2.8. Removal of arsenic with manganese oxide-coated sand

There is a need to develop cost-effective processes for use in small systems or home-treatment units in developing areas of the world, for removing As(III) and As(V) from ground water. Because of the ease of handling, sludge-free operation, and regeneration capability, processes based on the adsorption method appear promising. Hydrous manganese and iron and aluminum oxides have been considered the principal solid-phase components controlling the adsorption of arsenic in water [183] and these oxides, particularly the redox-sensitive manganese and iron hydroxides under oxidizing conditions, constitute significant sinks of arsenic in aquatic systems

[184]. A redox reaction between iron(III) and arsenite does not occur within 72 h. However, manganese oxides can oxidize arsenite to arsenate. The released Mn^{2+} ions adsorb onto the manganese dioxide, giving it a positive charge, thereby leading to an enhancement in the adsorption of arsenate. Driehaus et al. [185] observed $\delta\text{-MnO}_2$ to be efficient in arsenite oxidation and in adsorbing arsenate, with a low release of soluble manganese. Conceivably, oxidation/adsorption by manganese oxides is an effective process for removing arsenite and arsenate from water, and a matrix, such as sand, coated with manganese oxides would be an effective medium for removing arsenic(III) and arsenic(V) from water. Hence, a manganese oxide coated sand was developed as a cheap and sustainable sorbent to remove arsenic from water.

2.9. Characterization of manganese oxide-loaded sand:

The synthetic manganese oxide coated sand was characterized by several methods, including X-ray photoelectron spectroscopic (XPS), X-ray diffraction (XRD) analysis, EDX and specific surface area. The specific surface area was determined by single-point Brunauer-Emmett-Teller (BET) N_2 adsorption. The BET surface area of the manganese oxide-loaded sand was measured with an Accelerated Surface Area and Porosimetry system, ASAP 2010 (Micromeritics Instrument Corporation, Norcross, GA), using nitrogen adsorption/desorption isotherms. The crystallinity of the material was analyzed by powder X-ray diffraction analysis using Cu KR radiation. X-ray photoelectron spectroscopic (XPS) studies of the manganese oxide coated sand surfaces was conducted to determine the chemical state and abundance of Mn, O, and As in the near-surface of the sorbent.

2.10. Removal of As(III)

Based on the results from the preliminary experiments, the adsorption of As(III) onto the more effective sorbents was investigated. The time dependence of As(III) removal was evaluated. The adsorption capacity of the sorbents in removing As(III) was determined from adsorption isotherm experiment. The effect of pH and sorbent dosage on the removal efficiency of As(III) was also evaluated.

2.11. Column adsorption experiments

Adsorption of arsenic on manganese oxide coated sand was evaluated with continuous flow through systems after determining the adsorbent capacity resulting from the maximum removal efficiency for arsenic. Column adsorption studies was conducted to simulate flow through systems depending on the effective parameters on the adsorption process such as initial arsenic concentration, pH, ionic strength, sorbent dosage, co-existing ions , etc.

In order to achieve a permeable media for the column study, the manganese oxide adsorbent was mixed with quartz sand to result a media with a hydraulic conductivity of not less than 10^{-3} cm/sec. The column studies was carried out for a maximum period of 3 days. Arsenic solution was fed to the system from a reservoir at a given influent concentration, and effluent was collected at the bottom of the column. The concentration of arsenic in the effluent was monitored with time until the breakthrough of arsenic and subsequent exhaustion of the adsorbent occurs.

2.12. Modeling of column adsorption data

The movement of solute in a column can be modeled by a one-dimensional form of the advection--dispersion equation - plug flow dispersion reactor (PFDR) model:

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_d \frac{\partial^2 C}{\partial x^2} + r \quad (21)$$

where x is the spatial dimension, v_x is the interstitial velocity and D_d is the dispersion coefficient. The first term on the right side of the above equation shows the advective mass transport while the second term is indicative of the dispersive mass transport. The r is indicative of the reactive mass transport. At steady state conditions, the change of arsenic concentration with respect to time is zero ($\frac{\partial C}{\partial t} = 0$). The performance characteristics of the column was evaluated and simulated based on a plug flow dispersion reactor (PFDR) model.

3. REFERENCES

- [1] USEPA, 2001. Fact Sheet: Drinking Water Standard for Arsenic. <http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations_factsheet.cfm>.
- [2] Mandal, B.K. and Suzuki, K.T.: Arsenic round the world: a review, *Talanta*, 58:201–235, 2002.
- [3] Wedepohl, K.H.: The composition of the continental crust. *Geochim Cosmochim Acta*, 59 :1217–1232, 1995.
- [4] Kabata-Pendias, A., Pendias, H.: Trace elements in soils and plants, CRC Press, Boca Raton, FL, 2000.
- [5] Mohan, D., Pittman, C.U. Jr.: Arsenic removal from water/wastewater using adsorbents—A critical review, *J. Hazard. Mater.*, 142:1–53, 2007.

- [6] Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J. and Tullio, J.O.: Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina, *Appl. Geochem.* 17 (3): 259–284, 2002.
- [7] Kang, Y., Liu, G., Chou, C-L, Wong, M.H., Zheng, L., Ding, R.: Arsenic in Chinese coals: Distribution, modes of occurrence, and environmental effects, *Sci. Total Environ.* 412-413:1–13, 2011.
- [8] Peters, G.R., McCurdy, R.F. and Hindmarsh, T.J.: Environmental aspects of arsenic toxicity. Critical Reviews in *Environ. Sci. Technol.* 33(6):457-493, 1996.
- [9] Schoen, A., Beck, B., Sharma, R. and Dube, E.: Arsenic toxicity at low doses: epidemiological and mode of action considerations. *Toxicology and Applied Pharmacology*, 198(3):253-267, 2004.
- [10] Abedin, M., Cotter-Howells, J., and Meharg, A.A.: Arsenic uptake and accumulation in rice (*Oryza sativa* L.) irrigated with contaminated water. *Plant and Soil*, 240(2):311-319, 2002.
- [11] Arsenic in drinking water (1999). National Research Council. p:193-222. National Academy Press, Washington D.C.
- [12] Saha, K.C.: Diagnosis of arsenicosis. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 38(1):255-272, 2003.
- [13] Liu, J., Zheng, B., Aposhian, H.V., Zhou, Y., Chen, M.L., Zhang, A. and Waalkes, M.P. :Chronic Arsenic Poisoning from Burning High-Arsenic-Containing Coal in Guizhou, China. *Environmental Health Perspectives - New Series*, 110(2):119-122, 2002.
- [14] Watanabe, C., Kawata, A., Sudo, N., Sekiyama, M., Inaoka, T., Bae, M. and Ohtsuka, R.: Water intake in an Asian population living in arsenic-contaminated area. *Toxicology and Applied Pharmacology*, 198(3):272-282, 2004.
- [15] Das, D., Chatterjee, A., Mandal, B.K., Samanta, G., Chakraborty, D. and Chanda, B.: Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 2. Arsenic concentration in drinking water, hair, nails, urine, skin-scales and liver tissues (biopsy) of the affected people, *Analyst*, 120 :917–924, 1995.
- [16] Jain, C.K. and Ali, I.: Arsenic: occurrence, toxicity and speciation techniques, *Water Res.* 34 :4304–4312, 2000.
- [17] Rahman, M.M., Mukherjee, D., Sengupta, M.K., Chowdhury, U.K., Lodh, D., Chanda, C.R., Roy, S., Selim, M.D., Quamruzzaman, Q., Milton, A.H., Shahidullah, S.M., Rahman, Md. T. and Chakraborti, D.: Effectiveness and reliability of arsenic field testing kits: are the million dollar screening projects effective or not? *Environ. Sci. Technol.* 36. 2002.
- [18] Chatterjee, A., Das, D., Mandal, B.K., Chowdhury, T.R., Samanta, G. and Chakraborty, D.: Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 1. Arsenic species in drinking water and urine of the affected people, *Analyst*, 120:643–656, 1995.

- [19] Robertson, F.N.: Arsenic in ground water under oxidizing conditions, south-west United States. *Environ. Geochem. Health* , 11:171–176, 1989.
- [20] Roy, M., Nilsson, L. and Pal, P.: Development of groundwater resources in a region with high population density: a study of environmental sustainability. *J. Environ. Sci.* 5: 251–267, 2008.
- [21] Rahman, M.M., Sengupta, M.K.,Ahamed, S.,Chowdhury,U.K., Hossain, M.A.,Das, B.,Lodh,D., Saha,K.C., Pati,S. and Kaies,I.: The magnitude of arsenic contamination in groundwater and its health effects to the inhabitants of the Jalangi—one of the 85 arsenic affected blocks in West Bengal, India. *Sci. Total Environ.* 338 (3):189–200, 2005.
- [22] Chakraborti, D.,Sengupta,M.K.,Rahman,M.M.,Ahamed,S.,Chowdhury,U.K. and Hossain, M.A.: Groundwater arsenic contamination and its health effects in the Ganga–Meghna–Brahmaputra plain. *J. Environ. Monit.* 6 (6) : 74–83,2004.
- [23] Tseng, W.P., Chu, H.M., How, S.W., Fong, J.M.,Lin, C.S. and Yeh,S.: Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan, *J. Natl. Cancer Inst.* 40 (3): 453–463, 1968.
- [24]Berg,M.,Tran,H.C.,Nguyen,T.C.,Pham,H.V.,Schertenleib,R.and Giger,W.:Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat, *Environ. Sci. Technol.* 35 (13):2621– 2626, 2001.
- [25] Cebrian, M.E., Albores, A., Aguilar, M. and Blakely, E.: Chronic arsenic poisoning in the North of Mexico. *Hum. Toxicol.* 2 :121–133, 1983.
- [26] Shrestha, R.R.,Shrestha,M.P.,Upadhyay,N.P.,Pradhan,R.,Khadka,R.,Maskey,A.,Maharjan, M., Tuladhar, S., Dahal B.M. and Shrestha,K.: Groundwater arsenic contamination, its health impact and mitigation program in Nepal, *J. Environ. Sci. Health Part A: Toxic/Hazard. Substances Environ. Eng.* 38 (1):185–200, 2003.
- [27] Sun, G.: Arsenic contamination and arsenicosis in China, *Toxicol. Appl. Pharmacol.* 198 (3):268–271, 2004.
- [28] Thornburg, K., Sahai, N.: Arsenic occurrence, mobility, and retardation in sandstone and dolomite formations of the Fox River Valley, Eastern Wisconsin. *Environ. Sci. Technol.* 38 (19):5087–5094, 2004.
- [29] Bundschuh, J., Farias, B., Martin, R., Storniolo, A., Bhattacharya, P., Cortes, J., Bonorino, G. and Albouy, R.: Groundwater arsenic in the ChacoPampean Plain, Argentina: case study from Robles county, Santiago del Estero Province. *Appl. Geochem.* 19 (2):231–243, 2004.
- [30] Robinson,B.H., Brooks, R.R., Outred, H.A. and Kirkman, J.H.: The distribution and fate of arsenic in the Waikato River system, North Island, New Zealand, *Chem. Spec. Bioavailability*, 7 (3) :89–96,1995.

- [31] Caceres,D.D.,Pino,P.,Montesinos,N.,Atalah,E.,Amigo,H. and Loomis,D.: Exposure to inorganic arsenic in drinking water and total urinary arsenic concentration in a Chilean population, *Environ. Res*, 98 (2):151–159, 2005.
- [32] Vahter,M., Concha,G., Nermell,B., Nilsson,R., Dulout,F. and Natarajan,A.T.: A unique metabolism of inorganic arsenic in native Andean women. *Environmental Toxicology and Pharmacology*, 293(4):455-462, 1995.
- [33] Steinmaus,C., Yuan,Y., Bates,M.N. and Smith,A.H.:Case-Control Study of Bladder Cancer and Drinking Water Arsenic in the Western United States. *American Journal of Epidemiology*, 158(12):1193-1201, 2003.
- [34] Rossman,T.G., Uddin,A.N., Burns,F.J. and Bosland,M.C.:Arsenite Is a Cocarcinogen with Solar Ultraviolet Radiation for Mouse Skin: An Animal Model for Arsenic Carcinogenesis. *Toxicology and Applied Pharmacology*, 176(1):64-71, 2001.
- [35] Wang,J.P., Qi,L., Moore,M.R. and Ng,J.C.: A review of animal models for the study of arsenic carcinogenesis. *Toxicology Letters*, 133(1):17-31,2002.
- [36] [ATSDR] Agency for Toxic Substances and Disease Registry. 2007. Toxicological profile for arsenic. Draft for Public Comment. Atlanta GA [updated 2007 August; accessed 2008 January 14]. Available from: <http://www.atsdr.cdc.gov/toxprofiles/tp2.html>.
- [37] Rose, M., Lewis, J., Langford, N., Baxter, M., Origgi , S., Barber, M.: Arsenic in seaweed—forms, concentration and dietary exposure. *Food and Chemical Toxicology*, 45: 1263–1267, 2007.
- [38] [WHO] World Health Organization (WHO). Arsenic and arsenic compounds, 2nd edn. Environmental Health Criteria 224. Geneva CH [updated 2001; accessed 2008 April 2].Available from: <http://www.inchem.org/documents/ehc/ehc/ehc224.htm>
- [39] Kapaj,S., Peterson,H., Liber,K. and Bhattacharya,P.: Human Health Effects From Chronic Arsenic Poisoning—A Review. *Journal of environmental science and health part A*, 41:2399-2428,2006.
- [40] Kipping,M.D., in: J. Lenihan, W.W. Fletcher (Eds.), Arsenic, the Chemical Environment, Environment and Man. *Glasgow*, 6:93– 110,1997.
- [41] WHO (World Health Organisation), Environmental Health Criteria, 18: Arsenic, World Health Organisation, Geneva, 1981.
- [42] Guidelines for Drinking-Water Quality, vol. 1, third ed., World Health Organization, 2008, p. 491.
- [43] USEPA Fact Sheet: Drinking Water Standard for Arsenic (2001) http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations_factsheet.cfm.
- [44] Morales,K.H., Ryan,L., Tsung-Li,K., Meei-Maan,W. and Chien-Jen,C.: Risk of internal cancers from arsenic in drinking water. *Environmental Health Perspectives*,108(7):655-661. 2000.

- [45] WHO. (2005). Diagnosis and treatment of chronic arsenic poisoning. http://www.who.int/water_sanitation_health/dwq/arsenicun4.pdf.
- [46] National Research Council, 2000. Arsenic in Drinking Water. National Academy Press, Washington, DC.
- [47] Rossman, T.: Arsenic. In: Rom W and Markowitz S eds. Environmental and occupational medicine, 4th ed. Hagerstown, MD: Lippincott Williams & Wilkins.:1006–1017, 2007.
- [48] Ishinishi, N., Tsuchiya, K., Vahter, M. and Fowler, B.A.: Arsenic. In: Friberg L, Nordberg GF, Vouk V, eds. Handbook on the toxicology of metals. Amsterdam, NL: Elsevier Science. 1986
- [49] Welch, K., Higgins, I., Oh, M. and Burchfiel, C.: Arsenic exposure, smoking and respiratory cancer in copper smelter workers. *Arch Environ Health*, 37:325–335, 1982
- [50] Aposhian, H.V.: Biochemical toxicology of arsenic. 1989. *Rev Biochem Toxicol*. New York, NY: Elsevier/North Holland. 10:265–299, 1989
- [51] Smith, E., Naidu, R. and Alston, A.M.: Arsenic in the soil environment: A review. *Adv Agronom*, 64: 149-195, 1998.
- [52] Mohammad, S.: Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations, *Water Air Soil Poll.* 93:117–136, 1997.
- [53] Clifford, D.A. and C.C. Lin.: Ion Exchange, Activated Alumina, and Membrane Processes for Arsenic Removal from Groundwater, Proceedings of the 45th Annual Environmental Engineering Conference, University of Kansas, February 199. 1995.
- [54] Matschullat, J.: Arsenic in the geosphere-a review. *Sci Total Environ*, 249: 297-312, 2000.
- [55] Smedley, P.L. and Kinniburgh, D.G.: A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem*, 17:517-568, 2002.
- [56] Smedley, P.L. and Kinniburgh, D.G.: Sources and behaviour of arsenic in natural water, Chapter 1 in United Nations Synthesis Report on Arsenic in Drinking Water, 2005.
- [57] Wang, S. and Mulligan, C.N.: Occurrence of arsenic contamination in Canada: 3127 sources, behavior and distribution, *Sci. Total Environ.* 366:701–721, 2006.
- [58] Wagman, D.D., Evans, H.H., Parker, V.B., Schumm, R.H., Harlow, I., Bailey, S.M., Churney, K.L. and Butall, R.L.: The NBS tables of chemical thermodynamic properties. Selected values for inorganic and organic substances in SI units. *J. Phys. Chem*, 2:392 Ref. Data II, 1982.
- [59] Masscheleyn, P.H., Delaune, R.D. and Patrick, W.H. Jr.: Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil. *Environ. Sci. Technol*, 25:1414-1419, 1991.

- [60] Cullen,W.R. and Reimer,K.J.: Arsenic speciation in the environment. *Chemical review*, 89:713-764,1989.
- [61] Ferguson,J.F. and Gavis,J.: A review of the arsenic cycle in natural waters. *Water Res*, (11):1259-1274, 1972.
- [62] Gulens,J. and Champ,D.R.:Influence of redox environments on the mobility of arsenic in ground water. *Chemical modelling in aqueous systems*: 81-95, 1979.
- [63] AkhtarAhmad,S.,Ullah Sayed,M.H.S.,Shampa,B.,Haque Khan,M.,Faruquee,M.H., Abdul,J., bdul Hadi,S. and Kabir Talukder,H.: Arsenic in drinking water and pregnancy outcomes. *Environmental Health Perspectives*, 109(6):629-631, 2001.
- [64] Wilkie, J.A. and Hering, J.G.: Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids Surfaces A: Physicochemical and Engineering Aspects*, 107:97-110, 1996.
- [65] Gallagher, P.A.; Schewegel, C.A.; Wei, X. and Creed, J.T.: Speciation and preservation of inorganic arsenic in drinking water sources using EDTA with IC separation and ICP-MS detection. *Journal of Environmental Monitoring*, 3: 371-376,2001.
- [66] Brandhuber, P. and Amy, G.: Alternative methods for membrane filtration of arsenic from drinking water. *Desalination*, 140: 1-14,2001.
- [67] McNeill, L.S. and Edwards, M.; Arsenic removal during precipitate softening. *J. Am. Water Works Ass*, 89(1):75-86, 1997.
- [68]Genç-Fuhrman, H., Tjell, J.C. and McConchie, D.: Adsorption of arsenic from water using activated neutralised red mud. *Environ. Sci. Technol*, 38:2428-2434, 2004.
- [69] Sorg,T.J. and Logsdon,G.S.: Treatment technology to meet the interim primary drinking water regulations for inorganics. Part 2. *Journal American Water Works Association*, 71(8):379-387,1978.
- [70] Ng,K.S., Ujang,Z. and Le-Clech,P.: Arsenic Removal Technologies for Drinking Water Treatment. *Reviews in Environmental Science and Biotechnology*, 2(4):43-53, 2003.
- [71] Jong, T. and Parry, D.L.: Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale Upflow anaerobic bed reactor runs. *Water Res*, 37:3379- 3389, 2003.
- [72] Rott, U. and Friedle, M.: Eco-friendly and cost-efficient removal of arsenic, iron and manganese by means of subterranean ground-water treatment. *Water Supply*: 18(1), 632-635. 2000.
- [73] Bissen, M. and Frimmel, F.H.: Arsenic- a review. Part II: Oxidation of arsenic and its removal in water treatment, *Acta Hydrochimica Hydrobiology*, 31(2): 97-107, 2003.

- [74] Pande, S.P.; Deshpande, L.S.; Patni, P.M. and Lutade, S.L.: Arsenic removal studies in some ground waters of West Bengal, India. *Journal of Environmental Science and Health*, A32:7:1981-1987, 1997.
- [75] Gregor, J.: Arsenic removal during conventional aluminum-based drinking-water treatment. *Water Res*, 35:7:1659-1664, 2001.
- [76] Cheng, R.C.; Liang, S.; Wang, H. and Beuhler, M.D.: Enhanced coagulation for arsenic removal. *J. Am. Water Works Ass*, 86(9):79-90, 1994.
- [77] Hering, J.G.; Chen P.Y.; Wilkie, J.A. and Elimelech, M.; Arsenic removal from drinking water during coagulation. *Journal of Environmental Engineering*, 123(8):800-807, 1997.
- [78] McNeill, L. S. and Edwards, M.: Soluble arsenic removal at water treatment plants. *J. Am. Water Works Ass*, 87(4):105-113, 1995.
- [79] Sancha, A.M.: Removal of arsenic from drinking water supplies: Chile experience. *Water Supply*, 18(1): 621-625, 2000.
- [80] Scott, K.N.; Green, J.F.; Do, H.D.; McLean, S.J.: Arsenic removal by coagulation. *Journal American Water Works Association*, 87(4):114-126, 1995.
- [81] Hering, J.G.; Chen, P.Y.; Wilkie, J.A.; Elimelech, M. and Liang, S.: Arsenic removal by ferric chloride, *J. Am. Water Works Ass*, 88(4):155-167, 1996.
- [82] Holm, T.R.: Effects of CO_3^{2-} /bicarbonate, Si, and PO_4^{3-} on arsenic sorption to HFO. *J. Am. Water Works Ass*, 94(4):174-181, 2002.
- [83] Ghurye, G., Clifford, D. and Tripp, A.: Iron coagulation and direct microfiltration to remove arsenic from groundwater. *J. Am. Water Works Ass*. 96 (4):143–152, 2004.
- [84] Leupin, O.X. and Hug, S.J.: Oxidation and removal of arsenic(III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res*. 39:1729–1740, 2005.
- [85] Criscuoli, A., Majumdar, S., Figoli, A., Sahoo, G.C., Bafaro, P., Bandyopadhyay, S. and Drioli, E.: As(III) oxidation by MnO_2 coated PEEK-WC nanostructured capsules. *J. Hazard. Mater*. 211–212:281–287, 2012.
- [86] Pettine, M., Campanella, L. and Millero, F.J.: Arsenite oxidation by H_2O_2 in aqueous solutions. *Geochim. Cosmochim. Acta*, 63: 2727–2735, 1999.
- [87] Ghurye, G. and Clifford, D.: As(III) oxidation using chemical and solid-phase oxidants. *J. Am. Water Works Ass*, 96 (1):84–96, 2004.
- [88] Vasudevan, S., Mohan, S., Sozhan, G., Raghavendran, N.S. and Murugan, C.V.: Studies on the oxidation of As(III) to As(V) by in-situ-generated hypochlorite. *Ind. Eng. Chem. Res*, 45: 7729–7732, 2006.

- [89] Dodd, M.C., Vu, N.D., Ammann, A., Le, V.C., Kissner, R., Pham, H.V., Cao, T.H., Berg, M. and von Gunten, U., Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: relevance to drinking water treatment. *Environ. Sci. Technol.*, 40:3285–3292, 2006.
- [90] Kim, M.J. and Nriagu, J.: Oxidation of arsenite in groundwater using ozone and oxygen. *Sci. Total Environ.* 247:71–79, 2000.
- [91] Yoon, S.H. and Lee, J.H.: Oxidation mechanism of As(III) in the UV/TiO₂ system: evidence for a direct hole oxidation mechanism. *Environ. Sci. Technol.* 39:9695–9701, 2005.
- [92] Shih, M.C.: An overview of arsenic removal by pressure driven membrane processes. *Desalination*, 172:85–97, 2005
- [93] Choong, T.S.Y., Chuah, T., Robiah, Y., Gregory Koay, F. and Azni, I.: Arsenic toxicity, health hazards and removal techniques from water: an overview. *Desalination*, 217:139–166, 2007.
- [94] Velizarov, S., Crespo, J. and Reis, M.: Removal of inorganic anions from drinking water supplies by membrane bioprocesses. *Rev. Environ. Sci. Biotechnol.* 3:361–380, 2004.
- [95] Figoli, A., Cassano, A., Criscuoli, A., Mozumder, M.S.I., Uddin, M.T., Islam, M.A. and Drioli, E.: Influence of operating parameters on the arsenic removal by nanofiltration. *Water Res.* 44:97–104, 2010.
- [96] Kim, M.J.: Separation of inorganic arsenic species in groundwater using ion exchange method. *Bull. Environ. Contam. Toxicol.* 67:46–51, 2001.
- [97] Sarkar, S., Blaney, L.M., Gupta, A., Ghosh, D. and SenGupta, A.K.: Use of ArsenXnp, a hybrid anion exchanger for arsenic removal in remote villages in the Indian subcontinent. *React. Funct. Polym.* 67:1599–1611, 2007.
- [98] An, B., Fu, Z., Xiong, Z., Zhao, D. and SenGupta, A.K.: Synthesis and characterization of a new class of polymeric ligand exchangers for selective removal of arsenate from drinking water. *React. Funct. Polym.* 70:497–507, 2010.
- [99] Donia, A.M., Atia, A.A. and Mabrouk, D.A.: Fast kinetic and efficient removal of As(V) from aqueous solution using anion exchange resins. *J. Hazard. Mater.*, 191:1–7, 2011.
- [100] Kartinen, E.O. and Martin, C.J.: An overview of arsenic removal processes. *Desalination*, 103:79–88, 1995.
- [101] Benjamin, M.M., Sletten, R.S., Bailey, R.P. and Bennett, T.: Sorption and filtration of metals using iron oxide-coated sand. *Water Res.* 30 (11): 2609–2620, 1996.
- [102] Dambies, L., Vincent, T. and Guibal, E.: Treatment of arsenic-containing solutions using chitosan derivatives: uptake mechanism and sorption performance, *Water Res.* 36:3699–3710, 2002.

- [103] Mohan,D.,Pittman, C.U. Jr., Bricka, M., Smith, F.,Yancey, B., Mohammad,J.,Steele, P.H., Alexandre-Franco, M.F., Serrano,V.G. and Gong, H.: Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, *J. Colloid Interf. Sci*,310: 57–73,2007.
- [104] Altundogan,H.S.,Altundogan,S.,Tumen,F. and Bildik,M.: Arsenic removal from aqueous solutions by adsorption on red mud, *Waste Manage.* 20 (8):761–767, 2000.
- [105] Zhang, F.S. and Itoh, H.: Iron oxide-loaded slag for arsenic removal from aqueous system, *Chemosphere*, 60 (3):319–325, 2005.
- [106] Gu,Z., Fang,J. and Deng,B.: Preparation and evaluation of GAC-based ironcontaining adsorbents for arsenic removal, *Environ. Sci. Technol*,39 (10):3833–3843, 2005.
- [107] Vaughan R.L. Jr. and Reed, B.E.: Modeling As(V) removal by a iron oxide impregnated activated carbon using the surface complexation approach. *Water Res*, 39 (6):1005–1014,2005.
- [108] Chuang,C.L.,Fan, M.,Xu, M.,Brown,R.C.,Sung,S.,Saha,B. and Huang, C.P.: Adsorption of arsenic(V) by activated carbon prepared from oat hulls.*Chemosphere*, 61 (4):478–483,2005.
- [109] Mondal, P.,Balomajumder,C. and Mohanty,B.: A laboratory study for the treatment of arsenic, iron, and manganese bearing ground water using Fe³⁺ impregnated activated carbon: effects of shaking time, pH and temperature. *J. Hazard. Mater*, (144):420–426, 2007.
- [110] Lorenzen,L.,van Deventer,J.S.J. and Landi,W.M.: Factors affecting the mechanism of the adsorption of arsenic species on activated carbon. *Miner. Eng*, 8 (45):557–569, 1995.
- [111] Navarro,P. and Alguacil, F.J.: Adsorption of antimony and arsenic from a copper electrorefining solution onto activated carbon. *Hydrometallurgy*, 66 (1–3):101–105, 2002.
- [112] Jubinka, L. and Rajakovic, V.: The sorption of arsenic onto activated carbon impregnated with metallic silver and copper. *Sep. Sci. Technol.* 27 (11) :1423–1433,1992.
- [113] Eguez, H.E.,Cho,E.H.: Adsorption of arsenic on activated charcoal, *J. Metals* ,39:38–41, 1987.
- [114] Manning, B.A.,Goldberg,S.: Arsenic(III) and arsenic(V) adsorption on three California soils. *Soil Sci.*,162 (12) :886–895,1997.
- [115] Viraghavan, T., Thirunavukkarasu,O.S. and Suramanian, K.S.: Removal of arsenic in drinking water by iron oxide-coated sand and ferrihydrite-batch studies, *Water Qual. Res. J. Can.* 36 (1): 55–70,2001.
- [116] Dousov, B.,Grygar,T.,Martaus,A.,Fuitov,L.,Koloušek,D. and Machovi,V.: Sorption of As(V) on aluminosilicates treated with Fe(II) nanoparticles. *J. Colloid Interf. Sci.* 302 (2): 424–431,2006.

- [117] Xu, Y.H., Nakajima,T. and Ohki,A.: Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded shirasu-zeolite. *J. Hazard. Mater.* B92:275–287, 2002.
- [118] Murugesan,G.S., Sathishkumar,M. and Swaminathan, K.: Arsenic removal from groundwater by pretreated waste tea fungal biomass.*Bioresour.Technol*,97 (3) :483–487, 2006.
- [119] Kuriakose,S., Singh, T.S. and Pant, K.K.: Adsorption of As(III) from aqueous solution onto iron oxide impregnated activated alumina. *Water Qual. Res. J. Can*,39 (3) :258–266, 2004.
- [120] Singh, T.S. and Pant,K.K.: Experimental and modelling studies on fixed bed adsorption of As(III) ions from aqueous solution. *Sep. Purif. Technol*, 48 (3):288–296, 2006.
- [121] Singh, T.S. and Pant, K.K.: Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. *Sep. Purif. Technol*, 36:139–147, 2004.
- [122] Singh, T.S. and Pant, K.K.: Kinetics and mass transfer studies on the adsorption of arsenic onto activated alumina and iron oxide impregnated activated alumina, *Water Qual. Res. J. Can.* 41 (2) :147–156,2006.
- [123] Pena,M.E.,Korfiatis,G.P.,Patel,M.,Lippincott,L.,Meng,X.: Adsorption of As(V) and As(III) by nanocrystalline titanium dioxide. *Water Res.* 11:2327–2337, 2005.
- [124] Saha,B.,Bains,R. and Greenwood,F.: Physicochemical characterization of granular ferric hydroxide (GFH) for arsenic(V) sorption from water. *Sep. Sci. Technol.* 40 (14):2909–2932. 2005.
- [125] Roberts,L.C.,Hug,S.J.,Ruettimann,T.,Khan,A.W. and Rahman,M.T.: Arsenic removal with iron(II) and iron(III) in waters with high silicate and phosphate concentrations, *Environ. Sci. Technol*, 38 :307– 315,2004.
- [126] Raven,K.P.,Jain,A. and Loeppert,R.H.: Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol*, 32 :344–349, 1998.
- [127] Thirunavukkarasu, O.S., Viraghavan, T. and Suramanian, K.S.: Arsenic removal from drinking water using iron-oxide coated sand.*Water Air Soil Pollut*,142:95–111, 2003.
- [128] Hodi,M.,Polyak,K. and Hlavay,J.: Removal of pollutants for drinking water by combined ion-exchange and adsorption methods. *Environ. Int.* 21:325–331, 1995.
- [129] Wasay,S.A., Haron,M.J., Uchiumi,A. and Tokunaga, S.: Removal of arsenite and arsenate ions from aqueous solution by basic yttrium carbonate. *Water Res*, 30 (5) :1143–1148,1996.
- [130] Namasivayam,C. and Senthilkumar,S.: Removal of arsenic(V) from aqueous solution using industrial solid waste: adsorption rates and equilibrium studies. *Ind. Eng. Chem. Res*,37 (12) :4816–4822,1998.
- [131] Pattanayak,J.,Mondal,K.,Mathew,S. and Lalvani,S.B.: A parametric evaluation of the removal of As(V) and As(III) by carbon based adsorbents. *Carbon*, 38:589–596, 2000.

- [132] Genc-Fuhrman, H., Bregnhøj, H. and McConchie, D.: Arsenate removal from water using sand–red mud columns. *Water Res.* 39(13):2944–2954, 2005.
- [133] Altundogan, H.S., Altundogan, S., Tumen, F., Bildik, M.: Arsenic adsorption from aqueous solutions by activated red mud. *Waste Manage.* 22 :357–363, 2002.
- [134] Singh, T.S. and Pant, K.K.: Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina, *Sep. Purif. Technol.* 36:139–147, 2004.
- [135] Suzuki, T.M., Bomani, J.O., Matsunaga, H. and Yokoyama, T.: Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic, *React. Funct. Polym.* 43 (1–2):165–172, 2000.
- [136] Dutta, P.K., Ray, A.K., Sharma, V.K. and Millero, F.J.: Adsorption of arsenate and arsenite on titanium dioxide suspensions. *J. Colloid Interf. Sci.* 278:270–275, 2004.
- [137] Lenoble, V., Bouras, O., Deluchat, V., Serpaud, B. and Bollinger J.-C.: Arsenic adsorption onto pillared clays and iron oxides, *J. Colloid Interf. Sci.* 255 (1):52–58, 2002.
- [138] Bang, S., Patel, M., Lippincott, L., Meng, X.: Removal of arsenic from groundwater by granular titanium dioxide adsorbent, *Chemosphere* ,60 (3):389–397, 2005.
- [139] Seki, H., Suzuki, A., Maruyama, H.: Biosorption of chromium(VI) and arsenic(V) onto methylated yeast biomass. *J. Colloid Interf. Sci.* 281 (2):261–266, 2005.
- [140] Badruzzaman, M., Westerhoff, P., Knappe, D.R.U.: Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH). *Water Res.* 38 (18):4002–4012, 2004.
- [141] Ladeira, A.C.Q., Ciminelli, V.S.T.: Adsorption and desorption of arsenic on an oxisol and its constituents. *Water Res.* 38 (8): 2087–2094, 2004.
- [142] Lin, T.-F., Wu, J.-K.: Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. *Water Res.* 35 (8):2049–2057, 2001.
- [143] Jang, M., Shin, E.W., Park, J.K., Choi, S.I.: Mechanisms of arsenate adsorption by highly-ordered nano-structured silicate media impregnated with metal oxides. *Environ. Sci. Technol.* 37 (21): 5062– 5070, 2003.
- [144] Kanel, S.R., Manning, B., Charlet, L., Choi, H.: Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. *Environ. Sci. Technol.* 39 (5):1291–1298., 2005.
- [145] Kundu, S., Kavalakatt, S.S., Pal, A., Ghosh, S.K., Mandal, M., Pal, T.: Removal of arsenic using hardened paste of Portland cement: batch adsorption and column study. *Water Res.* 38 (17):3780–3790, 2004.
- [146] Kundu, S., Gupta, A.K.: Adsorptive removal of As(III) from aqueous solution using iron oxide coated cement (IOCC): evaluation of kinetic, equilibrium and thermodynamic models. *Sep. Purif. Technol.* 52 (2):165–172, 2006.

- [147] Say, R., Yilmaz, N. and Denizli, A.: Biosorption of cadmium, lead, mercury, and arsenic ions by fungus *Penicillium Purpurogenum*. *Sep. Sci. Technol.* 38 (9):2039–2053, 2003.
- [148] Singh, D.B., Prasad, G., and Rupainwar, D.C.: Adsorption technique for the treatment of As(V)-rich effluents. *Colloid Surf, A* 111 (1–2): 49–56, 1996.
- [149] Zhang, H. and Selim, H.M.: Kinetics of arsenate adsorption–desorption in soils. *Environ. Sci. Technol.* 39 (16):6101–6108, 2005.
- [150] Hlavay, J. and Polyak, K.: Determination of surface properties of iron hydroxide-coated alumina adsorbent prepared for removal of arsenic from drinking water. *J. Colloid Interf. Sci.* 284 (1): 71–77. 2005.
- [151] Reed, B.E., Vaughan, R. and Jiang, L.: As(III), As(V), Hg, and Pb removal by Fe-oxide impregnated activated carbon. *J. Environ. Eng.* 126:869–873, 2000.
- [152] Mohan, D., Pittman, C.U.Jr., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Serrano, V.G. and Gong, H.: Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production, *J. Colloid Interf. Sci.* 310(1):57-73, 2007.
- [153] Dias, A., Sa, R.G., Spitale, M.C., Athayde, M. and Ciminelli, V.S.T.: Microwave-hydrothermal synthesis of nanostructured Nabirnessites and phase transformation by arsenic(III) oxidation. *Materials Research Bulletin*, 43:1528-1538, 2008.
- [154] Oscarson, D.W., Huang, P.M., Defosse, C. and Herbillon, A.: Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature* 291: 50 – 51, 1981.
- [155] Manning, B.A., Fendorf, S.E., Bostick, B. and Suarez, D.L.: Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* 36 (5):976–981, 2002.
- [156] Chakravarty, S., Dureja, V., Bhattacharyya, G., Maity, S. and Bhattacharjee, S.: Removal of arsenic from groundwater using low cost ferruginous manganese ore. *Water Res.* 36 (3):625–632, 2002.
- [157] Ouvreard, S., Simonnot, M.O., Sardin, M.: Reactive behavior of natural manganese oxides toward the adsorption of phosphate and arsenate. *Ind. Eng. Chem. Res.* 41:2785–2791, 2002.
- [158] Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., Chaalal, O. and Islam, M.R.: Arsenic removal in drinking water—impacts and novel removal technologies. *Energy Sources*, 27: 209–219, 2005.
- [159] Shihabudheen M. Maliyekkal, Ligy Philip, T. Pradeep.: As(III) removal from drinking water using manganese oxide-coated-alumina: Performance evaluation and mechanistic details of surface binding. *Chem. Eng. J.* 153 (1-3):101-107, 2009.

- [160] Lenoble, V., Laclautre, C., Serpaud, B., Deluchat, V., Bollinger, J.-C.: As(V) retention and As(III) simultaneous oxidation and removal on a MnO₂-loaded polystyrene resin. *Sci. Total Environ.*, 326(1–3):197–207, 2004.
- [161] Deschamps, E., Ciminelli, V.S.T., Weidler, P.G., Ramos, A.Y., 2003. "Arsenic sorption onto soils enriched with manganese and iron mineral. *Clays clay Miner.* 51, 197–204
- [162] Wu, K., Liu, R., Liu, H., Zhao, X., and Qu, J.: Arsenic(III, V) Adsorption on Iron-Oxide-Coated Manganese Sand and Quartz Sand: Comparison of Different Carriers and Adsorption Capacities. *Environ. Sci. Technol.*, 28(9): 643–651, 2011.
- [163] Deschamps, E., Ciminelli, V.S.T. and Höll, W.H.: Removal of As(III) and As(V) from water using a natural Fe and Mn enriched sample. *Water Res.*, 39:5212–5220, 2005.
- [164] Zhang, G., Qu, J., Liu, H., Liu, R., Wu, R.: Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. *Water Res.* 1921–1928, 2007.
- [165] Lakshminathiraj, P., Narasimhan, B.R.V., Prabhakar, S., Raju, G.B.: Adsorption studies of arsenic on Mn-substituted iron oxyhydroxide. *J. Colloid Interf. Sci.*, 304:317–322, 2006.
- [166] Nesbitt, H.W., Canning, G.W. and Bancroft, G. M.: XPS study of reductive dissolution of 7 Ångström-birnessite by H₃AsO₃, with constraints on reaction mechanism. *Cosmochim. Acta*, 62: 2097–2110, 1998.
- [167] USEPA, 2000. Technologies and costs for removal of arsenic from drinking water. US Environmental Protection Agency, EPA/815/R-00/028.
- [168] Howell, R.J.: Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.*, 9 (3):279–286, 1994.
- [169] Aydın, H. and Baysal, G.: Adsorption of acid dyes in aqueous solutions by shells of bittim (*Pistacia khinjuk* stocks). *Desalination*, 196:248–259, 2006.
- [170] Langmuir, I.: The constitution and fundamental properties of solids and liquids. *J. Amer. Chem. Soc.* 38:2221–2295, 1916.
- [171] Freundlich, H.M.F.: Über die adsorption in losungen, *Z. Phys. Chem.* 57A :385–470, 1906.
- [172] Temkin, M.J. and Pyzhev, V.: Recent modifications to Langmuir isotherms, *Acta. Physiochim., URSS*, 12:217–222, 1940.
- [173] Dubinin, M.M. and Radushkevich, L.V.: Equation of the characteristic curve of activated charcoal. *Chem. Zentr.* 1 :875, 1947.
- [174] Islam, M., Mishra, P.C. and Patel, R.: Fluoride adsorption from aqueous solution by a hybrid thorium phosphate composite. *Chem. Eng. J.*, 166:978–985, 2011.

- [175] Lagergren, S.: About the theory of so-called adsorption of soluble substances, *Handlingar*, Band 24 (4):1–39, 1898.
- [176] Blanchard, G. and Maunaye, M., Martin, G.: Removal of heavy metals from waters by means of natural zeolites, *Water Res.*, 18:1501–1507, 1984.
- [177] Alkan, M., Demirbas, O., Celikcapa, S., Dogan, M.: Sorption of acid red 57 from aqueous solution onto sepiolite, *J. Hazard. Mater.* B116: 135–145, 2004.
- [178] Bekci, Z., Ozveri, C., Seki, Y., Yurdakoc, K.: Sorption of malachite green on chitosan bead, *J. Hazard. Mater.*, 154:254–261, 2008.
- [179] Ho, Y.S.: Removal of copper ions from aqueous solution by tree fern. *Water Res.* 37: 2323–2330, 2003.
- [180] American Coal Ash Association, Coal Combustion Product (CCP) Production & Use Survey Results, American Coal Ash Association, 2011, p. 1 - <http://www.acaa-usa.org>.
- [181] Jones, D.R., 1995. The leaching of major and trace elements from coal ash. In *Environmental Aspects of Trace Elements in Coal*: Swaine, D.J.; Goodarzi, F. (Eds.); . Springer.
- [182] Izquierdo, M. and Querol, X.: Leaching behaviour of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology*, 94:54–66, 2012.
- [183] Yan-Chu, H. Arsenic distribution in soils. Arsenic in the environment. Part I: Cycling and characterization, J. O. Nriagu, ed., Wiley, New York, 17–49, 1994.
- [184] Mok, W.M., and Wai, C.M.: Mobilization of arsenic in contaminated river waters. Arsenic in the environment. Part I: Cycling and characterization, J. O. Nriagu, ed., Wiley, New York, 99–117, 1994.
- [185] Driehaus, W., Seith, R., and Jekel, M.: Oxidation of arsenite(III) with manganese oxides in water treatment. *Water Res.*, 29(1):297–305, 1995.

Chapter II

II. COMPARISON OF ARSENIC REMOVAL EFFICIENCY OF PURE MANGANESE OXIDES IN A BATCH SYSTEM

1. INTRODUCTION

Arsenic has been recognized as one of the most toxic and ubiquitous element in the environment [1]. Long-term drinking water exposure to arsenic has been linked to the cancer of the kidney, bladder skin, lung and the cardiovascular and neurological systems [2]. Considering arsenic high toxicity and the serious effect of arsenic on human health, World Health Organization as well as USEPA have specified the maximum contaminant level (MCL) of arsenic in drinking water as 10 $\mu\text{g/L}$ [3, 4].

Many countries are affected by high level of arsenic concentrations in surface and ground water [5]. Concentration of arsenic in some regions in Bangladesh is as high as 1000 $\mu\text{g/L}$ [6]. Natural geochemical contamination through soil leaching, industrial wastewaters, hydrothermal activities and mining are the main source of contamination [7,8].

There are two primary forms of arsenic in environment; organic and inorganic. Organic species of arsenic are mainly found in foodstuffs and have the form of mono methyl arsenic acid (MMAA), dimethyl arsenic acid (DMAA), and arseno-sugars. Arsenic may exist in water in different oxidation states (+5,+3,0,-3)[9,10] but Arsenite (As III) and arsenate (As V) are two predominant valence states of inorganic arsenic species. As(III) ,the more toxic form, exists as an uncharged species (H_3AsO_3) or anionic species (H_2AsO_3^-) in a moderately reducing environment whereas

As(V) species consist primarily of monovalent (H_2AsO_4^-) or divalent (HAsO_4^{2-}) anions in natural waters [11, 12]. In natural surface waters, As(V) is the dominant species while natural ground waters contain mainly As(III) due to the dominant reducing conditions [13].

Therefore, applying effective methods and appropriate materials to selectively remove the excess amount of arsenic from drinking water are required. The method used to bring down the arsenic concentration to the standard level should be simple, effective, selective and not remove all present ions in water [14]. Various methods like lime softening [15], precipitation-coprecipitation[16],membrane process[17],ion exchange[18] and adsorption[19] have been used for removing of arsenic. Adsorption has been recognized as a superior method for arsenic treatment. Various adsorbents like mineral oxides, activated carbons, biological materials, or polymer resins, have been used for the adsorption of arsenic.[5,20,21].

Investigations have shown that manganese oxides are effective oxidizer of the more toxic species ,As(III), to As(V) in water treatment unit and natural environment and make the sorption process easier and effective [15,22]. Manganese oxides extremely affect the mobility and fate of many pollutants in environment and can easily participate in different redox reactions and strongly adsorb numerous ions [23].

Manning et al. [24] have suggested that MnO_2 materials used at near neutral pH in drinking water filtering and environmental remediation would play a beneficial role as both an efficient oxidant of As(III) and a sorbent for As(V). A low cost ferruginous manganese ore (FMO) with the major mineral phases of pyrolusite and goethite was studied for the removal of arsenic from groundwater [9]. The results showed that FMO can adsorb both As(III) and As(V) without any pre-treatment in

the pH range of 2-8 with the maximum adsorbed arsenic(III) of 0.53 mg/g at pH of 6.3 and the maximum adsorbed As(V) of 15.38 mg/g at a pH of 6.5 . The adsorption of arsenate has also been studied by natural manganese oxides by monocomponent column experiments [25]. The maximum arsenate adsorption of 2.2299 $\mu\text{mol/g}$ was obtained from a solution of 0.67 mM sodium arsenate (50 ppm arsenic) and 1mM sodium chloride at pH 7.9.

Thirunavukkarasu et al. [26] applied manganese greensand in the column studies to examine the removal of arsenic in drinking water. They indicated that manganese greensand was found to be efficient in removing As(III) to a level below 25 $\mu\text{g/L}$. Also, iron addition enhanced arsenic removal in filtration studies where in the case of Fe:As(III) ratio of 20:1, the maximum solid phase concentration was estimated at 22.3 $\mu\text{g/g}$ based on the weight of manganese greensand; whereas it was estimated at 2.5 $\mu\text{g/g}$ for Fe:As(III) ratio of 7:1. The performance of manganese oxide-coated-alumina (MOCA) in removing As(III) and its interaction with As(III) in drinking water was studied and compared to activated alumina[27]. The sorption process was found to be pH dependent and the optimum removal was observed between a pH of 4 and 7.5. The predicted maximum As(III) sorption capacity of 29.15 mg/g was obtained from Langmuir model at $\text{pH}=7 \pm 0.2$ which was higher than that of activated alumina (19.63 mg g^{-1}) .

A MnO_2 -loaded polystyrene resin(R- MnO_2) has been demonstrated as a strong solid sorbent for arsenic retention where the R- MnO_2 maximal capacities were 0.7 and 0.3 mmol/g towards As(III) and As(V), respectively[7]. Deschamps et al. [28] investigated the arsenic adsorption onto some soils enriched in Mn and Fe. They have claimed that the presence of naturally occurring Mn oxides

promotes the effective oxidation of As (III) to As(V). Also, the Mn minerals in their study showed a significant uptake of both the arsenite and arsenate.

Wu et al.[29] showed that using a manganese sand carrier instead of a quartz sand carrier for arsenic (As) (III,V) adsorption to iron-oxide-coated sand can improve the adsorption capacity of the sorbent. The maximum adsorption capacities (q_m) of As(III) and As(V) by iron-oxide-coated manganese sand (IOCMS) were obtained as 2.216 mg/g and 5.452 mg/g, respectively; which were nearly 3 and 10 times higher than those by iron-oxide-coated quartz sand (IOCQS), respectively. Deschamps et al. [8] demonstrated the high adsorption capacity of a Fe and Mn enriched sample as a sorbent in batch and column experiments for removing As(III) and As(V) from water. At pH 3.0, the maximum uptake of 8.5 and 14.7 mg/g were obtained for As(V) and for As(III)-treated materials, respectively. The oxidation of As(III) to As(V) of both adsorbed and dissolved As-species were promoted by Mn-minerals. Column experiments with the sorbent for an initial As-concentration of 100 μ g/L showed a very efficient elimination of As(III). Zhang et al.[30] developed a novel Fe–Mn binary oxide adsorbent from low cost materials which could completely oxidize As(III) to As(V) and was effective for both As(V) and As(III) removal, specially the As(III). The maximal adsorption capacities of As(V) and As(III) were found to be 0.93 mmol/g and 1.77 mmol/g, respectively in a 200 mg/L arsenic suspension at pH 5.0 ± 0.1 . A Mn-substituted iron oxyhydroxide (MIOH) has been used as a sorbent for the adsorption of arsenite and arsenate from water [31]. The maximum uptake of arsenite and arsenate onto MIOH was found to be 4.58 and 5.72 mg/g, respectively. The high removal rate of arsenite was related to the probable oxidation of arsenite by manganous oxyhydroxide to the easily removable arsenate ions.

Manganese oxide has been mostly used in combination to the other sorbents for removal of arsenic from aqueous solutions but to best of our knowledge there is no study on As adsorption using different types of bearing manganese oxides. Therefore, manganese oxides with different oxidation states were tested for arsenate removal. Adding the mineral oxides to small volumes of water has been identified by USEPA as a feasible process to remove arsenic from water [32]. The aim of this work is to investigate the effect of different manganese oxides on the adsorption of arsenate. Zeta potential measurement was carried out to investigate the nature of adsorption.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Sodium Arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 99% purity, ACS grade), magnesium chloride (MgCl_2 , 99.1% purity, ACS grade), calcium chloride (CaCl_2 , 98.8% purity, ACS grade), sodium bicarbonate (NaHCO_3 , 100.1 % purity, ACS grade), hydrochloric acid (HCl , ACS plus grade), sodium hydroxide (NaOH) and sodium sulfate (Na_2SO_4 , 99.3% purity, ACS grade) were of analytical reagent grade and no further purification was done on them. Deionized (DI) water was prepared in the laboratory with a resistance greater than 18 M Ω . Sodium Arsenate and Mn_3O_4 were obtained from Sigma-Aldrich (St. Louis, MO) company while the other manganese oxides were obtained from Alfa Aesar company (Ward Hill, MA). The rest of the chemicals were obtained from Fisher scientific (Fair Lawn, NJ).

2.2. Sorbent Characterization

The BET surface area of different manganese oxides were measured with an Accelerated Surface Area and Porosimetry system, ASAP 2010 (Micromeritics Instrument Corporation, Norcross, GA), using nitrogen adsorption/desorption isotherms.

2.3. Batch Adsorption Tests

The experiments were conducted with dry sorbent suspension of different concentrations. Each solid sorbent was immersed in 50 mL of As(V) solution in high density polyethylene (HDPE) bottles. An As(V) stock solution(1000 mg/L) was prepared by dissolving 4.165 g Sodium arsenate in 1 L DI water. A certain volume of the stock solution was subsequently diluted for a desired level of As(V) solutions during the experiment. Two solutions of 2.5 mM and 5.5 mM sodium bicarbonate were prepared by adding 2.5 mM magnesium chloride (MgCl_2), 2 mM calcium chloride (CaCl_2) and 1 mM sodium sulfate(Na_2SO_4) to each of these solutions to synthesize a more realistic solution considering the effect of other co-existing ions.

After adding the adsorbent, the solution was shaken thoroughly in a tumbler at 25 °C. The adsorption kinetics of arsenate on the sorbents was investigated with varying contact times. The suspensions were centrifuged to separate the aqueous phase from the adsorbent. The pH, TDS and alkalinity were measured. The centrifuged solutions were filtered with a 0.45 μm cellulose acetate filter and the concentration of arsenate in the filtrate was analyzed with graphite furnace atomic

absorption spectroscopy (GFAAS) with Zeeman background correction. For arsenic analysis, all measurements were carried out using an electrodeless lamp (EDL) lamp at 193.7 nm and the modifier used was palladium-magnesium modifier. The atomization and pre-treatment temperature were 2000 and 1200 °C, respectively. The detection limit of arsenic was estimated to be 1 µg/L. The uptake of As(V) on the sorbents was determined as:

$$q = \frac{(C_0 - C_e)}{m} \times A \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of As(V) in the solution (mg/L), q is the adsorbed As(V) (mg/kg), m is the adsorbent dosage (kg) and A is the solution volume (L). The removal percent (%) was calculated using the following equation:

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

2.4. Adsorption isotherm experiments

In order to find the As(V) retention onto different manganese oxides, various dosage of the sorbent were mixed in HDPE bottles with 50 mL of the arsenic (V) solution. The bottles were shaken in a tumbler at 16 rpm for a period of time determined from the adsorption kinetics experiment and required for the adsorption equilibrium. Afterwards, the bottles were taken from the shaker and the samples were analyzed similar to the batch adsorption tests.

2.5. Zeta potential measurement

The zeta potential of all manganese oxides was measured by a Zeta-meter system 3.0(Zeta meter Inc, VA). A suspension of 100 mg/L of the sorbent was prepared. The pH of the samples were adjusted from 3 to 12 using 0.1 M HCl and 0.1 M NaOH solutions.

3. RESULTS AND DISCUSSION

3.1. Characterization of manganese oxides

Fig.1 to 4 show the X-ray diffraction (XRD) of different types of manganese oxide, (MnO , Mn_2O_3 , Mn_3O_4 and MnO_2) which can be used to determine their chemical composition. From Fig.1, the XRD results indicated good agreement with MnO (JCPDS card No 78-0424). Powder XRD revealed good agreement with tetragonal Mn_2O_3 (JCPDS card No 41-1442) (Fig.2). As seen in Fig.3, the Mn_3O_4 XRD was found to be similar to tetragonal Mn_3O_4 (JCPDS card No 24-0734). Also, a good agreement was found between the XRD pattern of MnO_2 in this study (Fig.4) and MnO_2 (JCPDS card No 41-0142). All these results confirmed that the applied manganese oxide sorbents in this study were pure and crystalline adsorbents.

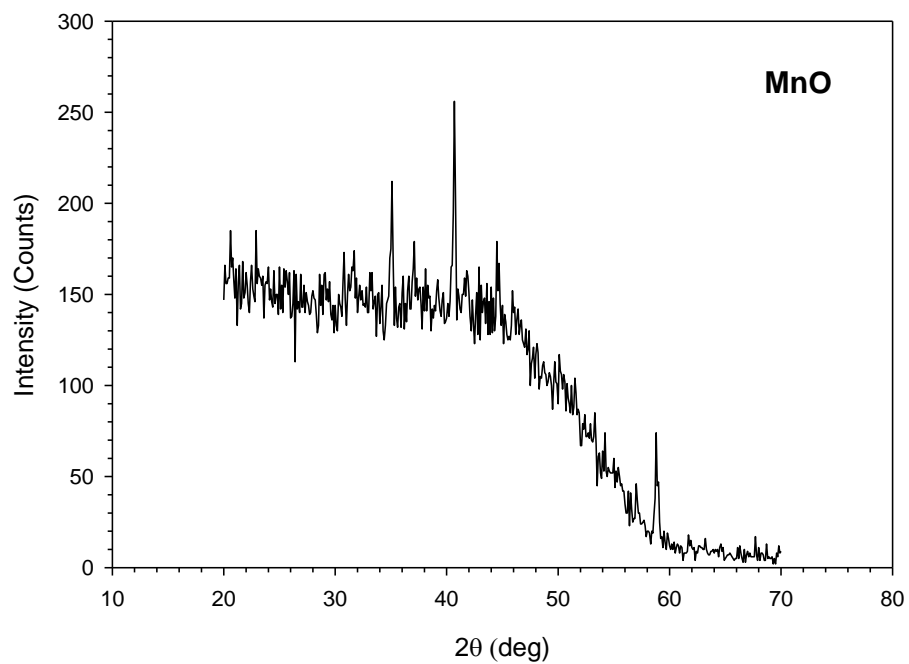


Fig. 1. XRD pattern of MnO powder

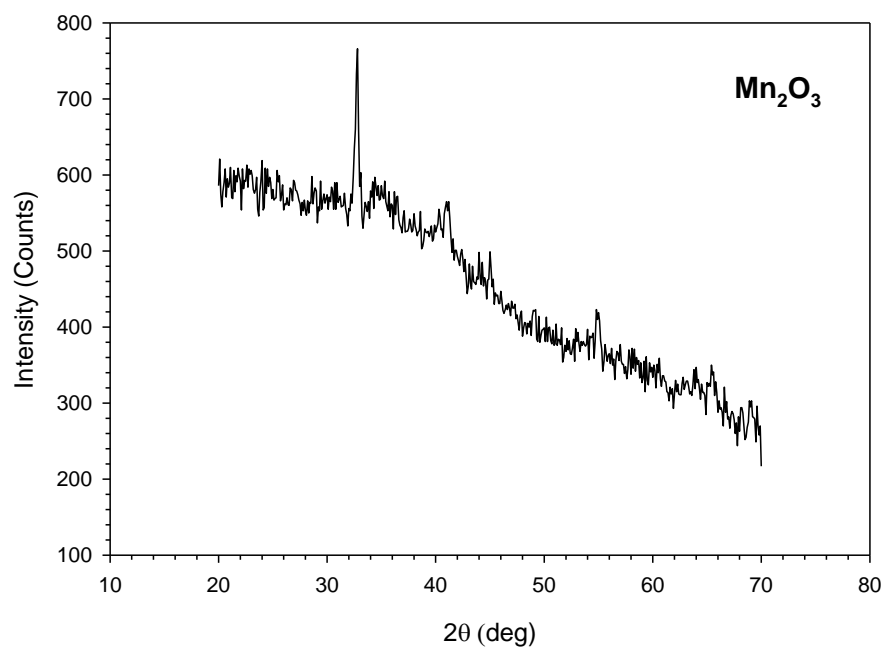


Fig. 2. XRD pattern of Mn_2O_3 powder

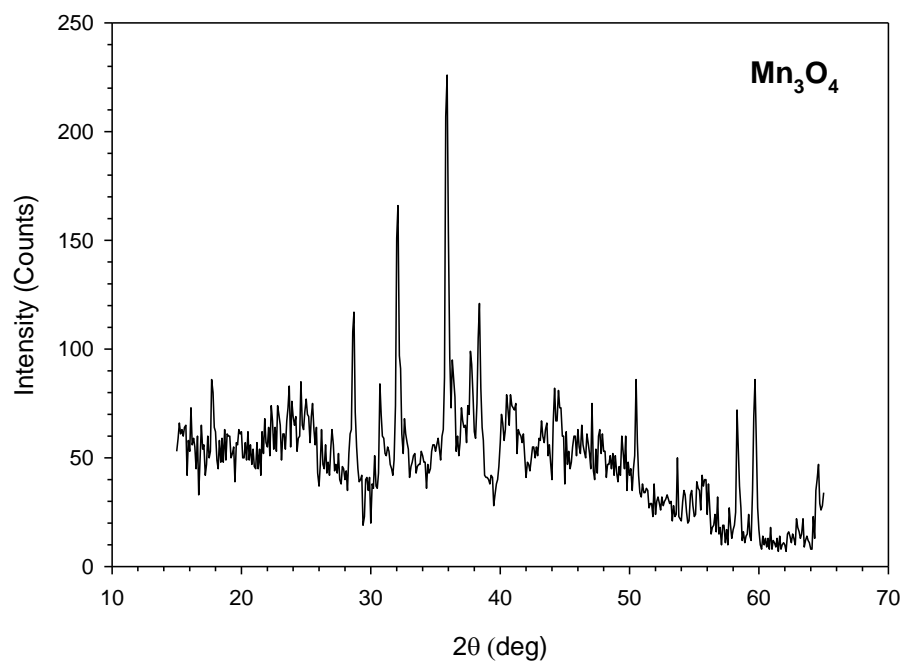


Fig. 3. XRD pattern of Mn_3O_4 powder

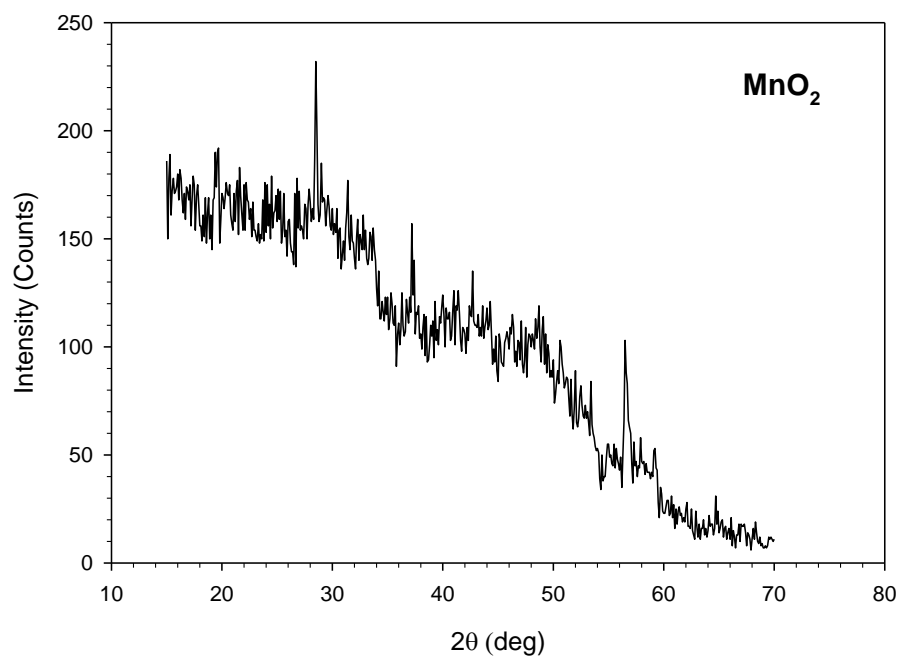


Fig. 4. XRD pattern of MnO_2 powder

3.1.1. Surface area

The BET surface area was determined to know the specific surface area of the four types of manganese oxides used in this study. Table 1 show the surface area of all four types of manganese oxides. The Mn_3O_4 was found to have the highest surface area. The arsenic adsorption capacity of the manganese oxides are reported per surface area to clearly compare the removal efficiency of manganese oxides.

Table 1. BET surface area of Manganese Oxides

| | Material | BET Surface Area(m^2/g) |
|---|-------------------------|---|
| 1 | MnO | 0.4754 ± 0.0098 |
| 2 | MnO_2 | 1.9516 ± 0.0030 |
| 3 | Mn_2O_3 | 2.2039 ± 0.0126 |
| 4 | Mn_3O_4 | 3.4101 ± 0.0357 |

3.1.2. Surface Charge Study

The mechanisms of arsenic contaminants adsorption by manganese oxides may depend on the surface charge characteristics of the adsorbents. Zeta potential was measured in order to determine some information about the whole charge of manganese oxides particles and to help to explain the interaction between solution-solid interfaces. The zeta potential of manganese oxides were measured in a 1 mM NaCl solution and the results are shown in Fig.5-8.

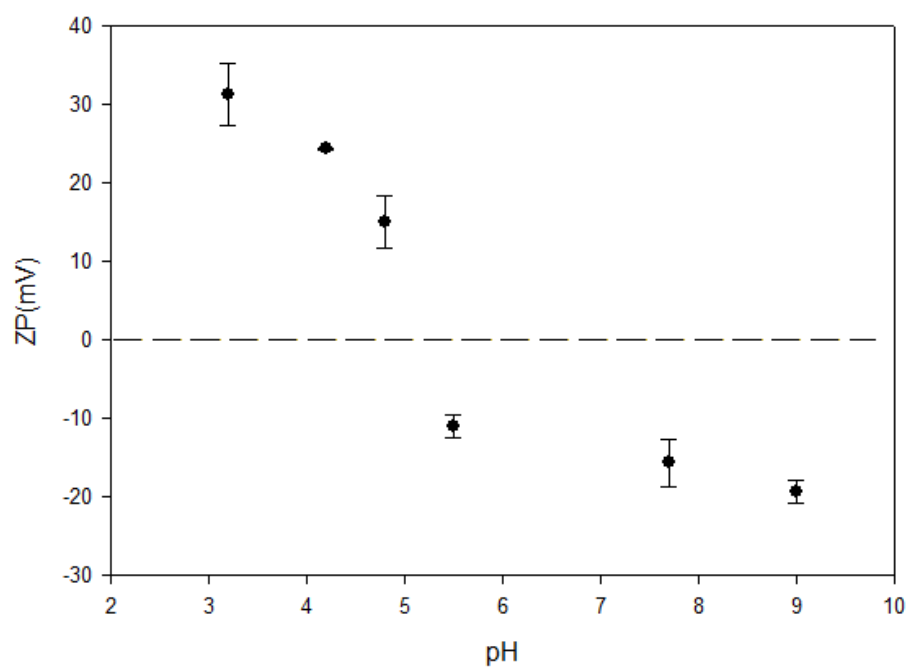


Fig. 5. Zeta potential of MnO in DI solution

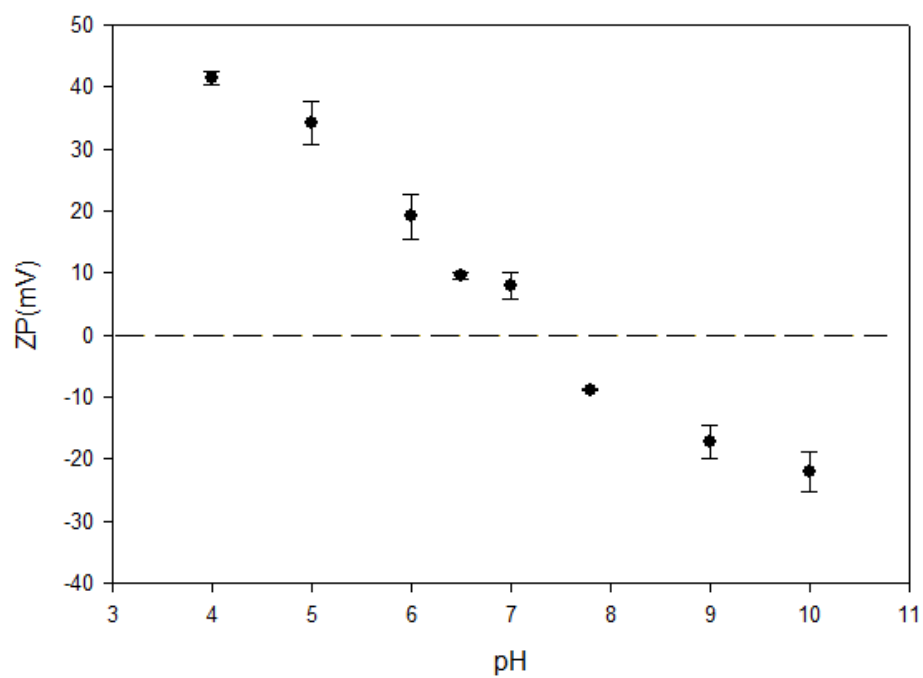


Fig. 6. Zeta potential of Mn₂O₃ in DI solution

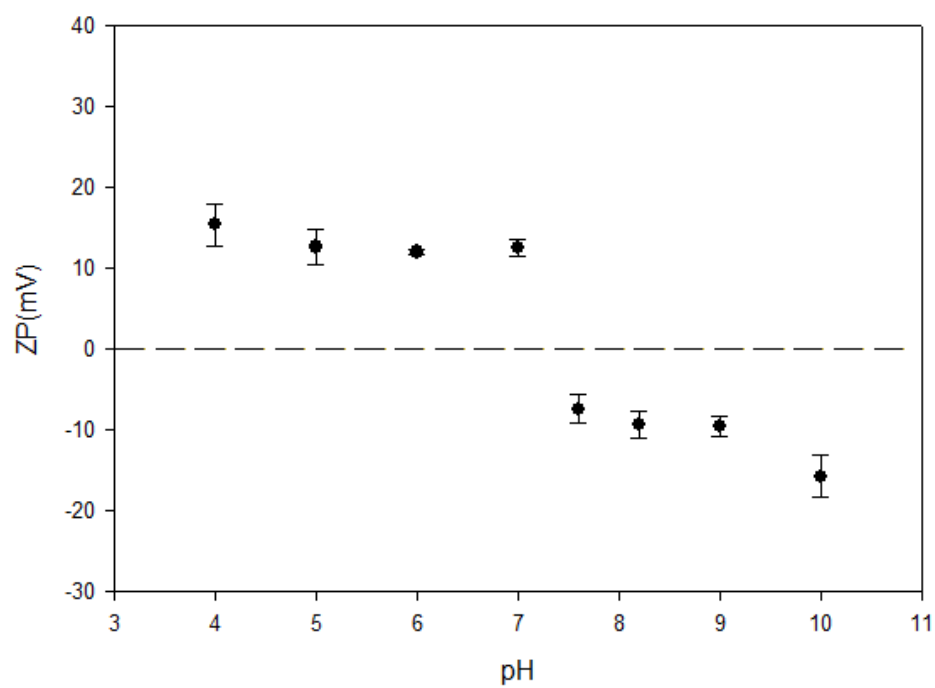


Fig. 7. Zeta potential of Mn_3O_4 in DI solution

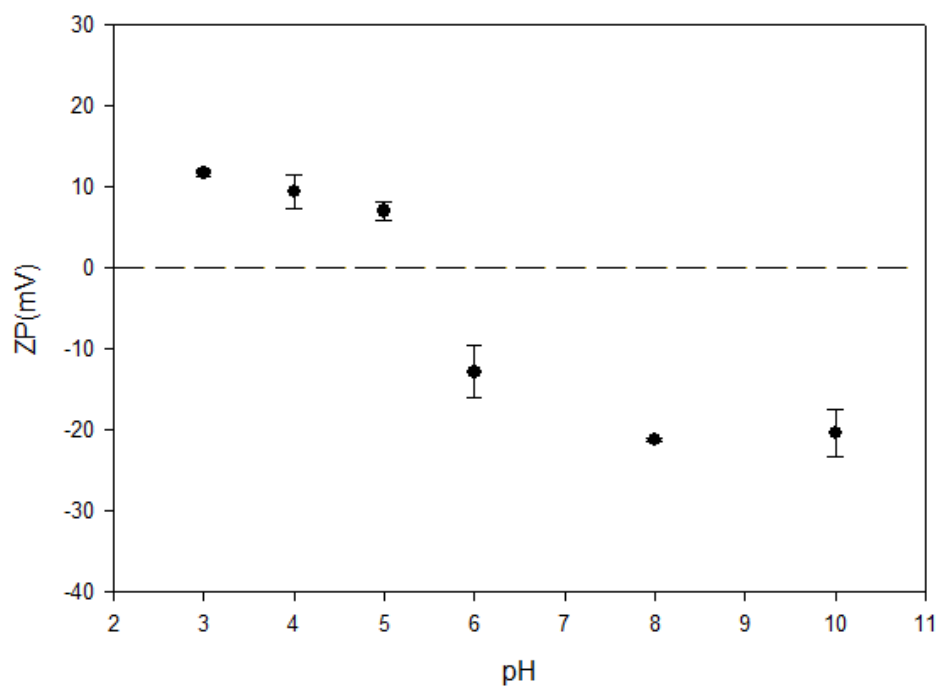


Fig. 8. Zeta potential of MnO_2 in DI solution

The PZC of MnO, Mn₂O₃, Mn₃O₄ and MnO₂ was obtained at pH of 5.2, 7.38, 7.41 and 5.35, respectively. Below these pH, the adsorbent surface is predominantly positively charged and above this pH it is negatively charged. At pH_{pzc}, the ions may adsorb onto the surface through the formation of outer-sphere complexes via van der Waals forces. The MnO and MnO₂ indicated negative zeta potential values over the most range of pH studied (Fig. 5 and 8). These values became increasingly negative as the pH values of the suspension increased. Mn₂O₃ and Mn₃O₄ maintained positive zeta potential values over the most range of pH studied. Mn₂O₃ exhibited ZP value as high as 41.5 mV at pH = 4.0. Within the moderate acidic to neutral pH range which most frequently encountered in the environment (pH = 5.0 to 7.0), the ZP values of Mn₂O₃ and Mn₃O₄ ranged from 34.3 to 8 mV and 12.5 to 12.6 mV, respectively which implies that adsorption of arsenic anions by Mn₂O₃ and Mn₃O₄ may be possible through electrostatic attraction under environmental conditions. Strong changes in zeta potential values were observed in all manganese oxides. As can be seen the PZC values increases as the surface area increases. This phenomenon correlated very well with the arsenic removal efficiency in DI solution by manganese oxides.

3.2. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of As(V) from solutions with different ionic backgrounds including DI solution, 2.5 mM HCO₃⁻ and 5.5 mM HCO₃⁻ solution was evaluated for four different types of manganese oxides. The pH, TDS, conductivity and alkalinity of 2.5 mM HCO₃⁻ and 5.5 mM HCO₃⁻ solution are tabulated Table 2.

Table 2. Characteristics of DI solution, 2.5 mM HCO_3^- and 5.5 mM HCO_3^- solution.

| Solution | pH | TDS (mg/L) | Conductivity ($\mu\text{S}/\text{cm}$) | Alkalinity (mg/L as CaCO_3) |
|-------------------------|-------|------------|---|--|
| 2.5 mM HCO_3^- | 7.946 | 953 | 1926 | 79 |
| 5.5 mM HCO_3^- | 8.018 | 1200 | 2420 | 175 |

Different amounts of the sorbents was exposed to the solutions with the As(V) initial concentrations of 1 mg/L. The results are presented in Fig.9 to 11.

The results indicated that the removal efficiency of As(V) increased with the adsorbent dosage in all DI solution, 2.5 mM HCO_3^- and 5.5 mM HCO_3^- solution. This might be due to the increase in the number of active sites in unit volume of solution. Also, no significant increment in the removal tendency was observed at higher adsorbent doses which can be due to this fact that As(V) adsorption occurs in two stages, which are fast formation of a mono layer followed by a slow plateau stage [33].

The results show that for Mn_2O_3 and Mn_3O_4 , the removal of As(V) increased with sorbent dosage up to a dosage of 10 g/L. After that, the removal efficiency was found to be more or less constant and close to 99%. The Mn_2O_3 and Mn_3O_4 sorbents showed promising performance in removing the As(V) from all three solutions even with the low level of adsorbent dosage while MnO_2 and MnO worked well just with the high sorbent dosage. In order to meet the EPA standard level for arsenic

in drinking water a 10 g/L of Mn_2O_3 and Mn_3O_4 is needed while this dosage is 10 times higher for MnO and MnO_2 adsorbents.

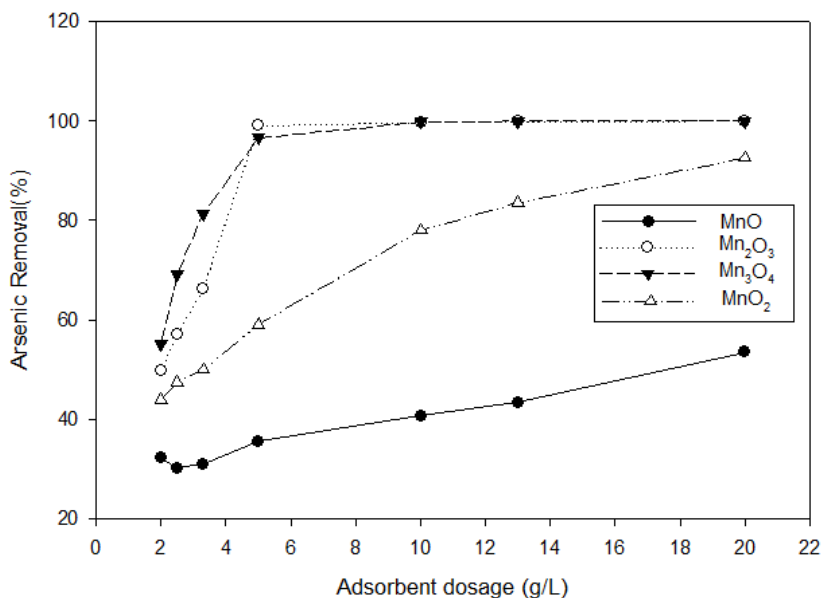


Fig.9. The effect of adsorbent dosage on the removal of As(V) from DI solution

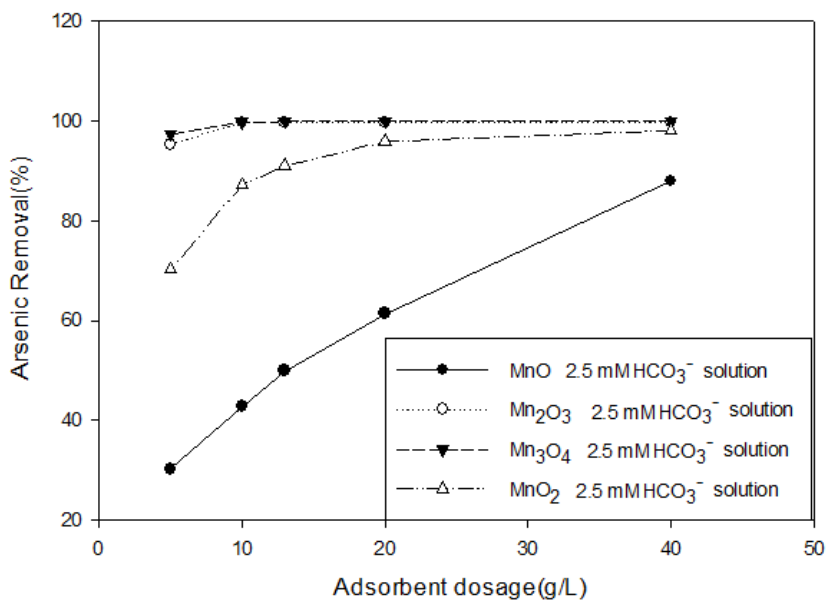


Fig.10. The effect of adsorbent dosage on the removal of As(V) from 2.5 Mm HCO_3^- solution

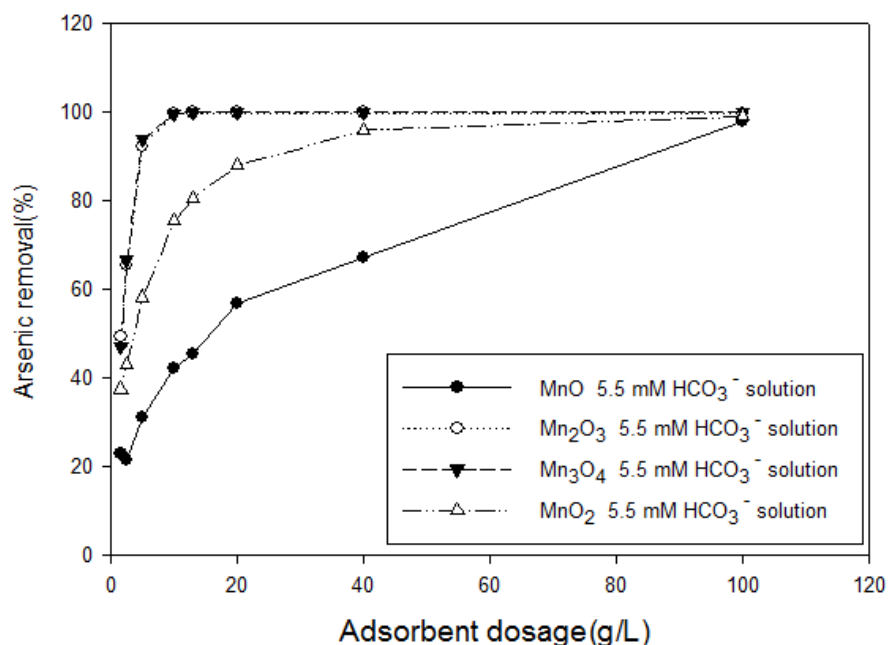


Fig.11. The effect of adsorbent dosage on the removal of As(V) from 5.5 Mm HCO_3^- solution

3.3. Effect of contact time

The effect of contact time on the As(V) removal efficiency was investigated. The main purpose in this study was to establish the ideal conditions of the adsorbent capacity, by considering the contact time of the solution at the solid/liquid interface. A 5 g/L of each sorbent (MnO, Mn₂O₃, Mn₃O₄ and MnO₂) was exposed to 50 mL of 2.5 Mm HCO_3^- solution. The adsorption data for arsenic uptake versus contact time for a fixed adsorbent amount is shown in the Fig. 12, giving identical abrupt increase in adsorption specially for Mn₂O₃ and Mn₃O₄ at low times before reaching the plateaus. According to these data, equilibrium was achieved at less than 10 hr for all manganese oxides. However, to be sure on the best adsorption conditions at different

concentrations levels, to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with 24 h of contact time. This short time period required to attain equilibrium suggests an excellent affinity of the As(V) for Mn_2O_3 and Mn_3O_4 from aqueous solution.

The data from Fig.12 show that the As(V) adsorption process onto Mn_2O_3 is faster than the one with Mn_3O_4 . In the other word, the available active sites on the surface of Mn_2O_3 get saturated in a shorter time. As expected, MnO and MnO_2 were not able to remove significant amount of arsenic in solution in different time intervals. The equilibrium arsenate uptake onto MnO , Mn_2O_3 , Mn_3O_4 and MnO_2 was found to be 40.42 mg/kg, 185.03 mg/kg, 132.3 mg/kg and 98.99 mg/kg, respectively.

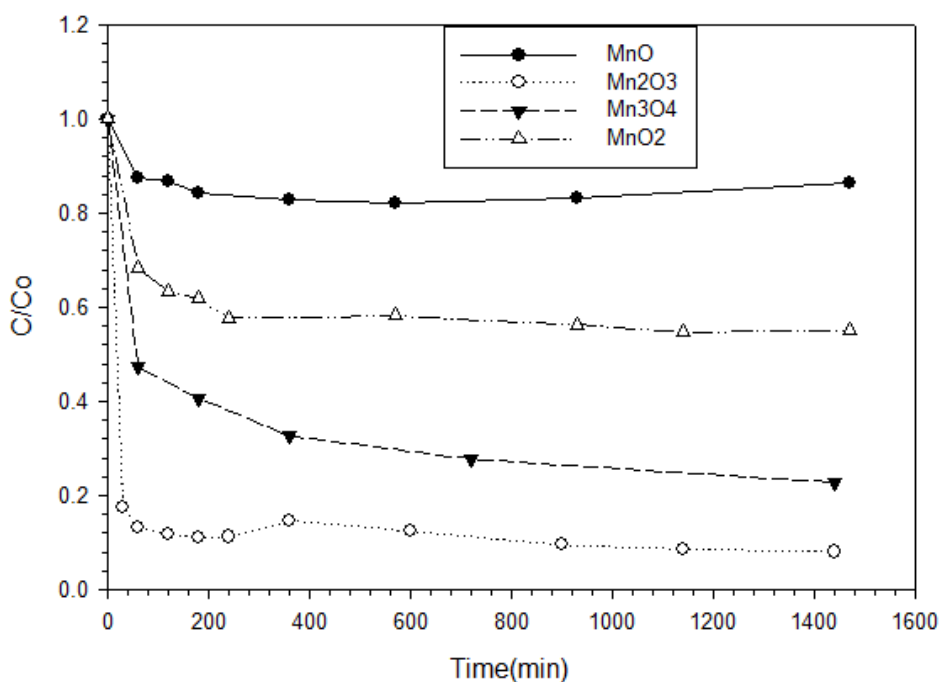


Fig.12 Effect of contact time on As(V) removal efficiency-5 g/L sorbent.1 mg/L initial arsenic concentration.

3.4. Kinetic modelling

The evaluation of the kinetics of the adsorption process is an important issue before scaling up to industrial process scale. In this study, kinetic experiments were carried out by the batch procedure for a period of 24 h.

Several kinetic models have been used to determine the rate constants of different systems. Widely used kinetic models are those based on the decrease of available active sites to interact with solute (adsorption capacity) and have been successfully used to determine rate constants and characteristics of the sorption process (e.g., pseudo-first order model [34], pseudo-second order model [35]. The term “pseudo” is used to distinguish the use of solute concentration from solid concentrations [36].

The pseudo-first order model and the pseudo second-second order method can be written as Eq.3 and Eq.4, respectively:

$$\frac{dq}{dt} = k_1 \times (q_e - q_t) \quad (3)$$

$$\frac{dq}{dt} = k_2 \times (q_e - q_t)^2 \quad (4)$$

where q_e and q_t are the adsorption capacities(mg/kg) at equilibrium and at time t , respectively. k_1 is the adsorption rate constant(min^{-1}) of pseudo-first order adsorption and k_2 is the adsorption rate constant($\text{g.mg}^{-1}.\text{min}^{-1}$) of pseudo-second order adsorption.

The linearized forms of the Lagergren pseudo-first order and pseudo-second order equations are given in Eq.5 and Eq.6, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2} \right) \left(\frac{1}{q_e^2} \right) + \frac{t}{q_e} \quad (6)$$

The theoretical equilibrium sorption capacity, q_e calculated, and the rate constant k_1 can be obtained from the intercept and slope of a linear plot of $\ln(q_e - q_t)$ against t , respectively. k_2 can be obtained from the intercept of a linear plot of t/q_t against t . Fig.13 and Fig.14 show the pseudo-first order model and the pseudo second-second order model fits for As(V) adsorption onto MnO, Mn₂O₃, Mn₃O₄ and MnO₂, respectively.

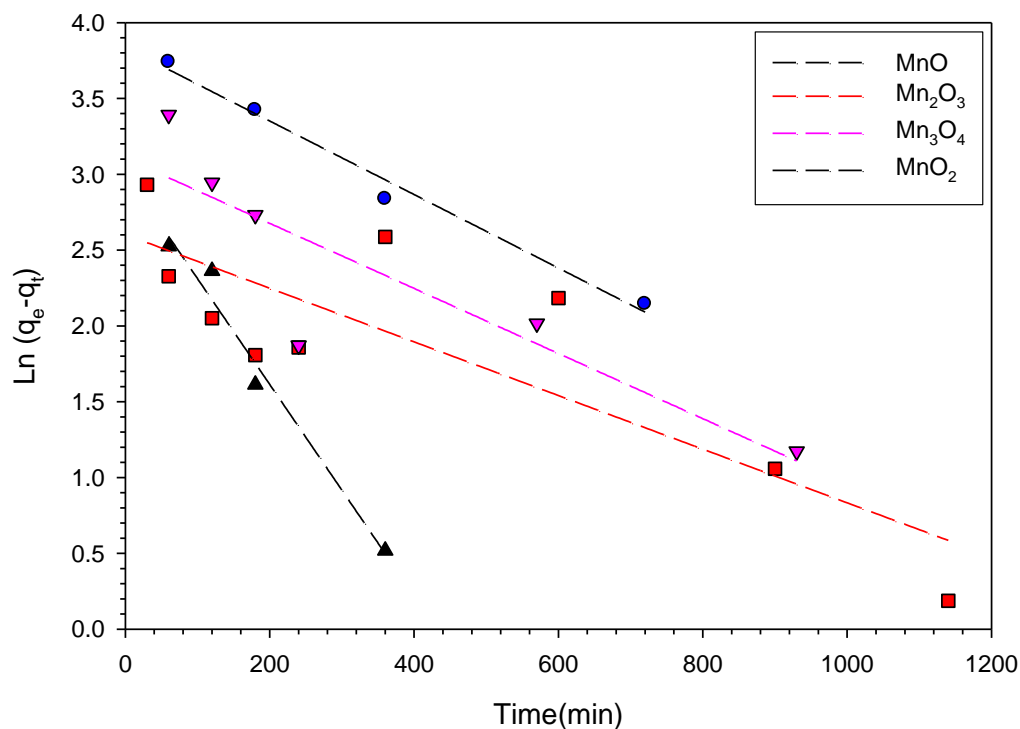


Fig.13. Test of pseudo-first kinetic model kinetic model for As(V) adsorption on MnO, Mn₂O₃, Mn₃O₄ and MnO₂ (T=298.15 K, adsorbent dosage=5 g/L)

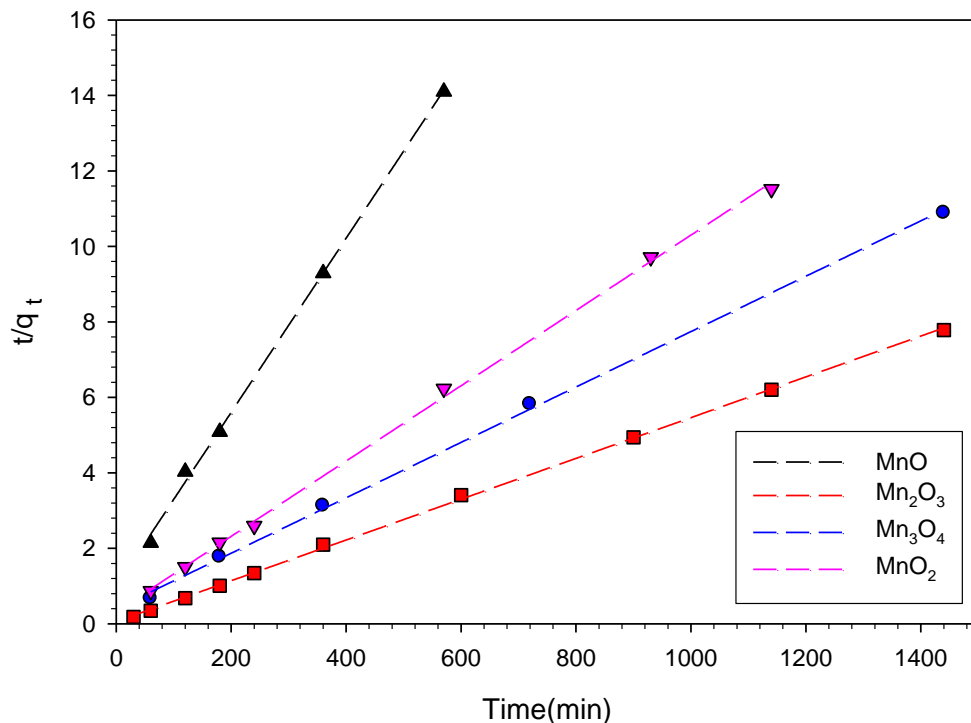


Fig.14. Test of pseudo-second order kinetic model kinetic model for As(V) adsorption on MnO, Mn₂O₃, Mn₃O₄ and MnO₂ (T=298.15 K, adsorbent dosage=5 g/L)

The kinetic parameters of above models are listed in Table 3. The correlation coefficients for the linear plots of the pseudo-second order rate law were found to be close to 1.0 for the all studied manganese oxides. Moreover, the calculated values of q_e were very close to the experimental data. This suggests that the sorption system is the pseudo-second order reaction. The equilibrium As(V) adsorption capacity onto Mn₂O₃ and Mn₃O₄ was found to be higher than the other manganese oxides in all time increments. The higher As(V) adsorption rate onto Mn₂O₃ versus Mn₃O₄ is indicative of a faster As(V) removal by Mn₂O₃ than Mn₃O₄.

Table 3. Kinetic parameters of Pseudo-first-order and Pseudo-second-order for the adsorption of arsenic onto MnO, Mn₂O₃, Mn₃O₄ and MnO₂.

| | q_{exp} | PSEUDO-FIRST-ORDER | | | PSEUDO-SECOND- ORDER | | |
|--------------------------------|-----------|--------------------|-------|--------|----------------------|--------|--------|
| | | K_1 | q_e | R^2 | K_2 | q_e | R^2 |
| MnO | 40.42 | 0.007 | 20.29 | 0.9757 | 0.0005 | 43.29 | 0.9986 |
| Mn ₂ O ₃ | 185.03 | 0.0018 | 13.48 | 0.7111 | 0.0005 | 185.19 | 0.9996 |
| Mn ₃ O ₄ | 132.3 | 0.0024 | 46.3 | 0.9851 | 0.0001 | 136.98 | 0.9990 |
| MnO ₂ | 98.99 | 0.0021 | 22.31 | 0.7821 | 0.0003 | 100 | 0.9990 |

The mechanism of adsorption is generally considered to involve three steps, one or any combination of which can be the rate-controlling mechanism: (i) mass transfer across the external boundary layer film of liquid surrounding the outside of the particle; (ii) adsorption at a site on the surface (internal or external) and the energy will depend on the binding process (physical or chemical); this step is often assumed to be extremely rapid; (iii) diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism [37].

The intraparticle diffusion equation is represented as:

$$q_t = k_{id}t^{1/2} + c \quad (7)$$

where q_t (mg/kg) is the adsorption capacities(mg/kg) at time t (min) and k_{id} (mg.kg⁻¹.min^{-1/2}) is the rate constant of intraparticle diffusion. The value of k_{id} and c can be obtained from the slope and intercept of the plot of q_t versus $t^{1/2}$, respectively (Fig.15). The straight line passing the through the origin indicates that the intraparticle diffusion model is the main rate determining step for the adsorption process.

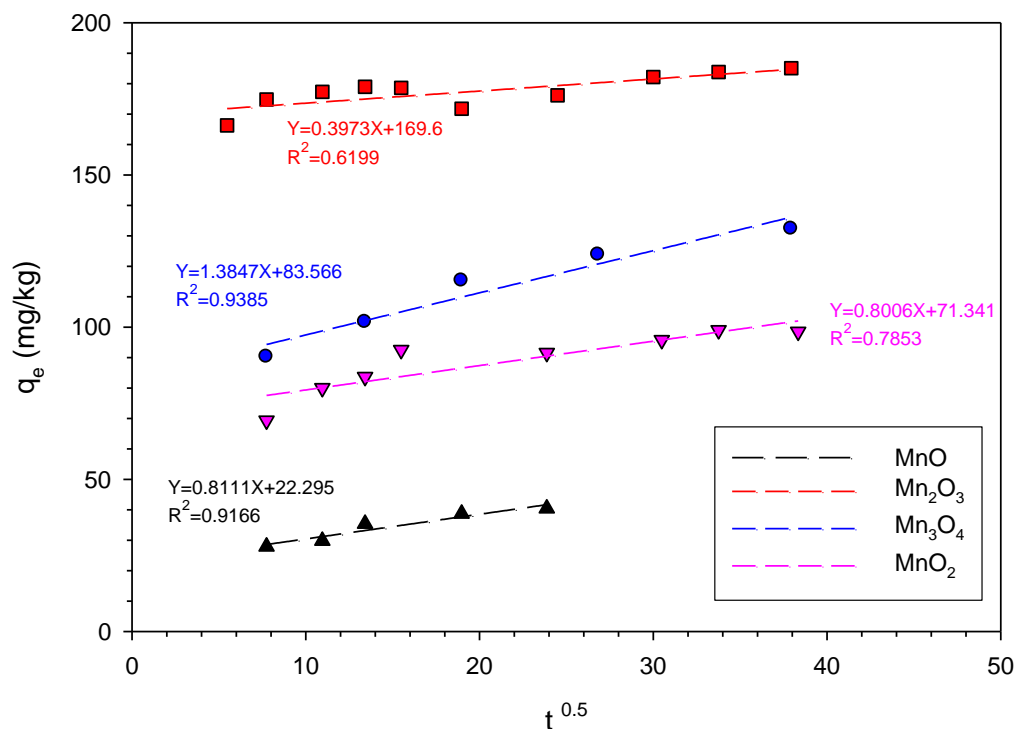


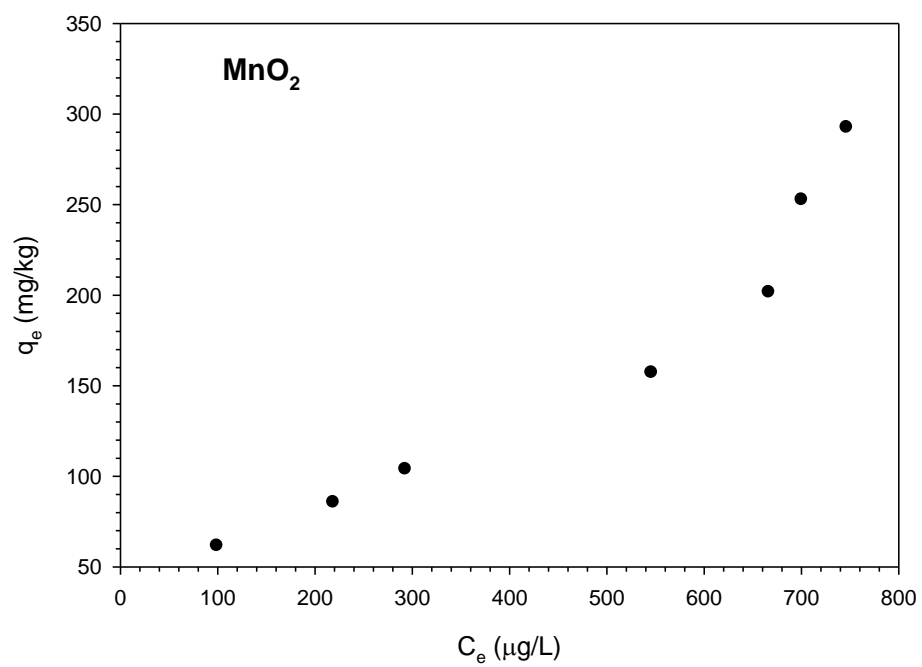
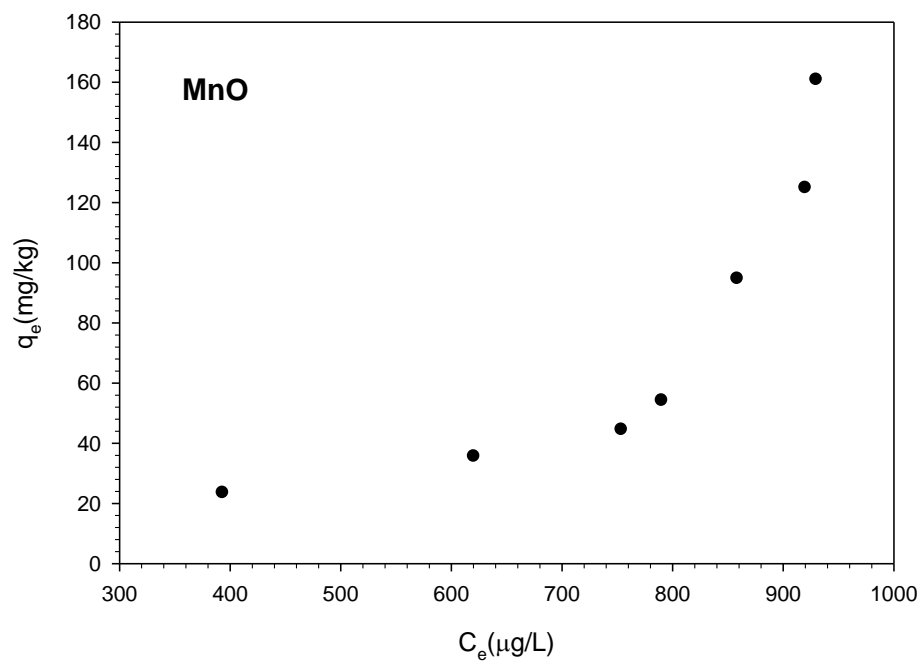
Fig.15. Test of intraparticle diffusion model for As(V) adsorption on MnO, Mn₂O₃, Mn₃O₄ and MnO₂ (T=298.15 K, adsorbent dosage=5 g/L)

As seen from Fig.15, the value of c obtained from the intraparticle diffusion model is not zero and the correlation coefficient is not satisfactory for manganese oxides adsorbent, indicating that the intraparticle diffusion may not be the controlling factor in determining the kinetics of the process. Due to crystallinity of the applied sorbents, the external mass transfer is taking place.

3.5. Adsorption isotherm experiments

The abilities of four common isotherms, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D-R) were investigated to model the arsenate adsorption equilibrium data at 25 °C using an initial arsenate concentration of 1 mg/L in DI, 2.5mM HCO_3^- and 5.5mM HCO_3^- solution. The correlation coefficient was used to select the best –fit isotherm model. The capacity of the manganese oxides sorbents at different residual concentration of arsenic in three studied solutions is shown in Fig 16-18. The similar adsorption pattern was obtained in different solutions.

From Fig.16-18 and for As(V) adsorption onto Mn_2O_3 than Mn_3O_4 in all solutions, first the arsenate uptake increased sharply which is indicative of the accessible sites on the surface of Mn_2O_3 and Mn_3O_4 for As(V) adsorption. By increasing the arsenic concentration, a plateau was obtained, representing that all active adsorption sites in Mn_2O_3 and Mn_3O_4 surface were occupied. However, for As(V) adsorption onto MnO and MnO_2 , the arsenate uptake increased slowly by increasing the arsenic concentration at lower As(V) concentration while at higher arsenic concentration the arsenate uptake raised rapidly indicting the unfavorable adsorption of arsenate on MnO and MnO_2 .



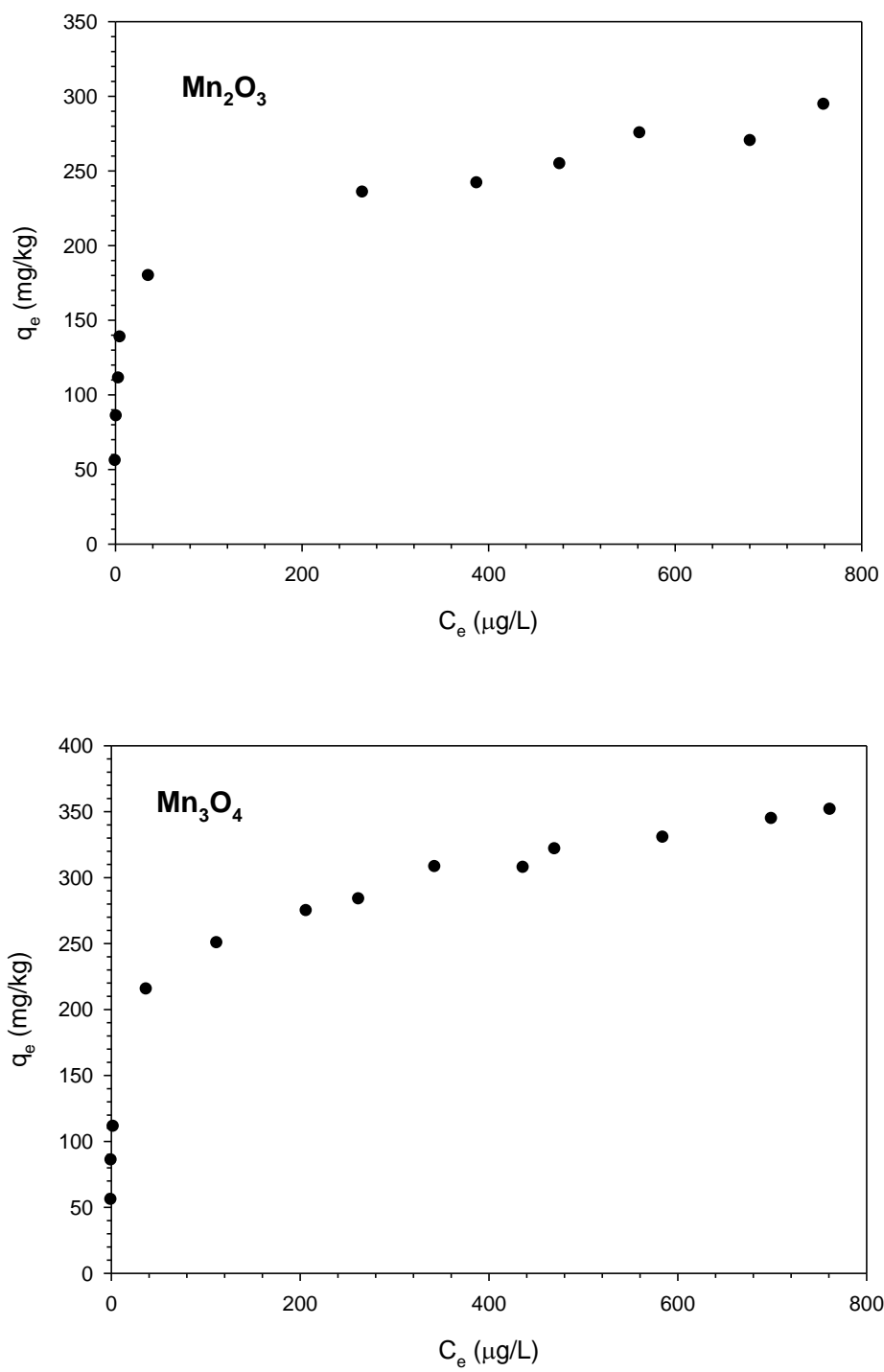
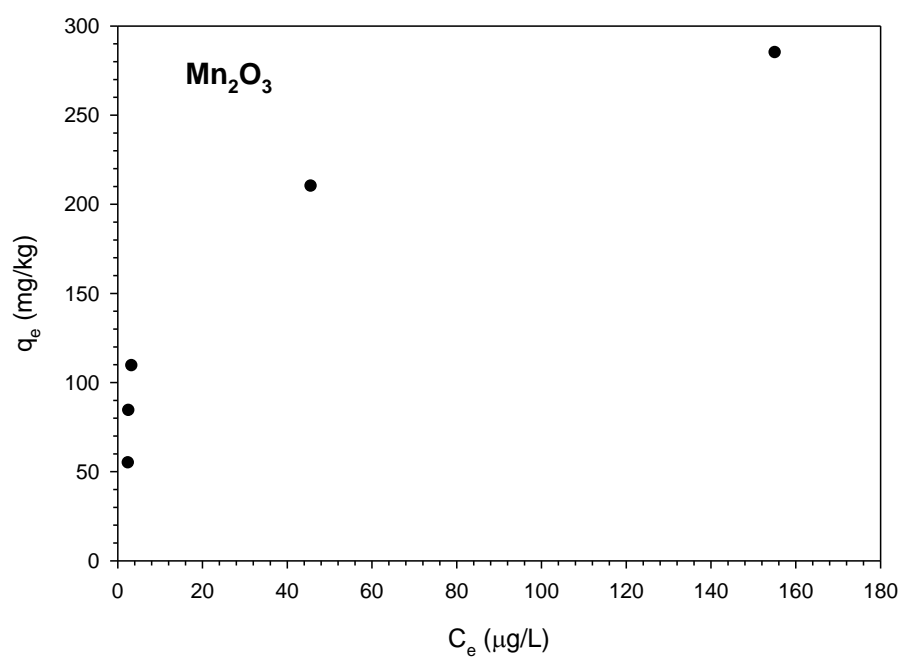
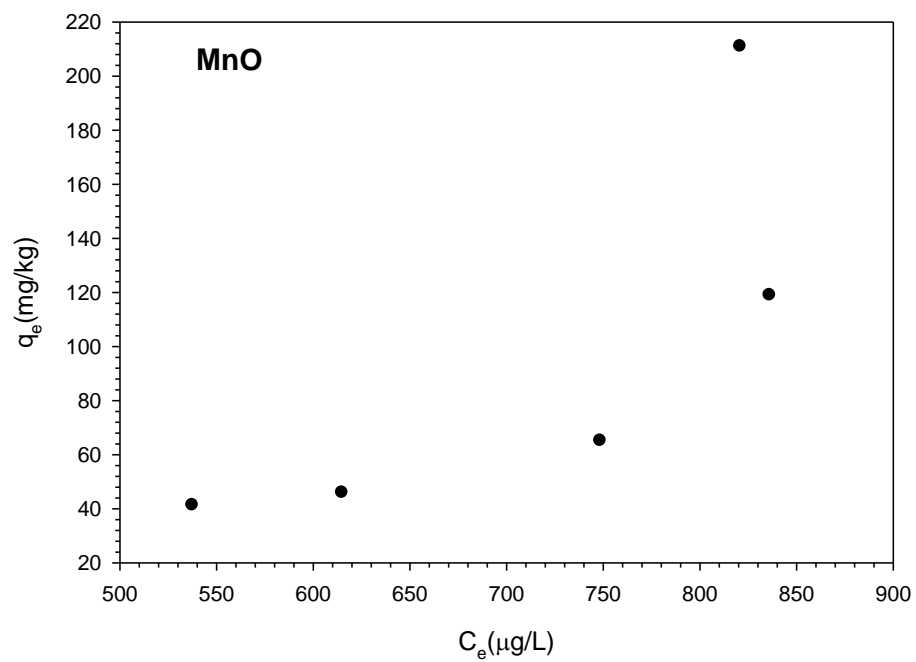


Fig.16. Adsorption capacity of the sorbents in DI solution



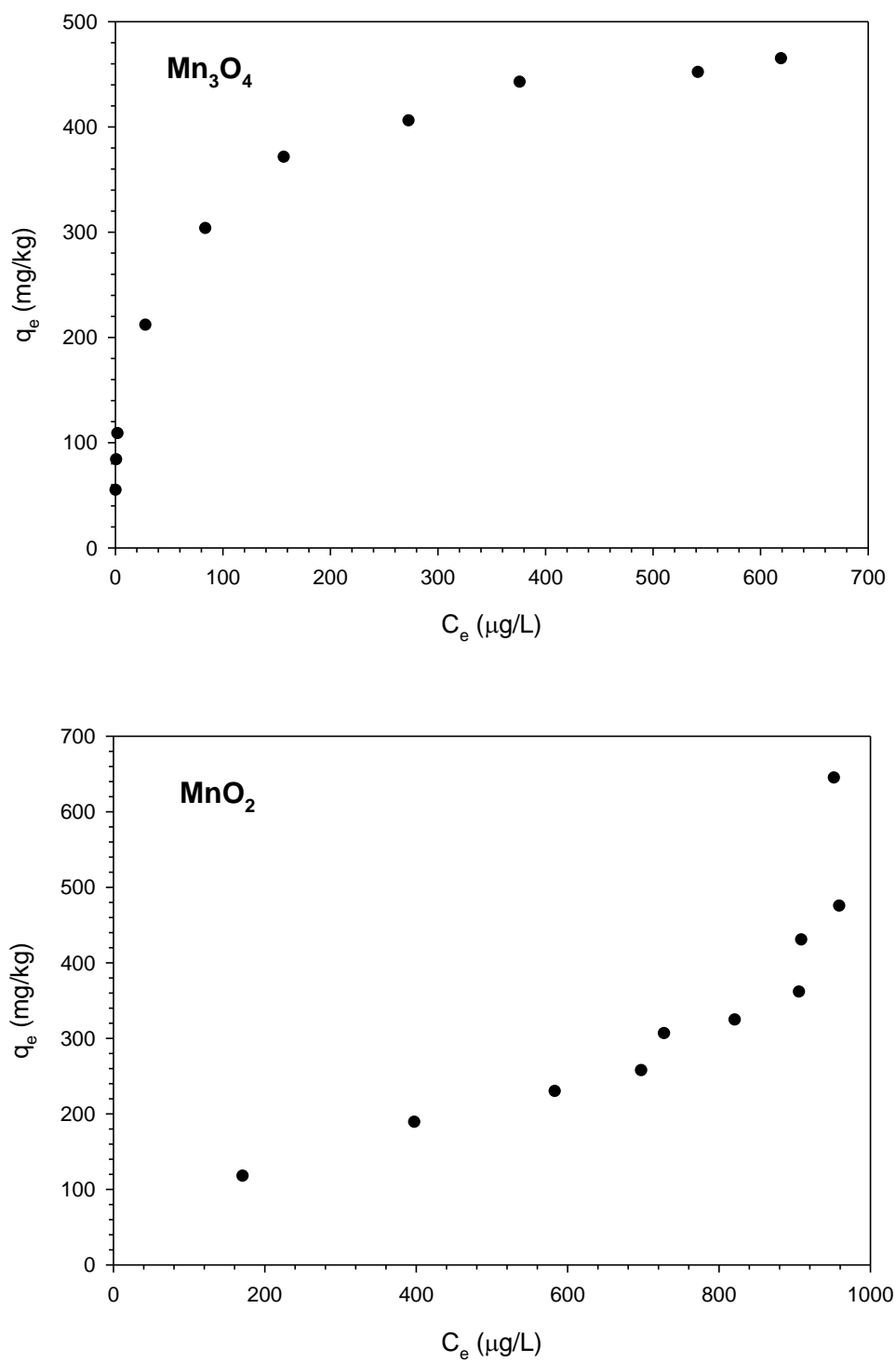
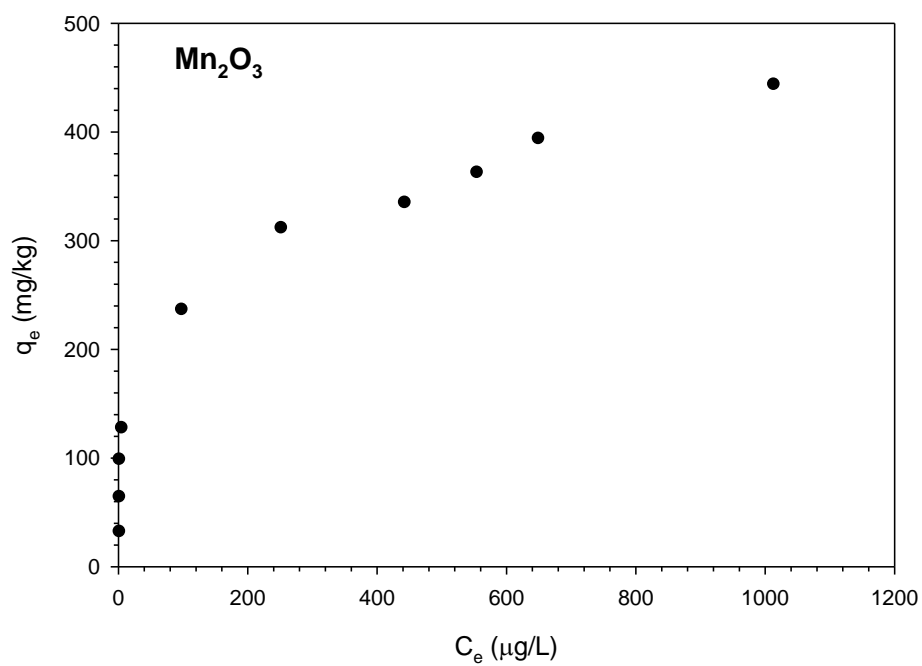
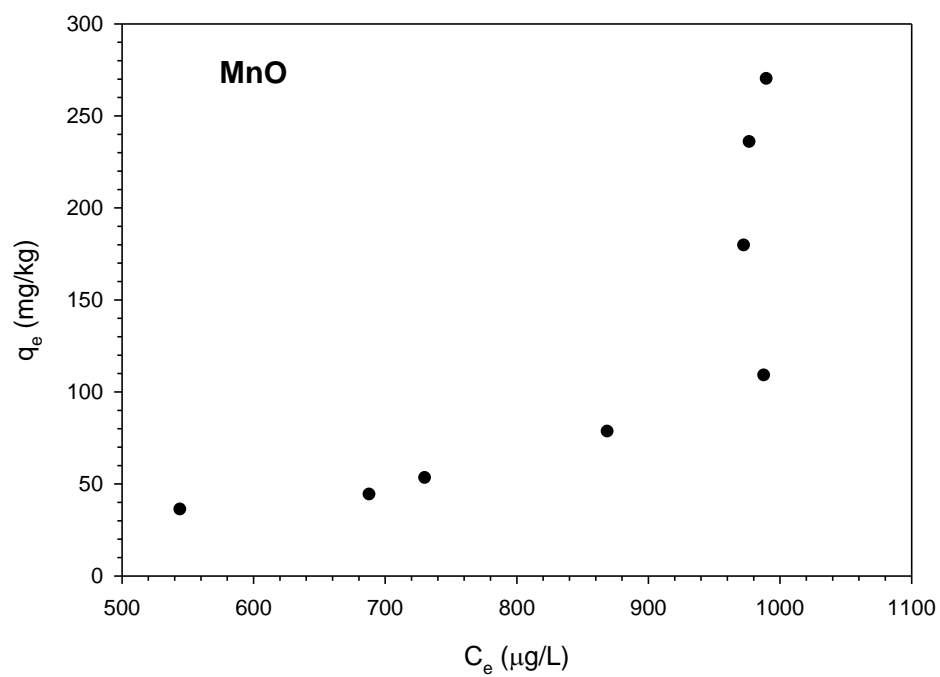


Fig.17. Adsorption capacity of the sorbents in 2.5M HCO_3^- solution



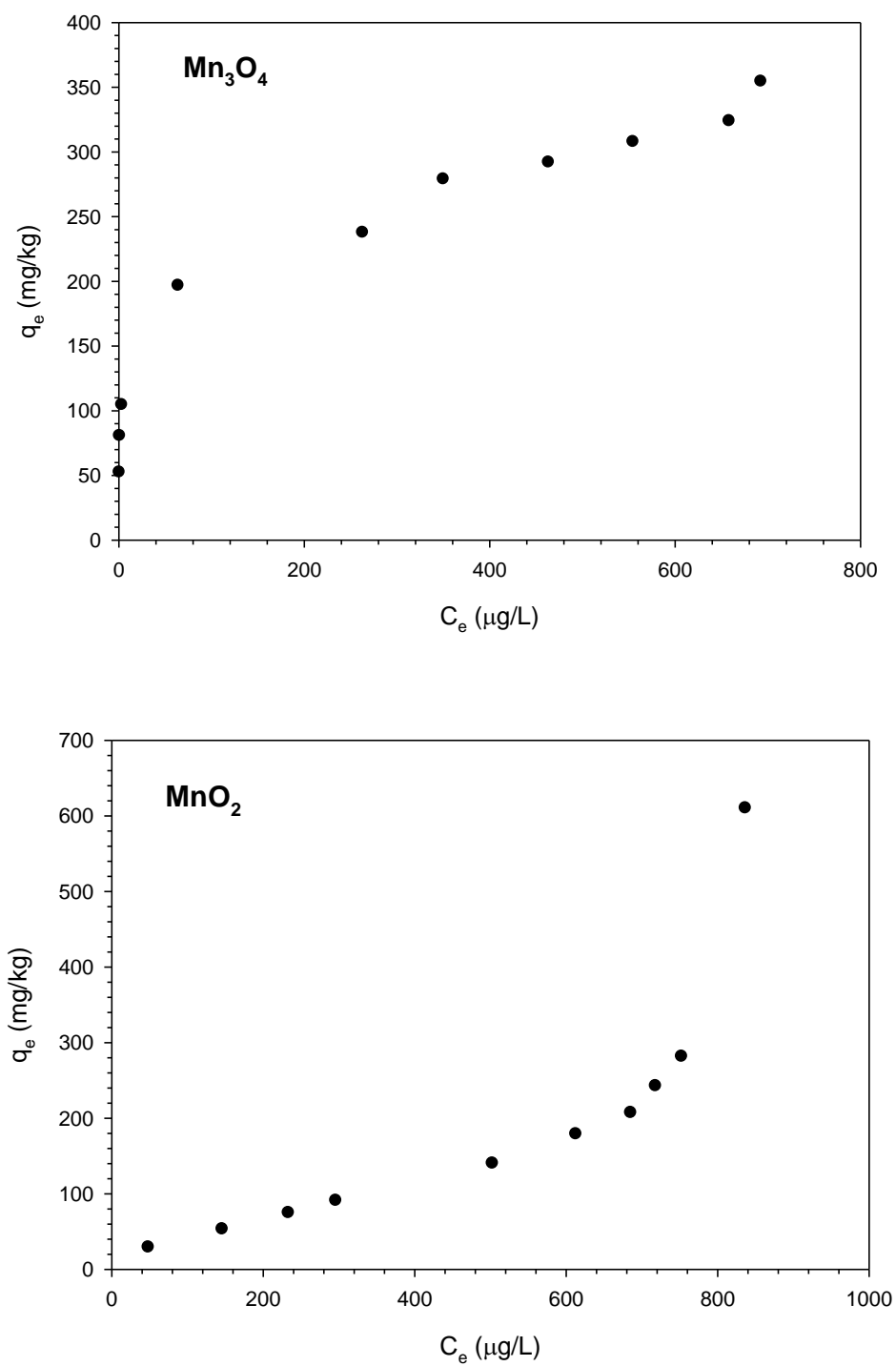


Fig.18. Adsorption capacity of the sorbents in 5.5Mm HCO_3^- solution

Langmuir isotherm assumes that adsorption occurs on a structurally homogenous surface, that is, all the adsorption sites are equivalent and adsorbed molecules do not interact. It can model the monolayer coverage of the adsorption surface and the adsorption that occurs through the same mechanism. The Langmuir isotherm commonly expressed as the following equation [38]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

where q_e is the amount of As(V) adsorbed per unit weight of adsorbent (mg/kg), q_m is maximum As(V) adsorbed (mg/kg) corresponding to complete coverage of available sites, K_L is Langmuir constant related the free energy or net enthalpy of adsorption and C_e is the concentration of adsorbate in solution at equilibrium (mg/L). The linear form of Langmuir model is as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (4)$$

Values of q_m and K_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e . (Fig.19 to 21). The As(V) adsorption on MnO and MnO₂ did not follow the Langmuir isotherm.

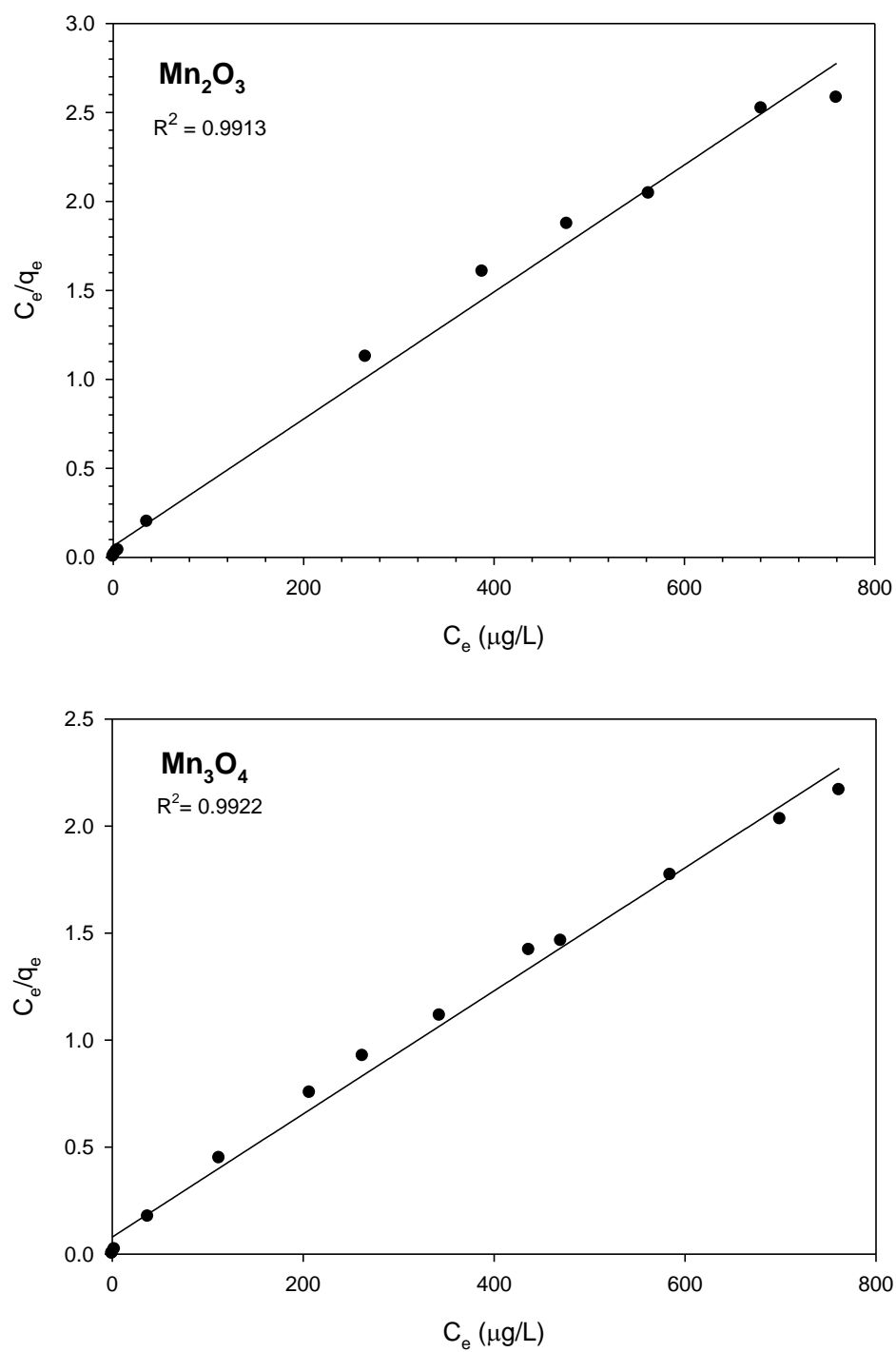


Fig.19. Langmuir isotherm models for As(V) adsorption onto the sorbents in DI solution

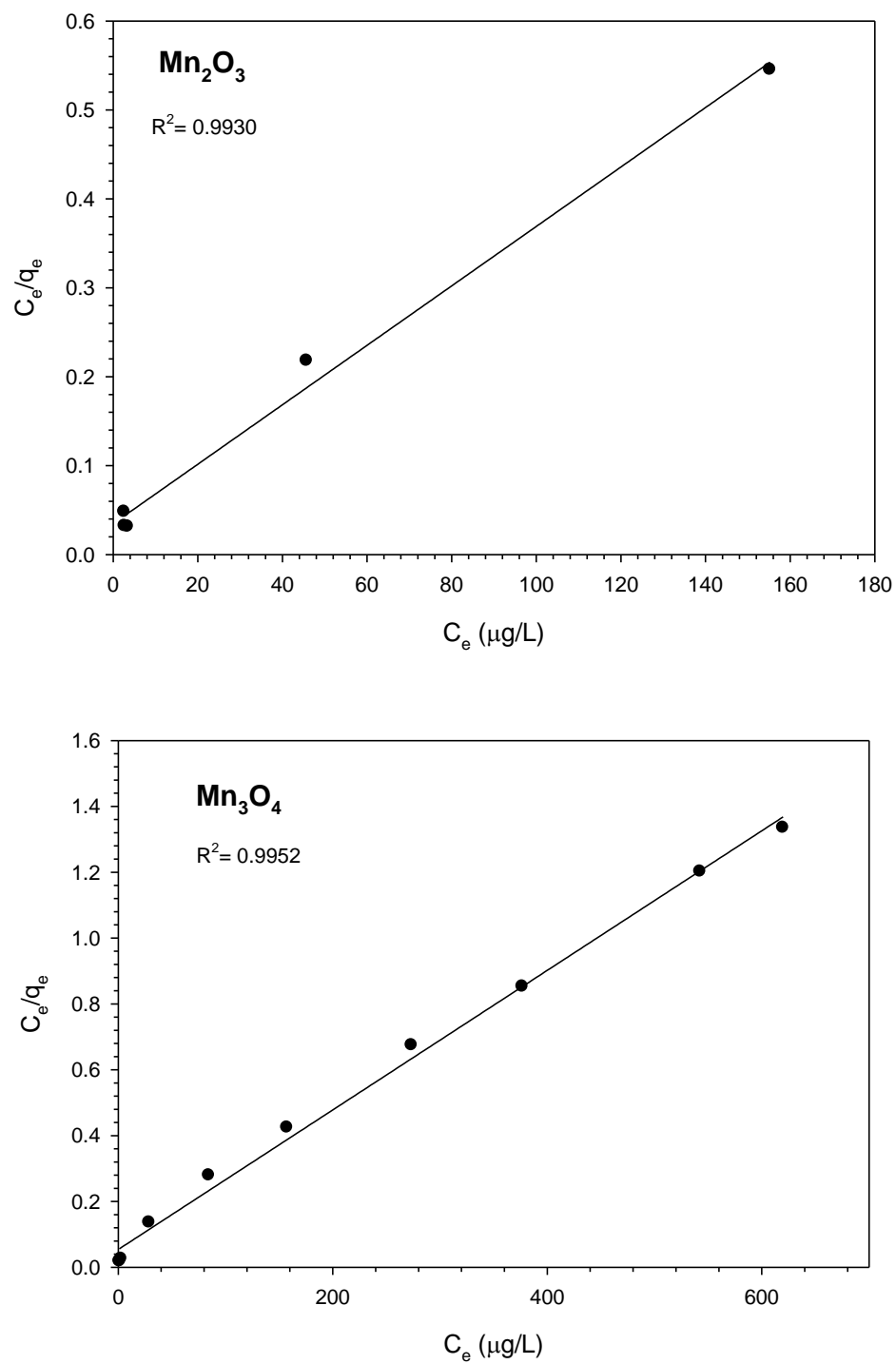


Fig.20. Langmuir isotherm models for As(V) adsorption onto the sorbents 2.5Mm HCO_3^- solution

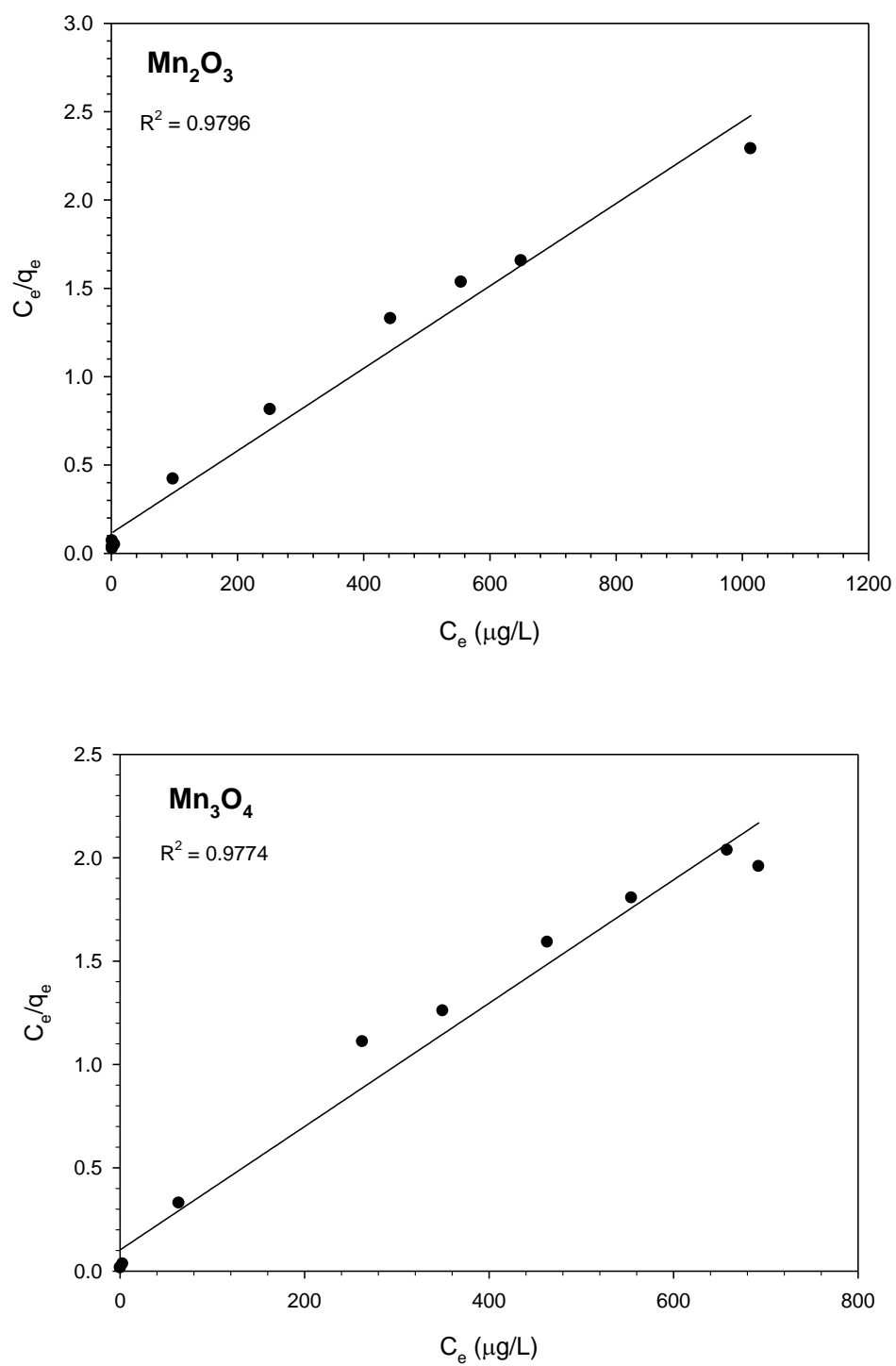


Fig.21. Langmuir isotherm models for As(V) adsorption onto the sorbents 5.5Mm HCO_3^- solution

The Freundlich isotherm model has been employed for interpreting both multilayer sorption and sorption on heterogeneous surfaces [39]. Freundlich model assumes a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites. This empirical equation can be represented as:

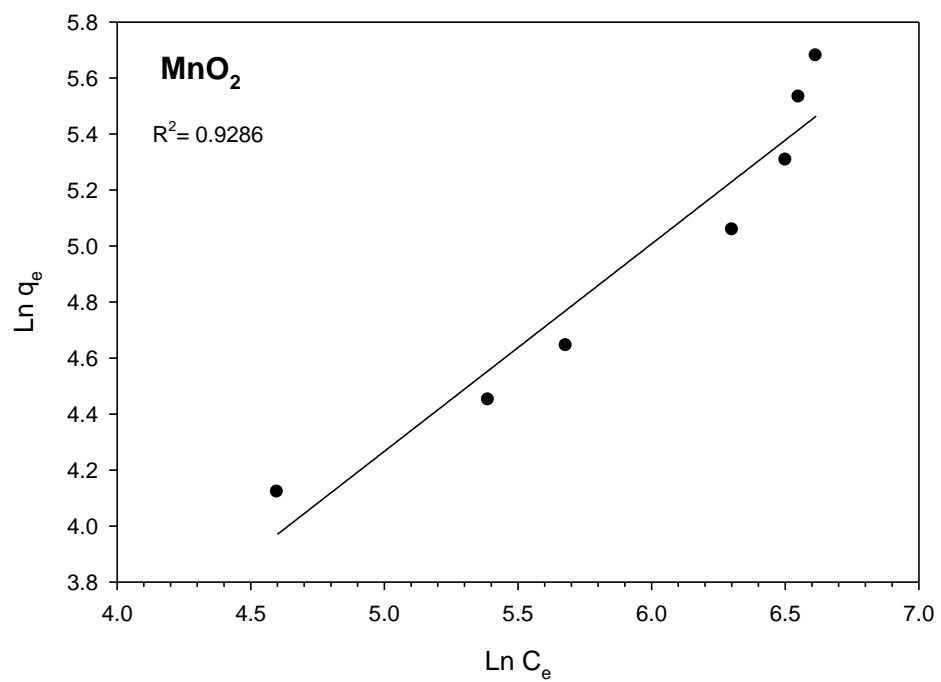
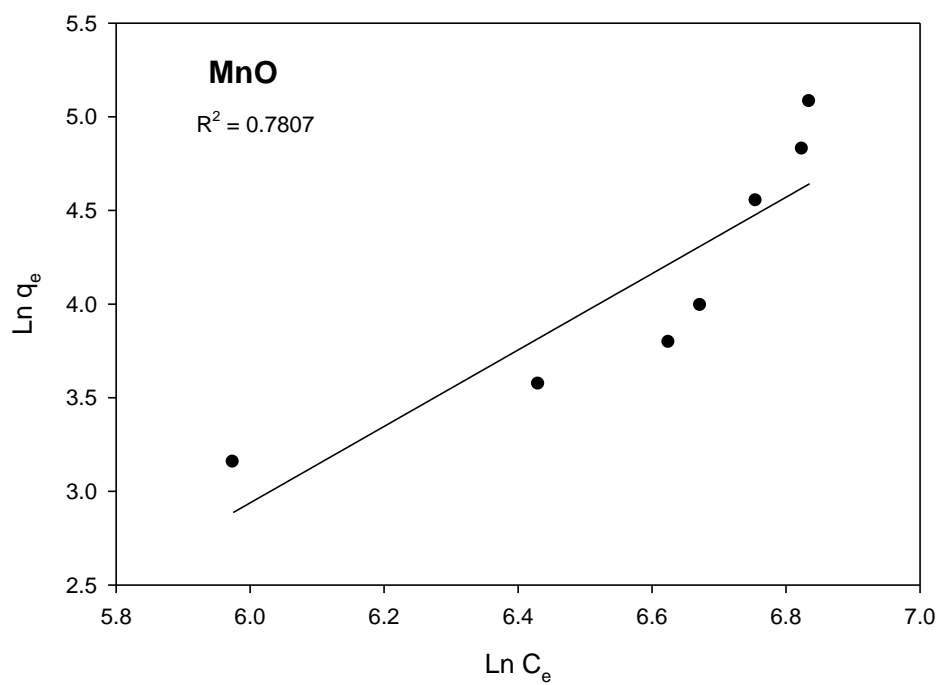
$$q_e = K_F C_e^{1/n} \quad (5)$$

where K_F is the Freundlich constant indicating the adsorption capacity and $1/n$ is a constant that shows the adsorption intensity or strength. $1/n$ values less than one shows good adsorption intensity.

The linearized form of the Freundlich is represented by the following equation:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (6)$$

The intercept and the slope of the plot of $\ln q_e$ versus $\ln C_e$ gives the K_F and $1/n$ values. (Fig.22-24).



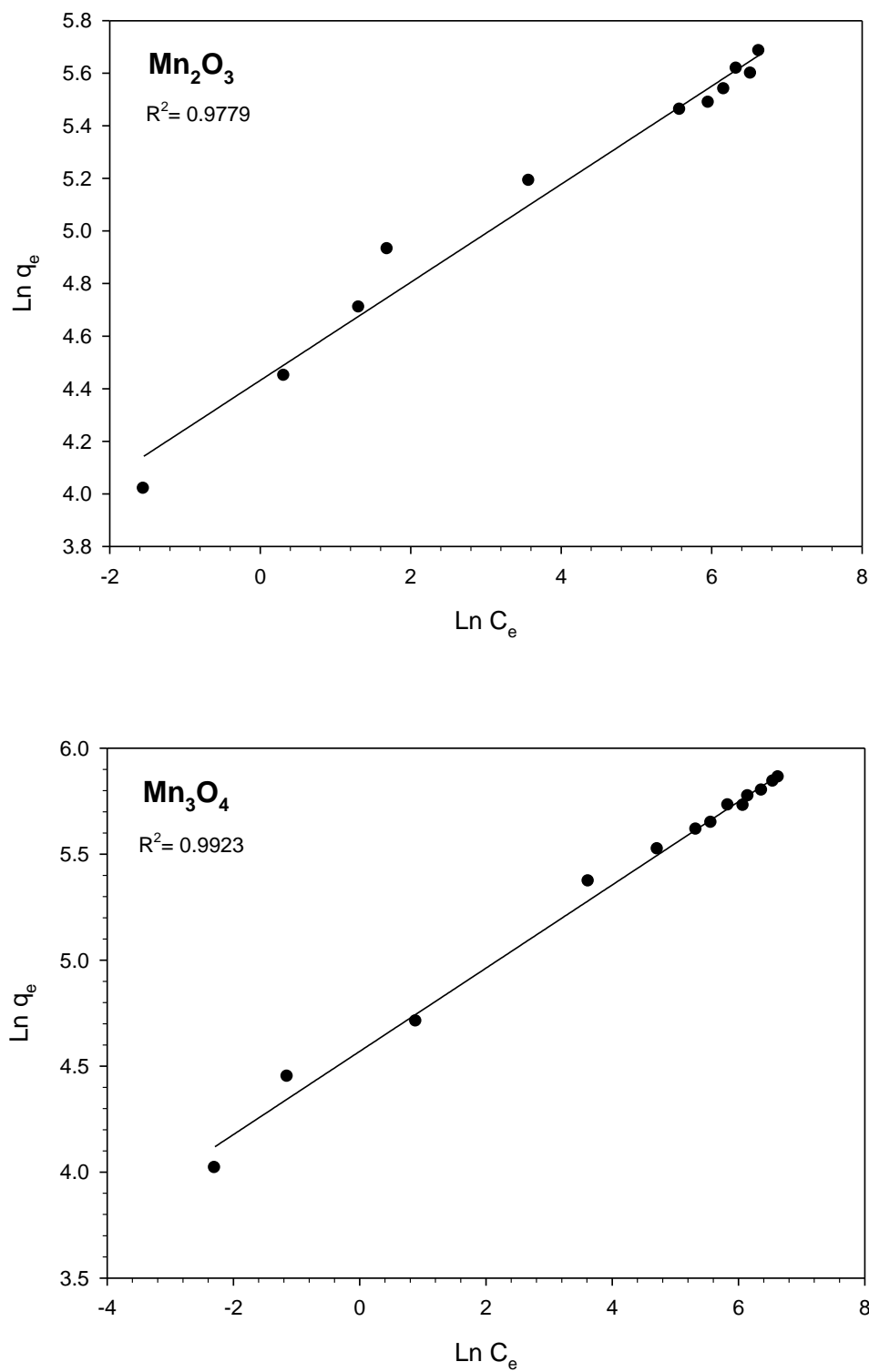
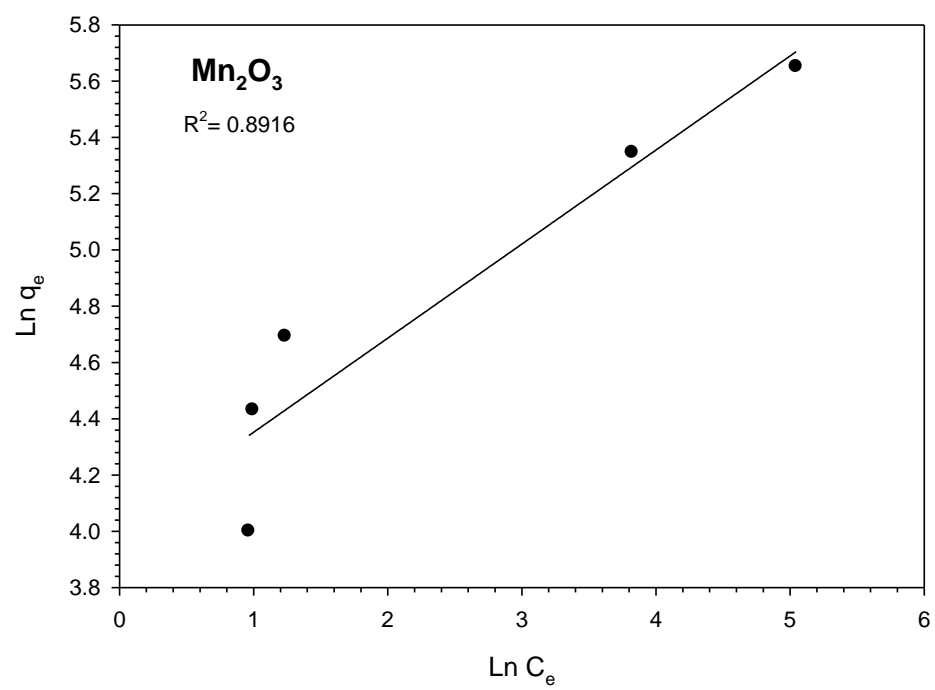
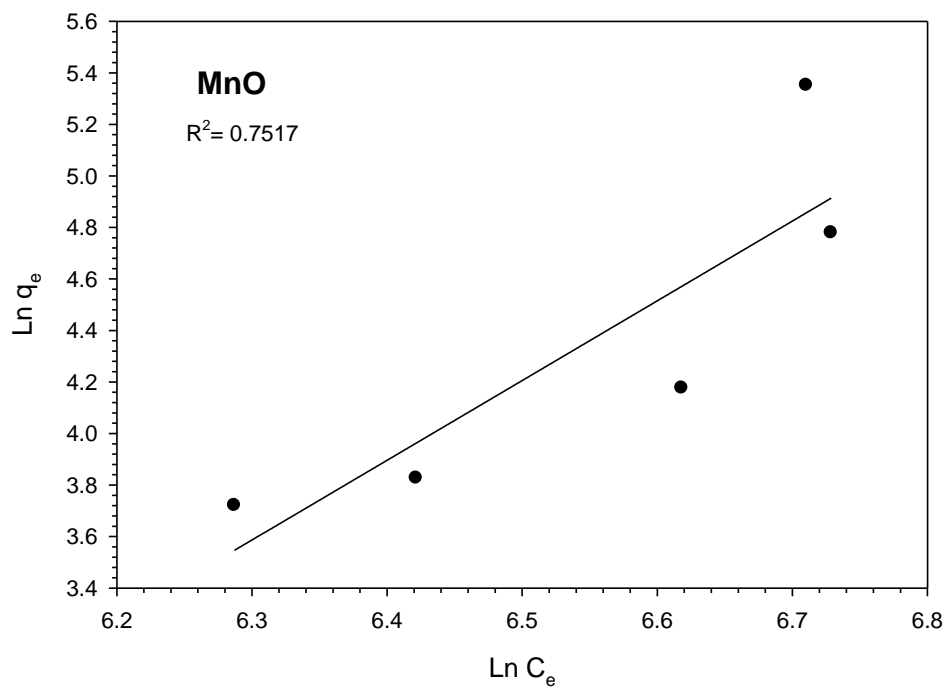


Fig.22. Freundlich isotherm models for As(V) adsorption onto the sorbents in DI solution



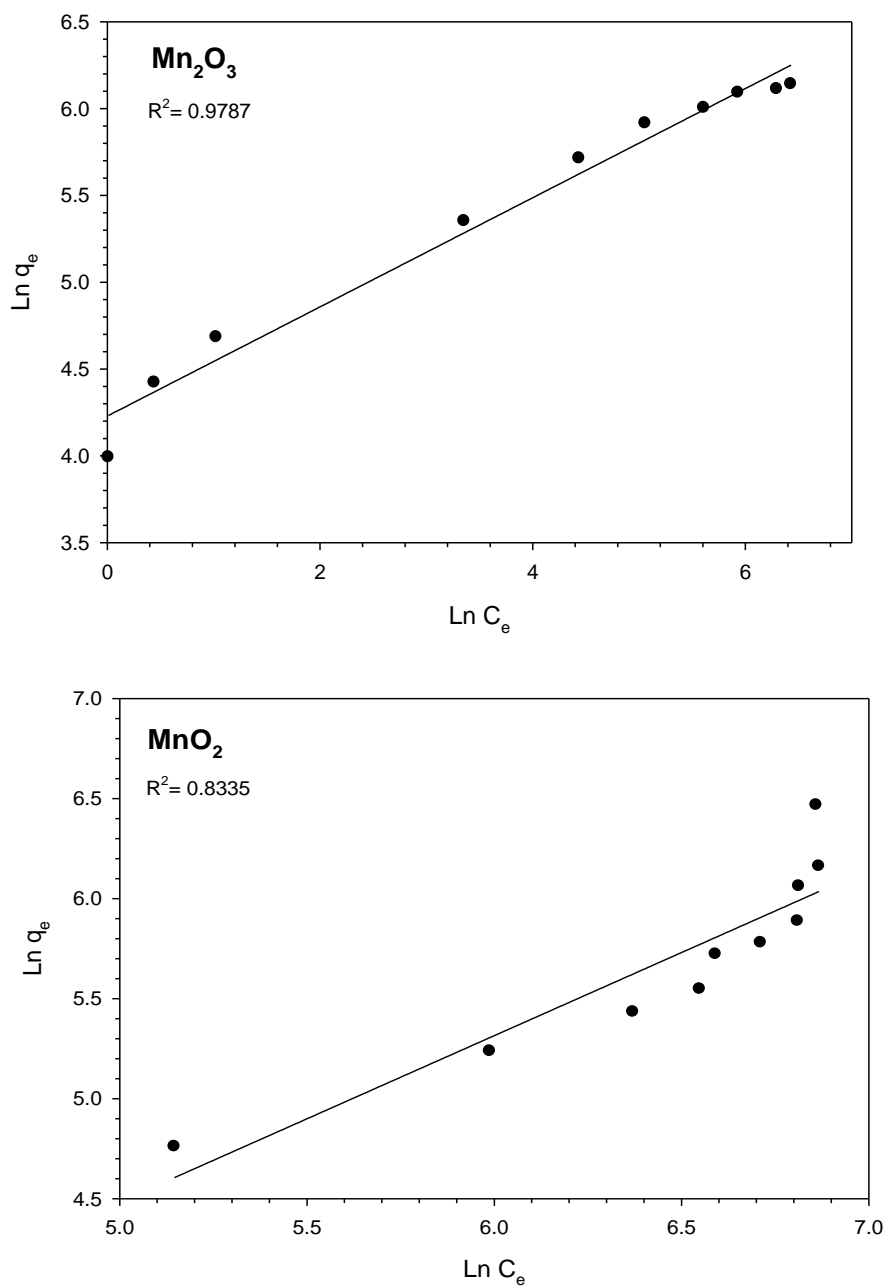
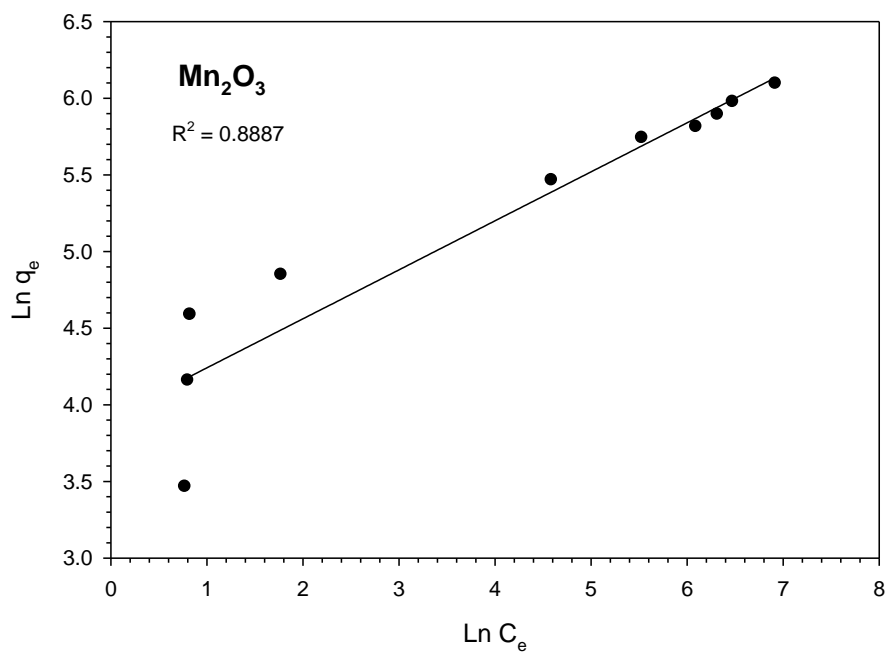
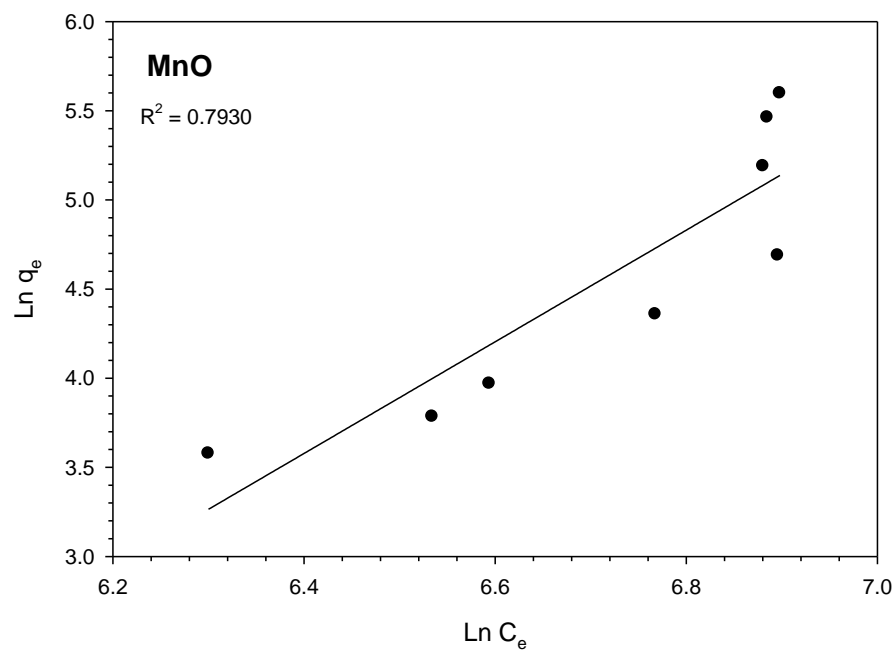


Fig.23. Freundlich isotherm models for As(V) adsorption onto the sorbents in 2.5Mm HCO_3^-



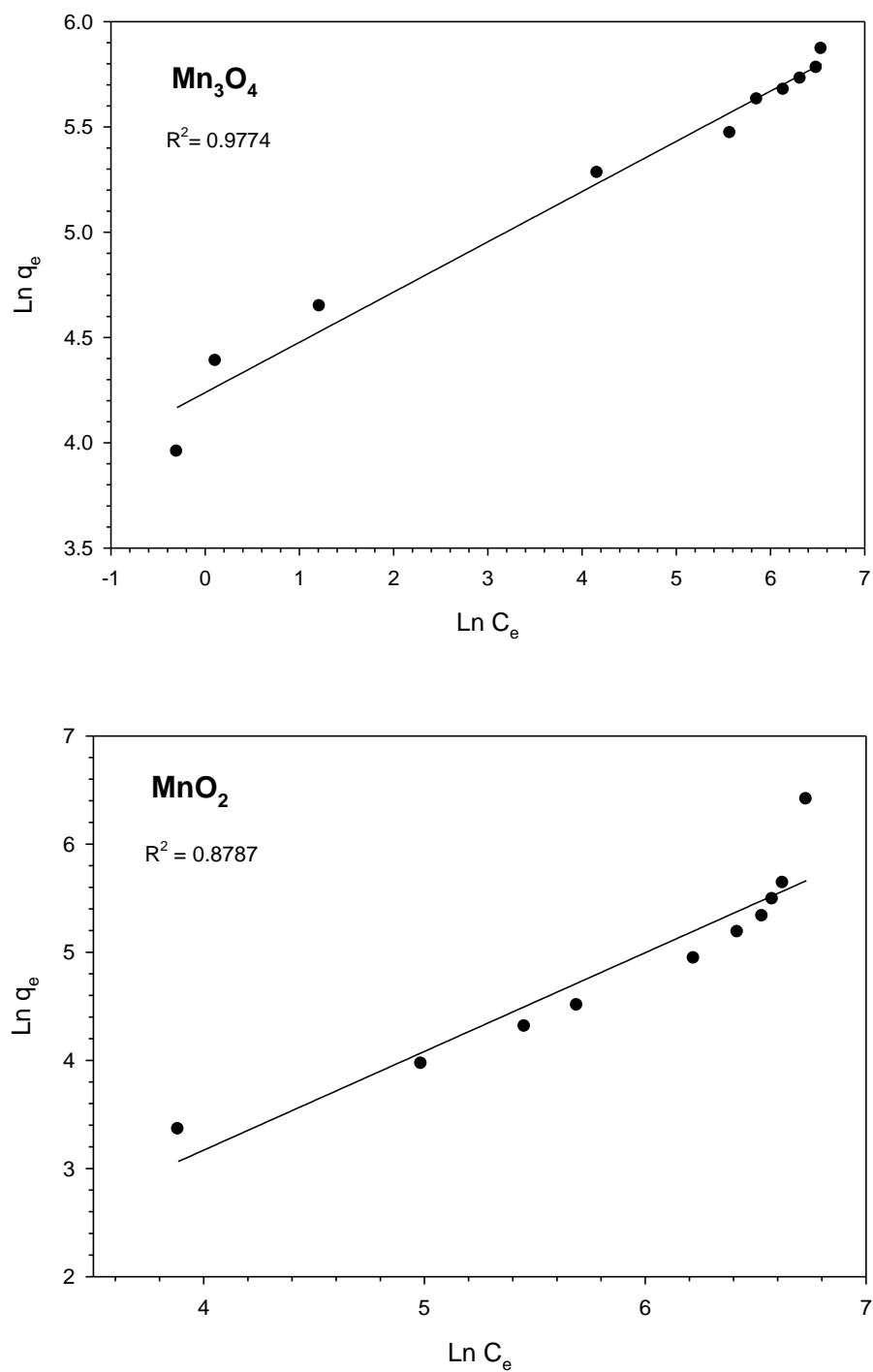


Fig.24. Freundlich isotherm models for As(V) adsorption onto the sorbents in 5.5Mm HCO_3^-

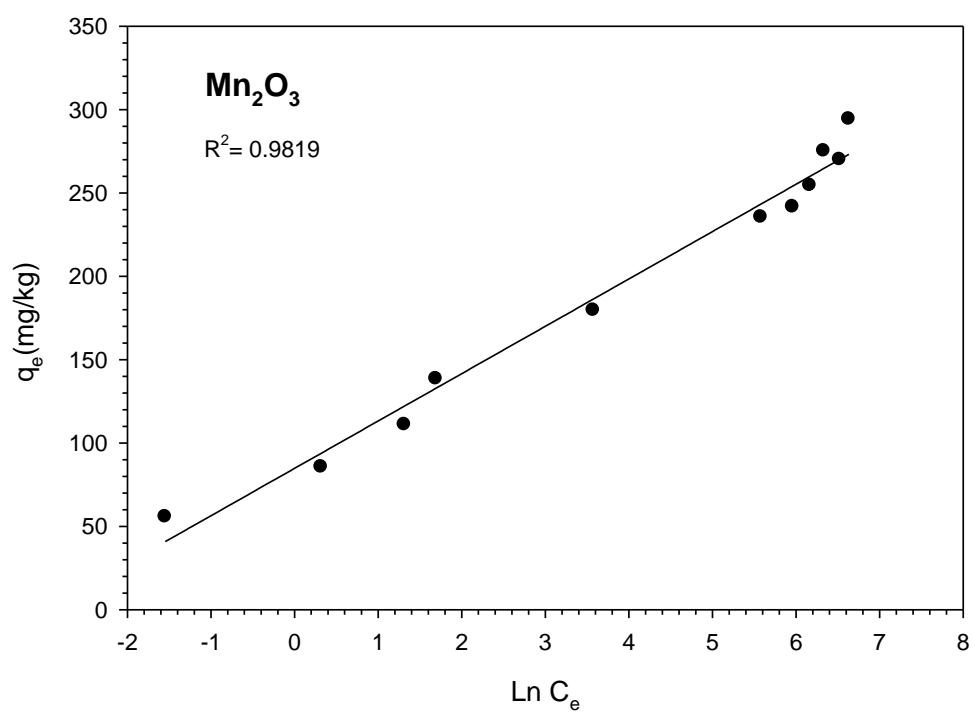
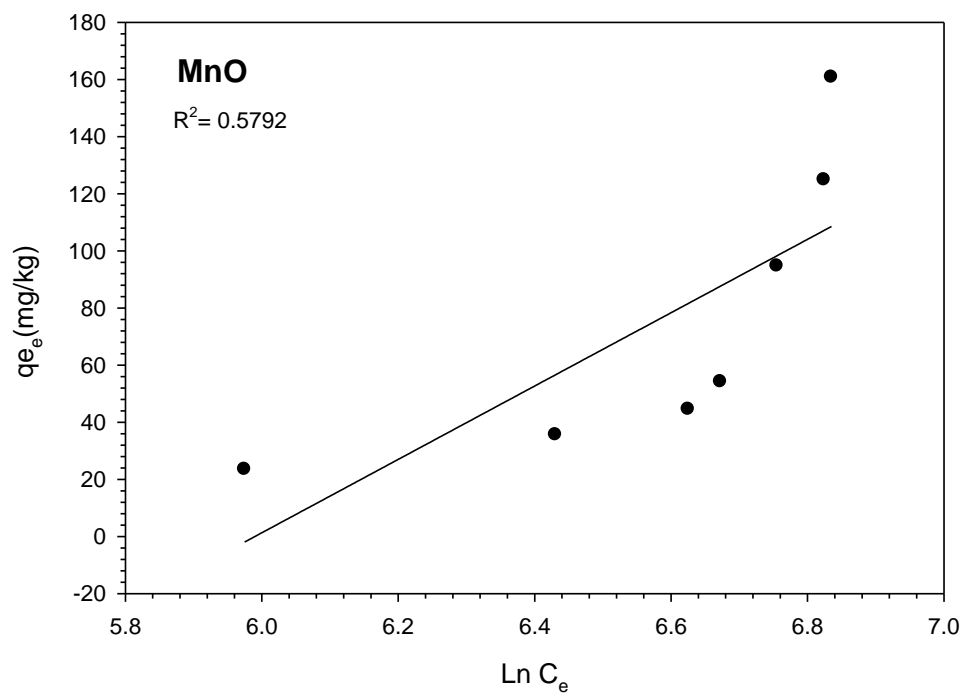
The Temkin isotherm [40] model assumes that the heat of adsorption of all the molecules in the layer would decrease linearly with coverage due to adsorbate/adsorbent interactions:

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \quad (12)$$

and linearized as:

$$q_e = \left(\frac{RT}{b}\right) \ln(A) + \left(\frac{RT}{b}\right) \ln(C_e) \quad (13)$$

where A (L/g) is the equilibrium binding constant relating to the maximum binding energy and determines the Temkin adsorption potential, b (J/mol) is corresponded to the heat of adsorption, and T and R are the temperature (K) and gas constant (8.314 J/mol.K), respectively. Temkin isotherm can be applied with assumption of uniform distribution of binding energies up to some maximum binding energy. The Temkin isotherm constants (b and A) can be determined from the slope and intercept of a plot of q_e versus $\ln C_e$ as shown in Fig. 25-27.



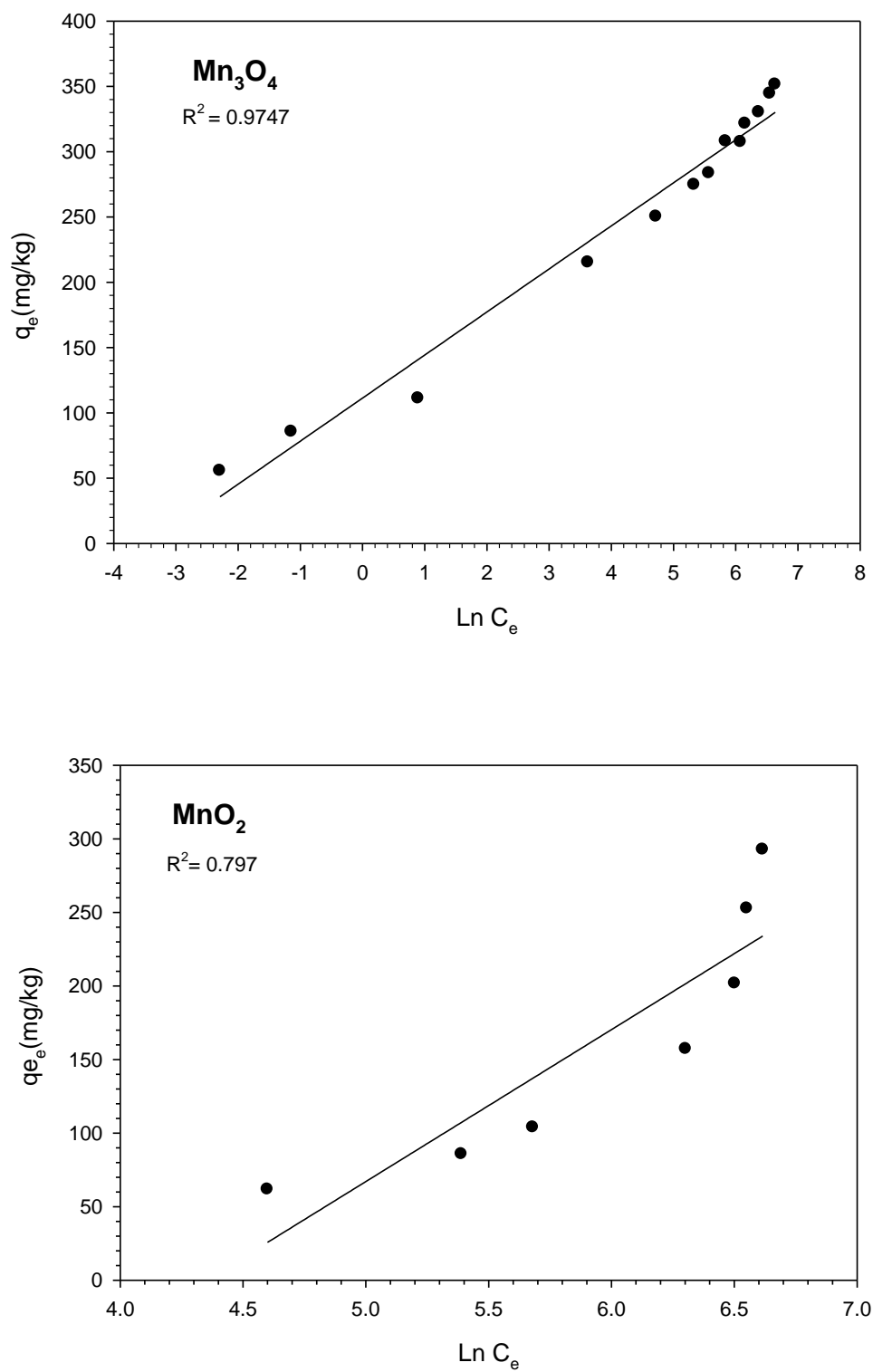
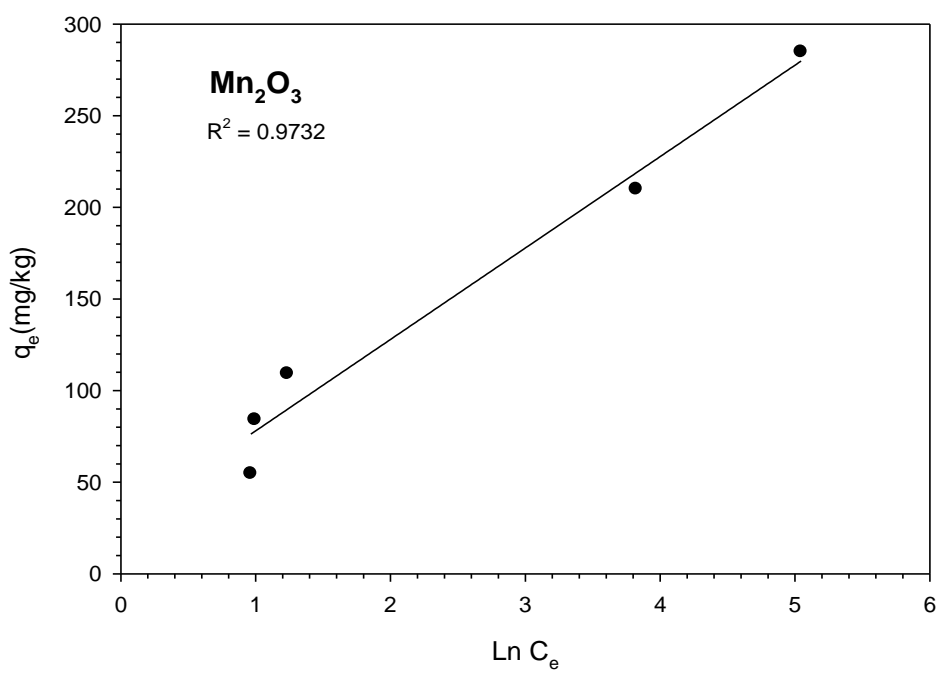
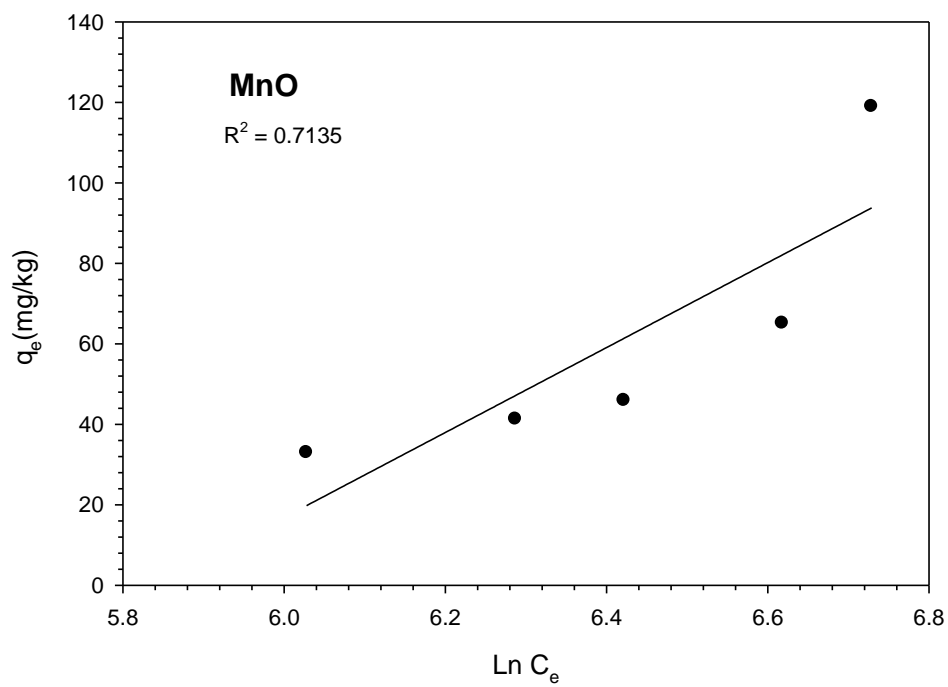


Fig.25. Temkin isotherm models for As(V) adsorption onto the sorbents in DI solution



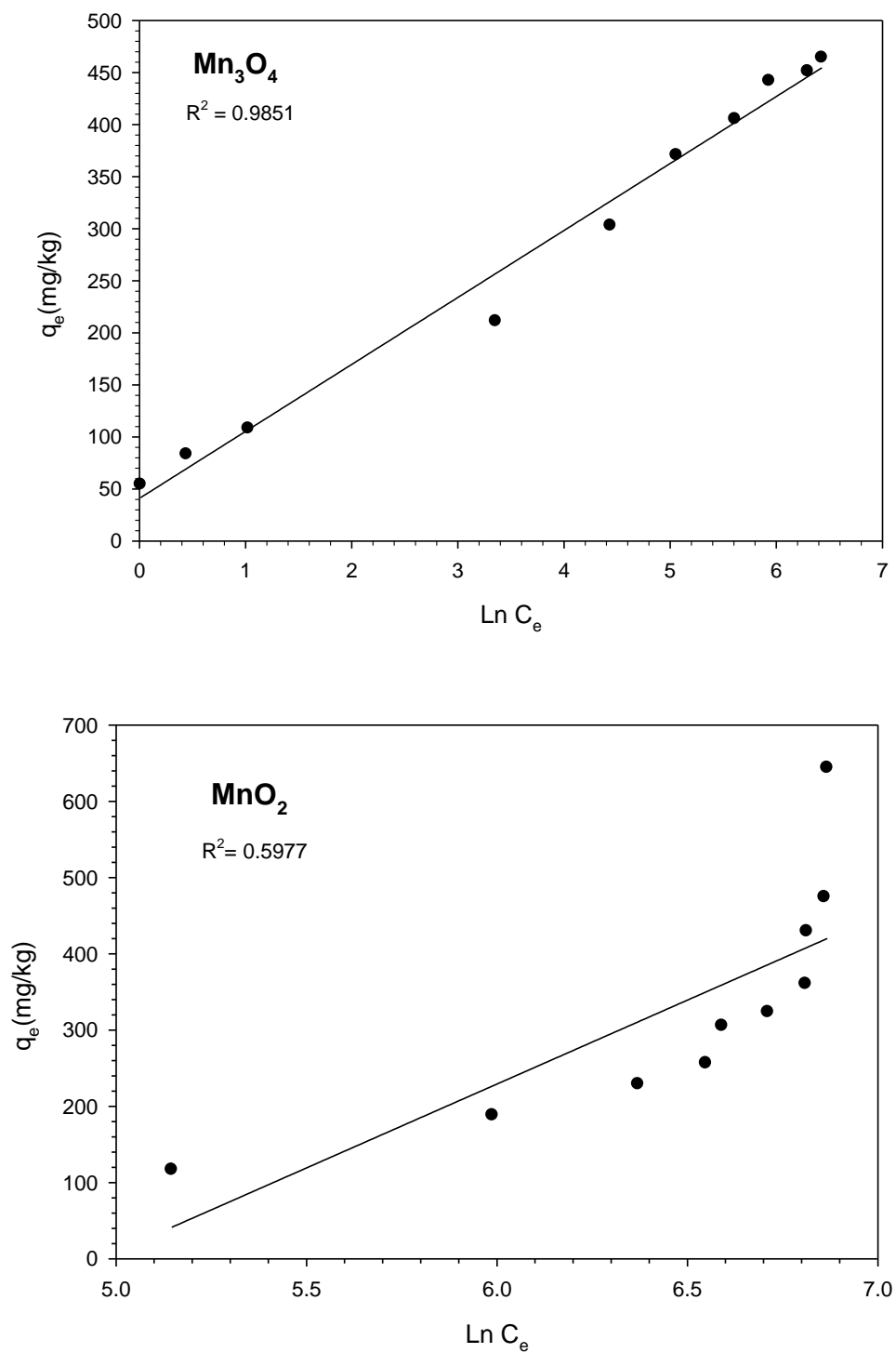
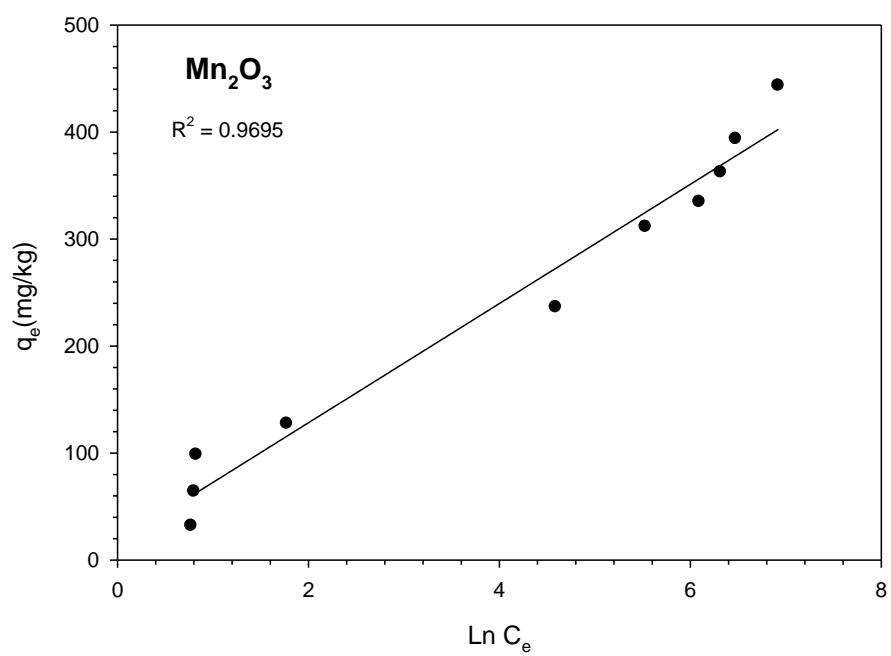
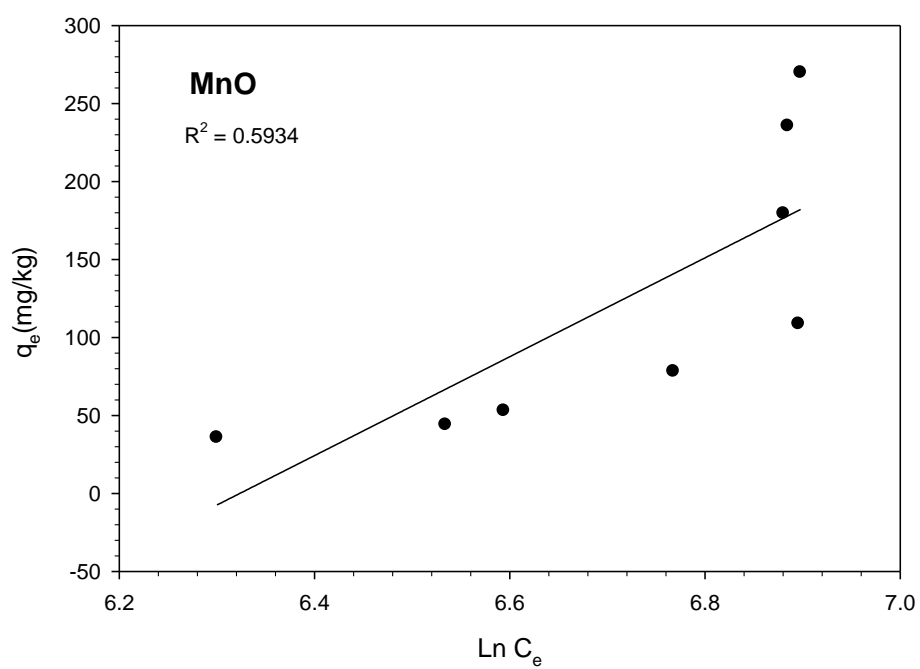


Fig.26. Temkin isotherm models for As(V) adsorption onto the sorbents in 2.5Mm HCO_3^- solution



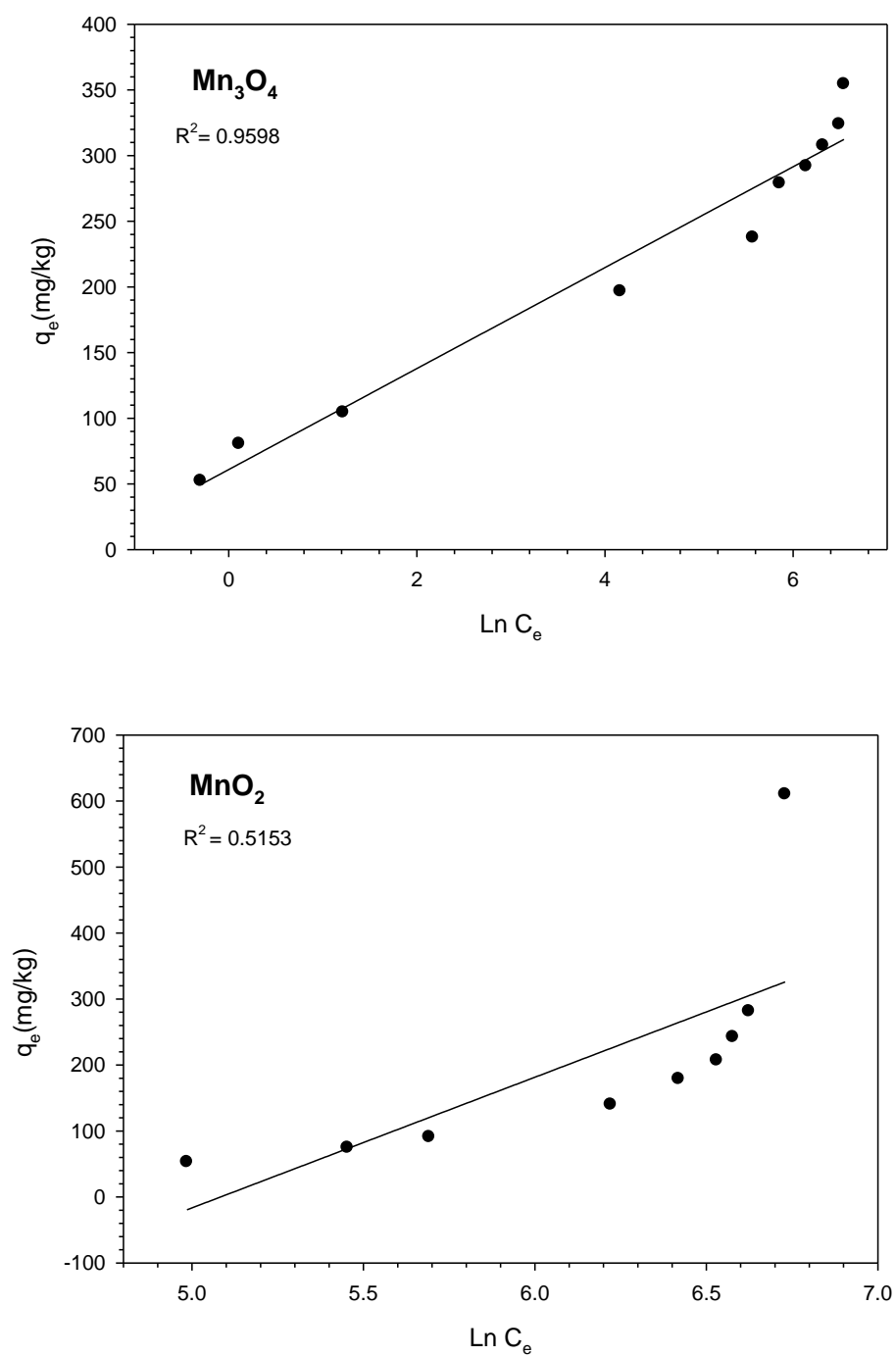


Fig.27. Temkin isotherm models for As(V) adsorption onto the sorbents in 5.5Mm HCO_3^- solution

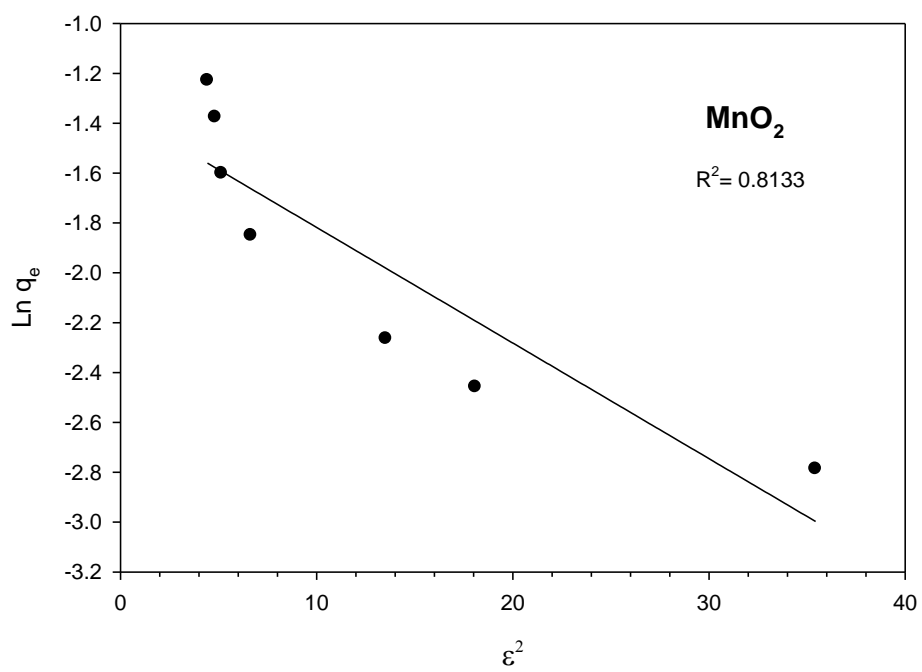
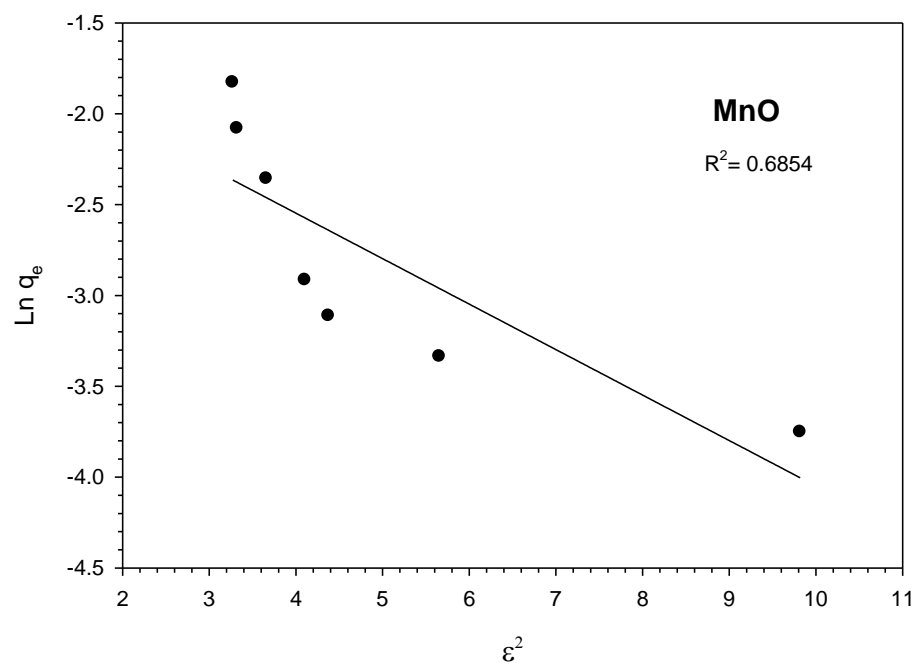
In order to evaluate the nature of the sorption, the adsorption equilibrium data were also fitted with Dubinin–Radushkevich (D-R) adsorption equation. This model envisages the process mechanisms and determines the mean free energy of the sorption which is defined as the free energy change for removing a molecule from its location in the sorption space to an infinite distance in solution from the sorption surface [41]. D-R adsorption isotherm can be expressed as:

$$q_e = q_m \exp(-K_{DR} \varepsilon^2) \quad (9)$$

where q_e is the amount of the adsorbate adsorbed per unit weight of adsorbent (mg/kg), ε (Polanyi potential) is $RT \ln(1 + 1/C_e)$, C_e is the equilibrium concentration of adsorbate in aqueous solution (mg/L), q_m is the adsorption capacity (mg/kg), K_{DR} is a constant related to adsorption energy (mol². kJ²)⁻¹, and R and T are the gas constant and temperature (K), respectively. The linearized form of the D-R equation is expressed as follow:

$$\ln q_e = \ln q_m - K_{DR} E^2 \quad (10)$$

q_m and K can be determined from the intercept and slope of the plot $\ln q_e$ versus ε^2 , respectively as shown in Fig 28-30.



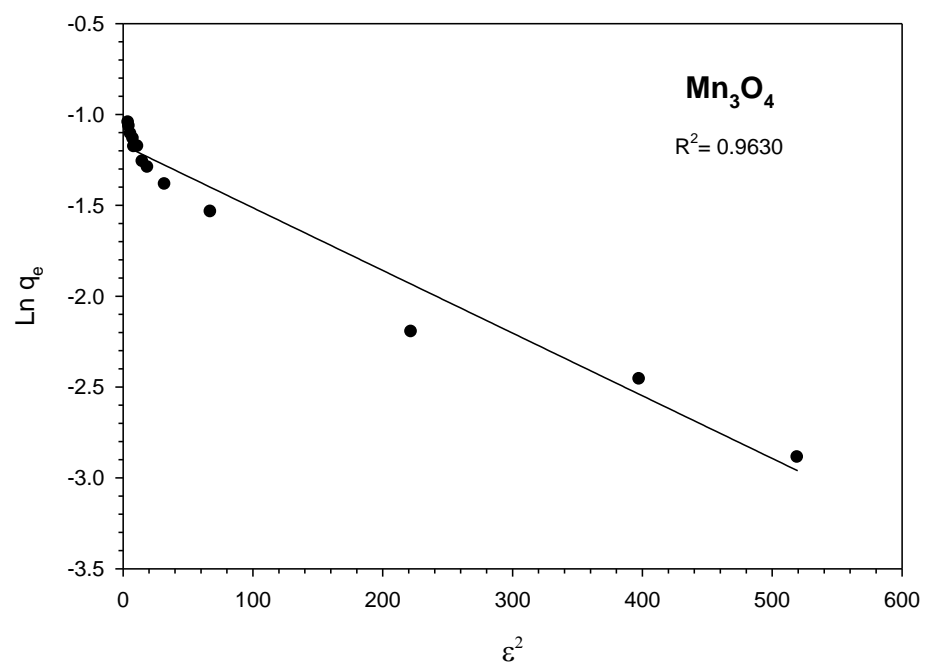
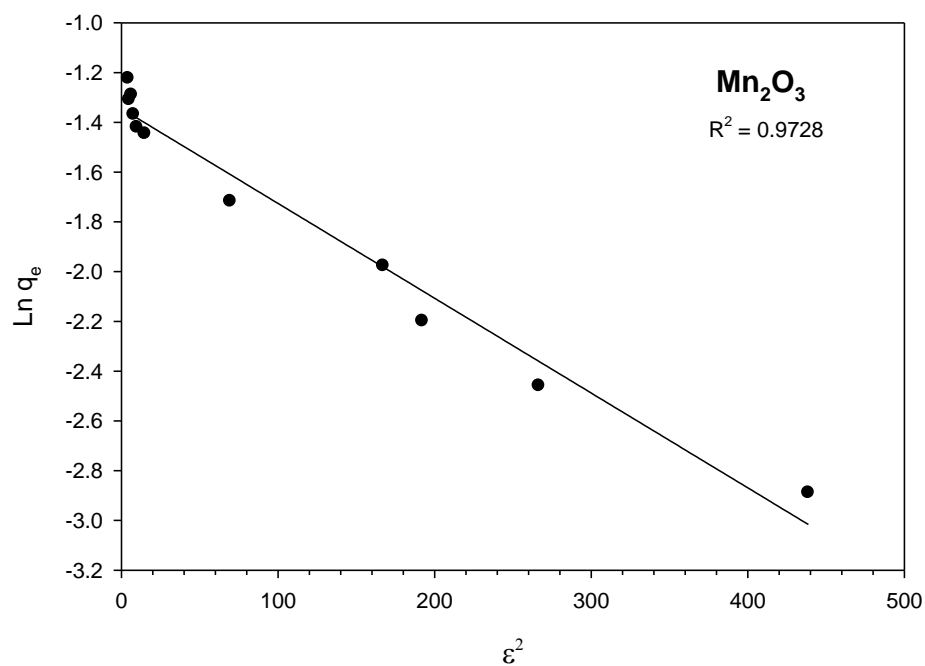
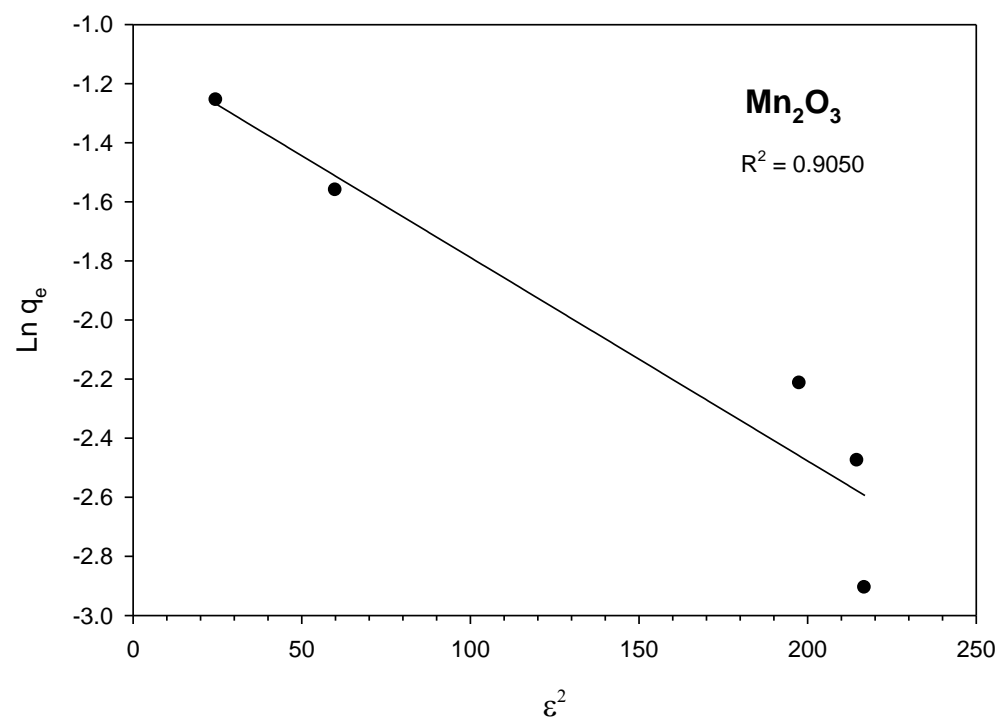
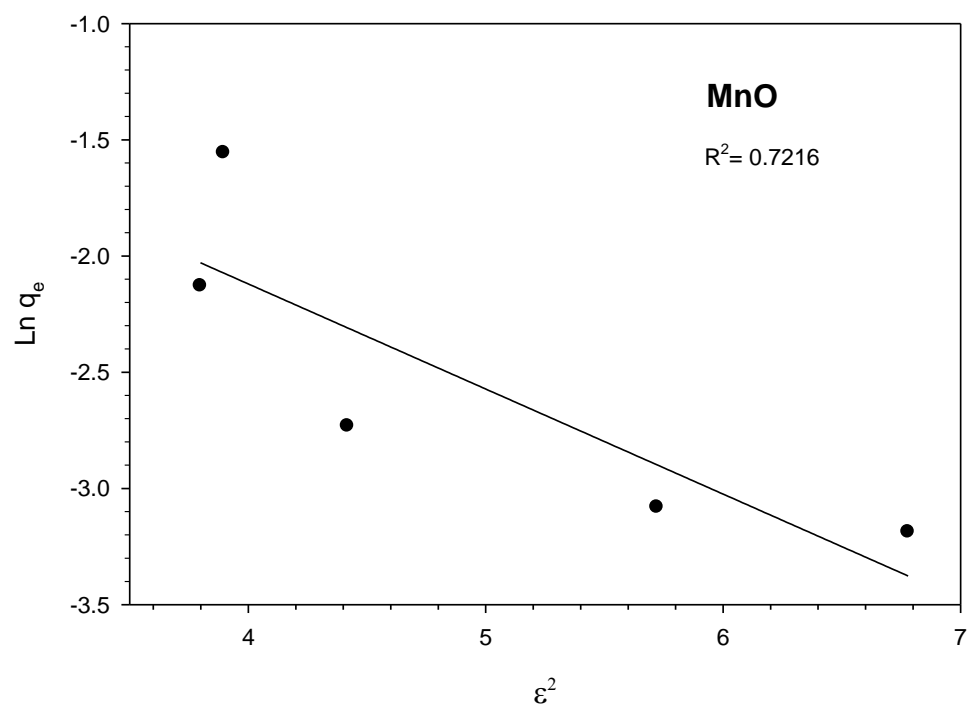


Fig.28. D-R isotherm models for As(V) adsorption onto the sorbents in DI solution



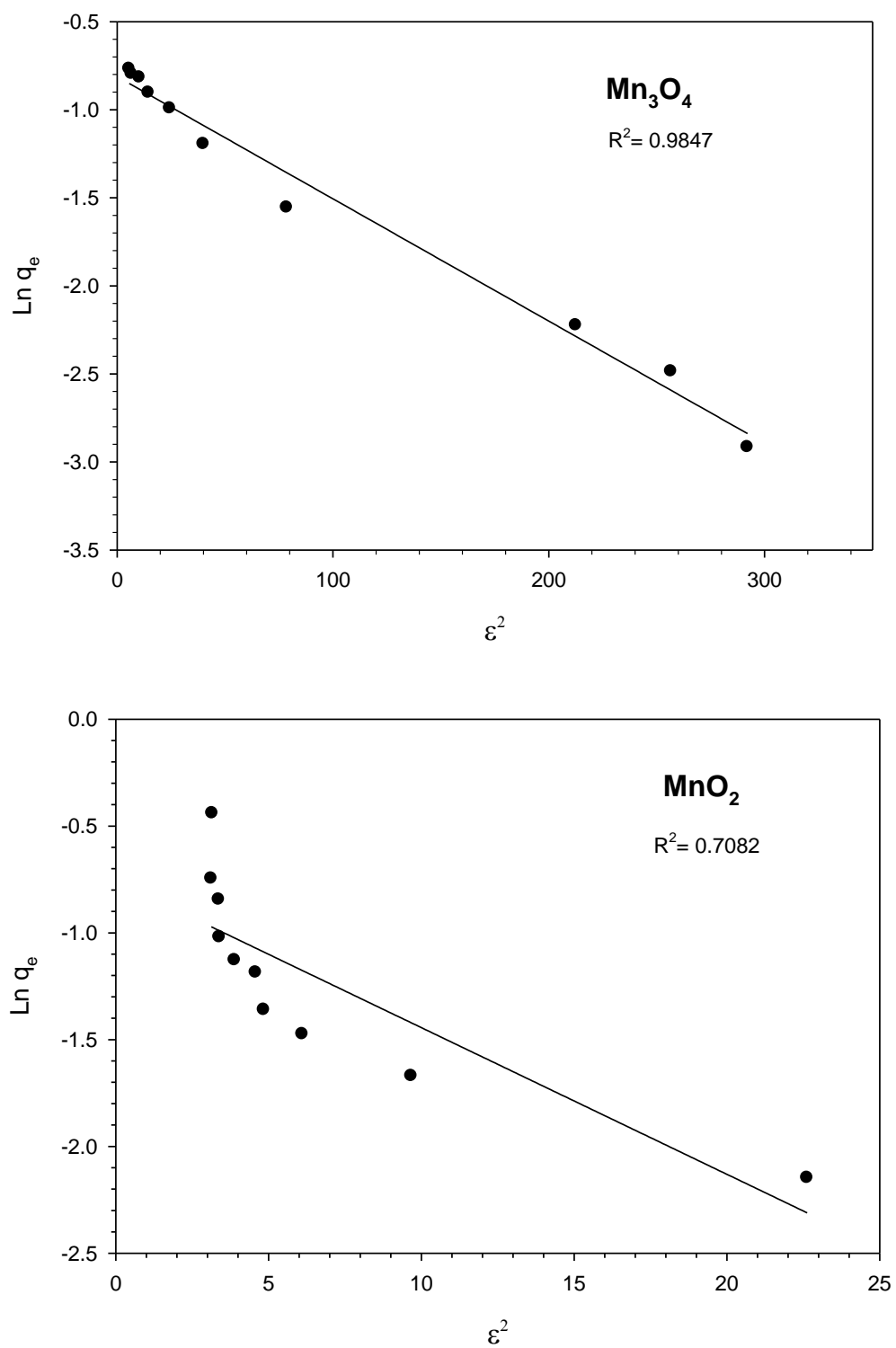
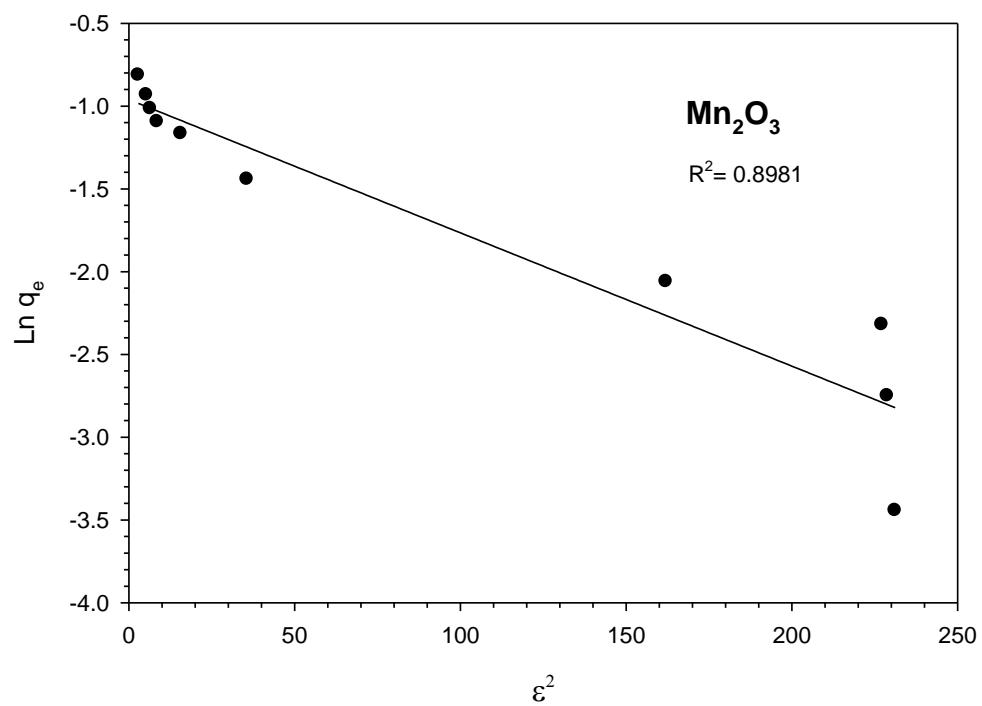
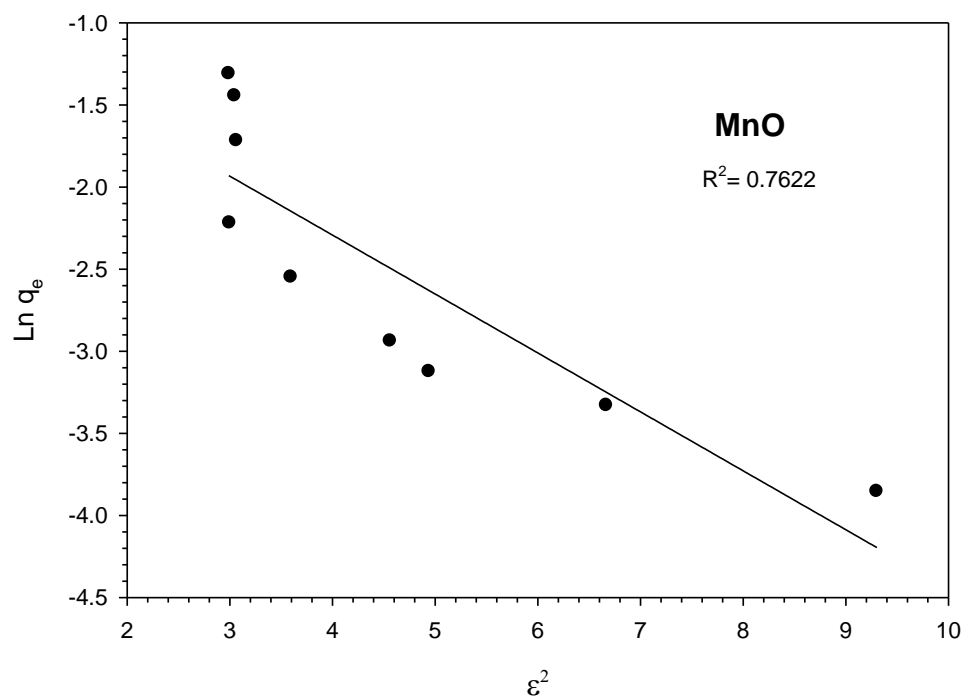


Fig.29. D-R isotherm models for As(V) adsorption onto the sorbents in 2.5Mm HCO_3^- solution



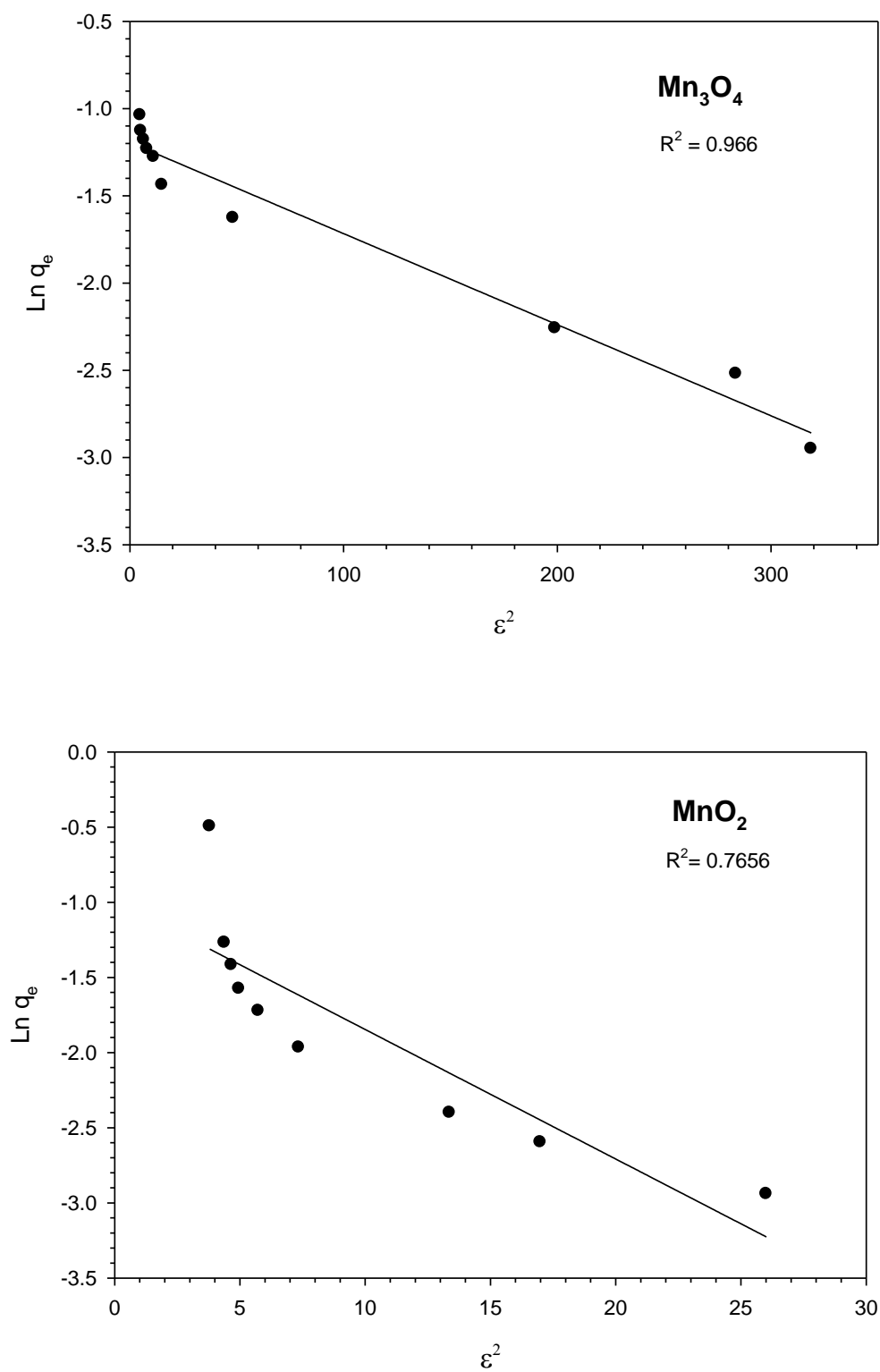


Fig.30. D-R isotherm models for As(V) adsorption onto the sorbents in 5.5Mm HCO_3^- solution

The type of adsorption such as physisorption or chemisorption can be determined by calculating the mean free energy (E) in the system using the following equation: [41]:

$$E = \frac{1}{\sqrt{(2K_{DR})}} \quad (11)$$

where R, T, and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively. If the magnitude of E is less than 8 kJ/mol the sorption process is of physical sorption; if E is in the range of 8 to 16 kJ /mol the sorption is supposed to proceed via chemisorption. The adsorption parameters obtained from the isotherm plots are listed in Table 4-6.

Table 4. Adsorption parameters for arsenic (V) adsorption in DI solution

| | Langmuir | | | | Freundlich | | | Temkin | | | D-R | |
|--------------------------------|----------|--------|--------|--------|--------------|--------|--------|--------------|-------------|--------|-------|--------|
| | q_m | K_L | R_L | R^2 | K_F | $1/n$ | R^2 | $A(L/\mu g)$ | $b(kJ/mol)$ | R^2 | E | R^2 |
| MnO | - | - | - | - | 9.08 E-05 | 2.0408 | 0.7807 | 0.0025 | 0.0193 | 0.5793 | 1.41 | 0.6854 |
| Mn ₂ O ₃ | 277.78 | 0.0571 | 0.0155 | 0.9913 | 84.06 | 0.1866 | 0.9779 | 19.77 | 11.61 | 0.9819 | 11.43 | 0.9728 |
| Mn ₃ O ₄ | 344.83 | 0.0366 | 0.0240 | 0.9922 | 96.50 | 0.1963 | 0.9923 | 29.27 | 13.306 | 0.9747 | 12.13 | 0.963 |
| MnO ₂ | - | - | - | - | 1.75 | 0.7410 | 0.9286 | 0.0129 | 0.0240 | 0.7970 | 3.28 | 0.8133 |

Table 5. Adsorption parameters for As(V) adsorption in 2.5Mm HCO_3^- solution

| | Langmuir | | | | Freundlich | | | Temkin | | | D-R | |
|-------------------------|----------|--------|--------|--------|------------|--------|--------|------------------|--------------------|--------|------|--------|
| | q_m | K_L | R_L | R^2 | K_F | $1/n$ | R^2 | $A(\text{L/ug})$ | $b(\text{kJ/mol})$ | R^2 | E | R^2 |
| MnO | - | - | - | - | 1.224 E-07 | 3.0956 | 0.7517 | 0.0029 | 0.0234 | 0.7135 | 1.05 | 0.7216 |
| Mn_2O_3 | 303.03 | 0.0948 | 0.0107 | 0.9930 | 55.57 | 0.3344 | 0.8916 | 1.76 | 0.0497 | 0.9732 | 8.51 | 0.9050 |
| Mn_3O_4 | 476.19 | 0.0389 | 0.0232 | 0.9952 | 68.66 | 0.3144 | 0.9787 | 1.89 | 0.0385 | 0.9851 | 8.51 | 0.9747 |
| MnO_2 | - | - | - | - | 1.39 | 0.831 | 0.8335 | 0.007 | 0.0113 | 0.5977 | 2.69 | 0.7082 |

Table 6. Adsorption parameters for As(V) adsorption in 5.5Mm HCO_3^- solution

| | Langmuir | | | | Freundlich | | | Temkin | | | D-R | |
|-------------------------|----------|--------|--------|--------|------------|--------|--------|------------------|--------------------|--------|------|--------|
| | q_m | K_L | R_L | R^2 | K_F | $1/n$ | R^2 | $A(\text{L/ug})$ | $b(\text{kJ/mol})$ | R^2 | E | R^2 |
| MnO | - | - | - | - | 7.08 E-08 | 3.131 | 0.793 | 0.0018 | 0.0078 | 0.5934 | 2.47 | 0.7622 |
| Mn_2O_3 | 434.78 | 0.0202 | 0.0407 | 0.9796 | 50.47 | 0.3197 | 0.8887 | 1.35 | 0.0444 | 0.9695 | 7.86 | 0.8981 |
| Mn_3O_4 | 333.33 | 0.0293 | 0.0316 | 0.9794 | 69.2761 | 0.2386 | 0.9774 | 4.88 | 0.0645 | 0.9598 | 9.8 | 0.9660 |
| MnO_2 | - | - | - | - | 0.6175 | 0.9129 | 0.8787 | 0.0062 | 0.0125 | 0.5153 | 2.41 | 0.7656 |

Freundlich values of $1/n$ show the favorability of adsorption of As(V) onto Mn_2O_3 , Mn_3O_4 and MnO_2 . The adsorption capacity of MnO was much lower than the other sorbents indicating that MnO doesn't have favorable affinity to As(V) as other sorbents. The high $1/n$ value for MnO in all three solutions also confirmed that unfavorable adsorption of arsenate onto MnO. These results are in good agreement with the results obtained from Fig.9-11. As it can be seen from the Table 4-6, the isotherm models for the As(V) adsorption onto MnO didn't fit the equilibrium data well. The general arsenate adsorption capacity of the manganese oxides was in the order of $Mn_3O_4 > Mn_2O_3 > MnO_2 > MnO$.

The K_L constant in Langmuir isotherm generally shows that the adsorbate affinity to bind with adsorbent in the solution. The K_L values resulted from Langmuir isotherm model in this study showed that the solution with high alkalinity (5.5mM HCO_3) decreased the As(V) affinity to bind with adsorbents. Tan et.al. [42] proposed a dimensionless constant separation, R_L , obtained from Langmuir isotherm to predict whether the adsorption process is favorable or unfavorable. The R_L can be written as:

$$R_L = \frac{1}{1 + K_L C_0}$$

where C_0 is the initial As(V) concentration($\mu g/L$) and K_L is the Langmuir constant($L/\mu g$). The value of R_L between 0 to 1 indicate the favorable type of the system. The R_L values of the As(V) adsorption onto Mn_2O_3 and Mn_3O_4 (Table 3-5) was in the range of 0 to 1 indicating the favorable adsorption system on the applied sorbents.

Temkin adsorption isotherm relatively described the As(V) adsorption data for Mn_2O_3 and Mn_3O_4 which may be due to the linear dependence of heat of adsorption at low or medium coverage. Since b is related to the heat of adsorption, the positive value of the constant $B(B=RT/b)$ for all manganese oxides in DI, 2.5mM HCO_3^- and 5.5mM HCO_3^- solution represents an exothermic process [43]. Based on values of Temkin constant (A), the As(V) adsorption potential for the manganese oxides were as : $\text{Mn}_3\text{O}_4 > \text{Mn}_2\text{O}_3 > \text{MnO}_2 > \text{MnO}$. The adsorption potential of Mn_3O_4 and Mn_2O_3 in DI solution was found to be much higher than in 2.5mM HCO_3^- and 5.5mM HCO_3^- which can be due to the presence of other ions in 2.5mM HCO_3^- and 5.5mM HCO_3^- solutions which can compete with arsenic ions to adsorb onto the limited activate site on the adsorbents' surface.

In order to evaluate the nature of the sorption, the adsorption equilibrium data were also fitted with Dubinin–Radushkevich (D-R) adsorption equation. The mean free energy of As(V) adsorption onto Mn_3O_4 and Mn_2O_3 (obtained from the D-R adsorption equation) was found to be more than 8 kJ/mol indicating that chemisorption governs the adsorption of arsenate onto the surface of Mn_3O_4 and Mn_2O_3 . The low values of mean free energy (<8 kJ/mol) of As(V) adsorption onto MnO_2 and MnO is indicative of physisorption nature of arsenate by adsorption process by MnO_2 and MnO .

3.6. General Comparison of Different Manganese Oxide Sorbents in Solutions with Different Ionic Background

The arsenic adsorption capacity of all manganese oxides at the arsenic standard level ($10\text{ }\mu\text{g/L}$) was compared in three different solutions with different ionic background. The results are shown

in Fig.31. The results confirmed the higher arsenic removal efficiency of Mn_3O_4 and Mn_2O_3 versus MnO_2 and MnO in DI, 2.5mM HCO_3^- and 5.5mM HCO_3^- solutions. The adsorption capacity of the sorbents decreased by presence of other ions in the solution and increasing the concentration of bicarbonate. The lower uptake of arsenate in 2.5mM HCO_3^- versus DI water can be due to the higher pH of the solution (Table 2) and the competing effect of other ions specially bicarbonate on the limited active sites on the surface of the sorbents. The arsenic removal efficiency decreased even more by increasing the concentration of bicarbonate to 5.5 mM. Since the pH does not change significantly by increasing the bicarbonate concentration from 2.5 mM to 5.5 mM (Table 2), the lower arsenic removal in 5.5mM HCO_3^- might be due to just the competing effect of bicarbonate anions with the arsenate anions causing the lower adsorption of arsenate onto the sorbent.

The adsorption capacity of the sorbents was also compared considering their surface area (Fig.32). As seen in Fig.32, Mn_2O_3 was able to uptake more arsenic per surface area than Mn_3O_4 . Also the arsenate adsorption capacity of MnO per its surface area was found to be higher than MnO_2 .

In general the results showed that the arsenic removal efficiency of manganese oxides with the oxidation states of 3 (Mn^{3+}) or the combination of oxidation number of 2 and 3 (Mn^{2+} , Mn^{3+}) were able to remove higher amount of arsenic versus the other manganese oxides with the oxidation number of 2+ (Mn^{2+}) or 4+ (Mn^{4+}). In the following chapter, the removal ability of Mn_3O_4 in adsorption of arsenate and the removal ability of Mn_2O_3 to remove As(V) and As(III) will be studied in detail and the effect of different parameters like contact time, sorbent dosage, pH ,co-existing ions and sorbent reusing on the arsenic removal efficiency will be investigated.

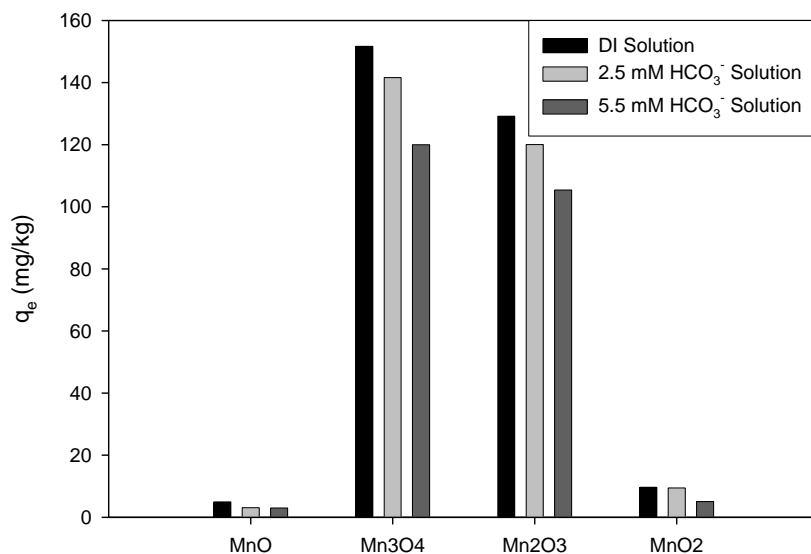


Fig 31. General comparison of arsenic adsorption capacity of different manganese oxides in solutions with different ionic background

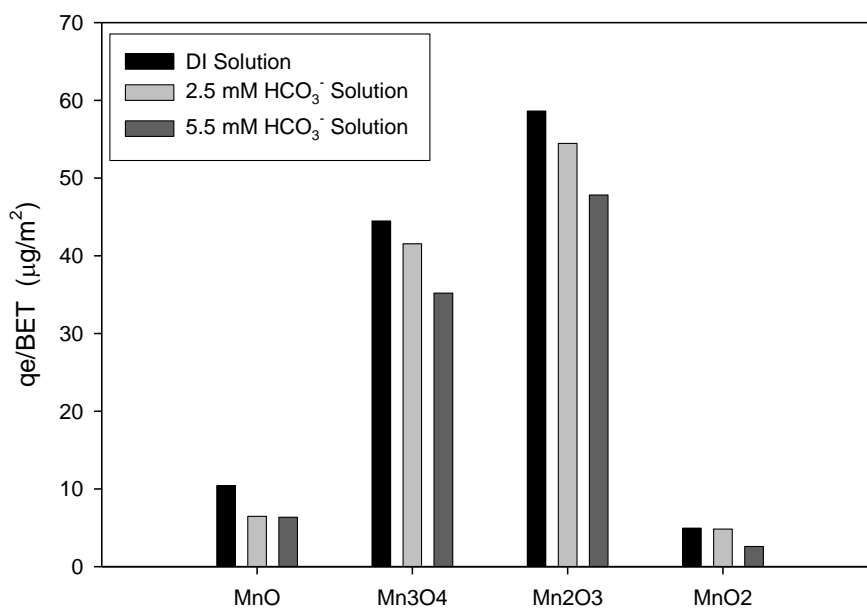


Fig 32. General comparison of arsenic adsorption capacity of different manganese oxides in solutions with different ionic background considering their BET surface area.

4. CONCLUSION

The arsenate removal efficiency of different manganese oxides (MnO, Mn₃O₄, Mn₂O₃ and MnO₂) with different oxidation states were compared. The XRD patterns of the sorbents confirmed that the applied manganese oxide sorbents in this study were pure adsorbents. The BET surface area of the sorbents was in this order: Mn₃O₄ > Mn₂O₃ > MnO₂ > MnO. From the adsorbents surface charge analysis, the PZC of MnO, Mn₃O₄, Mn₂O₃ and MnO₂ was obtained at pH of 5.2, 7.41, 7.38 and 5.35, respectively indicated that the Mn₂O₃ and Mn₃O₄ maintained positive zeta potential values over the most range of pH studied.

The effect of adsorbent dosage on the removal of As(V) from solutions with different ionic backgrounds including DI solution, 2.5 mM HCO₃⁻ and 5.5 mM HCO₃⁻ solution was evaluated for four different types of manganese oxides. The Mn₂O₃ and Mn₃O₄ showed promising performance in removing the As(V) from all three solutions even with the low level of adsorbent dosage while MnO₂ and MnO worked well just with the high sorbent dosage. A 10 g/L of Mn₂O₃ and Mn₃O₄ was found to be needed in order to meet the EPA standard level for arsenic in drinking water while this dosage was 10 times higher for MnO and MnO₂ adsorbents.

The effect of contact time on the As(V) removal efficiency onto manganese oxides showed that the equilibrium can be achieved at less than 10 hr for all manganese oxides. The kinetics modeling results suggested that the adsorption process was the pseudo-second order reaction where a higher equilibrium As(V) adsorption capacity was obtained for Mn₂O₃ and Mn₃O₄ versus the other manganese oxides in all time increments. Also, the As(V) removal by Mn₂O₃ was found to be faster than Mn₃O₄. The results from intraparticle diffusion model indicated that a combination of

both the external and internal mass transfer were the rate limiting step in arsenic adsorption process for all manganese oxides.

The abilities of four common isotherms, Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D-R) were investigated to model the arsenate adsorption equilibrium data at 25 °C using an initial arsenate concentration of 1 mg/L in DI, 2.5mM HCO_3^- and 5.5mM HCO_3^- solution. The results showed that the general arsenate adsorption capacity of the manganese oxides was in the order of $\text{Mn}_3\text{O}_4 > \text{Mn}_2\text{O}_3 > \text{MnO}_2 > \text{MnO}$. The results of Langmuir and Freundlich model showed the favorable adsorption system on Mn_3O_4 and Mn_2O_3 . According to the results obtained from Temkin model, the As(V) adsorption onto the sorbents in DI, 2.5mM HCO_3^- and 5.5mM HCO_3^- solution was found to be an exothermic process. Also, the As(V) adsorption potential for Mn_3O_4 and Mn_2O_3 was higher than MnO_2 and MnO . The mean free energy of As(V) adsorption onto Mn_3O_4 and Mn_2O_3 , obtained from the Dubinin–Radushkevich (D-R) adsorption model, indicated that chemisorption governs the adsorption of arsenate onto the surface of Mn_3O_4 and Mn_2O_3 . The low values of mean free energy (< 8 kJ/mol) of As(V) adsorption onto MnO_2 and MnO was indicative of physisorption nature of arsenate by adsorption process by MnO_2 and MnO .

The arsenic adsorption capacity of all manganese oxides at the arsenic standard level (10 $\mu\text{g/L}$) was compared in three different solutions with different ionic background. The results confirmed the higher arsenic removal efficiency of Mn_3O_4 and Mn_2O_3 versus MnO_2 and MnO in DI, 2.5mM HCO_3^- and 5.5mM HCO_3^- solutions. The adsorption capacity of the sorbents decreased in 2.5mM HCO_3^- and 5.5mM HCO_3^- solutions due to the higher pH of the solutions and the competing effect of other ions specially bicarbonate on the limited active sites on the surface of the sorbents.

In general the results showed that the arsenic removal efficiency of manganese oxides with the oxidation states of 3 (Mn^{3+}) or the combination of oxidation number of 2 and 3 (Mn^{2+} , Mn^{3+}) were able to remove higher amount of arsenic versus the other manganese oxides with the oxidation number of 2+ (Mn^{2+}) or 4+ (Mn^{4+}).

5. REFERENCES

- [1] Zhao,Z., Jia,Y., Xu,L., Zhao,S : Adsorption and heterogeneous oxidation of As(III) on ferrihydrite. *Water Res*, 45 (19):6496–6504, 2011.
- [2] Kapaj,S.,Peterson,H.,Liber,K. and Bhattacharya,P.: Human Health Effects From Chronic Arsenic Poisoning—A Review, *Journal of environmental science and health part A*,41:2399-2428, 2006.
- [3] World Health Organization: *Guidelines for Drinking-Water Quality*,1: 491, 2008.
- [4] USEPA Fact Sheet: Drinking Water Standard for Arsenic, 2001. http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations_factsheet.cfm.
- [5] Mohan, D., Pittman,C.U.Jr.: Arsenic removal from water/wastewater using adsorbents—A critical review. *Journal of Hazardous Materials*, 142: 1–53, 2007.
- [6] Harvey,C.F., Swartz,C.H., Badruzzaman,A.B.M., Keon-Blute,N.,Yu,W.,Ali,M.A., Jay,J.,Beckie,R.,Niedan,V.,Brabander,D.,Oates,P.M.,Ashfaq,K.N.,Islam,S.,Hemond,H.F. and Ahmed, M.F.: Arsenic mobility and groundwater extraction in Bangladesh, *Science*, 298:1602–1606, 2002.
- [7] Lenoble,V., Laclautre,C., Serpaud,B., Deluchat,V.and Bollinger,J-C.: As(V) retention and As(III) simultaneous oxidation and removal on a MnO_2 -loaded polystyrene resin. *Sci Total Environ*, 326: 197–207, 2004.
- [8] Deschamps,E., Ciminelli,V.S.T., Höll,W.H. :Removal of As(III) and As(V) from water using a natural Fe and Mn enriched sample, *Water Res* ,39:5212–5220, 2005.

- [9] Chakravarty,S., Dureja,V., Bhattacharya,G., Maity,S. and Bhattacharjee,S.: Removal of arsenic from ground water using low cost ferruginous manganese ore, *Water Res*, 36 :625–632, 2002.
- [10] Mohammad,S.: Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations, *Water Air Soil Poll.* 93: 117–136, 1997.
- [11] Clifford, D.A. and Lin, C.C.: Ion Exchange, Activated Alumina, and Membrane Processes for Arsenic Removal from Groundwater, Proceedings of the 45 th Annual Environmental Engineering Conference, University of Kansas, February 19, 1995.
- [12] Matschullat,J.: Arsenic in the geosphere-a review. *Sci Total Environ*, 249:297-312, 2000.
- [13] Smedley, PL. and Kinniburgh, DG.: A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem*, 17:517-568, 2002.
- [14] Zhao,X. Holl,W.H.:Elimination of cadmium trace contamination from drinking water.*water Res.*36 :851-858,2002.
- [15] Wang,Y, Reardon, EJ.: A sideriteylimestone reactor to remove arsenic and cadmium from wastewaters. *Appl Geochem*, 16:1241 –1249, 2001.
- [16] Meng, X., Korfiatis, GP. Bang, S. and Bang, KW. Combined effects of anions on arsenic removal by iron hydroxides. *Toxicol Lett*, 133: 103 –111, 2002.
- [17] Sancha,AM, O’Ryan,R, Perez,O. The removal of arsenic from drinking water and associated costs: the Chilean case. Interdisciplinary perspectives on drinking water risk assessment and management. Proceedings of the Santiago Symposium, IAHS publ.260 2000:17–25. 1998.
- [18] Clifford,D. and Lin,CC.: Arsenic (III) and arsenic (V) removal from drinking water in San Ysidro, New Mexico, EPAy 600yS2-91y011, US EPA, Cincinnati 199.
- [19] Pattanayak,J, Mondal,K, Mathew,S and Lalvani,SB.:A parametric evaluation of the removal of As(V) and As(III) by carbonbased adsorbents. *Carbon*, 38: 589 –596, 2000.
- [20] Benjamin,M.M.,Sletten,R.S.,Bailey, R.P. and Bennett,T.:Sorption and filtration of metals using iron-oxide-coated sand, *Water Res.* 30 (11) :2609–2620, 1996.
- [21] Dambies, L.,Vincent, T. and Guibal, E.:Treatment of arsenic-containing solutions using chitosan derivatives: uptake mechanism and sorption performance, *Water Res.* 36 :3699–3710, 2002.
- [22] Dias,A.,Sa,RG.,Spitale,MC,Athayde,M. and Ciminelli,VST.: Microwave-hydrothermal synthesis of nanostructured Nabirnessites and ph ase transformation by arsenic(III) oxidation. *Materials Research Bulletin*, 43:1528-1538, 2008.
- [23] Oscarson,D.W. ,Huang,P.M. ,Defosse,C. and Herbillon,A.: Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature*, 291:50 – 51, 1981.

- [24] Manning, B.A., Fendorf, S.E., Bostick, B. and Suarez, D.L.: Arsenic(III) oxidation and As(V) adsorption reactions on synthetic birnessite, *Environ. Sci. Technol.*, 36 (5) :976–981, 2002.
- [25] Ouvreard, S., Simonnot, M.O. and Sardin, M.: Reactive behavior of natural manganese oxides toward the adsorption of phosphate and arsenate, *Ind. Eng. Chem. Res.*, 41: 2785–2791, 2002.
- [26] Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., Chaalal, O and Islam, M.R.: Arsenic removal in drinking water—impacts and novel removal technologies, *Energy Sources*, 27:209–219, 2005.
- [27] Maliyekkal, S.M., Philip, L. and Pradeep, T.: As(III) removal from drinking water using manganese oxide-coated-alumina: Performance evaluation and mechanistic details of surface binding, *Chemical Engineering Journal*, 153 (1-3):101-107, 2009.
- [28] Deschamps, E., Ciminelli, V.S.T., Weidler, P.G., Ramos, A.Y.: Arsenic sorption onto soils enriched with manganese and iron mineral. *Clays clay Miner.*, 51: 197-204, 2003.
- [29] Wu, K., Liu, R., Liu, H., Zhao, X., and Qu, J.: Arsenic(III,V) Adsorption on Iron-Oxide-Coated Manganese Sand and Quartz Sand: Comparison of Different Carriers and Adsorption Capacities. *Environmental Engineering Science*, 28(9): 643-651, 2011.
- [30] Zhang, G., Qu, J., Liu, H., Liu, R. and Wu, R.: Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. *Water Res.*, 41:1921-1928. 2007.
- [31] Lakshminathiraj, P., Narasimhan, B.R.V., Prabhakar and Raju, S.G.B.: Adsorption studies of arsenic on Mn-substituted iron oxyhydroxide. *Journal of Colloid and Interface Science*, 304:317–322, (2006).
- [32] USEPA. Technologies and costs for removal of arsenic from drinking water. US Environmental Protection Agency, EPA/815/R-00/028, 2000.
- [33] Mondal, P., Majumder, C. and Mohanty, B.: Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated ground water by Fe³⁺ impregnated activated carbon. *Journal of Hazardous Materials*, 150(3): 695–702. 2008.
- [34] Ho, Y.S. and McKay, G.: The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *Can. J. Chem. Eng.*, 76:822–827, 1998.
- [35] Ho, Y.S. and McKay, G.: Pseudo-second order model for sorption processes. *Process Biochem.*, 34:451–465, 1999.
- [36] Ho, Y.S.: Review of second-order models for adsorption systems. *J. Hazard. Mater.*, B136:681–689, 2006.
- [37] Cheunga, W.H., Sze Tob, Y.S., McKay, G.: Intraparticle diffusion processes during acid dye adsorption onto chitosan. *Bioresource Technology*, 98(15):2897–2904, 2007.

- [38] Langmuir, I.: The constitution and fundamental properties of solids and liquids, *J. Amer. Chem. Soc.* 38:2221-2295, 1916.
- [39] Freundlich, H.M.F.: Über die adsorption in losungen. *Z. Phys. Chem.* 57A:385-470, 1906.
- [40] Temkin, M.J. and Pyzhev, V.: Recent modifications to Langmuir isotherms, *Acta. Physiochim*, URSS 12:217–222, 1940.
- [41] Dubinin, M.M., Radushkevich, L.V.: Equation of the characteristic curve of activated charcoal, *Chem. Zentr*, 1:875, 1947.
- [42] Tan, I.A.W, Ahmad, A.L., Hameed, B.H.: Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon, *Journal of Hazardous Materials. J. Hazard. Mater*, 164: 473-482, 2009.
- [43] Karim, A.H., Jalil, A.A., Triwahyono, S., Sidik, S.M., Kamarudin, N.H.N., Jusoh, R. Jusoh, N.W.C. and Hameed, B.H: Amino modified mesostructured silica nanoparticles for efficient adsorption of methylene blue. *Journal of Colloid and Interface Science*, 386 (1):307-314, 2012.

Chapter (III)

III. ADSORPTION AND REMOVAL OF ARSENIC(V) USING CRYSTALLINE MANGANESE (II,III) OXIDE: KINETICS, EQUILIBRIUM, EFFECT OF pH AND IONIC STRENGTH

1. INTRODUCTION

Arsenic is a naturally occurring metalloid that is present throughout the environment in water, soil, air and food. [1] The consumption of high levels of arsenic concentration by humans has been linked to the cancer of the skin, bladder, lung and kidney and the neurological and cardiovascular systems. [2] Considering the severe effect of arsenic on human health and to limit the exposure to arsenic, the World Health Organization (WHO) as well as the U.S. Environmental Protection Agency (EPA) recommend a maximum contaminant level (MCL) of arsenic in drinking water of 10 µg/L. [3,4] Many countries are affected by high levels of arsenic in surface water and ground water. Contamination through soil leaching, industrial wastewaters, hydrothermal activities and mining are the main source of contamination. [5,6] The presence of various concentrations of arsenic within the shallow zones of ground water has been reported in many countries. Concentration of arsenic in some regions in Bangladesh is as high as 1000 µg/L. [7]

Arsenic may exist in water in different oxidation states (+5,+3,0,-3) [8] but As(III) [arsenite] and As(V) [arsenate] are the predominant valence states of inorganic arsenic species. As(III), the most toxic form, exists as an uncharged species (H_3AsO_3) or anionic species (H_2AsO_3^-) in a moderately reducing environment, whereas As(V) species are H_2AsO_4^- or HAsO_4^{2-} anions in natural waters.

[9] In natural surface waters, As(V) is the dominant species while natural ground waters contain mainly As(III) due to the dominant reducing conditions. [10]

The technologies employed to remove arsenic from water should be simple, effective, selective, and not remove all ions present in water. [11] Several methods have been used for removal of arsenic but they usually suffer from one or more drawbacks, scope of application and limitations.[12] However, adsorption [13] has been recognized as a superior method for removal of arsenic owing to its lower cost, flexibility and simplicity of design, high efficiency, easy handling and high selectivity. Different sorbents have been used as promising media for removal of arsenic from water.[14]

Manganese oxides have been used in mixed-oxide sorbents such as iron-manganese [15] and cerium–manganese [16] or as loaded/substituted material for enhancement of arsenic sorption from aqueous solutions. Manning et al. [17] have suggested that birnessite (MnO_2) used at near neutral pH in drinking water treatment and environmental remediation may play a beneficial role as both an efficient oxidant of As(III) and a sorbent for As(V). A low cost ferruginous manganese ore (FMO) with the major mineral phases of pyrolusite and goethite has been studied for the removal of arsenic from groundwater.[8] The adsorption of arsenate has also been studied by natural manganese oxides by monocomponent column experiments. [18] The maximum arsenate adsorption of $2.23 \mu\text{mol/g}$ was obtained from a solution of 0.67 mM sodium arsenate (50 mg/L arsenic) and 1 mM sodium chloride at pH 7.9. Thirunavukkarasu et al.[19] applied manganese “greensand” in column studies to examine the removal of arsenic in drinking water. A MnO_2 - loaded polystyrene resin (R-MnO_2) has been demonstrated as a strong solid sorbent for arsenic

retention where the R-MnO₂ maximal capacities were 0.7 mmol/g and 0.3 mmol/g towards As(III) and As(V), respectively.[5] Deschamps et al.[20] investigated the adsorption of arsenic onto some soils enriched with manganese and iron. They claimed that the presence of naturally occurring manganese oxides promotes the effective oxidation of As(III) to As(V). Also, the manganese minerals in their study showed a significant uptake of both the As(III) and As(V). Wu et al. [21] showed that using a manganese sand carrier instead of a quartz sand carrier for arsenic adsorption to iron-oxide-coated sand can improve the adsorption capacity of the sorbent. Manganese-substituted iron oxyhydroxide (MIOH) has been used as sorbent for the adsorption of As(III) and As(V) from water. [22]

Manganese oxides affect the mobility and fate of many pollutants in the environment and can easily participate in different redox reactions and strongly adsorb numerous ions.[23] Manganese oxides are widely present around the globe and are available in countries facing arsenic groundwater contamination. The addition of mineral oxides to small volumes of water has been identified by U.S. EPA as a feasible process to remove arsenic from water.[24] In this study, crystalline manganese (II,III) oxide (Mn₃O₄) powder was evaluated as a relatively inexpensive sorbent for removal of As(V). The aim of this study was to investigate the effectiveness of Mn₃O₄ for adsorption and removal of As(V) from water and the effect of different parameters like contact time, sorbent dosage, pH, ionic strength and co-existing ions on the removal of As(V).

2. MATERIALS AND METHODS

2.1. Materials

All chemicals were of analytical reagent grade and no further purification was carried out. All solutions were prepared with de-ionized (DI) water with a resistance greater than 18 M Ω . The manganese (II,III) oxide powder (Mn₃O₄, 97 % purity, density of 4.8 g/mL at 25°C) with an average particle size of less than 325 U.S. mesh (44 μ m) was obtained from Sigma-Aldrich (St. Louis, MO). Sodium arsenate (Na₂HAsO₄·7H₂O, 99% purity, ACS grade) was purchased from Sigma-Aldrich. The other chemicals were obtained from Fisher scientific (Fair Lawn, NJ). The calcium chloride (CaCl₂, 98.8% purity, ACS grade), sodium sulfate (Na₂SO₄, 99.3% purity, ACS grade) and sodium bicarbonate (NaHCO₃, 100 % purity, ACS grade) were used to prepare a synthetic solution representative of natural waters with bicarbonate alkalinity and total hardness considering the effect of solution ionic strength. The stock solution of As(V) was prepared with sodium arsenate in DI water.

2.2. Sorbent characterization

X-ray powder diffraction(XRD) patterns were obtained on a Siemens D5000 with Cu K α radiation, $\lambda=1.5418$ Å, at 40 KV and 30 mA . The pattern were obtained from 15° to 65° 2 θ with a step size of 0.02° 2 θ , counting for 10 s/step to better resolve the peaks . The BET surface area of the Mn₃O₄ was measured with an Accelerated Surface Area and Porosimetry system, ASAP 2010 (Micromeritics Instrument Corporation, Norcross, GA), using nitrogen adsorption/desorption isotherms. The zeta potential of the sorbent was measured by a Zeta-meter system 3.0 (Zeta meter

Inc,VA). A suspension of 100 mg/L Mn_3O_4 in 1mM NaCl solution was prepared. The pH of the samples were adjusted from 3 to 10 using 0.1 M HCl and 0.1 M NaOH solutions.

2.3. Batch Adsorption Experiments

An initial arsenic concentration of 1 mg/L was chosen to determine the adsorption capacity of the sorbent. The experiments were performed with dry sorbent suspensions of different dosages in DI water and the synthetic solution. The synthetic solution was prepared from the stock solution of As(V), and contained 2.5 mM sodium bicarbonate (NaHCO_3), 1 mM calcium chloride (CaCl_2) and 0.5 mM sodium sulfate (Na_2SO_4). The solid sorbent was added to 50 mL of As(V) solution in high density polyethylene (HDPE) bottles. After the addition of sorbent to the bottles, the bottles were shaken in a rotating tumbler at 16 rpm in the dark, and the suspensions were left to equilibrate for 24 hr at 25 °C. After the shaking period, the suspensions were then centrifuged to separate the aqueous phase from the sorbent. The supernatant was filtered with a 0.45 μm cellulose acetate filter and the concentration of arsenic in the filtrate was analyzed.

For the kinetics experiments, 0.25 g of Mn_3O_4 was mixed with 50 mL of a 1 mg/L solution of As(V) at 25 °C. To investigate the effect of the solution pH on the adsorption of As(V), 0.25 g of Mn_3O_4 was added to 50 mL of 1 mg/L solution of As(V). The initial pH of the solution in DI water was adjusted to 2-10 using 0.1 M HCl and 0.1 M NaOH solutions. In order to find the effect of ionic strength and the effect of co-existing ions on the adsorption of arsenic onto Mn_3O_4 , different concentrations of sulfate, phosphate, bicarbonate and calcium were selected to evaluate the uptake of arsenic as function of individual ions added to DI water. The CaCl_2 , Na_2SO_4 , NaHCO_3 and

Na_2HPO_4 were used as sources of calcium, sulfate, bicarbonate and phosphate, respectively. A 50 mL volume of each co-existing ion solution with an initial arsenic concentration of 1 mg/L was mixed with 0.25 g Mn_3O_4 , and the experiments were performed in similar fashion to the batch adsorption tests.

2.4. Analytical Methods

The graphite furnace atomic absorption spectroscopy (GFAAS) with Zeeman background correction was used to determine the arsenic concentration in the adsorption tests. For arsenic analysis, all measurements were carried out using an electrodeless lamp (EDL) at 193.7 nm and the modifier used was palladium-magnesium modifier. The atomization and pre-treatment temperature were 2000 and 1200 °C, respectively. The detection limit of arsenic was estimated to be 1 µg/L. The uptake of arsenic(V) on the sorbents was determined as:

$$q = \frac{(C_0 - C_e)}{m} \times A \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of As(V) in the solution (mg/L), q is the adsorbed As(V) (mg/kg), m is the adsorbent dosage (kg) and A is the solution volume (L).

3. RESULTS AND DISCUSSION

3.1. Characterization of Sorbent

The chemical composition of manganese (II,III) oxide powder was determined by X-ray diffraction (XRD). The XRD pattern of the Mn_3O_4 sorbent is shown in Fig. 1. The XRD pattern revealed good agreement with Mn_3O_4 (JCPDS card No 24-0734). The appearance of the narrow and strong peaks in the XRD pattern of the sorbent was indicative of its crystalline structure. The BET surface area was determined to be $3.41 \text{ m}^2/\text{g}$.

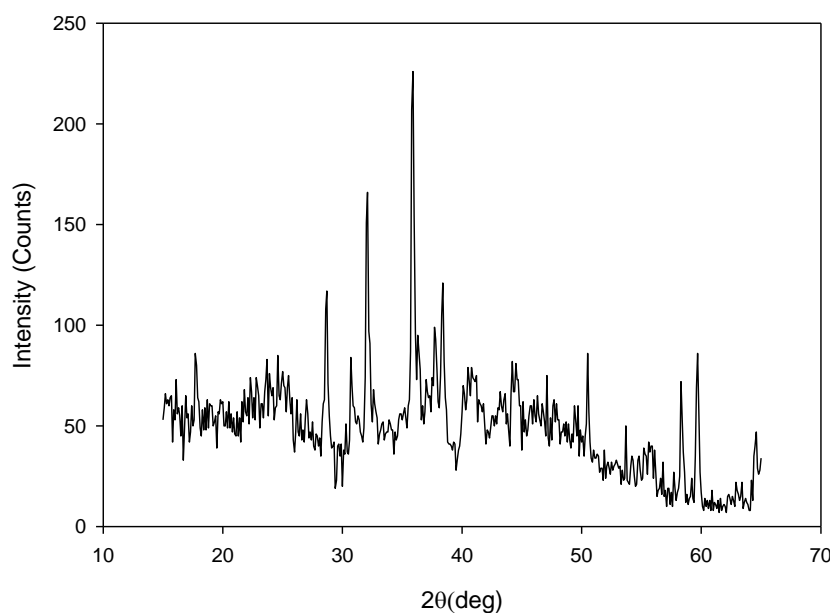


Fig. 1. XRD pattern of the Mn_3O_4

3.2. Effect of Sorbent Dosage

The removal of arsenic was determined as function of sorbent dosage by increasing the sorbent dosage from 1 to 20 g/L at an initial As(V) concentration of 1 mg/L and a solution volume (50 mL) of DI water or synthetic solution. The results presented in Fig. 2 show that the uptake of arsenic from both DI water and synthetic solution increased with increasing dosage of the sorbent. The pH of the solutions was not kept constant in order to determine how the presence of the sorbent affected the arsenic removal efficiency when the solution was naturally exposed to different dosages of the sorbent. The solution pH for different dosages of Mn_3O_4 was in the range of 6.6-6.9 in DI water and 7.9-8.3 in the synthetic solution.

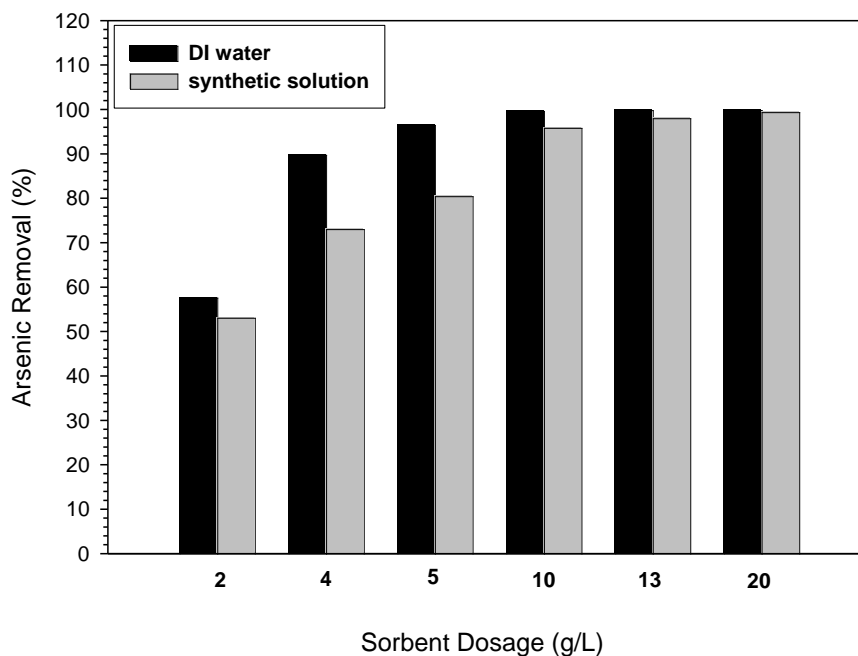


Fig.2. Effect of sorbent dosage on the removal of As(V) using Mn_3O_4 from a 1 mg/L solution.

A dosage of 20 g/L Mn_3O_4 was applied for the synthetic solution at pH 8.2 to achieve the WHO and U.S. EPA standards. A 20 g/L of Mn_3O_4 decreased the As(V) concentration from 1000 $\mu\text{g/L}$ down to 6.01 $\mu\text{g/L}$. However, in DI water, an adsorbent dosage of 10 g/L at pH 6.6 was sufficient to decrease the arsenic concentration from 1000 $\mu\text{g/L}$ down to 2.4 $\mu\text{g/L}$ (greater than 99% removal) which meets the WHO and U.S. EPA standards, indicating that the Mn_3O_4 sorbent has a greater adsorption capacity in DI water than in the synthetic solution. The effect of pH and competing ions on the adsorption of As(V) will be discussed later in the manuscript.

3.3. Influence of Contact Time and Adsorption Kinetics

The effect of contact time on removal of As(V) from the synthetic solution was determined at an initial As(V) concentration of 1 mg/L by taking samples at different time intervals and measuring the residual concentration of As(V) in the solution. A sorbent dosage of 20 g/L was used at pH 8.2. The data presented in Fig.3 show that arsenic adsorption increased over time, reaching equilibrium after 6 hr. Arsenic adsorption was high within the first 60 min, but thereafter the adsorption decreased and approached equilibrium. About 96% removal of arsenic was achieved within the first 60 min of contact between sorbent and solution, while only 1–3% of additional removal occurred in the following 17 hr. Grossl et al. [25] and Raven et al. [26] observed a similar trend while using ferrihydrite as sorbent. At equilibrium, about 99% of arsenic was adsorbed and the equilibrium adsorption capacity for As(V) was 49.8 mg/kg.

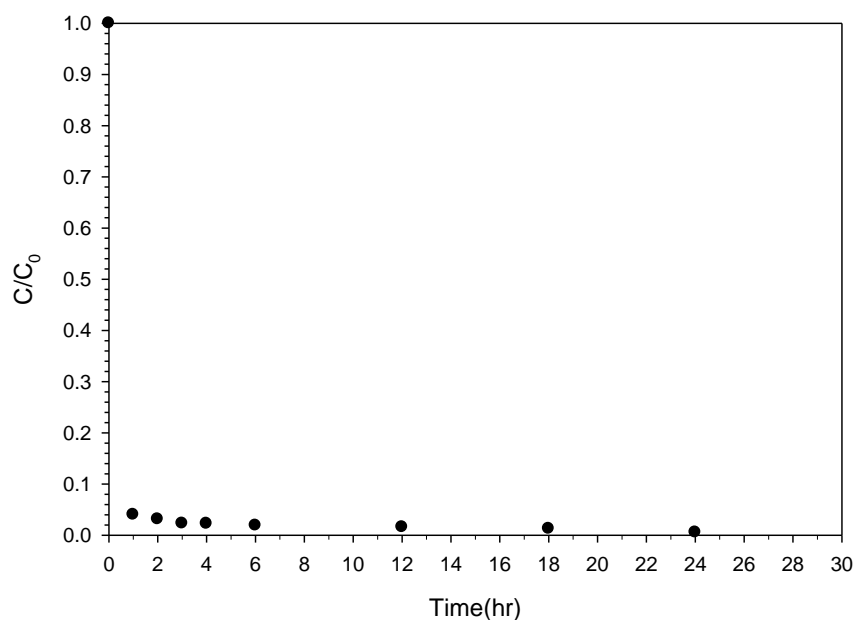


Fig.3. Effect of contact time on adsorption of As(V) from the synthetic solution (pH=8.2) onto 20 g/L Mn₃O₄ .

The Lagergren pseudo-first order model [27] and the pseudo-second order model [28] were employed to study the adsorption kinetics. The results of the uptake of As(V) by Mn₃O₄ powder at different time interval were used to understand the dynamics of the adsorption process and to evaluate the performance of the sorbent with the time. The pseudo-first order model is given as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where q_e and q_t are the adsorption capacities (mg/kg) at equilibrium and at time t , respectively, and k_1 is the adsorption rate constant (min^{-1}) of pseudo-first order adsorption. The integrated form of the Lagergren pseudo-first order is as follow:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The adsorption rate constant (k_1) and the theoretical value of the equilibrium adsorption capacity(q_e) can be obtained from the slope and the intercept of the linear plot of $\ln(q_e - q_t)$ versus t ,

respectively (Fig.4.a). The pseudo-second order model and its linearized form are given in Eq.4 and Eq.5, respectively:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2} \right) \left(\frac{1}{q_e^2} \right) + \frac{t}{q_e} \quad (5)$$

where k_2 is the adsorption rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$) of pseudo-second order adsorption and can be obtained from the intercept of a linear plot of t/q_t against t (Fig.4.b). It should be noted that all kinetic models were applied within the equilibrium time. The kinetic parameters of above models are shown in Table 1. The pseudo-second model provides the R^2 value of 0.999 and the predicted equilibrium adsorption value for the pseudo-second model was obtained as 50 mg/kg. The higher value of correlation coefficient and the comparable theoretical and experimental values of q_e in case of pseudo second order kinetics (Table 1) shows that the pseudo-second order model was able to accurately describe the adsorption kinetic data. The better fit of pseudo-second order model to the kinetic data suggests the existence of more than one rate-controlling step. [29]

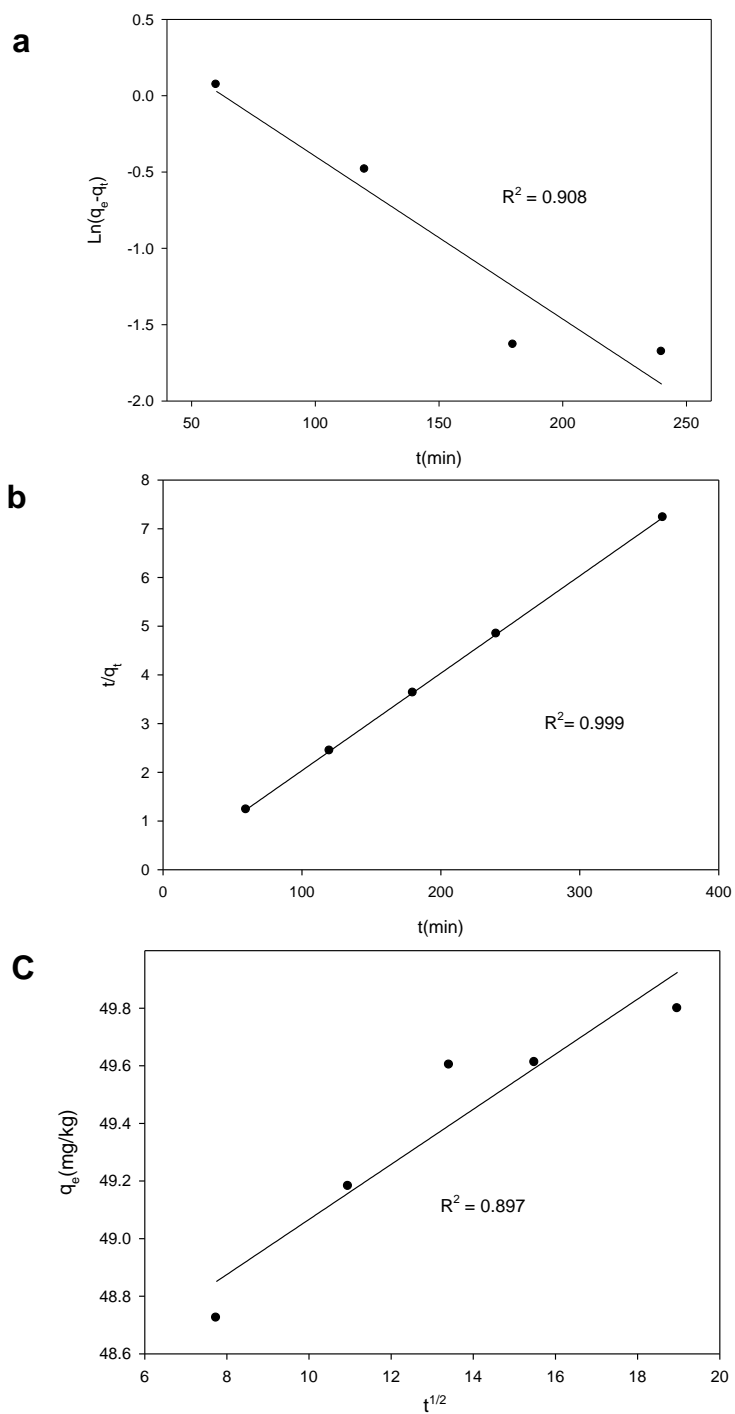


Fig.4. Test of (a) pseudo-first kinetics model and (b) pseudo-second order kinetics model (c) intraparticle diffusion model (pH=8.2, T=25°C, sorbent dosage = 5 g/L).

Table 1. Pseudo-first order and pseudo-second order kinetic parameters for adsorption of As(V) onto Mn₃O₄

| Experimental $q_e = 49.8$ mg/kg | | | | |
|---------------------------------|------------------------------------|---------------|-------|-------------|
| Order | $k_1(1^{st}), k_2(2^{nd}), k_{id}$ | q_e (mg/kg) | C | R^2 value |
| 1 st | 0.022 (min ⁻¹) | 13.63 | - | 0.908 |
| 2 nd | 0.011 (kg/mg.min ⁻¹) | 50 | - | 0.999 |
| Intraparticle diffusion | 0.7407 (mg/kg/min ^{0.5}) | - | 48.11 | 0.897 |

The three main steps occurring in the process of adsorption of arsenic (adsorbate) onto the Mn₃O₄ sorbent are:

1. Transport of adsorbate molecules from bulk solution to the external surface of the sorbent by diffusion through the boundary layer (film diffusion).
2. Diffusion of the adsorbate from the external surface into the pores of the sorbent (pore diffusion)
3. Adsorption of the adsorbate on the active sites on the internal surface of the sorbent pores

Determining the rate limiting step helps elucidate the adsorption mechanism for adsorption of As (V) onto the Mn₃O₄ sorbent. The last step (step 3) is very rapid and usually does not represent the rate-limiting step in the uptake of As(V).^[30] Hence, either pore diffusion or film diffusion or a combination of both may be the rate controlling steps. The experimental data can be modeled based on by Fick's 2nd law to determine the sole existence of intraparticle diffusion in the adsorption process as rate controlling step:

$$q_t = k_{id}t^{1/2} + c \quad (6)$$

where q_t (mg/kg) is the adsorption capacity at time t (min), k_{id} (mg.kg⁻¹.min^{-1/2}) is the rate constant of intraparticle diffusion and C (mg/kg) represents the boundary layer effect. Larger values of C are indicative of larger values of boundary layer thickness. ^[31] For q_t versus $t^{1/2}$, a straight line

passing through the origin($C=0$) indicates that the intraparticle diffusion model is the main rate determining step for the adsorption process. [32] The values of k_{id} and C were determined in Fig. 4c from the slope and intercept of the plot of q_t versus $t^{1/2}$, respectively. The non-zero value of C obtained from the intraparticle diffusion model for the present system (Fig.4c) indicates that mainly external mass transfer (film diffusion) was taking place in the adsorption process, which was expected due to the crystalline structure of the Mn_3O_4 sorbent.

3.4. Adsorption Equilibrium Isotherm Experiments

Equilibrium adsorption isotherms can provide essential physiochemical data for evaluating the applicability of the adsorption process [33]. Fig. 5 shows the adsorption isotherm data for the adsorption of As(V) onto the Mn_3O_4 sorbent in DI water and the synthetic solution. Two adsorption isotherm models, Langmuir and Freundlich, were employed to fit the equilibrium adsorption data at 25 °C using an initial As(V) concentration of 1 mg/L. The Dubinin–Radushkevich (D-R) adsorption equation was also used to predict the nature of the adsorption process.

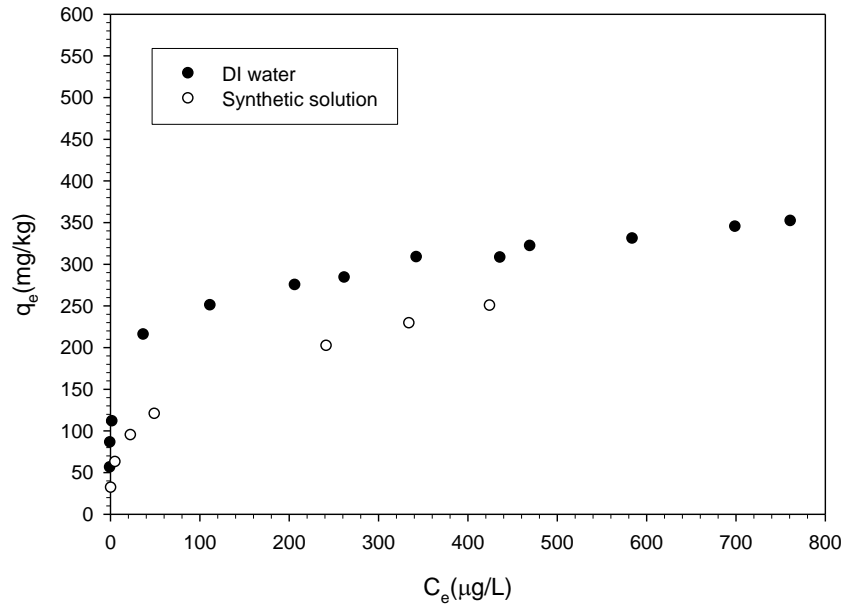


Fig. 5. Adsorption equilibrium isotherm data

The Langmuir adsorption model describes adsorption on homogeneous surfaces and assumes that the adsorbent surface consists of active sites with a uniform energy and therefore, the adsorption energy is constant. It can model the monolayer coverage of the adsorption surface and the adsorption that occurs through the same mechanism. The Langmuir isotherm can be described as the following equation: [34]

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where q_e is the amount of arsenic adsorbed per unit weight of adsorbent (mg/kg), q_m is maximum arsenic adsorbed (mg/kg) corresponding to complete coverage of available sites, K_L is Langmuir constant related to the free energy or net enthalpy of adsorption and C_e is the concentration of arsenic in solution at equilibrium (µg/L). The linear form of Langmuir model is as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (8)$$

where q_m and K_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e or $1/q_e$ versus $1/C_e$, respectively.

The Freundlich empirical equation and its linearized form are expressed as follow:

$$q_e = K_F C_e^{1/n} \quad (9)$$

$$\log q_e = \log K_F + (1/n) \log C_e \quad (10)$$

where K_F is the Freundlich constant indicating the adsorption capacity and $1/n$ is a constant that shows the adsorption intensity or strength. [35] The Freundlich isotherm model has been applied for describing both adsorption on heterogeneous surfaces and multilayer sorption.[36] The higher value of K_F indicates the higher level of adsorbate removal while $1/n$ values less than one indicate good adsorption intensity.[37] The Freundlich parameters K_F and $1/n$ can be determined from the intercept and slope of the plot of $\log q_e$ against $\log C_e$.

In order to evaluate the nature of the sorption, the adsorption equilibrium data were also fitted with Dubinin–Radushkevich (D-R) adsorption equation. This model envisages the process mechanisms and determines the mean free energy of the sorption which is defined as the free energy change for removing a molecule from its location in the sorption space to an infinite distance in solution from the sorption surface.[38] D-R adsorption isotherm can be expressed as:

$$q_s = q_m \exp(-K_{DR} \varepsilon^2) \quad (11)$$

and linearized as:

$$\ln q_s = \ln q_m - K_{DR} \varepsilon^2 \quad (12)$$

where q_m is the D–R constant, ε (Polanyi potential) is $RT \ln(1 + 1/C_e)$ and K_{DR} is a constant related to adsorption energy ($\text{mol}^2 \cdot \text{kJ}^2$)⁻¹. The q_m and K_{DR} can be determined from the intercept and slope of the plot $\ln q_e$ versus ε^2 , respectively. The type of adsorption such as physisorption or chemisorption can be determined by calculating the mean free energy (E) in the system using the following equation: [39]

$$E = \frac{1}{\sqrt{(2K_{DR})}} \quad (13)$$

If the magnitude of E is less than 8 kJ/mol the sorption process is of physical sorption, while if E is in the range of 8 to 16 kJ /mol, the sorption is supposed to proceed via chemisorption.

The adsorption parameters obtained from the adsorption isotherm plots are listed in Table 2. The adsorption data for both DI water and the synthetic solution followed the Langmuir and Freundlich equations with high R^2 values, indicating the favorable adsorption of As (V) onto the Mn_3O_4 sorbent. The maximum adsorption capacity of the sorbent q_m obtained from the Langmuir adsorption equation was 345 mg/kg and 256 mg/kg in DI water and synthetic solution, respectively. The values of Langmuir parameter q_m and the Freundlich parameter K_F are both greater for DI water than for the synthetic solution, indicating a greater adsorption capacity for DI water than for the synthetic solution. This result can be due to the presence of the other ions in the synthetic solution which can compete with arsenic for the limited active sites on the surface of the sorbent. The feasibility of isotherm criterion can be determined from a dimensionless constant separation, R_L , obtained from the Langmuir isotherm.[40] The R_L can be expressed as:

$$R_L = \frac{1}{1 + K_L C_0} \quad (14)$$

where K_L is the Langmuir constant (L/mg) and C_0 is the initial arsenic concentration (mg/L). The value of R_L demonstrates the nature of adsorption as linear ($R_L = 1$), irreversible ($R_L = 0$), unfavorable ($R_L > 1$), and favorable ($0 < R_L < 1$). With an initial As (V) concentration of 1 mg/L, the calculated value of R_L in DI water and the synthetic solution were 0.027 and 0.033, respectively, showing nearly irreversible adsorption of As (V) onto the Mn_3O_4 sorbent.

The adsorption equilibrium data were also fitted with Dubinin–Radushkevich (D-R) adsorption equation. The mean free energy of adsorption of As(V) onto Mn_3O_4 (obtained from the D-R adsorption equation) in DI water and synthetic solution was calculated as 12.13 kJ/mol and 8.11 kJ/mol, respectively, which was suggestive of the chemisorption of As(V) onto the surface of Mn_3O_4 .

The adsorption parameters presented in Table 2 show that the Freundlich parameter $1/n$ was smaller for DI water than for synthetic solution, while the Langmuir parameter K_L and the D-R parameter K_{DR} were larger for DI water than for synthetic solution. The smaller $1/n$ value, and the larger K_L and K_{DR} values for DI water show that the binding of As(V) onto Mn_3O_4 was stronger in DI water than in the synthetic solution. The stronger binding of As(V) for DI water may be attributed to the pH of DI water which was lower than the pH of synthetic solution, as discussed later as part of the effect of pH on adsorption.

Table 2. Adsorption parameters for adsorption of As(V) onto Mn₃O₄

| Langmuir | | | Freundlich | | | D-R | | |
|-----------------------------|-------------|-----------------------|---|-------------|-----------------------|--|-------------|-----------------------|
| | DI water | Synthetic solution | | DI water | Synthetic solution | | DI water | Synthetic solution |
| $q_m(\text{mg/kg})$ | 344.8 | 256.4 | K_F $(\text{mg/kg})(\text{L}/\mu\text{g})^{1/n}$ | 96.5 | 30.85 | K_{DR} $(\text{mol}^2/\text{kJ}^2)$ | 0.0034 | 0.0076 |
| $K_L(\text{L}/\mu\text{g})$ | 0.0366 | 0.0294 | $1/n$ | 0.196 | 0.346 | $E(\text{kJ/mol})$ | 12.13 | 8.11 |
| R^2 | 0.992 | 0.984 | R^2 | 0.992 | 0.996 | R^2 | 0.963 | 0.962 |

The maximum adsorption capacity of Mn₃O₄ in this study (256-345 mg/kg) was compared to several representative metal oxide sorbents (Table 3). When the adsorption capacities are compared in terms of sorbent mass (mg of As(V) removed per kg of sorbent), some of the sorbents have a greater adsorption capacity (TiO₂, goethite, activated alumina), while some others have a similar adsorption capacity (ferrihydrite, hematite, MnO₂). When the adsorption capacities are compared in terms of sorbent surface area [mg of As(V) removed per m² of sorbent], all other sorbents have adsorption capacities that are comparable to or lower than the surface normalized adsorption capacity of crystalline Mn₃O₄ sorbent (101.5 μg/m²).

Table 3. Comparison of Mn_3O_4 with other sorbents for As(V) adsorption capacity

| Adsorbent | pH | Concentration range | Surface area (m^2/g) | Capacity (mg/kg) | Capacity per surface area ($\mu\text{g}/\text{m}^2$) | Reference |
|---|-----------------------------------|---------------------------------|--|------------------------------------|--|--------------|
| hydrous titanium dioxide | 4.0 | 0.2–8.5 mg/l | 280 | 33400 | 119.3 | [41] |
| Goethite | 9.0 | 0–60 mg/L | 39 | 4,000 | 102.6 | [42] |
| Activated alumina | 7.0 | 50 mg/m ³ | 195 | 9,200 | 47.2 | [43] |
| Ferrihydrite (FH) | - | 325 $\mu\text{g}/\text{L}$ | 141 | 250 | 1.8 | [44] |
| MnO_2 | 7.9 | <1 mg/L | 17 | 172 | 10.1 | [18] |
| micro-/nano-structured MnO_2 spheres | - | 0.1–0.8 mM | 162.54 | 14500 | 89.2 | [45] |
| Hematite | 4.2 | 133.49 $\mu\text{mol}/\text{L}$ | 14.4 | 200 | 13.9 | [46] |
| Fe/GAC | - | 237–362 $\mu\text{g}/\text{L}$ | 631.3 | 3887.5 | 6.2 | [47] |
| Mn_3O_4 | 6.6–8.3 DI and synthetic solution | 1 mg/L | 3.4 | 256–345 | 75.3–101.5 | present work |
| Mn_3O_4 | 7.6 Groundwater | 1 mg/L | 3.4 | 76–119 | 22.4–35 | present work |

3.5. Effect of pH on Adsorption of As(V)

The speciation of As(V) is pH dependent and the corresponding stability of species pH values for As(V) are: H_3AsO_4 (pH 0–2), H_2AsO_4^- (pH 3–6), HAsO_4^{2-} (pH 7–11), and AsO_4^{3-} (pH 12–14). [48] Hence, pH can play an effective role for the adsorption of arsenic species. The pH dependence of As(V) adsorption has been reported for other sorbents. [49] In order to determine the optimum pH for adsorption of As(V) onto Mn_3O_4 powder, the uptake of arsenic as a function of pH was studied. Fig 6 shows the effect of pH on adsorption of arsenate in the pH range of 2.0–10.0 with an initial As(V) concentration of 1 mg/L. The initial pH before adsorption was the pH of the arsenic solution before the addition of Mn_3O_4 . The Mn_3O_4 sorbent most effectively adsorbed

arsenate in the pH interval 2.0–8.0 with nearly 92–97 % removal of arsenic. Stronger arsenic adsorption onto Mn_3O_4 powder was obtained at lower pH values. The adsorption of As(V) onto Mn_3O_4 decreased slightly in the pH range 2–9, while decreasing sharply when solution pH was greater than 9.

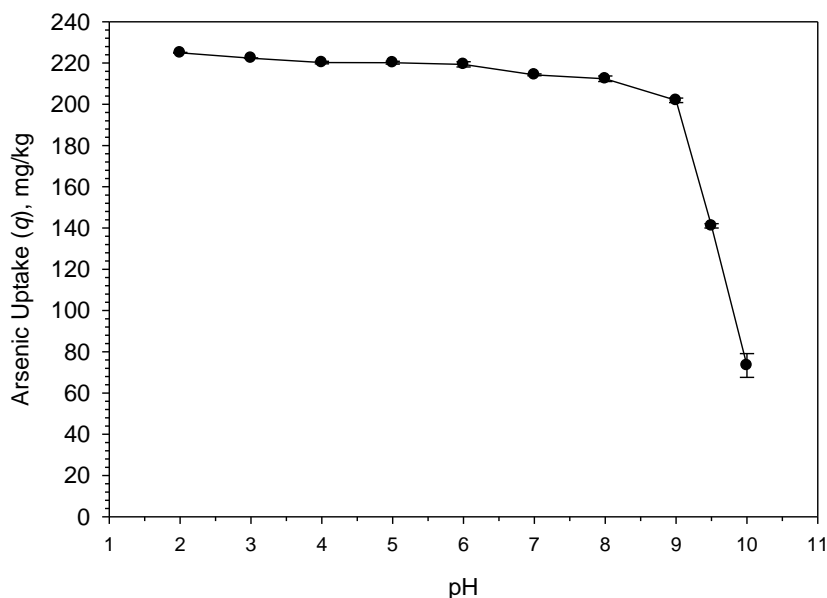


Fig. 6. Effect of pH on adsorption of As(V) onto Mn_3O_4 (5 g/L sorbent dosage) from a 1 mg/L solution.

The effect of pH on adsorption can be interpreted based on the surface charge of the sorbent. In order to observe the surface charges of the Mn_3O_4 suspensions and understand the interactions at the solid-solution interface, the zeta potential values were measured in a 1 mM NaCl solution. The point of zero charge (PZC) for Mn_3O_4 was determined as 7.32 (Fig.7a). Below the pH_{PZC} of 7.32, the Mn_3O_4 particles are predominantly positively charged and above this pH they are negatively charged. Adsorption of OH^- or H^+ on the neutral $\equiv\text{Metal-OH}^0$ site results in the net surface charge of Mn_3O_4 at the solid-solution interface. At the PZC or pH_{PZC} , cations and anions may adsorb onto the surface through the formation of outer-sphere complexes via van der Waals forces.

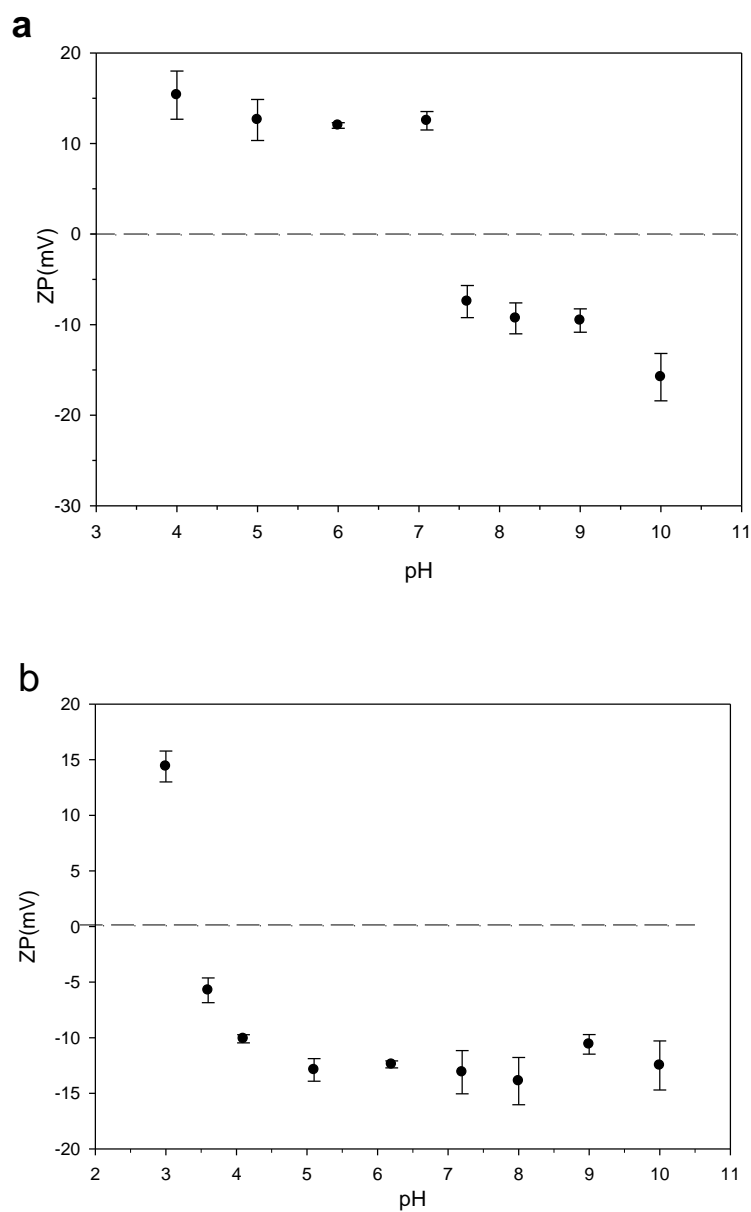


Fig. 7. Zeta potential of 0.1 g/L Mn_3O_4 as a function of pH in water (a): in the absence of arsenate, (b): in the presence of arsenate.

As solution pH increases from lower pH to 7.32, the lesser adsorption of As(V) can be due to the decreasing electrostatic attraction between the anionic As(V) species and the less positive surface of Mn_3O_4 . The lower adsorption of As(V) at $\text{pH} > 7.32$ can be attributed to an increase in repulsion

between the more negatively charged As(V) species and the negatively charged surface sites of Mn_3O_4 . In addition, the decrease in the uptake of As(V) on Mn_3O_4 at higher pH could be due to an increase in competing hydroxyl ions (OH^-) for adsorption sites with increasing pH which can cause a reduction in adsorption. [50] Similar results were also obtained by Chandra et al. [51] and Luo et al.[52], who investigated the adsorption of As(V) on magnetite-reduced graphene oxide composites and magnetite Fe_3O_4 -reduced graphene oxide- MnO_2 nanocomposites, respectively. The adsorption of As(V) onto Mn_3O_4 powder is of a wide pH range, which should be of advantage for practical operation.

The specific adsorption of ions onto the surface can change the PZC of the surface. The decrease in the PZC of the sorbent (Fig 7. b) clearly proves the adsorption of As(V) species onto the surface of Mn_3O_4 . Also, the anionic H_2AsO_4^- and HAsO_4^{2-} species are the predominant As(V) species in the pH range 4–8 which can contribute negative charge on the surface of the sorbent. Hence, the shift in the PZC value to the acidic side can be attributed to the formation of negatively charged surface complexes by specific adsorption of $\text{H}_x\text{AsO}_4^{x-3}$ ions onto the surface of Mn_3O_4 . [53] In the outer-sphere complexes, no certain chemical reaction can occur between the adsorbate and the surface that could change the surface charge of the sorbent. Therefore, the decrease in the PZC value of the suspension can be attributed to the formation of inner-sphere complexes by As(V) at the surface of Mn_3O_4 . [54]

Due to the nature of the As(V) solution in DI water which is not a buffered solution, the final pH of the solution after adsorption could change considerably during the experiments. Adding the sorbent to the solution is expected to shift the pH towards the point of zero charge, i.e. lower the

pH for $\text{pH} > \text{pzc}$ and increase the pH for $\text{pH} < \text{pzc}$. The measurements of the final pH of the solutions with different initial pH confirmed this claim.

3.6. Effect of Co-existing Ions on the Uptake of As(V)

The presence of co-existing ions, such as sulfate, bicarbonate, phosphate and calcium which are usually present in natural waters may affect the removal efficiency of arsenic from water. An initial As(V) concentration of 1 mg/L was used in all solutions with a sorbent dosage of 5 g/L. The effect of other ions on arsenic adsorption was investigated by increasing the concentration of HCO_3^- from 1 to 5.5 mM and increasing the concentrations of SO_4^{2-} , Ca^{2+} and PO_4^{3-} from 0.5 to 2 mM. The effect of co-existing ions on arsenic adsorption is shown in Fig. 8. The presence of bicarbonate and phosphate suppressed the adsorption of As(V), where phosphate had the greatest effect on adsorption. The decrease in the adsorption of As(V) in the presence of phosphate and bicarbonate could be attributed to competition between these anions and As(V) for the limited available adsorption sites on the surface of Mn_3O_4 . Calcium and sulfate did not show any noticeable influence on the adsorption of As(V).

The adsorption of As(V) decreased greatly at PO_4^{3-} concentrations up to 1 mM. With a further increase in the PO_4^{3-} concentration, adsorption of arsenic decreased slightly. The removal of As(V) decreased to 11% at the PO_4^{3-} concentration of 2 mM. The interference of phosphate on the adsorption of As(V) can be attributed to the similar behavior of arsenate and phosphate in solution in many aspects and the similar types of surface-complexes which can be formed by phosphate and arsenate. Zeng [55], Jian et al. [50] and Li et al. [56] have observed a negative effect and high interference of phosphate ions on the removal percent of arsenate while using Fe(III)-Si Binary

Oxide, ferrihydrite and hydrous cerium oxide nanoparticles as sorbents, respectively. Similarly, increasing the concentration of bicarbonate had negative effect on the adsorption of As(V). Increasing the concentration of bicarbonate up to 5.5 mM, decreased the removal of arsenic from 97% to 68%. Although the highest competitive effect was observed in the presence of PO_4^{3-} , HCO_3^- indicated a good competitive capacity.

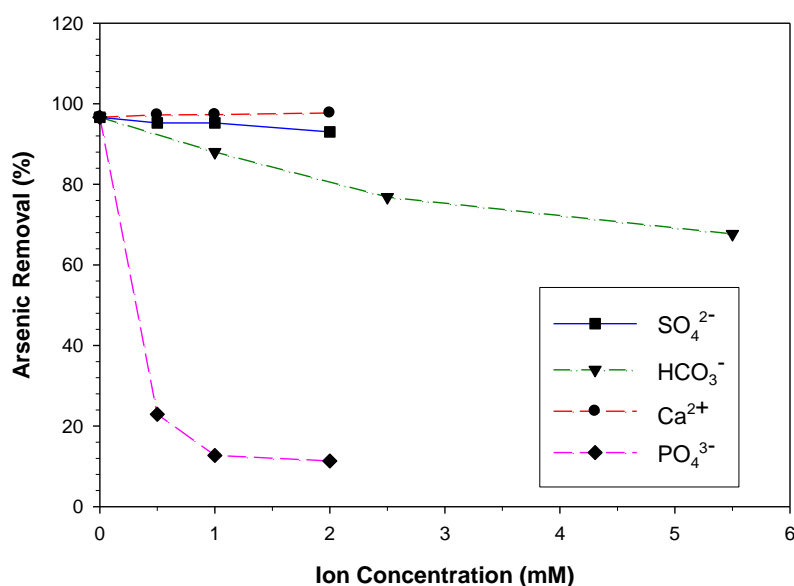


Fig. 8. Effect of coexisting ions on adsorption of As (V) onto Mn_3O_4

3.7. Sorbent Reuse

The sorbent can be a cost effective sorbent if the sorbent can be reused in multiple cycles of operation. The adsorption capacity of the sorbent was tested by exposing the same mass of sorbent (1 g) to the synthetic solution [1 mg/L As(V)] in several consecutive cycles of adsorption. The percent uptake of As(V) by Mn_3O_4 from the synthetic solution for each adsorption cycle was

99.5%, 75.6% and 69.8% for the first, the second and the third cycles of adsorption, respectively. The uptake of As(V) by 1 g of sorbent for the first, the second and the third cycles of adsorption corresponded to 40.6%, 30.9% and 28.5% of the total combined As(V) uptake (100%) achieved during the three cycles of adsorption, showing that nearly 60 percent of the total uptake of As(V) was achieved during the second and third cycles of adsorption. The results indicate that reusing the Mn_3O_4 sorbent from the first adsorption cycle in two extra consecutive cycles was conducive to the removal of substantial additional amounts of As(V) from the synthetic solution.

3.8. Batch Studies Using Arsenic Spiked Real Groundwater

Two different real-life groundwater samples were collected from central and northern Illinois. The composition of these two groundwaters is shown in Table 4. The arsenic removal with real groundwater spiked with 1mg/L As(V), without adding sodium bicarbonate, calcium chloride and sodium sulfate was studied in the batch system. The batch experiments were performed as before. Different ranges of adsorbent dosage (2-40 g/L) were exposed to the spiked groundwaters for 24hr for arsenic adsorption. The results were then compared with the synthetic and DI solution.

Table 4. Characteristics of real groundwaters

| Parameter | Groundwater #1 | Groundwater #2 |
|---|----------------|----------------|
| pH | 7.646 | 7.584 |
| TDS (mg/L) | 780 | 2670 |
| Alkalinity (mg/L as CaCO ₃) | 02.2 | 150 |
| Ca(mg/L) | 78.59 | 300.1 |
| Total Hardness (mg/L as CaCO ₃) | 273.6 | 796 |
| Fe (mg/L) | 3.62 | 4.22 |
| Mn(mg/L) | 0.664 | 0.705 |
| Conductivity (μS) | 1592 | 5120 |
| Mg (mg/L) | 45.61 | 67.71 |

Fig.9 represents the As(V) uptake at different arsenic concentrations in the groundwaters and Fig.10,represents the arsenic removal efficiency from the two studied groundwaters. Greater than 99% removal was obtained for both groundwaters using 20 g/L of Mn₃O₄ sorbent. The similar arsenic removal was observed at higher sorbent dosage (>10 g/L) while at lower Mn₃O₄ dosage,the higher arsenic adsorption was achieved from the second groundwater. Comparing to DI solution, the lower arsenic removal efficiency was obtained in groundwaters and the synthetic solution. As mentioned before,this might be due to the presence of other ions competing with arsenic on the limited activated sites on Mn₃O₄. As shown in Fig.2 and Fig.9, the similar arsenic removal efficiency was resulted from the real groundwaters versus the synthetic solution within the Mn₃O₄ dosages of 5-40 g/L. Based on the results, the crystalline Mn₃O₄ sorbent showed promising arsenic

removal efficiency from real groundwaters indicating its ability to be used as a practical efficient sorbent for arsenic removal.

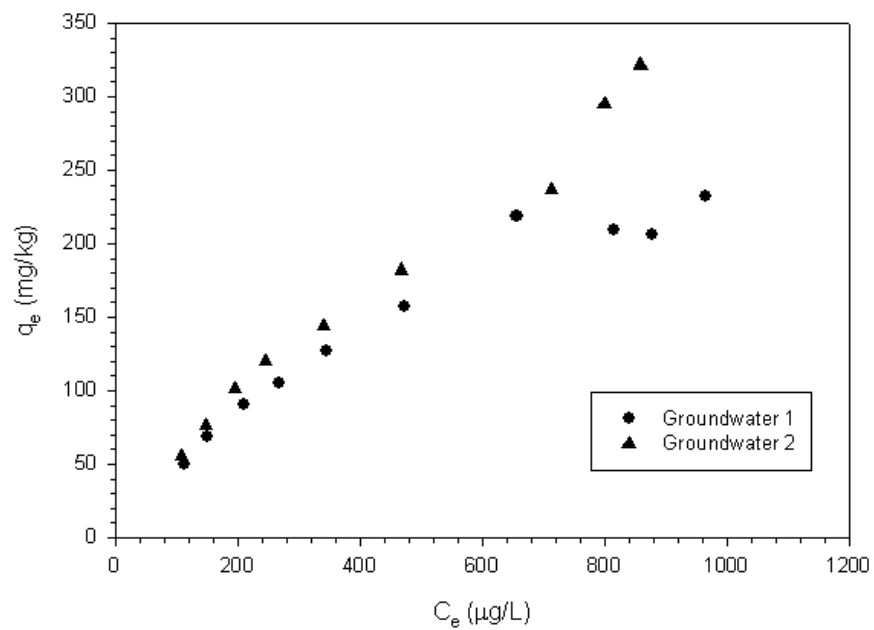


Fig.9. Arsenic uptake from arsenic spiked real ground waters at different concentrations

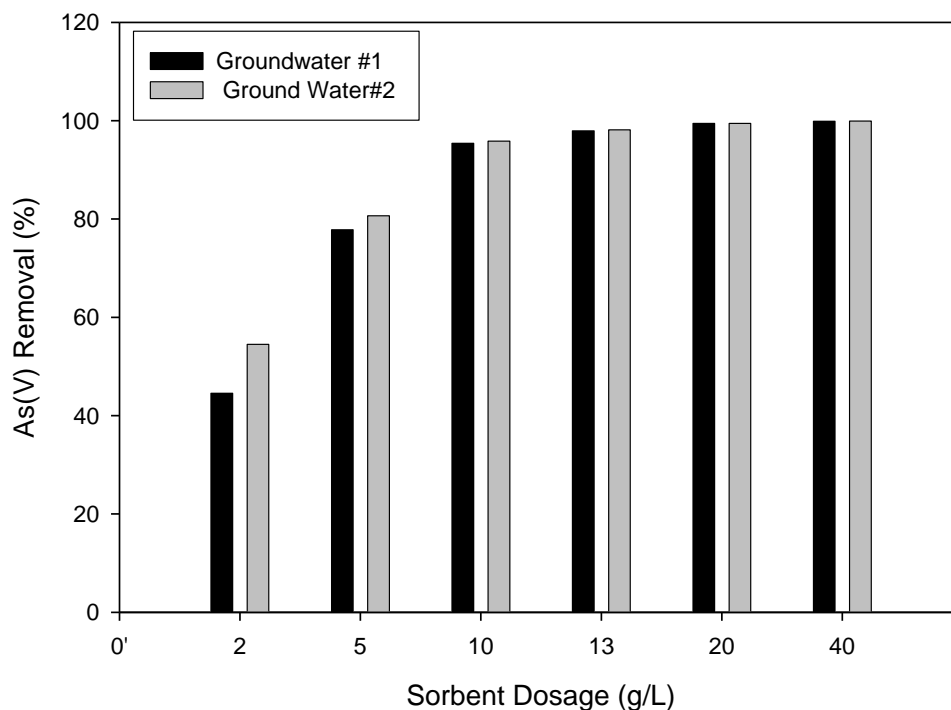


Fig. 10. Arsenic removal from arsenic spiked real ground water

4. CONCLUSION

This study showed the effectiveness of crystalline manganese oxide (II,III) powder (Mn_3O_4) for removal of As(V) from water. The surface charge analysis and zeta potential measurements confirmed the adsorption of arsenic onto the surface of Mn_3O_4 . The Mn_3O_4 sorbent was able to remove greater than 99% of arsenic under the condition of adsorbent dosage 20 g/L, pH of 6.6-8.3, temperature of 25°C and contact time of 24 hr. The adsorption process could be explained by the pseudo-second order kinetics model. The Langmuir, Freundlich and D-R adsorption equations were applied to equilibrium adsorption isotherm data. The maximum adsorption capacity of the sorbent in DI water and synthetic solution was found to be 345 mg/kg and 256 mg/kg, respectively. Chemical adsorption (chemisorption) governed the adsorption of As(V) onto the

surface of Mn_3O_4 . The removal of arsenic decreased with increasing pH. Experiments on the influence of other existing ions in water showed that adsorption of arsenic decreased in order of ions, phosphate > bicarbonate > calcium ~ sulfate. The data reported in this study contribute to a better understanding of the effect of different factors like co-existing ions, pH, sorbent dosage and surface charge on the removal of arsenic by manganese oxides. The arsenic removal ability of the Mn_3O_4 was tested in two different real groundwaters as well. The promising arsenic removal efficiency (>99%) was resulted by applying the crystalline Mn_3O_4 sorbent to the groundwaters indicating the Mn_3O_4 ability to be used as a practical efficient sorbent for arsenic removal. Based on the results obtained from this study, Mn_3O_4 powder was shown to be an effective and suitable sorbent for removal of As(V) from water.

5. REFERENCES

- [1] Huang,C., Ke,Q., Costa,M. and Shi,X.: Molecular mechanisms of arsenic carcinogenesis. *Mol Cell Biochem*,255(1-2): 57-66, 2004.
- [2] Kapaj,S., Peterson,H, Liber,K. and Bhattacharya,P.: Human Health Effects From Chronic Arsenic Poisoning—A Review. *J. Environ. Sci. Health Part A*,41(10):2399-2428,2006.
- [3] WHO(World Health Organisation).Guidelines for drinking water quality. Geneva,1993,p-41.
- [4] EPA. Implementation guidance for the arsenic rule. EPA report-816-D-02-005, Cincinnati, USA,1998.
- [5] Lenoble, V., Laclautre, C., Serpaud, B., Deluchat, V. and Bollinger, JC.: As(V) retention and As(III) simultaneous oxidation and removal on a MnO_2 -loaded polystyrene resin. *Sci Total Environ.* ,326(1-3):197-207.2004.
- [6] Deschamps,E., Ciminelli,V.S.T. and Höll, W.H.: Removal of As(III) and As(V) from water using a natural Fe and Mn enriched sample.*Water. Res.* ,39(20):5212-5220,2005.
- [7] Harvey,C.F.,Swartz ,C.H., Badruzzaman ,A.B.M., Keon-Blute ,N., Yu ,W., Ali, M.A., Jay ,J.,

Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaq, K.N., Islam, S., Hemond, H.F. and Ahmed, M.F.: Arsenic mobility and groundwater extraction in Bangladesh. *Science*, 298: 1602-1606, 2002.

[8] Chakraborty, S., Dureja, V., Bhattacharya, G., Maity, S. and Bhattacharjee, S.: Removal of arsenic from ground water using low cost ferruginous manganese ore. *Water. Res.*, 36(3): 625-632, 2002.

[9] Matschullat, J.: Arsenic in the geosphere-a review. *Sci Total Environ.*, 249(1-3):297-312, 2000.

[10] Smedley, P.L. and Kinniburgh, D.G.: A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem.*, 17(5):517-568, 2002.

[11] Zhao, X., Holl, W.H. and Yun, G.: Elimination of cadmium trace contamination from drinking water. *Water. Res.*, 36(4):851-858, 2002.

[12] Basu, T. and Ghosh, U.C.: Nano-structured iron(III)–cerium(IV) mixed oxide: Synthesis, characterization and arsenic sorption kinetics in the presence of co-existing ions aiming to apply for high arsenic groundwater treatment. *Applied Surface Science.*, 283 : 471–481, 2013.

[13] Pattanayak, J., Mondal, K., Mathew, S. and Lalvani, S.B.A.: Parametric evaluation of the removal of As(V) and As(III) by carbonbased adsorbents. *Carbon.*, 38(4):589-596, 2000.

[14] Mohan, D., Pittman, C.: Arsenic removal from water/wastewater using adsorbent-A critical review. *J Hazard Mater.*, 142(1-2):1-53, 2007.

[15] Zhang, S., Niu, H., Cai, Y., Zhao, X. and Shia, Y.: Arsenite and arsenate adsorption on coprecipitated bimetal oxide nanomaterials: MnFe_2O_4 and CoFe_2O_4 . *Chem. Eng. J.*, 158(3):599-607, 2010.

[16] Gupta, K., Bhattacharya, S., Chattopadhyay, D., Mukhopadhyay, A., Biswas, H., Dutt, J., Ranjan Ray, N. and Ghosh, U.C.: Ceria associated manganese oxide nanoparticles: Synthesis, characterization and arsenic(V) sorption behavior. *Chem. Eng. J.*, 172 (1):219-229, 2011.

[17] Manning, B.A., Fendorf, S.E., Bostick, B. and Suarez, D.L.: Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.*, 36(5):976-981, 2002.

[18] Ouvre, S., Simonnot, M.O. and Sardin, M.: Reactive behavior of natural manganese oxides toward the adsorption of phosphate and arsenate. *Ind. Eng. Chem. Res.* 41(11):2785-2791. 2002.

[19] Thirunavukkarasu, O.S., Viraraghavan, T., Subramanian, K.S., Chaalal, O., Islam, M.R.: Arsenic removal in drinking water—impacts and novel removal technologies. *Energy Sources*, 27(1-2):209-218, 2005.

[20] Deschamps, E., Ciminelli, V.S.T., Weidler, P.G., Ramos, A.Y.: Arsenic sorption onto soils enriched with manganese and iron mineral. *Clays and clay Miner.*, 51:197-204, 2003.

- [21] Wu, K., Liu, R., Liu, H., Zhao, X., Qu, J.: Arsenic(III, V) Adsorption on Iron-Oxide-Coated Manganese Sand and Quartz Sand: Comparison of Different Carriers and Adsorption Capacities. *Env. Eng. Science.*, 28(9):643-651, 2011.
- [22] Lakshmipathiraj, P., Narasimhan, B.R.V., Prabhakar, S. and BhaskarRaju, G.: Adsorption studies of arsenic on Mn-substituted iron oxyhydroxide. *J. Colloid Inter. Sci.*, 304(2):317-322, 2006.
- [23] Oscarson, D.W., Huang, P.M., Defosse, C. and Herbillon, A.: Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature.*, 291:50-51, 1981.
- [24] USEPA, Technologies and costs for removal of arsenic from drinking water. US Environmental Protection Agency, EPA report 815-R-00-028, 2000.
- [25] Grossl, P.R., Eick, M., Sparks, D.L., Goldberg, S. and Anisworth, C.C.: Arsenate and chromate retention mechanism on goethite. 2. Kinetic evaluation using pressure-jump relaxation technique. *Environ. Sci. Technol.*, 31(2) :321-326, 1997.
- [26] Raven, K.P., Jain, A. and Loeppert, R.H.: Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelope. *Environ. Sci. Technol.*, 32(3):344-349. 1998.
- [27] Lagergren, S. : Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar*, Band 24:1-39, 1898.
- [28] Blanchard, G., Maunaye, M. and Martin, G.: Removal of heavy metals from waters by means of natural zeolites. *Water. Res.*, 18(12):1501–1507, 1984.
- [29] Sen, T.K. and Sarzali, M.V.: Removal of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminum oxide (Al_2O_3): a kinetic and equilibrium study. *Chem. Eng. J.*, 142(3): 256-262, 2008.
- [30] Singh, T.S and Pant, K.K.: Kinetics and Mass Transfer Studies on the Adsorption of Arsenic onto Activated Alumina and Iron Oxide Impregnated Activated Alumina. *Water Qual. Res. J. Canada.*, 41:147, 2006.
- [31] Bekci, Z., Ozveri, C., Seki, Y. and Yurdakoc, K.: Sorption of malachite green on chitosan bead. *J. Hazard. Mater.*, 154 (1-3) :254–261, 2008.
- [32] Ho, Y.S.: Removal of copper ions from aqueous solution by tree fern. *Water. Res.*, 37(10) :2323-2330, 2003.
- [33] Aydin, H. and Baysal, G.: Adsorption of acid dyes in aqueous solutions by shells of bittim (*Pistacia khinjuk* stocks). *Desalination.*, 196 (1-3):248–259, 2006.

- [34] Langmuir, I.: The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.*, 38(11):2221-2295, 1916.
- [35] Freundlich, H.M.F.: Uber die adsorption in losungen. *Z Phys Chem.*, 57(A):385, 1906.
- [36] Ho, Y.S., Porter, J.F. and McKay, G.: Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water Air Soil Pollut.*, 141(1-4):1-33, 2002.
- [37] Raji, C. and Anirudhan, T.S.: Batch Cr(VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics. *Water. Res.*, 32(12):3772-3780, 1998.
- [38] Dubinin, M.M. and Radushkevich, L.V.: Equation of the characteristic curve of activated charcoal. *Chem. Zentr.*, 1:875, 1947.
- [39] Islam, M., Mishra, P.C. and Patel, R.: Fluoride adsorption from aqueous solution by a hybrid thorium phosphate composite. *Chem. Eng. J.*, 166(3):978-985, 2011.
- [40] Tan, I.A.W., Ahmad, A.L. and Hameed, B.H.: Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *J. Hazard. Mater.*, 164(2-3):473-482, 2009.
- [41] Piriälä, M., Martikainen, M., Ainassaari, K., Kuokkanen, T., Keiski, R.L.: Removal of aqueous As(III) and As(V) by hydrous titanium dioxide. *J. Colloid Interf. Sci.*, 353:257-262, 2011.
- [42] Lenoble, V., Laclautre, C., Deluchat, V., Serpaud, B. and Bollinger, J.-C.: Arsenic removal by adsorption on iron(III) phosphate, *J. Hazard. Mater.*, 123 (1-3):262-268, 2005.
- [43] Takanashi, H., Tanaka, A., Nakajima, T. and Ohki, A.: Arsenic removal from groundwater by a newly developed adsorbent. *Water Sci. Technol.*, 50 (8):23-32, 2004.
- [44] Gupta, V.K., Saini, V.K. and Jain, N.: Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *J. Colloid Interf. Sci.*, 288(1):55-60, 2005.
- [45] Zhang, T. and Sun, D.D.: Removal of arsenic from water using multifunctional micro-/nano-structured MnO₂ spheres and microfiltration. *Chem Eng J.*, 225:271-279, 2013.
- [46] Singh, D.B., Prasad, G. and Rupainwar, D.C.: Adsorption technique for the treatment of As(V)-rich effluents. *Colloid Surf. A*, 111(1-2):49-56, 1996.
- [47] Sigrist, M.E., Brusa, L., Beldomenico, H.R., Dosso, L., Tsendra, O.M., Gonzalez, M.B., Picck, C.L. and Vera, C.R.: Influence of the iron content on the arsenic adsorption capacity of Fe/GAC adsorbents. *J. of Env. Chem. Eng. J.*, 2:927-934, 2014.
- [48] Elizalde-Gonzalez, M.P., Mattusch, J., and Wennrich, R.: Application of natural zeolites for

preconcentration of arsenic species in water samples. *J. Environ. Monit.*, 3(1):22-26, 2001.

[49] Howell, R.J.: Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.*, 9(3): 279–286, 1994.

[50] Jain, A., Raven, K.P. And Loeppert, R.H.: Arsenite and Arsenate adsorption on ferrihydrite: surface charge reduction and net OH⁻ release stoichiometry. *Environ. Sci. Technol.*, 33(8) :1179-1184. 1999.

[51] Chandra, V., Park, J., Chun, Y., Lee, J.W., Hwang, I.C., Kim, K.S.: Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. *ACS Nano*, 4(7):3979–3986, 2010.

[52] Luo, X., Wang, X., Luo, S., Dong, R., Tu, X. and Zeng, G.: Adsorption of As (III) and As(V) from water using magnetite Fe₃O₄-reduced graphite oxide–MnO₂ nanocomposites. *Chem. Eng. J.*, 187: 45–52, 2012.

[53] Tripathy, S.S. and Raichur, A.M.: Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water. *Chem. Eng. J.*, 138(1-3):179-186. 2008.

[54] Stumm, W.: Chemistry of the Solid–Water Interface. New York: Wiley–Interscience, 1999.

[55] Zeng, L.: Arsenic Adsorption from Aqueous Solutions on an Fe(III)-Si Binary. *Water Qual. Res. J. Canada*, 39:267-275, 2004.

[56] Li, R., Li, Q., Gao, S. and Shang, J.K.: Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles: Part A. Adsorption capacity and mechanism. *Chem. Eng. J.*, 185–186 :127-135, 2009.

Chapter (IV)

IV. ADSORPTION OF ARSENIC(III) AND ARSENIC(V) ONTO CRYSTALLINE MANGANESE(III) OXIDE: EQUILIBRIUM, KINETICS, EFFECT OF pH AND IONIC STRENGTH.

1. INTRODUCTION

Arsenic contamination in drinking water and its side effects on human health which sometimes leads to potentially fatal diseases like skin and internal cancers have received increasing concern worldwide in the last decade [1,2]. Considering the severe effect of arsenic on human health and to limit the exposure to arsenic, the World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) recommended standard for arsenic in drinking water is 10 µg/L. Arsenic mainly exist in in the form of inorganic compounds, As(V) [arsenate] and the more harmful and mobile As(III) [arsenite] in natural waters. Natural ground waters contain mainly As(III) due to the prevalent reducing conditions while natural surface waters contain mostly As(V) [3].

The technologies employed to remove arsenic from water down to the standard level should be simple, effective, selective, and not remove all ions present in water [4]. Various arsenic removal technologies including ion exchange, precipitation and membrane processes have already been used [5]. Among the treatment processes, the adsorption technology has been considered as a simple and cost-effective process to remove arsenic contamination from aqueous environment [6]. A wide range of sorbents have been used as promising media for removal of arsenic from water, of which metal oxides were the most commonly used adsorbents. The functional groups on the

surfaces of metal oxides can react with the arsenic anions or molecules through the mechanisms of surface complex reaction or electrostatic adhesion [7]. However, problems still exist for current arsenic adsorption removal practice especially the adsorption of As(III). Since As (III) is more difficult to remove than As(V) at neutral pH conditions [8] , it is preferred to convert As(III) to As(V) [9]. The conversion of As(III) to As(V) in oxygenated water is thermodynamically favored. However, the rate of the transformation may take days, weeks or months depending on specific conditions [10].

Some types of manganese oxides may be an effective oxidizing agent of As(III) with a relative low oxidation potential and fit for specific oxidation of As(III) [11]. Manganese oxides have been used in mixed oxides sorbents or as loaded/substituted material for enhancement of arsenic sorption from aqueous solutions. Zhang et al. [12] synthesized Fe-Mn binary oxide (FMBO) for the simultaneous removal of As(III) and As(V). Gupta et al. [13] developed manganese associated nanoparticles agglomerate of Fe(III) oxide (MNFHO) for As(III) removal. Maliyekkal et al. [14] applied manganese oxide-coated-alumina (MOCA) for As(III) adsorption and they proposed the oxidation of As(III) by MOCA due to the manganese(II) release. Sun et al. [15] used manganese-modified activated carbon fiber (Mn-ACF) for removal of As(V) from aqueous solution. A hybrid polymer containing manganese and iron oxides as a sorbent was synthesized and developed for As(III) and As(V) removal [16]. He and Hering [17] studied the enhancement of As(III) sequestration by manganese oxides in the presence of iron(II).

However, to best of our knowledge no studies have been conducted so far on the As(III) oxidation/adsorption and As(V) adsorption behaviors of pure manganese oxide sorbents, which possess the advantages of extensive availability, low cost and oxidation potential of As(III). In the

present study, manganese (III) oxide (Mn_2O_3) powder was evaluated as a sorbent for removal of As(III) and As(V). The aim of this work was to investigate the removal efficiency of As(III) and As(V) by Mn_2O_3 powder in solutions with different ionic strength. Furthermore, the effect of different parameters like sorbent dosage, contact time, pH and ionic strength on the removal of As(V) and As(III) from aqueous solutions was studied. Arsenic adsorption was evaluated in the presence and absence of competing ions. Also, the mechanism for adsorption of As(III) and As(V) was investigated by adsorption equilibrium and kinetics experiments.

2. MATERIALS AND METHODS

2.1. Adsorbent Characterization

The BET surface area of the Mn_2O_3 sorbent was measured with an Accelerated Surface Area and Porosimetry system, ASAP 2010 (Micromeritics Instrument Corporation, Norcross, GA), using nitrogen adsorption/desorption isotherms. X-ray powder diffraction (XRD) patterns for the Mn_2O_3 sorbent were obtained on a Siemens D5000 with Cu $K\alpha$ radiation, $\lambda=1.5418 \text{ \AA}$, at 40 KV and 30 mA. The patterns were obtained from 15° to $65^\circ 2\theta$ with a step size of $0.02^\circ 2\theta$, counting for 10 s/step to better resolve the peaks.

2.2. Arsenic adsorption experiments

2.2.1. Chemicals and reagents

All chemicals were of analytical reagent grade and no further purification was carried out. All solutions were prepared with de-ionized (DI) water with a resistance greater than 18 M Ω . The manganese (III) oxide powder (Mn₂O₃, 98 % purity, density of 4.5 g/mL at 25°C) with an average particle size less than 325 U.S. mesh (44 μ m) was obtained from Alfa Aesar (Ward Hill, MA). Sodium arsenate (Na₂HAsO₄·7H₂O, 99% purity, ACS grade) and sodium meta-arsenite (NaAsO₂, 95% purity, ACS grade) were purchased from Sigma-Aldrich.

The other chemicals were obtained from Fisher scientific (Fair Lawn, NJ). The calcium chloride (CaCl₂, 98.8% purity, ACS grade), sodium sulfate (Na₂SO₄, 99.3% purity, ACS grade) and sodium bicarbonate (NaHCO₃, 100% purity, ACS grade) were used to prepare a solution, referred to as synthetic solution, representative of natural waters containing bicarbonate alkalinity and considering the effect of other co-existing ions. The As(III) and As(V) stock solutions were prepared with sodium meta-arsenite and sodium arsenate, respectively.

2.2.2 Batch Adsorption Experiments

A 1 mg/L solution of As(III) and a 1 mg/L solution of As(V) were prepared. The experiments were conducted with dry sorbent suspensions of different concentrations in DI water and in the synthetic solution. The experiments were carried out in high density polyethylene (HDPE) bottles, where different dosages of the sorbent were placed in the bottles and 50 mL of solution was added to the sorbent. The bottles were capped and shaken by hand to mix the slurry of sorbent and water before placing the bottles inside a rotating tumbler. The bottles were shaken in the tumbler at 16 rpm for 24 h and at 25 °C. After shaking, the bottles were removed from the tumbler, the contents of the bottles were then centrifuged at 9,000 rpm to separate the aqueous phase from the sorbent. The supernatant were filtered with a 0.45 μ m cellulose acetate filter and the concentration of

arsenic in the filtrate was analyzed using atomic absorption (AA). The adsorption of As (III) and As(V) on the sorbents was determined as:

$$q = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

where q is the adsorbed arsenic (mg/kg), C_0 and C_e are the initial and equilibrium (final) concentration of arsenic in the solution (mg/L), m is the adsorbent dosage (kg), and V is the solution volume (L).

2.2.3. Contact Time and Adsorption Kinetics Experiments

The adsorption kinetics of As(III) and As(V) for adsorption onto the sorbent was investigated using several time intervals. For the kinetics study, 0.25 g of Mn_2O_3 was mixed with 50 mL of 1 mg/L arsenic solution at 25 °C for 24 hr.

2.2.4. pH Experiments

The effect of pH on the adsorption of As(III) and As(V) was evaluated by determining the adsorption and removal of arsenic from water over a broad range of solution pH. For the pH experiments, 0.25 g of the Mn_2O_3 sorbent was mixed with 50 mL of 1 mg/L As(III) or 1 mg/L As(V) solution. The initial pH of the solution in DI water was adjusted to a pH of 2-10 using 0.1 M HCl and 0.1 M NaOH solutions.

2.2.5. Sorbent Surface Charge Measurement

The zeta potential of the sorbent was measured by a Zeta-meter system 3.0 (Zeta meter Inc, VA).

The pH of the samples were adjusted from 2 to 10 using 0.1 M HCl and 0.1 M NaOH solutions.

2.2.6. Co-existing ions experiments

The effect of co-existing ions on the removal efficiency of As(III) and As(V) by the Mn_2O_3 sorbent was studied by adding different concentrations of four individual ions including sulfate, phosphate, bicarbonate and calcium to DI water. A 50 mL volume of each solution with an initial arsenic concentration of 1 mg/L was mixed with 0.25 g Mn_2O_3 .

2.2.7. Sorbent re-use experiments

To evaluate the re-use of the Mn_2O_3 sorbent, the adsorption experiments were carried out in five consecutive adsorption cycles. For the first adsorption cycle, 1 g of the sorbent was mixed with 50 mL of a synthetic solution of 1 mg/L of As(III) or 1 mg/L of As(V) for 24 hr. For the second adsorption cycle, the same mass of the used sorbent from the first adsorption cycle was exposed to a fresh batch of arsenic solution. The other adsorption cycles were performed in similar fashion. The residual concentration and the removal of arsenic were determined for each adsorption cycle.

2.3. Analytical methods

To determine the arsenic concentration in solution, the graphite furnace atomic absorption spectroscopy (GFAAS) with Zeeman background correction was used. The detection limit of arsenic was 1 µg/L. All arsenic concentration measurements were carried out using an electrodeless lamp (EDL) at 193.7 nm and the modifier used was palladium-magnesium modifier. The atomization and pre-treatment temperature were 2000 and 1200 °C, respectively.

3. RESULTS AND DISCUSSION

3.1. Characterization of Mn₂O₃ sorbent

Fig.1 shows the X-ray diffraction (XRD) pattern of Mn₂O₃ powder which can be used to determine its chemical composition. The powder XRD results revealed good agreement with tetragonal Mn₂O₃ (JCPDS card No 41-1442). The appearance of the narrow and strong peaks in XRD pattern of the sorbent is indicative of its crystalline structure. The BET surface area was determined to be 2.20 m²/g.

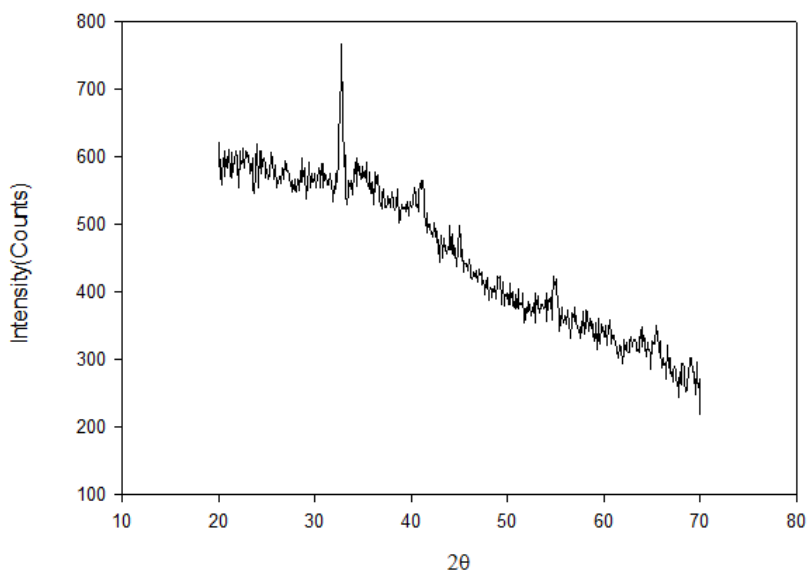


Fig. 1. XRD pattern of Mn_2O_3 powder

3.2. Effect of sorbent dosage

A 50 mL volume of DI water and synthetic solution with an initial concentration of 1 mg/L of As(III) or 1 mg/L of As(V) was used with different dosages of sorbent (1.6–20 g/L). It should be noted that the pH of the DI solution was not adjusted to investigate the “natural” effect of the sorbent dosage after adding to the system. The solution pH dropped after adding the sorbent. As mentioned before, the arsenic adsorption capacity is pH depended. Hence, due to the difference between pH of As(III) spiked DI and synthetic solution and As(V) spiked DI and synthetic solution, the removal efficiency of As(III) by the sorbent was not compared with As(V) removal efficiency. The comparison of the arsenic removal data presented in DI solution versus the synthetic solution is shown in Fig.2. Fig. 2 shows that the removal of As(III) and As(V) increased with the sorbent dosage for both DI water and synthetic solution. The removal of As(V) increased from 38.8% to

99.0% for DI solution and from 37% to 89.7% for synthetic solution when the sorbent dosage increased from 1.6 (not shown) to 5.0 g/L. The removal of As(III) increased from 66.4% to 98.9% for DI water and 55.9% to 96.4% for synthetic solution with increasing the sorbent dosage from 1.6 (not shown) to 5.0 g/L. The arsenic removal efficiency increased to a maximum of 99.9% in both DI water and synthetic solution as the sorbent dosage increased from 5 g/L to 20 g/L. Hence, a sorbent dosage of 5 g/L was applied in subsequent experiments.

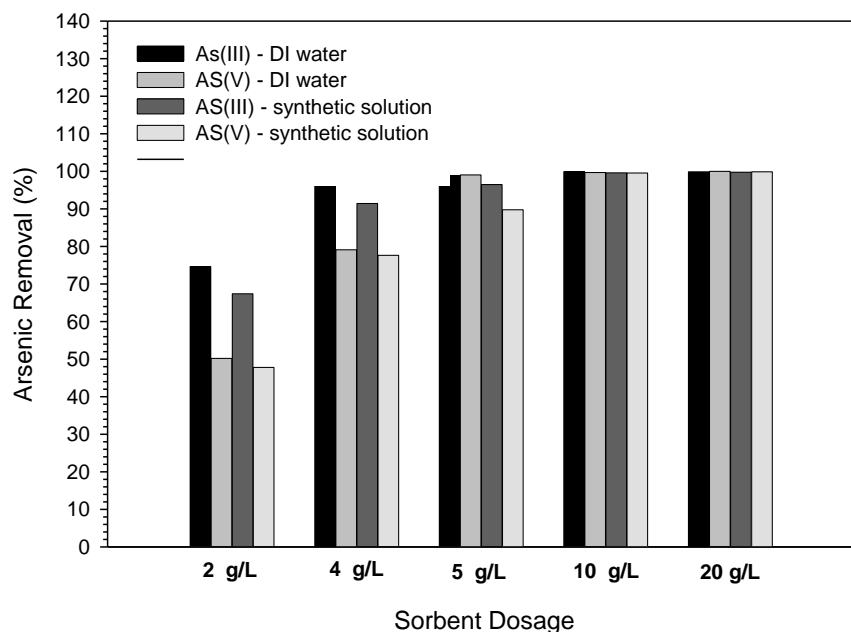


Fig.2. Effect of sorbent dosage on removal of arsenic using Mn_2O_3 from a 1 mg/L solution

3.3. Effect of contact time

The removal of arsenic was evaluated as a function of contact time. Fig. 3 shows the effect of contact time on the removal efficiency of As(III) and As(V) from the synthetic solution with an initial arsenic concentration of 1 mg/L using a sorbent dosage of 5 g/L. The data presented in Fig.

3 show that the rapid adsorption of As(III) and As(V) occurred within 30 min of contact time, where subsequently adsorption became slow and reached equilibrium within 10 hr. With further increase in contact time up to 24 hr, no significant removal of As(III) and As(V) was observed. Approximately 94% removal of As(III) and 87% removal of As(V) occurred within the first 60 min of contact, while only up to 5% of additional removal occurred in the following 23 h. The slower adsorption can be due to the decrease in concentration gradient between the bulk solution and the sorbent surface, which decelerates the transport of the arsenic species to the surface of Mn_2O_3 powder. A greater adsorption of As(III) than As(V) was observed at all time intervals.

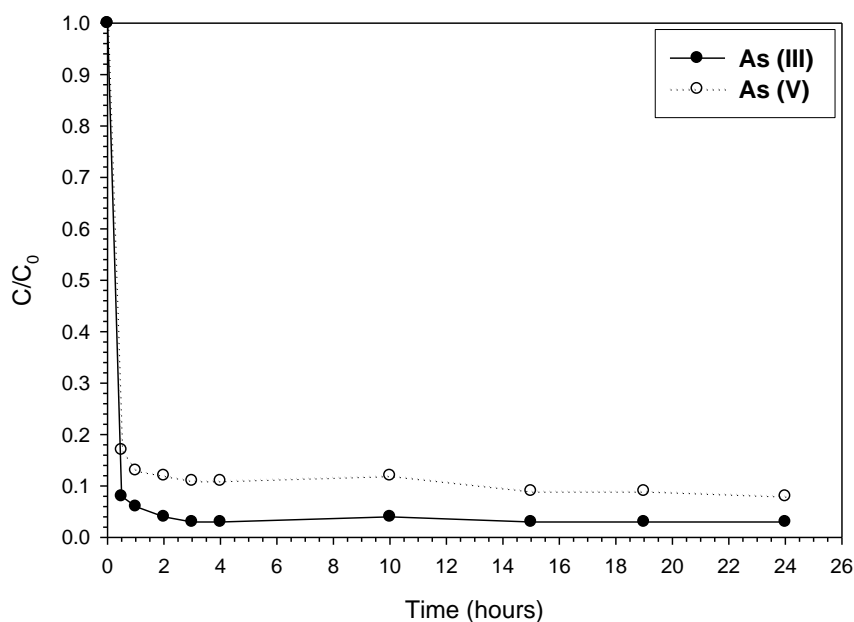


Fig. 3. Effect of contact time on removal of arsenic from a 1 mg/L synthetic solution by Mn_2O_3 (sorbent dosage = 5 g/L)

3.4. Adsorption kinetics

The rate of adsorption was obtained by studying the adsorption kinetics in the synthetic solution with an initial arsenic concentration of 1 mg/L at a sorbent dosage of 5g/L. To understand the dynamics of the adsorption process and evaluate the performance of the sorbent with time, two adsorption kinetic models were employed, the pseudo-first order [18] and the pseudo-second order models [19]. The pseudo-first order model is given as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2)$$

where q_e and q_t are the adsorption capacities (mg/kg) at equilibrium and at time t , respectively, and k_1 is the adsorption rate constant (min^{-1}) of pseudo-first order adsorption. The integrated form of the Lagergren pseudo-first order is as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The adsorption rate constant (k_1) and the theoretical value of the equilibrium adsorption capacity (q_e) can be obtained from the slope and the intercept of the linear plot of $\ln(q_e - q_t)$ versus t , respectively. The pseudo-second order model and its linear form are given in Eq.4 and Eq.5:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

$$\frac{t}{q_t} = \left(\frac{1}{k_2} \right) \left(\frac{1}{q_e^2} \right) + \frac{t}{q_e} \quad (5)$$

where k_2 is the adsorption rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$) of pseudo-second order adsorption and can be obtained from the intercept of a linear plot of t/q_t against t . The linearized pseudo-first order model and the pseudo-second order model were applied to the kinetics data for As(III) in Fig. 4.

The kinetic parameters obtained for the models are shown in Table 1. The pseudo-second model provided the higher R^2 value than the corresponding pseudo-first order model and there is a good agreement between the predicted adsorption capacity by pseudo-second order model and the experimental value which suggests that the pseudo-second order model is able to accurately predict the adsorption kinetics at equilibrium. The better application of pseudo-second order model to the kinetic data suggests the existence of more than one rate-controlling step [20]. The pseudo-second-order rate constant for As(III) adsorption was greater than the rate constant for As(V) adsorption, indicating that adsorption of As(III) was faster than adsorption of As(V).

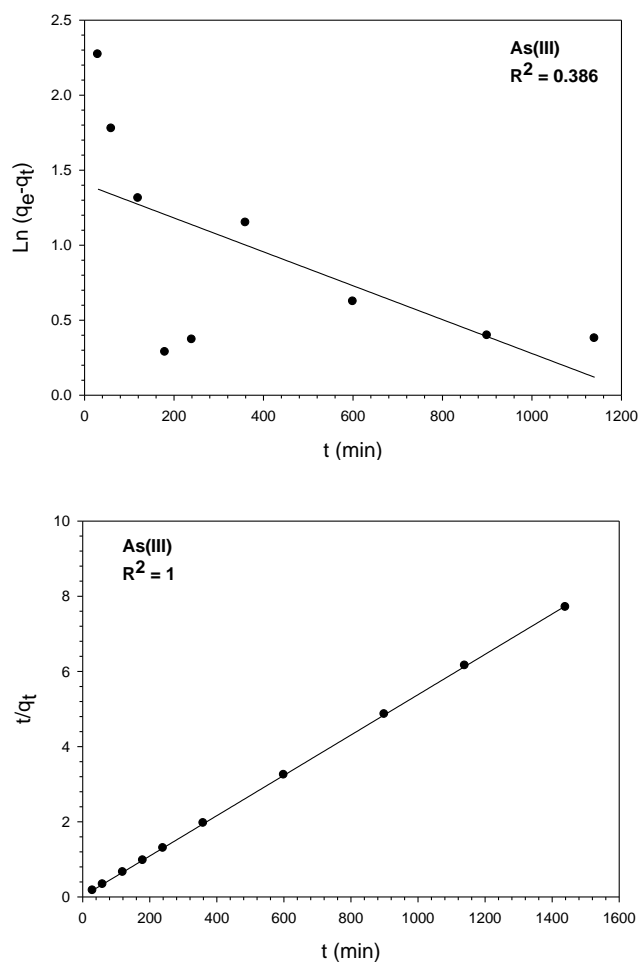


Fig. 4. Adsorption kinetics: pseudo-first order and pseudo-second order models
 1mg/L synthetic solution of As(III) [sorbent dosage = 5 g/L]

Determining the rate limiting step and the kinetic behavior of arsenic during adsorption onto Mn_2O_3 may help elucidate the adsorption mechanism of arsenic adsorption onto crystalline Mn_2O_3 . Film diffusion, pore diffusion and adsorption of the adsorbate on the active sites on the internal surface of the pores would be the three main steps occurring in the adsorption process of arsenic onto Mn_2O_3 . The third step is very rapid and usually

Table 1. Pseudo-first order and pseudo-second order kinetic parameters for adsorption of arsenic onto Mn₂O₃

| As(III) Experimental $q_e=186.75$ mg/kg | | | | |
|---|--|---------------------|--------|-------------|
| Order | $k_1(1^{st})$, $k_2(2^{nd})$, k_{id} | $q_e(\text{mg/kg})$ | C | R^2 value |
| 1 st | 0.011 | 4.085 | - | 0.386 |
| 2 nd | 0.002 | 185.16 | - | 1.00 |
| Intraparticle diffusion | 0.1903 | - | 179.98 | 0.558 |
| As(V) Experimental $q_e=185.03$ mg/kg | | | | |
| Order | $k_1(1^{st})$, $k_2(2^{nd})$, k_{id} | $q_e(\text{mg/kg})$ | C | R^2 value |
| 1 st | 0.0018 | 13.48 | - | 0.712 |
| 2 nd | 0.0005 | 185.19 | - | 0.999 |
| Intraparticle diffusion | 0.3973 | - | 169.6 | 0.6199 |

does not represent the rate-limiting step in the arsenic adsorption. A more comprehensive view of adsorption as a series of distinct steps can be explained by the intraparticle diffusion model [21].

The intraparticle diffusion was evaluated using the Weber–Morris equation [22] as follow:

$$q_t = k_{id}t^{\frac{1}{2}} + C \quad (6)$$

where q_t (mg/kg) is the adsorption capacities (mg/kg) at time t (min), k_{id} (mg.kg⁻¹.min^{-1/2}) is the rate constant of intraparticle diffusion and C represents the boundary layer effect. For q_t versus $t^{1/2}$, a straight line passing through the origin indicates that intraparticle diffusion is the main rate determining step for the adsorption process [23]. On the other hand, multi-linearity in the plot indicates that further complexity exist in the adsorption process. The value of k_{id} and C were determined from the slope and intercept of the plot of q_t versus $t^{1/2}$, respectively (Table 1). The non-zero values of C obtained from the Weber-Morris equation (Table 1) indicate that intraparticle diffusion was not the rate determining step in the adsorption of As(III) or As(V) onto Mn₂O₃. The

data presented in Fig. 5 show that multi-linearities resulted from the application of the intraparticle diffusion model to the adsorption kinetics data for As(III) and As(V). The data indicate that two steps rather than one step governed the adsorption of As(III) and As(V) onto Mn_2O_3 . The first linear segment of the plot for As(III) and As(V) adsorption have a very steep slope, designating the first step in the adsorption process which is film diffusion (external mass transfer) of arsenic from the bulk solution to the exterior surface of the Mn_2O_3 . The second linear segments of the plot do not have a steep slope, designating the second step in the adsorption process which corresponds to intraparticle diffusion of arsenic from the exterior surface of sorbent through the sorbent pores. Since the Mn_2O_3 sorbent is mostly crystalline (Fig. 1) and the second segment of the plots in Fig. 5 do not have a pronounced slope but are rather flat compared to the first segment of the plots in Fig. 5, therefore the rate limiting step during the adsorption of either As(III) or As(V) onto Mn_2O_3 would likely be external mass transfer.

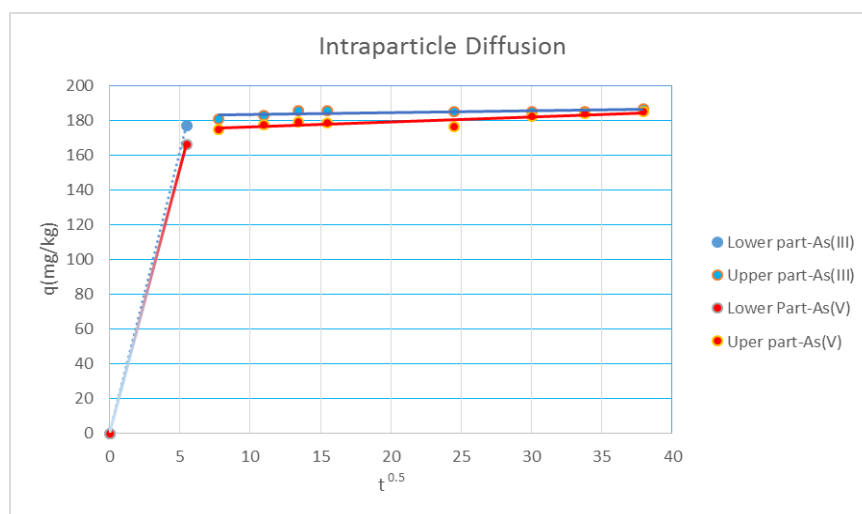


Fig. 5. The plots of intraparticle diffusion model for adsorption of As(III) and As(V) onto Mn_2O_3

3.5. Adsorption Equilibrium Isotherm Experiments

The equilibrium adsorption of both As(III) and As(V) was determined through adsorption isotherm experiments. The data from the adsorption isotherm experiments are presented in Fig. 6a and 6b for As(III) and As(V), respectively. The adsorption data from Fig. 6a and 6b show that the uptake of As(III) and As(V) increased sharply for lesser masses of sorbent, which is indicative of the accessible sites on the surface of Mn_2O_3 for adsorption. By increasing the arsenic concentration, site saturation of Mn_2O_3 surface occurred and a plateau was reached, representing that all active adsorption sites in Mn_2O_3 surface were occupied. The pH of the 1mg/L As(III) and 1mg/L As(V) DI solution before adsorption were 8.86 and 7.99, respectively while the pH of the 1mg/L As(III) and 1mg/L As(V) synthetic solution before adsorption were measured as 8.19 and 8.3 respectively. The arsenic adsorption capacity of the sorbents were compared in DI solution versus synthetic solution. No comparison was done between As(III) and As(V) adsorption in the solutions. The sorbent adsorbed more As(III) and As(V) from DI water than from synthetic solution.

The adsorption data were analyzed using three adsorption isotherm models: Langmuir, Freundlich and Temkin equations which are usually applied to single component adsorption [24]. The Dubinin–Radushkevich (D-R) adsorption equation was also employed to predict the nature of the adsorption process. The Freundlich [25] empirical model can be written as follow:

$$q_e = K_F C_e^{1/n} \quad (7)$$

where $1/n$ is a constant indicating the adsorption intensity or strength, K_F is the Freundlich constant indicating the adsorption capacity and C_e is the concentration of arsenic in solution at equilibrium ($\mu\text{g/L}$). Its linearized form is expressed as follow:

$$\log q_e = \log K_F + (1/n) \log C_e \quad (8)$$

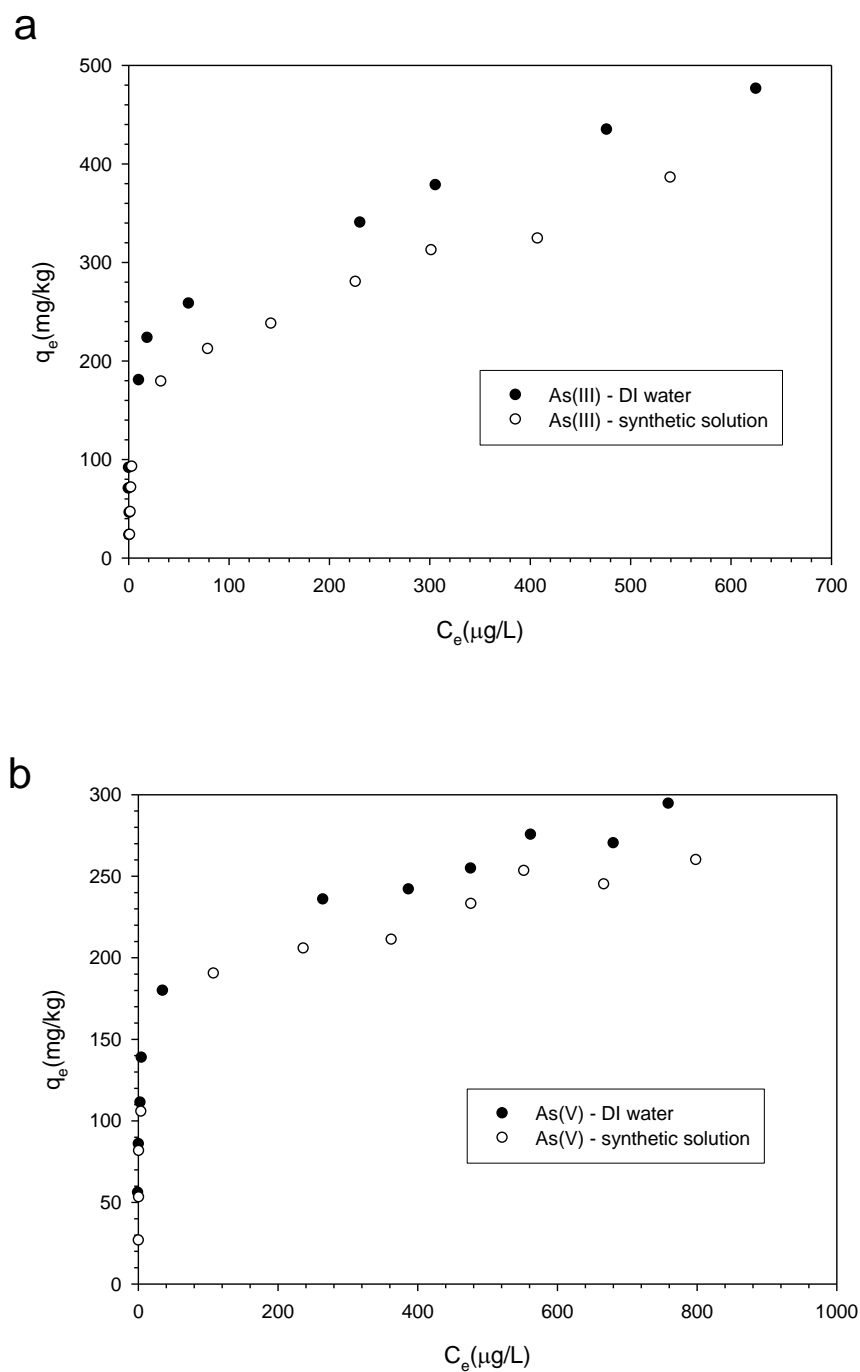


Fig. 6. Adsorption equilibrium isotherm data for adsorption of arsenic onto Mn_2O_3 : (a) As(III),
(b) As(v)

where K_F and $1/n$ can be determined from the intercept and slope of the plot of $\log q_e$ against $\log C_e$ (Fig. 2S). The Freundlich isotherm model is an empirical model describing multilayer sorption sites and heterogeneous sorption energies [26]. Freundlich model assumes that the adsorption sites are exponentially distributed with respect to the heat of adsorption. The binding energy and adsorption intensity rises proportionally by surface density for $1/n < 1$ [27]. The higher value of K_F indicates the higher level of adsorbate removal.

The Langmuir adsorption model [28] can be represented as the following equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (9)$$

where q_e is the amount of arsenic adsorbed per unit weight of adsorbent (mg/kg), q_m is maximum arsenic adsorbed (mg/kg) corresponding to complete coverage of available sites and K_L is Langmuir constant related to the free energy or net enthalpy of adsorption. The linear form of Langmuir model is as:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (10)$$

where q_m and K_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e or $1/q_e$ versus $1/C_e$, respectively. The Langmuir equation can model the monolayer coverage of the adsorption surface. It predicts that the adsorption runs on the homogeneous surfaces and assumes that the adsorbent surface consists of a finite number of active sites with a uniform energy and therefore, the adsorption energy is constant.

The Temkin isotherm model [29] assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate/sorbent interactions. Temkin isotherm equation can be applied with the assumption of uniform distribution of binding energies up to some maximum binding energy. Temkin isotherm is written by the following equation:

$$q_e = \left(\frac{RT}{b}\right) \ln(AC_e) \quad (11)$$

and linearized as:

$$q_e = \left(\frac{RT}{b}\right) \ln(A) + \left(\frac{RT}{b}\right) \ln(C_e) \quad (12)$$

where b (J/mol) is corresponded to the heat of adsorption, and T and R are the temperature (K) and gas constant (8.314 J/mol.K), respectively. The A (L/g) is the equilibrium binding constant relating to the maximum binding energy and determines the Temkin adsorption potential. The Temkin isotherm constants (b and A) can be determined from the slope and intercept of a plot of q_e versus $\ln C_e$.

The Dubinin–Radushkevich (D-R) [30] adsorption model may to be employed to evaluate the nature of the sorption and distinguish between chemical and physical adsorption. The D-R adsorption model can be expressed using the following equation:

$$q_e = q_m \exp(-K_{DR} \varepsilon^2) \quad (13)$$

where q_m is the D–R constant, ε (Polanyi potential) is $RT \ln(1 + 1/C_e)$ and K_{DR} is a constant related to adsorption energy ($\text{mol}^2 \cdot \text{kJ}^2$)⁻¹. The linearized form of the D-R equation is expressed as follows:

$$\ln q_e = \ln q_m - K_{DR} \varepsilon^2 \quad (14)$$

q_m and K_{DR} can be determined from the intercept and slope of the plot $\ln q_e$ versus ε^2 , respectively. The mean free energy (E) of adsorption per molecule of the adsorbate, when it is transferred to the surface of the adsorbent from infinity in the solution can be calculated from the constant K_{DR} as follow [31]:

$$E = \frac{1}{\sqrt{(2K_{DR})}} \quad (15)$$

For a magnitude of E less than 8 kJ/mol, the sorption process indicates physical adsorption, while if E is in the range of 8 to 16 kJ /mol, the sorption is supposed to proceed via chemisorption.

The adsorption parameters obtained from the Freundlich, Langmuir, Temkin and D-R equations for adsorption of As(III) and As(V) from DI water and synthetic solution are presented in Table 2. The small values of the Freundlich parameter $1/n$ for As(III) and As(V) adsorption from both DI water and synthetic solution are indicative of good adsorption intensity. According to the $1/n$ values, 29, 33, 19 and 26% of the active adsorption sites have equal energy level in the As(III)-DI solution, As(III)-synthetic solution, As(V)-DI solution and As(III)-synthetic solution, respectively. The K_F value can be considered as a relative indicator of the adsorption capacity of the Mn_2O_3 sorbent for a narrow sub-region having equally distributed energy sites for the adsorption of As(III) and As(V) [32]. The greater $1/n$ and lower K_F values for adsorption of As(III) and As(V) from the synthetic solution can be due to the presence of the other ions in the solution which may compete with arsenic ions for the limited active sites on the surface of the sorbent. The effect of co-existing ions on the arsenic removal efficiency will be discussed later.

Table 2. Adsorption parameters for arsenic adsorption onto Mn₂O₃

| | | As(III)+DI | As(III)+ synthetic solution | As(V)+DI | As(V)+ synthetic solution |
|------------|------------------------------|------------|-----------------------------------|----------|---------------------------------|
| Langmuir | $q_m(\text{mg/kg})$ | 454.55 | 370.37 | 277.78 | 256.41 |
| | $K_L (\text{L}/\mu\text{g})$ | 0.038 | 0.025 | 0.057 | 0.042 |
| | R^2 | 0.9816 | 0.9708 | 0.9913 | 0.9915 |
| Freundlich | $1/n$ | 0.2871 | 0.3308 | 0.1866 | 0.2613 |
| | K_F | 76.32 | 47.79 | 84.06 | 48.14 |
| | R^2 | 0.9126 | 0.9616 | 0.9779 | 0.8678 |
| Temkin | $b(\text{J/mol})$ | 44.8 | 46.1 | 87.2 | 79.2 |
| | $A (\text{L}/\mu\text{g})$ | 3.46 | 0.99 | 19.76 | 3.89 |
| | R^2 | 0.9527 | 0.9704 | 0.9819 | 0.9749 |
| D-R | K_{DR} | 0.0057 | 0.0078 | 0.0038 | 0.0062 |
| | E (kJ/mol) | 9.37 | 8.00 | 11.47 | 8.98 |
| | R^2 | 0.8901 | 0.9630 | 0.9728 | 0.9005 |

The data in Table 2 show that the values of q_m and K_L are lower for synthetic solution than for DI water, which indicates the higher affinity of the As(III) and As(V) to bind with the Mn₂O₃ sorbent in DI water. The feasibility of isotherm criterion can be determined from a dimensionless constant separation, R_L , obtained from the Langmuir isotherm which is indicative of the isotherm shape.

The R_L could be represented by the following equation:

$$R_L = \frac{1}{1 + K_L C_0} \quad (16)$$

where C_0 is the initial arsenic concentration ($\mu\text{g/L}$) and K_L is the Langmuir constant ($\text{L}/\mu\text{g}$). The value of R_L demonstrates the nature of adsorption as linear ($R_L = 1$), irreversible ($R_L = 0$), unfavorable ($R_L > 1$), and favorable ($0 < R_L < 1$) [33]. The calculated value of R_L for adsorption of

As(III) and As(V) from DI water and synthetic solution ranged between 0.017 and 0.038, indicating nearly irreversible adsorption of As(III) and As(V) onto the Mn_2O_3 sorbent. The high R^2 values of Temkin isotherm model showed that the Temkin adsorption isotherm can relatively describe the arsenic adsorption data for the DI and synthetic solution which may be due to the linear dependence of heat of adsorption at low or medium surface coverage. The b value in Temkin isotherm model is related to the heat of adsorption. The positive values of the constant B ($B=RT/b$) for As(III) and As(V) adsorption represents an exothermic process [34]. The smaller Temkin constant (A) for the synthetic solution indicate the lesser arsenic adsorption potential of the sorbent in the presence of co-existing ions. The mean free energy (E) of arsenic adsorption onto Mn_2O_3 (obtained from the D-R adsorption equation) for DI water and synthetic solution was calculated as 9.4 kJ/mol , 8.0 kJ/mol , 11.5 kJ/mol and 9.0 kJ/mol for As(III)-DI water, As(III)-synthetic solution, As(V)-DI water and As(V)-synthetic solution, respectively. The mean free energy (E) is suggestive of the chemisorption of As (V) onto the surface of Mn_2O_3 which is in good agreement with the results of adsorption kinetics experiment, where the applicability of pseudo-second order model for kinetic data suggested the occurrence of chemisorption.

The the larger K_L values from the Langmuir equation, the smaller $1/n$ values from the Freundlich equation, and the larger E values from the D-R equation for adsorption of As(V) and As(III) onto Mn_2O_3 in DI solution versus the synthetic solution indicate that the binding of arsenic to the active sites of the Mn_2O_3 sorbent in DI solution was stronger than in synthetic solution. However, the adsorption data from the adsorption isotherm experiments (Fig. 6a, 6b) show that the crystalline Mn_2O_3 sorbent was capable of removing more As(III) than As(V). The greater removal of As(III) was primarily due to the pH of adsorption and the sorbent point of zero charge (PZC), where

greater uptake of As(III) than As(V) occurred in the pH range of the adsorption isotherm experiments (6-8), as discussed later as part of the pH effect on adsorption.

The average adsorption capacity (q_m) of the Mn_2O_3 sorbent (Table 2) is 413 mg/kg for As(III) and 267 mg/kg for As(V). The adsorption capacity of an established sorbent such as activated alumina has been reported as 3,480 mg/kg for As(III) and 15,900 mg/kg for As(V) [35]. When adsorption capacity is reported in terms of the sorbent surface area, the adsorption capacity of the Mn_2O_3 sorbent becomes 188 $\mu\text{g}/\text{m}^2$ for As(III) and 121 $\mu\text{g}/\text{m}^2$ for As(V), while the adsorption capacity of the activated alumina sorbent becomes 30 $\mu\text{g}/\text{m}^2$ for As(III) and 137 $\mu\text{g}/\text{m}^2$ for As(V). Table 3 and 4 compare the As(III) and As(V) removal efficiency of the crystalline Mn_3O_4 investigated in this study versus the other sorbents in terms of maximum adsorption capacity and the surface-normalized adsorption capacities. The results show that, the surface-normalized adsorption capacities of the Mn_2O_3 sorbent for As(III) and As(V) are comparable to or greater than that of the other studied sorbents, rendering Mn_2O_3 as a viable sorbent for removal of As(III) and As(V) from water.

Table 3. Comparison of Mn_2O_3 with other sorbents for As(III) adsorption capacity

| Adsorbent | pH | Concentration range | Surface area (m^2/g) | Capacity (mg/kg) | Capacity per surface area ($\mu\text{g}/\text{m}^2$) | Reference |
|--|---------|---------------------|--|------------------------------------|--|------------|
| Fe_3O_4 –RGO– MnO_2 | 7 | 1.4–80.0 mg/L | 111.5 | 14040 | 125.9 | [36] |
| MIOH | 6.0–7.0 | 0.2–25 mg/L | 101 | 4580 | 45.4 | [37] |
| Fe_3O_4 | 7 | 0.1 mg/L | 57.6 | 1000 | 17.4 | [38] |
| KMnO_4 -modified iron oxide | 3 | 70 mg/L | 229 | 27400 | 119.7 | [39] |
| Mn_2O_3 | - | 1 mg/L | 2.2 | 413 | 188 | This study |

Table 4. Comparison of Mn_2O_3 with other sorbents for As(V) adsorption capacity

| Adsorbent | pH | Concentration | Surface area (m^2/g) | Capacity (mg/kg) | Capacity per surface area ($\mu\text{g}/\text{m}^2$) | Reference |
|--|---------|---------------|--|------------------------------------|--|------------|
| Fe_3O_4 –RGO– MnO_2 | 7.0 | 1.4–80.0 mg/L | 111.5 | 12220 | 109.6 | [36] |
| hydrous titanium dioxide | 4.0 | 0.2–8.5 mg/l | 280 | 33400 | 119.3 | [40] |
| MnO_2 | 7.9 | <1 mg/L | 17 | 172 | 10.1 | [41] |
| MIOH | 6.0–7.0 | 1–50 mg/L | 101 | 5720 | 56.6 | [37] |
| Mn_2O_3 | - | 1 mg/L | 2.2 | 267 | 121 | This study |

3.6. Effect of pH on adsorption

The pH of solution may affect the surface charge of adsorbents. Also, the speciation of arsenic and manganese, arsenic-manganese interactions, and arsenic adsorption can be affected by changing the pH of solution [42]. The As(V) is present in solution as the following stable forms at different pH values: H_3AsO_4 (pH 0–2), H_2AsO_4^- (pH 3–6), HAsO_4^{2-} (pH 7–11), and AsO_4^{3-} (pH 12–14). The As(III) is present in solution as the following stable forms at different pH values: H_3AsO_3 (pH 0–9), H_2AsO_3^- (pH 10–12), HAsO_2^{2-} (pH=13), and AsO_3^{3-} (pH =14) [43, 44]. The uptake of arsenic as a function of equilibrium solution pH is shown in Fig. 7. At pH values less than 9.0 (pH 3–10), the removal efficiency of As(III) (1 mg/L solution) with Mn_2O_3 ranged between 91–95% where the uptake of As(III) was relatively independent of solution pH. On the other hand, the uptake of As(V) showed greater dependence on pH with the highest uptake at pH 2 and the lowest uptake at pH 10. Comparable uptake of As(III) and As(V) was observed at pH values less than 5, whereas As(V) adsorption decreased with increasing pH over the pH range from 2 to 10. The uptake of As(III) by Mn_2O_3 was greater than the uptake of As(V) at solution pH between 5 and 9.

The pH dependence of arsenic adsorption onto Mn_2O_3 can be explained in terms of ionization of both adsorbates [45]. According to the pK_a values for arsenic acid [H_3AsO_4] in Table 5, H_2AsO_4^- is the predominant species in the pH range of 3–6 while HAsO_4^{2-} is the predominant species in the pH range of 6–9. The surface charge analysis of the sorbent showed that Mn_2O_3 sorbent has a net positive charge in the pH range of 3–6.3 enhancing the adsorption of As(V) species onto Mn_2O_3 by Coulombic attraction. A significant reduction in As(V) adsorption occurred above pH 6.5, which coincided

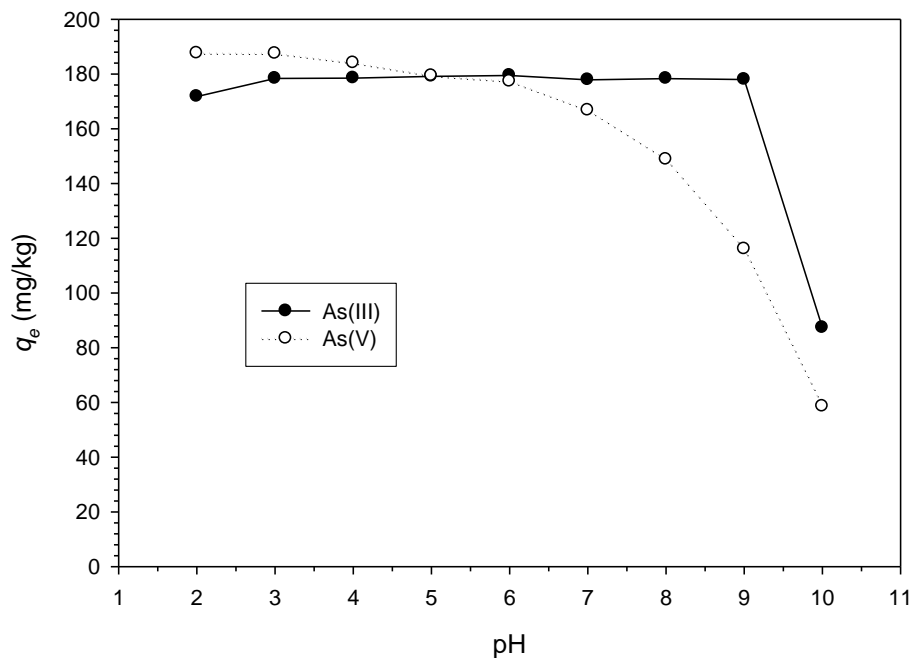


Fig.7. Effect of pH on adsorption of As(V) and As(III) onto Mn_2O_3 sorbent from 1 mg/L solution of arsenic (sorbent dosage =5 g/L)

approximately with the second $\text{p}K_a$ (6.7) of H_3AsO_4 . At pH higher than the point of zero charge (PZC) of the sorbent (6.3), the negative surface charge of Mn_2O_3 would tend to repulse the H_2AsO_4^- and HAsO_4^{2-} ions in the solution, leading to a decrease in adsorption of As(V).

Table 5. $\text{p}K_a$ values of As(III) and As(V).

| Arsenic Species | | $\text{p}K_{a1}$ | $\text{p}K_{a2}$ | $\text{p}K_{a3}$ |
|-----------------|--------------------------|------------------|------------------|------------------|
| As(III) | H_3AsO_3 | 9.1 | 12.1 | 13.4 |
| As(V) | H_3AsO_4 | 2.1 | 6.7 | 11.2 |

According to the $\text{p}K_a$ values of arsenous acid [H_3AsO_3] in Table 5, the neutral species H_3AsO_3^0 ($\text{p}K_{a1} = 9.1$) is the dominant As(III) species at pH 2-9. Hence, the adsorption of As(III) would

have lesser effect on the negative surface charge of the Mn_2O_3 sorbent than the adsorption of negatively charged As(V) species. The adsorption of As(III) did not decrease with increasing pH within the pH range of 3-9. However, the lower adsorption of As(III) at high solution pH (>9) would be due to an increased repulsion between the negatively charged As(III) species (H_2AsO_3^-) and negatively charged surface of Mn_2O_3 . Inflections in the adsorption of anions at pH values close to their pK_a has been reported [46]. The adsorption behavior of As(III) and As(V) onto Mn_2O_3 in this study was similar to other studies in which ferrihydrite and zerovalent iron were applied as sorbents to remove arsenic from aqueous solutions [47,48].

The higher uptake of As(V) in the acidic region may also be interpreted by the effect of pH on the charge of the sorbent surface, based on the point of zero charge (PZC) of the sorbent. The decreasing adsorption of As(V) from pH 3 to pH 6.27 can be due to the decreasing electrostatic attraction between the surface of Mn_2O_3 and anionic As(V) species like H_2AsO_4^- . At pH higher than 6.27, there is more repulsion between the more negatively charged As(V) species like $\text{H}_2\text{AsO}_4^{2-}$ and the negatively charged surface sites of Mn_2O_3 . Alternatively, an increase in competing hydroxyl ions (OH^-) for adsorption sites on surface of Mn_2O_3 can lower the uptake of As(V) by Mn_2O_3 at higher pH [49]. Overall, the adsorption of both As (III) and As(V) onto Mn_2O_3 powder occurred over a broad pH range, which should be of advantage for practical operation of an adsorber unit.

3.7. Surface Charge and pH

The interaction between solution-solid interfaces can be explained by surface charge of the sorbent using zeta potential measurements. The zeta potential measurements for Mn_2O_3 at equilibrium with

As(III) and As(V) in a 1 mM NaCl solution are shown in Fig. 8. A metal surface in water at neutral to slightly alkaline pH may be represented in general by the metal (M) hydroxide group as $=M-OH$. The PZC of Mn_2O_3 occurred at pH 6.27 (pH_{pzc}). Below this pH, the Mn_2O_3 surface is predominantly positively charged, and the protonated metal surface groups may be represented as $=M-OH_2^+$. Above the pH_{pzc} , the metal surface is negatively charged. At pH_{pzc} , the ions may adsorb onto the surface through the formation of outer-sphere complexes via van der Waals forces. The specific adsorption of ions onto the surface can change the PZC of the surface. The zeta potential values suggest that the surface charge of the Mn_2O_3 sorbent is reduced in the presence of either As(III) or As(V). The PZC of the Mn_2O_3 surface in a solution of 0.1 mg/L and 1 mg/L of As(III) or As(V) was found to shift toward the acidic region. The presence of 0.1 mg/L and 1 mg/L of As(III) in solution decreased the PZC of the sorbent from 6.3 down to 3.8 and 3.4, respectively. The presence of 0.1 mg/L and 1 mg/L of As(V) in solution decreased the PZC of the sorbent from 6.3 down to 3.9 and 3.5, respectively. These results show that the higher the arsenic concentration, the lower the zeta potential and corresponding values of PZC, which was similar to results reported by Dou et al. [50] where an Fe–Ce bimetal oxide adsorbent was used for arsenate adsorption. Tripathy and Raichur [51] have shown that the negatively charged species adsorbed on neutral surface site can shift the pH of PZC to lower pH. Under the experimental conditions, As(V) species ($H_2AsO_4^-$ and $HAsO_4^{2-}$) are negatively charged, leading to a

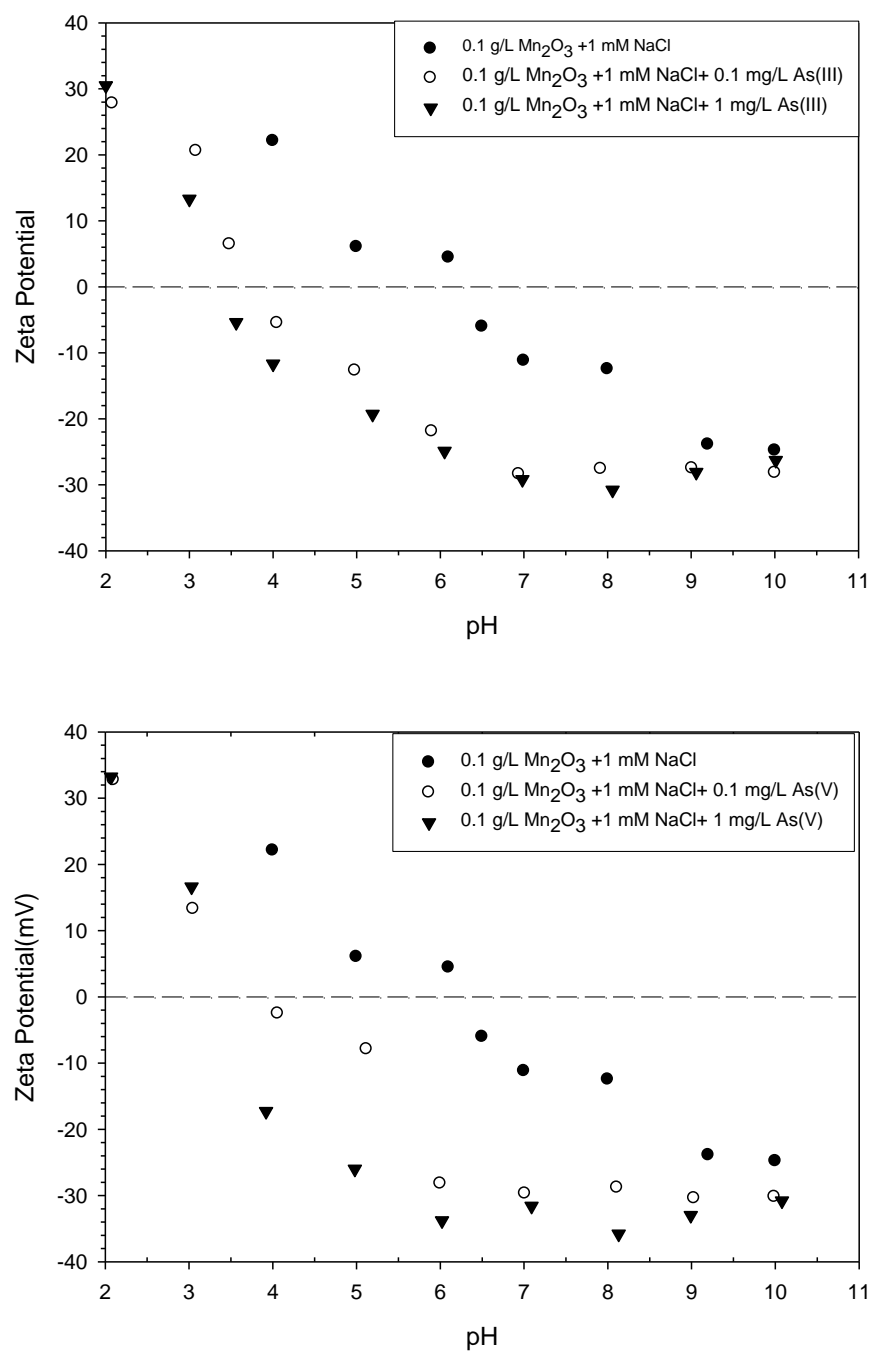
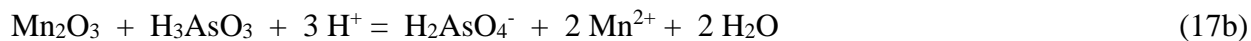
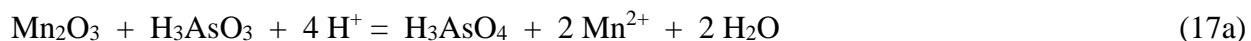


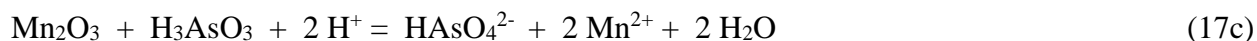
Fig. 8. Zeta potential of Mn_2O_3 as a function of solution pH in the presence of As(III) and As(V)

negatively charged Mn_2O_3 surface upon adsorption of As(V) species. Since As(III) exists as a neutral molecule of H_3AsO_3 at the same conditions (pH 3-9), therefore its adsorption onto neutral Mn_2O_3 should not change the PZC. The decrease in the PZC value of the Mn_2O_3 sorbent in presence of As(III) (Fig.8) may be attributed to the oxidation of As(III) to As(V) on the Mn_2O_3 surface. The surface charge of the sorbent can not be changed in the outer-sphere complexes where no certain chemical reaction takes place between the sorbent and adsorbate to change the sorbent surface charge. Therefore, the decrease in the PZC value of Mn_2O_3 was mainly due to the formation of inner-sphere complexes by As(V) species at the surface of Mn_2O_3 [46]. The surface charge analysis of the Mn_2O_3 sorbent indicates that H_3AsO_3 was likely oxidized to As(V) species on the surface of Mn_2O_3 , with As(V) species forming inner-sphere complexes on the surface of Mn_2O_3 .

3.8. Mechanism for oxidation of As(III) by Mn_2O_3

Different reactions may occur between Mn_2O_3 and As(III) at pH 2-9, leading to the formation of different As(V) species over a broad pH range of 2-9. According to the acid dissociation constants of arsenic species (Table 5), As(III) exists as arsenous acid (H_3AsO_3) at pH 2-9, while As(V) exists as H_3AsO_4 , H_2AsO_4^- and HAsO_4^{2-} at pH 2-9. Based on the zeta potential values obtained over the pH range of 2-9 (Fig. 8), the likely mechanisms responsible for the oxidation of As(III) to As(V) on the surface of Mn_2O_3 are given by Eq. 17 (a-c):





Based on the pK_a values in Table 5 and the reactions in Equations 17a, 17b and 17c, the surface oxidation of As(III) to As(V) will mainly proceed from arsenous acid (H_3AsO_3) as follows: to arsenic acid (H_3AsO_4) at pH 2-3, to dihydrogen arsenate (H_2AsO_4^-) at pH 3-6.7, and to hydrogen arsenate (HAsO_4^{2-}) at pH 6.7-9.

3.9. Effect of ionic strength and co-existing ions on adsorption of arsenic

The coexisting ions usually exist in water which could interfere with the uptake of arsenic by sorbent through competitive adsorption with arsenic for adsorption sites. Therefore, the effect of common ions in water like sulfate, bicarbonate, calcium and phosphate on the adsorption and removal of As(III) and As(V) were determined. The concentration of bicarbonate ranged from 1 mM to 5.5 mM. The concentration of calcium, sulfate and phosphate was each held at 0.5, 1.0 and 2.0 mM. In order to avoid the precipitation and conversion of ions in acidic or alkaline solutions, the solution pH was not adjusted. The corresponding solution pH with the presence of calcium, sulfate, phosphate and bicarbonate ions were in the range of 5.9-6.2, 5.9 -6.5, 7.6-8.5 and 7.8-8.2, respectively. The arsenic removal data as function of ion concentration are shown in Fig. 9. The presence of calcium and sulfate did not show any noticeable influence on the adsorption of As(V) and As(III) which may be due to the fact that the interaction of calcium and sulfate ions with the adsorption sites of Mn_2O_3 is weaker than As(III) and As(V) species [52]. Similar results were reported by other studies [45, 53]. Addition of bicarbonate decreased the removal efficiency of As(III) and As(V). Increasing the concentration of bicarbonate up to 5.5 mM decreased the

removal of As(V) from 99% to 62 %. The removal of As(III) and As(V) decreased greatly by the addition of 0.5 mM of phosphate

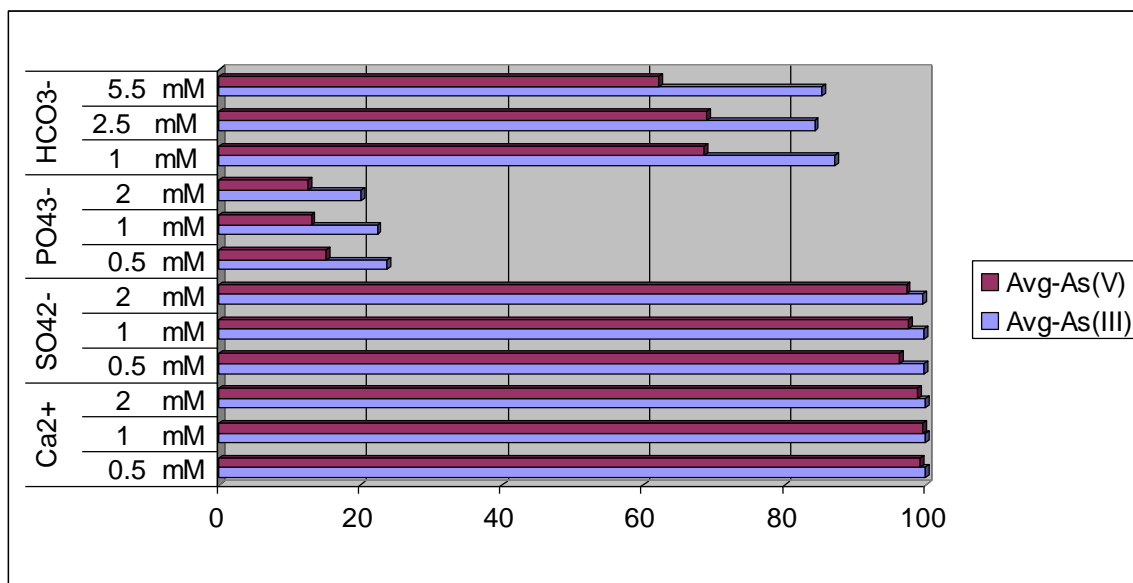


Fig. 9. Percent removal of As(III) and As(V) as function of co-existing ions (sorbent dosage = 5 g/L)

to solution. With a further increase in phosphate concentration, adsorption of As(III) and As(V) decreased slightly. The removal of As(V) decreased to 12.5 % at phosphate concentration of 2 mM. Similar to As (V), the adsorption of As(III) decreased with increasing concentration of phosphate. Phosphate and negatively charged species of As(V) are tetrahedral anions which are able to form the inner-sphere complexes on the surface of adsorbent [54]. The decrease in the adsorption of arsenic in the presence of phosphate and bicarbonate could also be attributed to competition between these anions and arsenic on limited available adsorption sites on the surface of Mn₂O₃ sorbent. In addition, the presence of bicarbonate (pH 7.8-8.2) and phosphate (pH 7.6-8.5) in solution resulted in more alkaline conditions which was unfavorable for adsorption of both As(III)

and As(V) onto Mn_2O_3 . Zhang et al. [55] have observed a negative effect of bicarbonate and high interference of phosphate ions on As(III) and As(V) adsorption while using on coprecipitated bimetal oxide magnetic nanomaterials: MnFe_2O_4 and CoFe_2O_4 . Frau et al. [56] showed that the adsorptive capacity of ferrihydrite for As(V) decreased in the presence of phosphate and bicarbonate as a consequence of their competitive effect. Li et al. [6] demonstrated that there is a negative effect and high interference of phosphate ions on As(V) adsorption on hydrous cerium oxide nanoparticles.

3.10. Re-use of manganese (III) oxide sorbent

The re-use of the sorbent is an important factor in determining its potential for practical application since it can reduce the operational cost and make the process economical [57]. The results presented in Fig. 10 show that greater than 99% removal of both As(III) and As(V) was achieved in each of the first and second adsorption cycles, while removal of arsenic decreased in the last three adsorption cycles. In the third adsorption cycle,

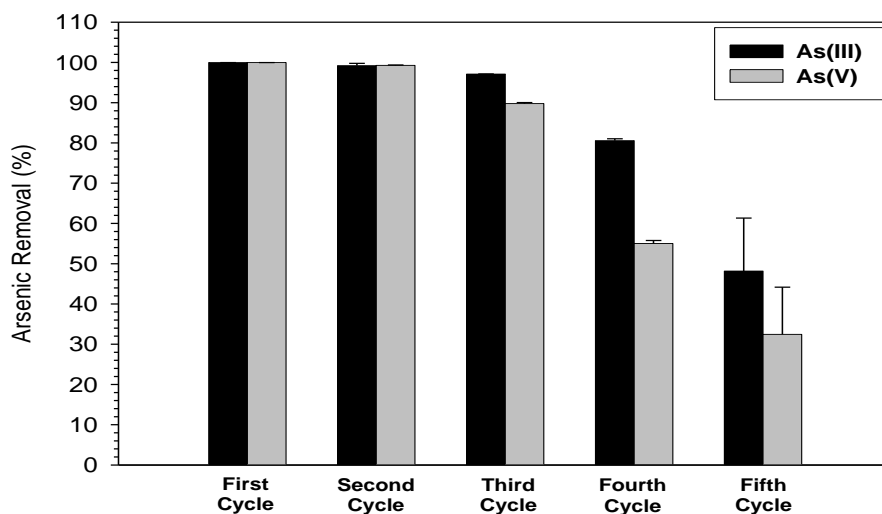


Fig. 10. Re-use of Mn_2O_3 sorbent in five adsorption cycles

97.1% and 90% removal of As(III) and As(V) were obtained, respectively. Adsorption of arsenic further decreased in the fourth and fifth adsorption cycles. The removal of As(III) was 80.6% and 48.2 %, and the removal of As(V) was 55% and 32.4% in the fourth and fifth adsorption cycles, respectively. After five adsorption cycles, the total uptake of As(III) [86 %] was greater than the total uptake of As(V) [74%]. Nearly 80 percent of the total uptake of both As(III) and As(V) was achieved during the second, third, fourth and fifth cycles of adsorption. The results show that re-using the Mn_2O_3 sorbent from the first adsorption cycle in four extra adsorption cycles was conducive to the removal of substantial additional amounts of As(III) and As(V) from the synthetic solution.

3.11. Arsenic removal from real groundwater

The arsenic removal ability of Mn_2O_3 was tested in two different real groundwater samples collected from northern Illinois. The composition of these two groundwaters is indicated in Table 6. The As(V) and As(III) removal with real groundwater spiked with 1mg/L As(V) or 1mg/L As(III), without adding sodium bicarbonate, calcium chloride and sodium sulfate was studied in the batch system. The batch experiments were performed as before. Different ranges of adsorbent dosage (2-40 g/L) were exposed to the spiked groundwaters for 24hr for arsenic adsorption. The results are shown in Fig.11.

Table 6. Characteristics of real groundwaters

| Parameter | Groundwater #1 | Groundwater #2 |
|---|----------------|----------------|
| pH | 7.646 | 7.584 |
| TDS (mg/L) | 780 | 2670 |
| Alkalinity (mg/L as CaCO_3) | 202.2 | 150 |
| Ca(mg/L) | 78.59 | 300.1 |
| Total Hardness (mg/L as CaCO_3) | 273.6 | 796 |
| Fe (mg/L) | 3.62 | 4.22 |
| Mn(mg/L) | 0.664 | 0.705 |
| Conductivity (μS) | 1592 | 5120 |
| Mg (mg/L) | 45.61 | 67.71 |

The higher arsenic removal efficiency was resulted at higher sorbent dosage as expected. For As(III) removal, increasing the sorbent dosage from 10 g/L to 40 g/L didn't significantly enhance the As(III) removal efficiency. The higher arsenite adsorption was obtained for GW#2 versus GW#1 specially at lower sorbent dosages. For As(V) spiked groundwater, the 20 g/L of crystalline Mn_2O_3 was able to remove greater than 99.5% of initial As(V) concentration from both groundwaters. For As(III) spiked groundwaters, the 20g/L and 13 g/L of the sorbent was needed to meet the arsenic standard limit in drinking water for GW#1 and GW#2, respectively. The very low dosage of Mn_2O_3 (2.5 g/L) removed almost 70% and 50 % of As(III) and As(V) initial concentration from GW#2 solution, respectively. The corresponding removal efficiency of As(III) and As(V) from GW#1 was obtained as 55% and 48% ,respectively. In general, the results indicated that an optimum dosage of 20 g/L of the crystalline Mn_2O_3 sorbent was able to remove a greater than 99.5% of arsenic from contaminated groundwaters and meet the standard level showing its ability to be used as a practical efficient sorbent for arsenic removal from contaminated groundwater.

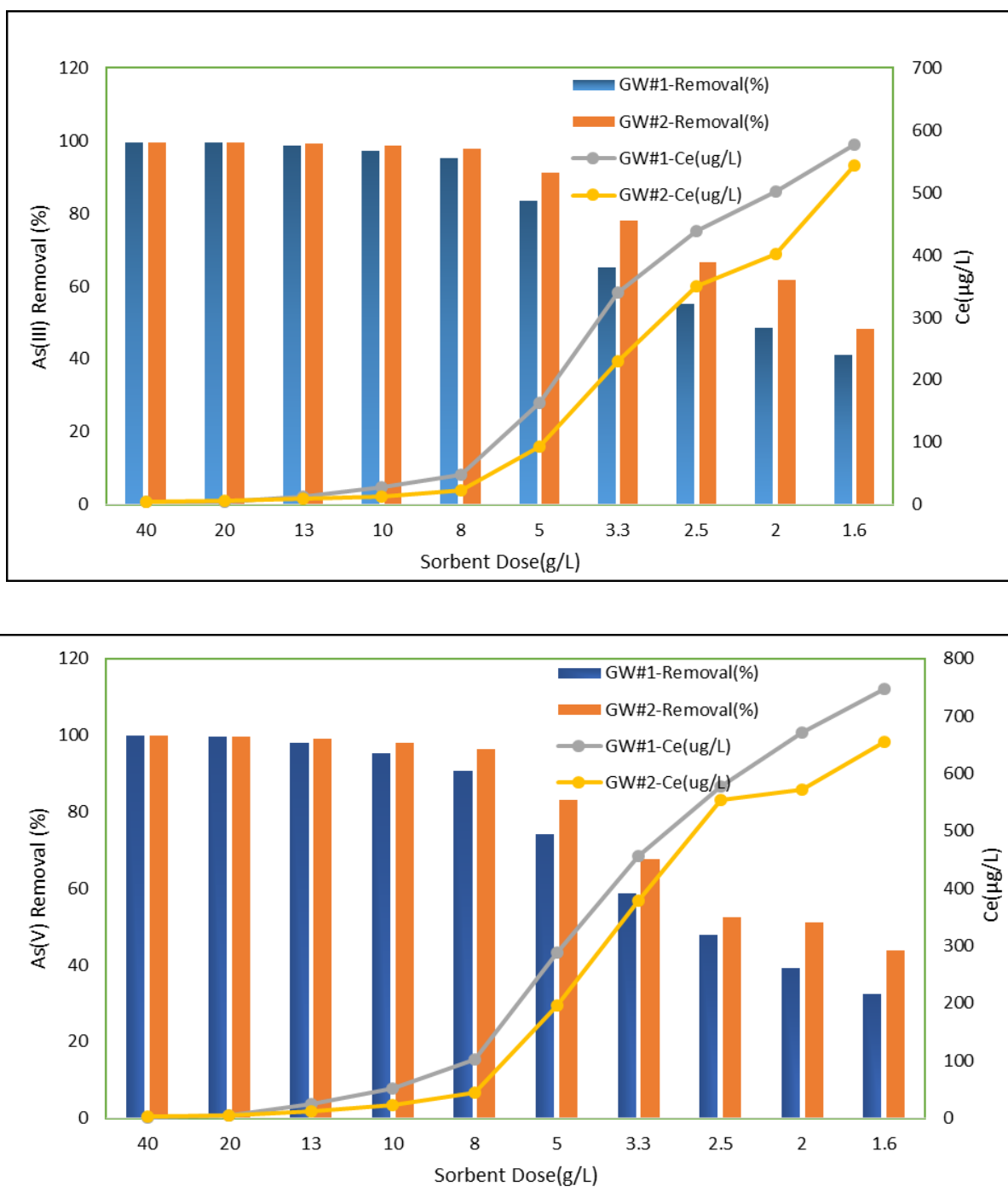


Fig.11. As(III) and As(V) removal from two different arsenic spiked real ground waters:GW#1 and GW#2

4. CONCLUSIONS

This study investigated the adsorption of As(V) and As(III) onto crystalline manganese (III) oxide (Mn_2O_3) in batch systems. The arsenic removal efficiency increased to a maximum of 99.9% in both DI water and synthetic solution as the sorbent dosage increased from 5 g/L to 20 g/L. Favorable adsorption of As(III) and As(V) onto Mn_2O_3 occurred. Moreover, a higher removal of As(III) than As(V) was obtained while the binding of As(V) onto Mn_2O_3 was found to be stronger than that of As(III). Fairly rapid adsorption of As(III) and As(V) occurred within 60 min of contact time. The pseudo-second order kinetic model was found to best correlate to the experimental data for adsorption of As(III) and As(V) onto Mn_2O_3 . Second-order kinetics and the D-R equation parameters were suggestive of arsenic chemisorption. Adsorption of As(III) was relatively independent of solution pH while the adsorption of As(V) showed greater dependence on pH with the highest uptake at pH 2. The surface charge analysis of the sorbent indicated that H_3AsO_3 was likely oxidized to the arsenate species on the surface of Mn_2O_3 , with As(V) species forming inner-sphere complexes on the surface of Mn_2O_3 . According to the acid dissociation constants of As(III) and As(V) species, zeta potential measurements and the effect of pH on adsorption, a likely mechanism responsible for the oxidation of As(III) to As(V) on the surface of Mn_2O_3 was proposed. The presence of phosphate and bicarbonate reduced arsenic removal efficiency, whereas the presence of calcium and sulfate did not show any noticeable effect on the adsorption of arsenic. The arsenic removal ability of Mn_2O_3 was tested in two different arsenic spiked real groundwater samples collected from northern Illinois. The results showed that an optimum dosage of 20 g/L of the crystalline Mn_2O_3 sorbent was able to remove a greater than 99.5% of As(III) and As(V) from contaminated groundwaters and meet the standard level. Based

on effective adsorption and sorbent re-use capacity, crystalline Mn_2O_3 was a potentially sustainable sorbent for removal of both As(III) and As(V) from water.

5. REFERENCES

- [1] Mandal, B.K. and Suzuki, K.T.: Arsenic round the world: a review. *Talanta*, 58 :201–235, 2002.
- [2] Sharma,A.K.,Tjell,J.C.,Sloth,J.J. and Holm,P.E.: Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. *Applied Geochemistry*.41:11–33, 2014.
- [3] Smedley, PL. and Kinniburgh, DG.: A review of the source, behaviour and distribution of arsenic in natural waters.*Appl Geochem.*,17(5):517-568,2002.
- [4] Zhao,X, Holl,W.H. and Yun,G.: Elimination of cadmium trace contamination from drinking water. *Water. Res.*,36(4):851-858,2002.
- [5] Mondal,P.,Majumder,C.B. and Mohanty,B.: Laboratory based approaches for arsenic remediation from contaminated water: recent developments. *Journal of Hazardous Materials* ,B137:464–479,2006.
- [6] Li,R.,Li,Q.,Gao,S. and Shang,J.K.: Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles: Part A. Adsorption capacity and mechanism. *Chem.Eng.J.*,185– 186 :127-135,2012.
- [7] Wu,K., Liu,T.,Xue,W. and Wang,X.: Arsenic(III) oxidation/adsorption behaviors on a new bimetal adsorbent of Mn-oxide-doped Al oxide, *Chem. Eng. J.* 192(2012) 343–349.
- [8] Driehaus,W., Seith,R. and Jekel,M.: Oxidation of arsenate(III) with manganese oxides in water treatment. *Water Research*, 29: 297–305,1995.
- [9] Ferguson, M.A.,Hoffmann,M.R. and Hering,J.G.: TiO_2 -Photocatalyzed As(III) Oxidation in Aqueous Suspensions: Reaction Kinetics and Effects of Adsorption. *Environ. Sci.Technol.*39 :1880–1886,2005.

- [10] Edwards, M.: Chemistry of arsenic removal during coagulation and Fe-Mn oxidation, *Water Works Assoc.* 86(9): 64-78, 1994.
- [11] Oscarson, D.W.,Huang, P.M.,Defosse,C. and Herbillon,A.: Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments.*Nature.*,291:50-51, 1981.
- [12] Zhang, G.S.,Qu, J.H.,Liu,H.J.,Liu,R.P. and Wu,R.C.: Preparation and evaluation of a novel Fe-Mn binary oxide adsorbent for effective arsenite removal. *Water Res.* 41:1921–1928, 2007.
- [13] Gupta,K.,Maity,A. and Ghosh,U.C.: Manganese associated nanoparticles agglomerate of iron(III) oxide: Synthesis, characterization and arsenic(III) sorption behavior with mechanism. *J. Hazard. Mater.*184:832–842, 2010.
- [14] Maliyekkal,S.M., Philip,L. and Pradeep,T.: As(III) removal from drinking water using manganese oxide-coated-alumina: Performance evaluation and mechanistic details of surface binding. *Chem. Eng. J.* 153:101–107, 2009.
- [15] Sun,Z.,Yu,Y.,Pang,S. and Du,D.. Manganese-modified activated carbon fiber (Mn-ACF): Novel efficient adsorbent for Arsenic. *Applied Surface Science*, 284:100–106, 2013.
- [16] Jacukowicz-Sobala, I., Ociński,D. and Kociolek-Balawejder,E.: Synthesis and Evaluation of a Novel Hybrid Polymer Containing Manganese and Iron Oxides as a Sorbent for As(III) and As(V) Removal. *Ind. Eng. Chem. Res.* 52:6453–6461, 2013.
- [17] He,Y.T.,Hering,J.G.: Enhancement of arsenic(III) sequestration by manganese oxides in the presence of iron(II). *Water Air Soil Pollut.*203:359–368, 2009.
- [18] Lagergren, S .: Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar, Band 24:1-39, 1898.
- [19] Ho,Y.S. and Mackay,G.. The kinetics of sorption of divalent metal ions onto sphagnum moss peat.*Water Res.* 34 (2000) 735–742.
- [20] Sen, T.K. and Sarzali, M.V.: Removal of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminum oxide (Al_2O_3): a kinetic and equilibrium study. *Chem. Eng. J.* 142(3):256-262, 2008.
- [21] D'Arcy, M.,Weiss,D.,Bluck,M. and Vilar,R.: Adsorption kinetics, capacity and mechanism of arsenate and phosphate on a bifunctional $\text{TiO}_2\text{-Fe}_2\text{O}_3$ bi-composite. *Journal of Colloid and Interface Science*, 364:205–212, 2011.
- [22] Weber, W.J. and Morris, J.C.: Kinetics of adsorption on carbon from solution. *Journal of Sanitary Engineering Division American Society of Civil Engineers*, 89 (1963) 31–59.

[23] Ho, Y.S.: Removal of copper ions from aqueous solution by tree fern. *Water. Res.*, 37(10): 2323-2330, 2003.

[24] Lodeiro, P., Kwan, S.M., Perez, J.T., González, L.F., Gérente, C., Andrès, Y. and McKay, G.: Novel Fe loaded activated carbons with tailored properties for As(V) removal: Adsorption study correlated with carbon surface chemistry. *Chem. Eng. J.*, 215–216 :105–112, 2013.

[25] Freundlich, H.M.F.: Über die adsorption in losungen. *Z Phys Chem.*, 57(A):385, 1906.

[26] Veličković, Z., Vuković, G.D., Marinković, A.D., Moldovan, M., Perić-Grujić, A.A., Uskoković, P.S. and Ristić, M.Đ.: Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multiwall carbon nanotubes. *Chem. Eng. J.* 181–182:174–181, 2012.

[27] Ntim, S.A. and Mitra, S.: Adsorption of arsenic on multiwall carbon nanotube–zirconia nanohybrid for potential drinking water purification. *J Colloid Interface Sci.* 375:154–159, 2012.

[28] Langmuir, I.: The constitution and fundamental properties of solids and liquids, I. Solids. *J. Am. Chem. Soc.*, 38(11):2221–2295, 1916.

[29] Temkin, M.J., Pyzhev, V.: Kinetics of ammonia synthesis on promoted iron catalysts. *Acta. Physiochim.*, URSS 12:217–222, 1940.

[30] Dubinin, M.M. and Radushkevich, L.V.: Equation of the characteristic curve of activated charcoal. *Chem. Zentr.*, 1 :875, 1947.

[31] Islam, M., Mishra, P.C. and Patel, R.: Fluoride adsorption from aqueous solution by a hybrid thorium phosphate composite. *Chem. Eng. J.*, 166(3):978–985, 2011.

[32] Mane, V.S. and Babu, P.V.V.: Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust. *Desalination*, 273:321–329, 2011.

[33] Kocabas-Ataklı, Z.Ö. and Yürüm, Y.: Synthesis and characterization of anatase nano-adsorbent and application in removal of lead, copper and arsenic from water. *Chem. Eng. J.* 225: 625–635, 2013.

[34] Karim, A.H., Jalil, A.A., Triwahyono, S., Sidik, S.M., Kamarudin, N.H., Jusoh, R., Jusoh, N.W., Hameed, B.H.: Amino modified mesostructured silica nanoparticles for efficient adsorption of methylene blue. *J Colloid Interface Sci.*, 386:307–14, 2012.

[35] Lin, T.F., Wu, J.K.: Adsorption of arsenite and arsenate within activated alumina grains: Equilibrium and kinetics. *Water Res.* 35:2049–2057, 2001.

[36] Luo, X., Wang, X., Luo, S., Dong, R., Tu, X. and Zeng, G.: Adsorption of As (III) and As(V) from water using magnetite Fe₃O₄-reduced graphite oxide–MnO₂ nanocomposites. *Chem. Eng. J.*,

187: 45–52, 2012.

[37] Lakshmipathiraj,P., Narasimhan,B.R.V., Prabhakar,S. and BhaskarRaju,G.: Adsorption studies of arsenic on Mn-substituted iron oxyhydroxide.*J. Colloid .Inter. Sci.*, 304(2):317-322, 2006.

[38] Simeonidis, K., Gkinis,Th.,Tresintsi,S., Martinez-Boubeta,C., Vourlias,G., Tsiaoussis,I., Stavropoulos,G., Mitrakas,M. and Angelakeris, M.: Magnetic separation of hematite-coated Fe_3O_4 particles used as arsenic adsorbents.*Chemical Engineering Journal*, 168:1008-1015, 2011.

[39] Huang,Y-H.,Shih,Y-J. and Cheng,F-J.: Novel KMnO_4^- modified iron oxide for effective arsenite removal. *Journal of Hazardous Materials*, 198, (2011)1-6.

[40] Piriälä, M.,Martikainen, M.,Ainassaari,K.,Kuokkanen,T. and Keiski,R.L.: Removal of aqueous As(III) and As(V) by hydrous titanium dioxide. *J. Colloid Interf. Sci.*, 353:257–262, 2011.

[41] Ouvrard, S.,Simonnot,M.O. and Sardin ,M.: Reactive behavior of natural manganese oxides toward the adsorption of phosphate and arsenate.*Ind. Eng. Chem. Res.* 41(11):2785-2791.2002.

[42] Martinsona, C.A. and Reddy, K.J.: Adsorption of arsenic(III) and arsenic(V) by cupric oxide nanoparticles. *J Colloid Interface Sci.* 336 (2009) 406–411.

[43] Chammui,Y., Sooksamiti,P., Naksataa,W.,Thiansemc,S. and Arqueropanyo, O.: Removal of arsenic from aqueous solution by adsorption on Leonardite. *Chem. Eng. J.*, 240:202–210, 2014.

[44] Elizalde-Gonzalez, M.P.,Mattusch,J. and Einicke,W.D., Wennrich.R.: Sorption on natural solids for arsenic removal. *Chem. Eng. J.* 81:187–195, 2001.

[45] Jain,A. and Loeppert,R.H.: Effect of competing ions on the adsorption of arsenate and arsenite by ferrihydrite. *J.Environ. Qual.* 29:1422-1430,2000.

[46] Stumm, W. Chemistry of the solid-water interface; Wiley: New York, 1992.

[47] Raven, K.P., Jain, A. and Loeppert, R.H.: Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelope. *Environ. Sci. Technol.*, 32(3):344-349.1998.

[48] Manning,B.A.,Fendorf,S.E. and Goldberg,S... Surface Structures and Stability of Arsenic(III) on Goethite: Spectroscopic Evidence for Inner-Sphere Complexes*Environ. Sci. Technol.* 32:2383-2388,1998.

[49] Manna,BR ., Dey, S.,Debnath,S. and Ghosh,UC.: Removal of arsenic from groundwater using crystalline hydrous ferric oxide (CHFO). *Water Qual. Res. J. Canada* , 38:193–210, 2003.

[50] Doua,X., Zhang,Y., Zhao,B.,Wu,X.,Wu,Z. and Yang,M.: Arsenate adsorption on an Fe–Ce bimetal oxide adsorbent: EXAFS study and surface complexation modeling. *Colloids and*

Surfaces A: Physicochem. Eng. Aspects 379:109–115, 2011.

[51] Tripathy, S.S. and Raichur, A.M.: Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water. *Chem. Eng. J.*, 138(1-3):179-186, 2008.

[52] Badruddoza, A.Z.M., Shawon, Z.B.Z., Rahman, M.T., Hao, K.W., Hidajat, K. and Uddin, M.S.: Ionically modified magnetic nanomaterials for arsenic and chromium removal from water. *Chem. Eng. J.* 225:607–615, 2013.

[53] Gao, Y. and Mucci, A.: Individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater. *Chem. Geol.* 199:91–109, 2003.

[54] Zeng, H., Fisher, B. and Giammar, D.E.: Individual and Competitive Adsorption of Arsenate and Phosphate To a High-Surface-Area Iron Oxide-Based Sorbent. *Environ. Sci. Technol.* 42:147–152, 2008.

[55] Zhang, S., Niu, H., Cai, Y., Zhao, X. and Shia, Y.: Arsenite and arsenate adsorption on coprecipitated bimetal oxide nanomaterials: MnFe_2O_4 and CoFe_2O_4 . *Chem. Eng. J.*, 158(3):599-607, 2010.

[56] Frau, F., Addari, D., Atzei, D., Biddau, R., Cidu, R. and Rossi, A.: Influence of Major Anions on As(V) Adsorption by Synthetic 2-line Ferrihydrite. Kinetic Investigation and XPS Study of the Competitive Effect of Bicarbonate. *Water Air Soil Pollut.* 205(2010) 25–41.

[57] Li, X., Qi, Y., Li, Y., Zhang, Y., He, X., Wang, Y.: Novel magnetic beads based on sodium alginate gel crosslinked by zirconium(IV) and their effective removal for Pb^{2+} in aqueous solutions by using a batch and continuous systems. *Bioresource Technology*, 142:611–619, 2013.

Chapter (V)

V. ADSORPTION AND REMOVAL OF ARSENIC FROM COAL FLY ASH LEACHATE USING MANGANESE OXIDE SORBENT

1. INTRODUCTION

Fly ash can be produced by combustion of coal in thermal power plants [1]. Fly ash is fine particulate inorganic matter obtained from electrostatic precipitators, mechanical processes, and fabric filters from the flue gas produced by the combustion of pulverized coal in the boiler assembly [2]. An estimated 780 Mt of coal ash are produced worldwide every year from Coal-based power generation [3]. In 2010, 67.7 million short tons of fly ash were generated by coal-fired power plants in the US, accounting for 52.0% of the total coal combustion products (CCPs) [4]. These ashes are normally disposed-off in large ash ponds or dry landfills along with other unused CCPs to get dried up.

Fly ash contains a broad array of trace elements in concentrations greater than 50 mg/kg, many of which are of environmental concern [5]. The phase transformations of the mineral matter in coal during high temperature combustion may make the trace elements in the original coal matrix susceptible to leaching [6]. Some elements contained in fly ash are likely to be released from the storage/disposal/application site when ash comes in contact with water [5]. Leaching of these trace elements can potentially pose health hazards to humans when they transfer into the groundwater

and reach to the domestic area. Thus special attention is to be needed to control and manage these toxic as leached from fly ash.

The leachability of mineral components and the behavior of dissolved components mainly depends on the redox potential (Eh), the combustion conditions, the concentration in fly ash, the concentration and mode of occurrence in the feed coal and, most importantly, the pH [7]. The effect of leaching solution pH on column leaching has been investigated [8]. Arsenic is one of the common hazardous pollutants found in coal fly ash [9]. The mode of occurrence of arsenic in coal is an important factor that influences the behavior of the element. It has been reported that arsenic occurs in the coal mostly as pyritic, organic and arsenate [10, 11], while the X-ray absorption fine structure (XAFS) spectroscopy studies showed that all the arsenic in fly ash appears to be present as arsenate, possibly combined with alumino-silicate slag and calcium ortho-arsenate [12,13,14]

Arsenic is enriched on fly ash particles as a consequence of the condensation of volatile arsenic species onto the surfaces of the particles. There is concern that leaching of this arsenic will result in contamination of aquatic disposal sites. The behavior of arsenic during disposal of coal-combustion waste products is a significant cause for concern because of its toxicity, environmental persistence, and tendency to bio-accumulate. The main concern is that pollution from the ash leaches out and contaminates nearby groundwater that is used for drinking. The World Health Organization (WHO) guideline value for arsenic in drinking water is 10 mg/L [15]. Also, arsenic has been determined to be a class A human carcinogen by the US EPA [16]. Therefore, applying effective methods and appropriate materials to selectively adsorb the excess amount of arsenic from ash leachate is required.

Various methods like lime softening [17], precipitation-coprecipitation [18], membrane process [19], ion exchange [20], and adsorption [21] have been used for adsorption of arsenic. Adsorption has been recognized as a superior method for arsenic treatment. Various adsorbents like mineral oxides, activated carbons, biological materials, or polymer resins have been used for the adsorption of arsenic from water [22].

Investigations have shown that manganese oxides are effective oxidizer of the more toxic species of As (III) to As(V) in water treatment unit and natural environment and make the sorption process easier and effective [23,24]. Manganese oxides extremely affect the mobility and fate of many pollutants in environment and can easily participate in different redox reactions and strongly adsorb numerous ions [25]. In last chapters, it was shown that the arsenate adsorption onto Mn_2O_3 and Mn_3O_4 were much higher than the other two manganese oxide sorbents (MnO and MnO_2). A 10g/L of Mn_2O_3 was able to remove greater than 99% of arsenate in solutions with different ionic background. In this chapter, the main focus is on applying manganese (III) oxide (Mn_2O_3) as a sorbent to adsorb the arsenic leached from fly ash. The effect of time and adsorbent dosage on the adsorption process efficiency of arsenic from a synthetic solution were investigated and the capability of Mn_2O_3 powder for removal of arsenic from three different alkaline ash leachates (called PZ8-3, PZ8-4 and PZ8-5) was studied.

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

Sodium hydroxide (NaOH) and hydrochloric acid (HCl, ACS plus grade) were of analytical reagent grade and were obtained from Fisher scientific (Fair Lawn, NJ, USA). The manganese oxide (Mn_2O_3) was obtained from Alfa Aesar company (Ward Hill, MA). Deionized water (DI) was prepared in the laboratory with a resistance greater than 18 M Ω .

2.2. Synthetic solution and Ash Samples

The synthetic solution was prepared by dissolving 1 mM HCO_3^- , 0.25 mM CaCl_2 , 0.25 mM Na_2SO_4 and 0.4 mg/L sodium arsenate [As(V)] in DI water. The coal fly ash used in the present study was collected from the retired ash basin at the Brunner Island site belonging to PPL Generation Co. in Pennsylvania. Three ash samples were obtained from the PZ8-3, PZ8-4 and PZ8-5 locations collected from a depth of 24 to 32 ft, 30 to 34 ft and 20 to 25 ft, respectively. U.S. EPA Method 3050B was used for the acid digestion of ash to determine the concentration of various elements in ash including aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chromium, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, selenium, silver, sodium, strontium and zinc. Ion chromatography (Dionex, CA) was used to analyze the chloride, fluoride and sulfate content of the ash. An elemental analyzer (EA) was used to analyze the inorganic carbon content of the ash. The moisture content and organic carbon content were obtained using a drying oven (105°C) and a muffle furnace (375°C), respectively (ASTM D 2974-87). The particle size distribution of the ash was determined (ASTM D 422). The pH of ash was determined by mixing 10 g of ash with 10 mL of deionized (DI) water using a 1:1 (g:mL) ratio (ASTM 4972).

2.3. Leaching Experiments

Leaching of ash was carried out by batch extraction of ash samples with DI water for 48 h. 200 g of ash were mixed with 2.0 L of DI water using a solid:liquid extraction ratio of 1 g:10 mL, and the mixture was shaken at 16 rpm. After 48 h of extraction, the ash-water slurry was centrifuged at 9500g for 10 min to separate the ash from the leachate. The leachate solution was then filtered using a 0.45 μm cellulose acetate membrane. Filtered leachate samples were analyzed for pH, alkalinity and arsenic concentration.

2.4. Batch Adsorption Tests

The ash leachate was equilibrated with the manganese oxide sorbent (Mn_2O_3) using a sorbent:solution ratio of 1g:50mL. All batch adsorption experiments were conducted in 50 mL high density polyethylene (HDPE) bottles. After the addition of the sorbent and the leachate to bottles, the mixture was shaken thoroughly in a tumbler in the dark at 16 rpm and 25 °C over a period of time. The suspensions were centrifuged at 9500 rpm to separate the aqueous phase from the sorbent. After centrifugation, the pH and alkalinity of the supernatant were measured. The pH was measured with a pH meter (Thermo scientific Orion, MA). The centrifuged solutions were filtered with 0.45 μm cellulose acetate membrane filters. The filtered samples for analysis of residual arsenic were preserved by adding concentrated HNO_3 (trace metal grade, Fisher Scientific) and were stored in polyethylene bottles. The concentration of arsenic in the filtrate was analyzed with graphite furnace atomic absorption spectroscopy (GFAAS) with Zeeman background correction. For arsenic analysis, all measurements were carried out using an electrodeless lamp (EDL) lamp at 193.7 nm and the modifier used was palladium-magnesium modifier. The

atomization and pre-treatment temperature were 2000 and 1200 °C, respectively. The detection limit of arsenic was estimated to be 1 µg/L.

All batch adsorption experiments were carried out in triplicate and at room temperature. The arsenic uptake by Mn₂O₃ was calculated as:

$$q = \frac{(C_0 - C_e)}{m} \times V \quad (\text{Eq.1})$$

where q is the adsorbed arsenic (mg/kg), C₀ and C_e are the initial and equilibrium concentration of arsenic in the solution (mg/L), respectively, V is the leachate volume (L), and m is the adsorbent dosage (kg). The arsenic removal percent (%) was calculated using the following equation:

$$\text{Removal}(\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (\text{Eq.2})$$

Different dosages (0.05-2 g) of the sorbent were used to investigate the effect of sorbent dosage. For the kinetics study, 0.5 g of Mn₂O₃ was mixed with 50 mL of the ash leachate at 25 °C for different periods of time.

2.5. Adsorption isotherm experiments

Different dosages of the sorbent were mixed in HDPE bottles with 50 mL of the leachate solution to determine the adsorption capacity of the sorbent. The bottles were shaken in a tumbler in the dark at 16 rpm for a period of time required for the adsorption equilibrium determined from the adsorption kinetics experiment. Afterwards, the bottles were removed from the tumbler and the samples were analyzed similar to the batch adsorption tests.

3. RESULTS AND DISCUSSION

3.1. Surface Analysis of Ash Particles

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) with X-ray electron diffraction spectroscopy (XEDS), Raman Spectroscopy and X-ray diffraction(XRD) were performed for one of the studied ash sample, PZ8-3 (24-32 ft), as an example for analyzing the surface of ash particles. TEM analysis concluded that the ash sample was heterogeneous (Figure 1) and amorphous alumina was present in ash. SEM analysis showed that the ash particles were heterogeneous, and XEDS showed that the ash surface contained mostly oxygen and carbon and appreciable amounts of aluminum and silicon, in addition to calcium and iron (Figure 2). Raman spectroscopy revealed the presence of amorphous inorganic carbon in the ash. XRD results (not shown here) confirmed the presence of crystalline iron (III) oxide and silica in the ash.

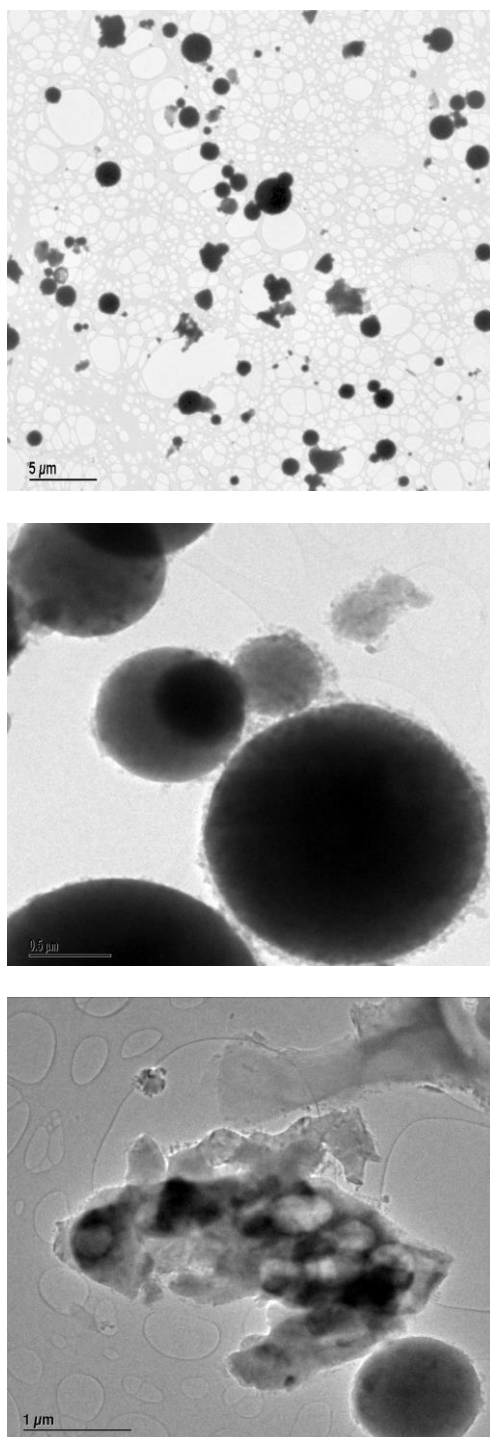


Fig.1. Transmission electron images of ash sample PZ8-3 (24-32')

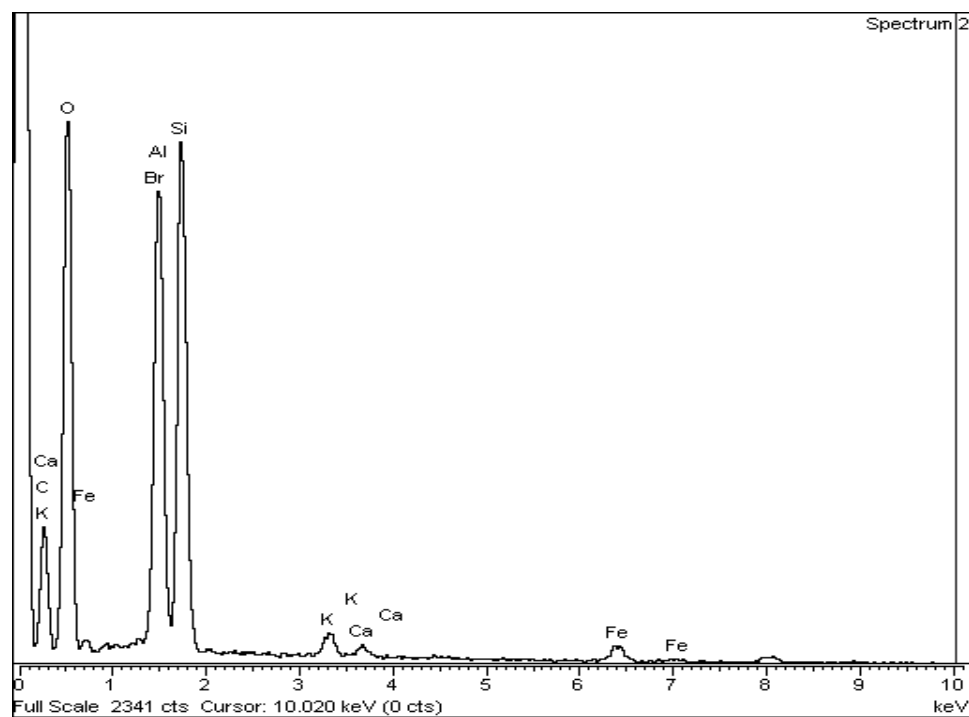
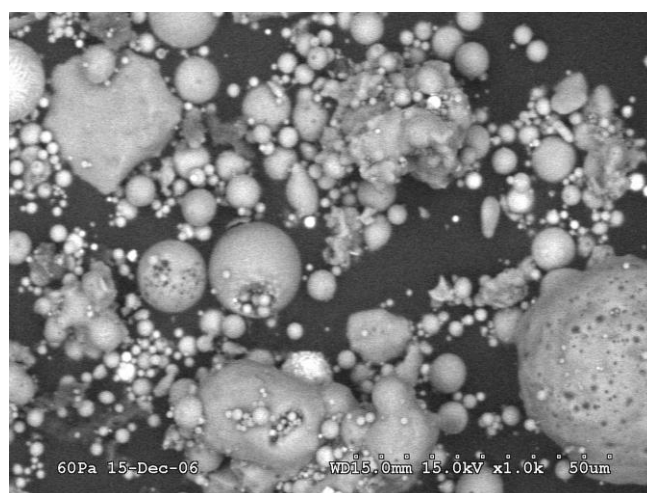


Fig. 2. Scanning electron micrograph and SEM/XEDS elemental analysis of ash sample PZ8-3 (24-32')

3.2. Ash and Ash leachate characterization

The physical and chemical properties of the ash samples used in the present study (PZ8-3, PZ8-4 and PZ8-5) are shown in table 1, table 2 and table 3. The physical properties of the ash samples showed that all three ash samples were alkaline in nature with pH of more than 7. The moisture content of the PZ8-3, PZ8-4 and PZ8-5 ash samples were found to be 20.2, 26.1 and 23.8, respectively. The chemical content of the ash samples indicated that the arsenic content of ash PZ8-3, PZ8-4 and PZ8-5 were much less than calcium and iron content and it was 108.19 , 152 and 213 mg/kg, respectively.

Table 1. Physical properties of ash samples

| Sample | pH | Eh (mV) | Moisture (%) | Specific Gravity | Porosity | OM (%) | IC (%) | Sand (%) | Silt (%) | Clay (%) |
|---------------|------|------------|-----------------|---------------------|----------|-----------|-----------|-------------|-------------|-------------|
| PZ8-3(24-32') | 7.91 | 213.1 | 20.2 | - | - | - | 1.5 | 30.3 | 57.2 | 12.5 |
| PZ8-4(30-34') | 8.08 | 216 | 26.1 | 2.03 | 0.35 | 0.55 | 2.19 | 20.6 | 60.4 | 19 |
| PZ8-5(20-25') | 7.39 | 219 | 23.8 | 2.12 | 0.37 | 0.76 | 2.34 | 14.4 | 52.2 | 33.4 |

Table 2. Chemical content of ash samples PZ8-4 and PZ 8-5 (mg/kg)

| | PZ 8-4 | PZ 8-5 | | PZ8-4 | PZ 8-5 | | PZ8-4 | PZ 8-5 | | PZ8-4 | PZ 8-5 |
|-----------|--------|--------|-----------|-------|--------|-----------|-------|--------|------------------------------------|-------|--------|
| | 30-34 | 20-25 | | 30-34 | 20-25 | | 30-34 | 20-25 | | 30-34 | 20-25 |
| Al | 18800 | 24100 | Mg | 938 | 1170 | Ca | 4760 | 4500 | Sr | 254 | 278 |
| Sb | 0.34 | 0.27 | Mn | 54.8 | 76 | Cr | 36.9 | 52.7 | Zn | 62.7 | 102 |
| As | 152 | 213 | Mo | 3.4 | 5.5 | Cu | 35.9 | 59.3 | F- | 2.3 | 7.1 |
| Ba | 451 | 418 | Ni | 26.7 | 38.6 | Fe | 28300 | 23200 | SO₄⁻² | 70 | 275 |
| Be | 3.4 | 4.9 | Se | 4.6 | 7.9 | Pb | 28.9 | 45.7 | Na | 299 | 381 |
| Ag | 0.19 | 0.26 | Li | 36 | 47 | B | 23 | 21 | | | |

Table 3. Concentration of several chemical constituents of ash samples from PZ8-3

| | Depth (feet) | As (mg/kg) | Fe (mg/kg) | Ca (mg/kg) | Mn (mg/kg) |
|--------------|-----------------|---------------|---------------|---------------|---------------|
| PZ8-3 | 24-32 | 108.19 | 38638.26 | 5409.36 | 85 |

Ash leachate were generated using fly ash PZ8-3(24-32') ,PZ8-4(30.5-34.5') and PZ8-5(20-25') by extracting of fly ash with DI water at 16 rpm for 48 hours at a mass (g) to volume (ml) ratio of 1:10. The properties of synthetic solution as well as ash leachates including pH, total dissolved solids (TDS), alkalinity and initial arsenic concentration are shown in Table 4. The analysis showed that the ash leachates contained only As(V) .

Table 4. Ash leachate characteristics

| Properties | Synthetic Solution | PZ8-3(24-32') | PZ8-4(30.5-34.5') | PZ8-5(20-25') |
|---|--------------------|---------------|-------------------|---------------|
| pH | 7.921 | 7.079 | 7.705 | 7.531 |
| TDS(mg/L) | 140 | 77 | 83 | 139 |
| Alkalinity (mg/L as CaCO ₃) | 26.67 | 21.7 | 16 | 12.7 |
| Initial Arsenic (V) (mg/L) | 0.435 | 0.37 | 0.450 | 0.330 |

3.3. Effect of sorbent dosage

The adsorbent dose is an important parameter in adsorption studies because it determines the adsorbent capacity for a given initial concentration of ash leachate. Also, the dosage of Mn₂O₃ adsorbent is a key parameter to control both the availability and the accessibility of adsorption sites. The removal of arsenic from all three different ash leachates and the synthetic solution as a function of sorbent dosage is shown in Fig.3.

As shown in Fig.3 and for actual leachates PZ85 and PZ83, the adsorption capacities of the sorbent decreased slowly as the used sorbent dosage decreased from 20 g/L to 5 g/L. Further decrease in the sorbent dosage led to significant decrease of arsenic removal. For PZ84 solution, a lower

arsenic adsorption capacity was obtained specially at dosages lower than 10 g/L. The decrease can be attributed to decreased surface area and the sorption sites. Since the particle size range constant, the surface area will be directly proportional to the mass of adsorbent in the solution. The arsenic removal efficiency from synthetic solution was not significantly decreased even at lower sorbent dosages.

In general, the sorbent showed promising removal efficiency for all three leachates. However, the arsenic removal was found to be higher in PZ8-5 leachates specially at lower dosages of the applied sorbent. A 10 g/L of Mn_2O_3 sorbent was able to remove greater than 98% of arsenic from ash leachates. The results indicated that a 5 g/L of the sorbent are needed to meet the EPA standard limit ($<10 \mu\text{g/L}$) for PZ8-3 and PZ85 leachates, respectively while for PZ8-4, a 10 g/L of Mn_2O_3 needs to be applied to drop the arsenic concentration of the leachate to less than $10 \mu\text{g/L}$.

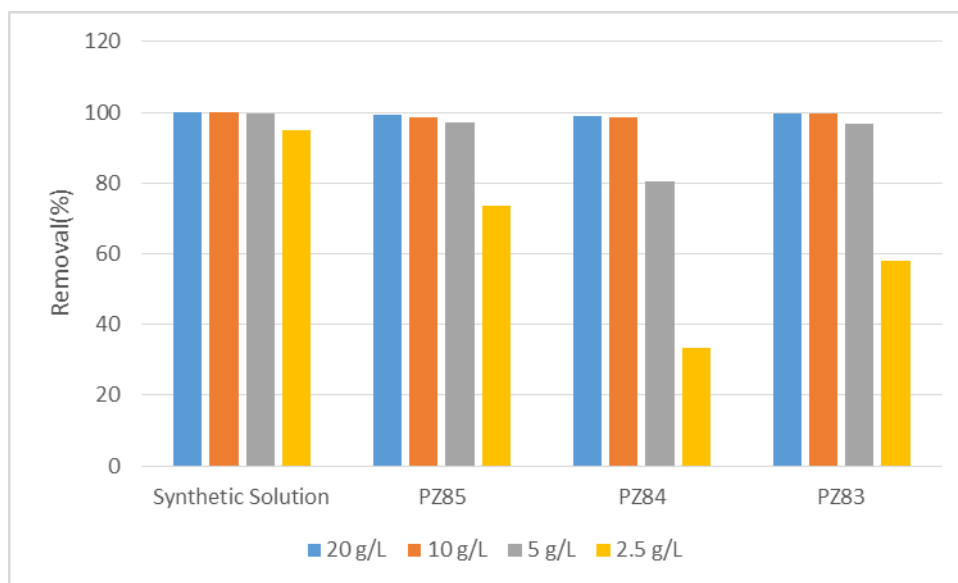


Fig.3. Effect of Mn_2O_3 dosage on the removal of arsenic from synthetic solution after 24 h

3.4. Effect of contact time

The kinetics of the sorption processes of arsenic onto the sorbent can indicate the efficiency and behavior of the sorbent and would help to understand the dynamics of the adsorption process. To determine the effect of contact time on the arsenic adsorption, the adsorbent was exposed to the synthetic solution and the leachates at different time intervals.

Variations in the percentage adsorption of arsenic by 10 g/L of Mn_2O_3 as a function of contact time for different leachates are shown in Fig.4. As shown in Fig.4, a 10 g/L of the applied sorbent was able to remove greater than 98% of initial arsenic in 30 min indicating the fast arsenic adsorption by Mn_2O_3 . A similar pattern was obtained for all three leachates. For all three leachates, an abrupt increases in adsorption was occurred at low times before reaching the plateaus.

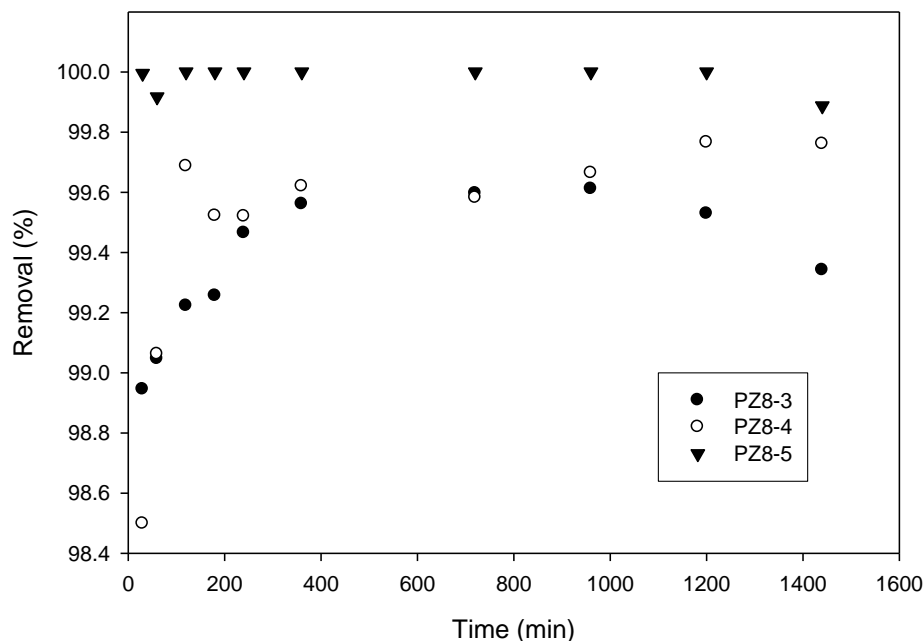


Fig.4. Effect of contact time on the removal of arsenic from ash leachates using 10 g/L of Mn_2O_3

In order to achieve the non-zero residual arsenic concentration for kinetic modeling, the arsenic removal was obtained at different contact times for a Mn_2O_3 dose of 4 g/L. The modeling was carried out for one of the leachate, PZ8-3, as an example and was compared to the kinetic modeling of arsenic removal from the synthetic solution (Fig.5). As depicted, the adsorption of As(V) onto Mn_2O_3 powder was rapid in the initial stages up to 60 min, and was almost same at high contact time. This behavior could be attributed to the availability of a large number of active sites for rapid surface arsenic ions binding during the first stage of adsorption process, while the second stage was the possible slow intra-particle diffusion of metal ions into the adsorbent. The results showed that the sorbent was able to decrease the concentration of arsenic below the

standard limit of $10 \mu\text{g l}^{-1}$ within 60 min. The equilibrium arsenate uptake for Mn_2O_3 for the leachate and the synthetic solution was found to be 84.4 mg/kg and 107.2 mg/kg, respectively. Based on the q_e values, the equilibrium time for arsenic adsorption in the synthetic solution was found to be 3hr while in leachate a 24hr equilibrium time was considered.

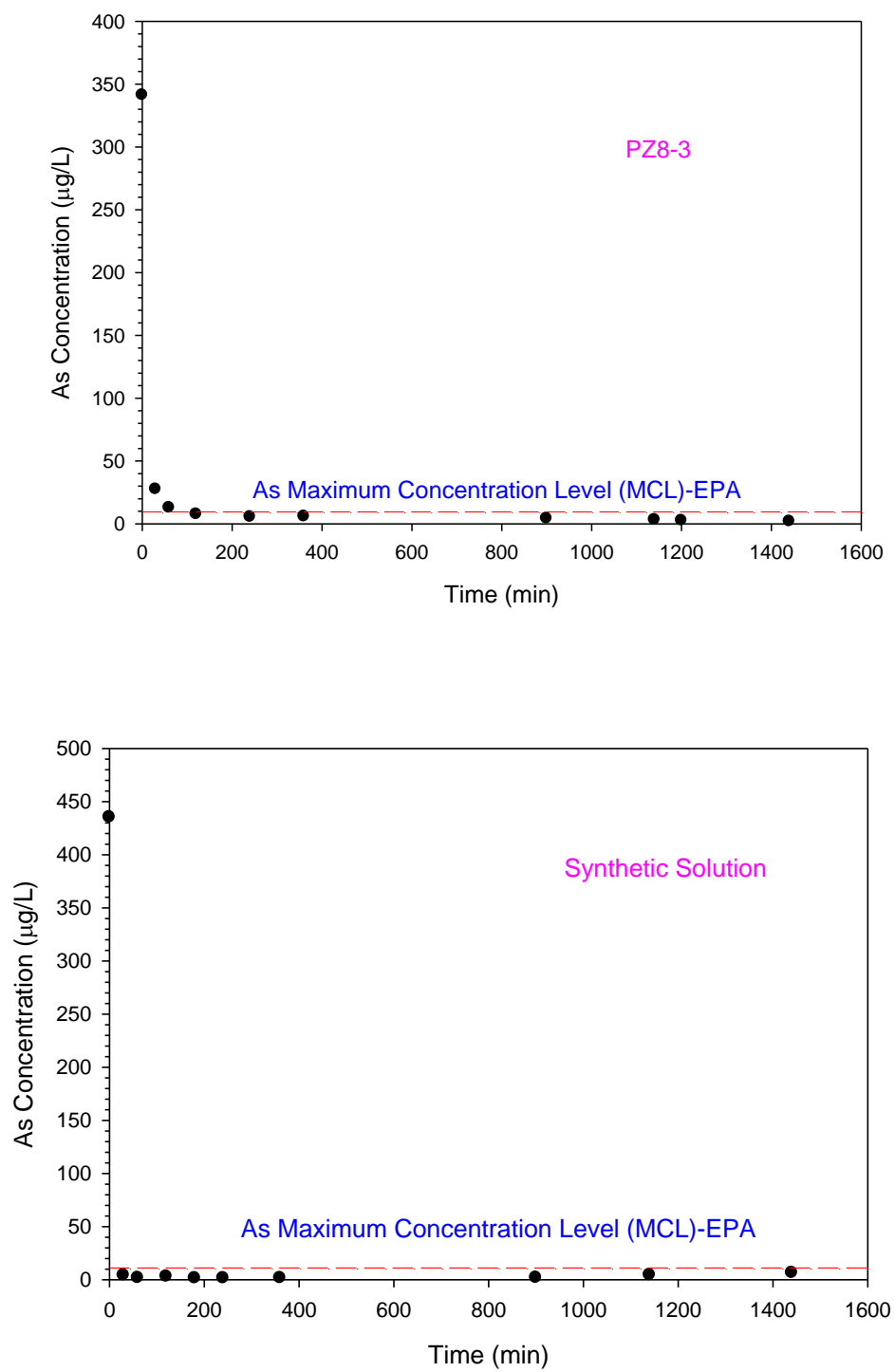


Fig.5. Effect of contact time on the removal of arsenic using 4 g/L of Mn_2O_3

3.5. Adsorption kinetics

Adsorption kinetics experiments were performed to investigate the mechanism of adsorption. The feature constants of sorption were obtained using a pseudo-first-order (Lagergren) model and pseudo-second-order model.

One of the most widely used sorption rate equations is the Lagergren rate equation [26], which is expressed by Eq. (3):

$$\frac{dq}{dt} = k_1 \times (q_e - q_t) \quad (1)$$

where k_1 is the adsorption rate constant (min^{-1}) of pseudo-first order adsorption and q_e and q_t are the adsorption capacities (mg/kg) at equilibrium and at time t , respectively. The values of k_1 and q_e can be determined by the slope of linear plots of $\ln(q_e - q_t)$ versus t (Fig. 6). It should be noted that the experimental data before the equilibrium time was considered for the kinetic study. The parameters of the pseudo-first-order model are summarized in Table 5. The coefficient of determination value for both leachate and synthetic solution was low and the calculated sorption capacity values obtained from this kinetic model did not give reasonable values compared with the experimental sorption capacity, implying that the arsenic sorption process by Mn_2O_3 did not follow the pseudo-first-order sorption rate expression of Lagergren.

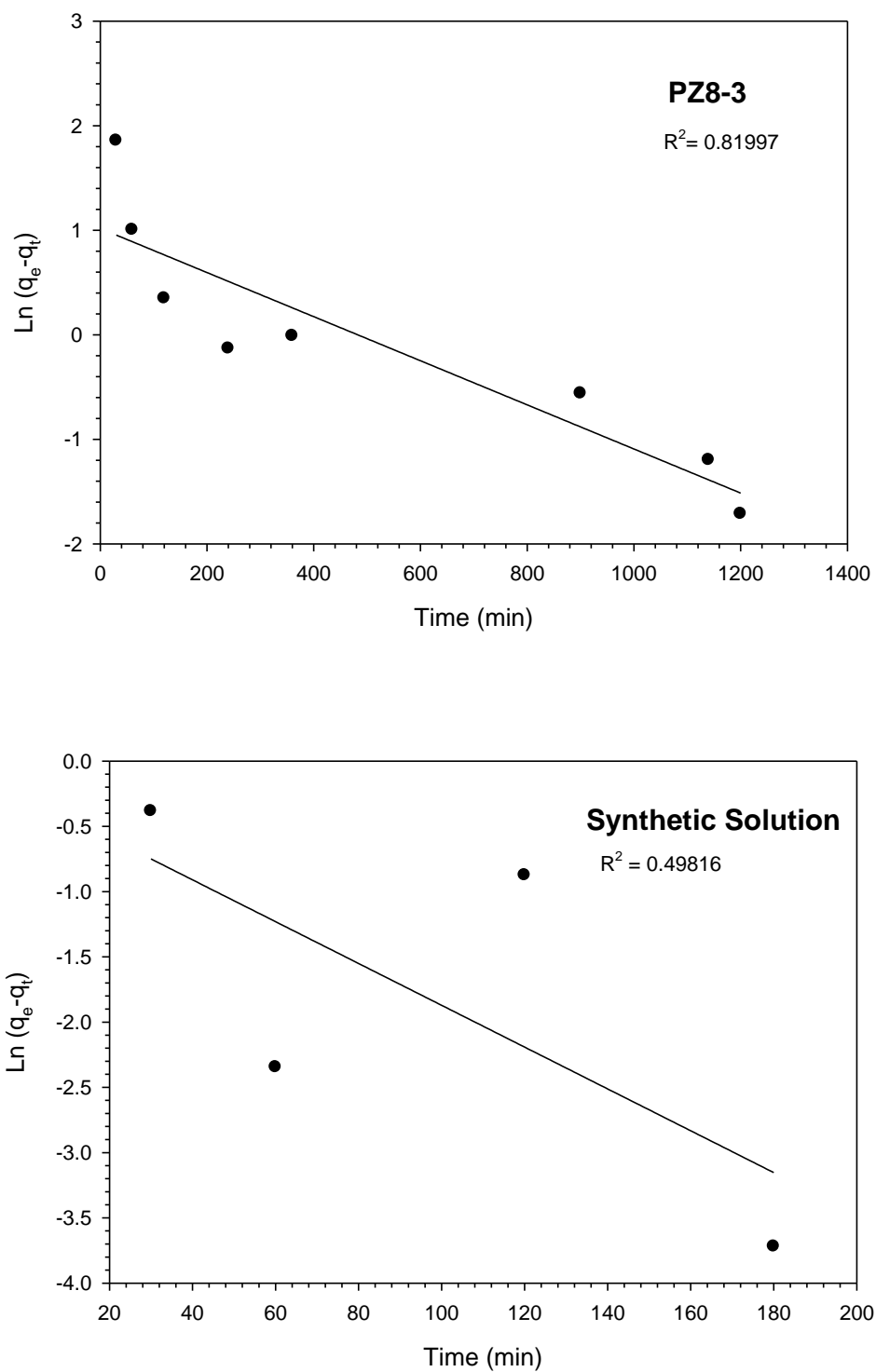


Fig.6. Test of pseudo-first order kinetic model for arsenic adsorption (adsorbent dosage=4 g/L)

The pseudo-second order model has proposed by Ho in 1995 as follows [27]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2} \right) \left(\frac{1}{q_e^2} \right) + \frac{t}{q_e} \quad (6)$$

where k_2 is the adsorption rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$) of pseudo-second order adsorption. Kinetic constants q_e and k_2 were calculated from the slope and intercept of the plot t/q_t versus t (Fig. 7) and were presented in Table 5.

A linear relationship existing between experimental data and pseudo-second-order model and the correlation coefficient (R^2) suggested a strong relationship between the parameters and also explained that the sorption process of arsenic followed pseudo-second-order kinetics. Moreover, the calculated q_e values were completely consistent with the experimental data in both ash leachate and synthetic solution.

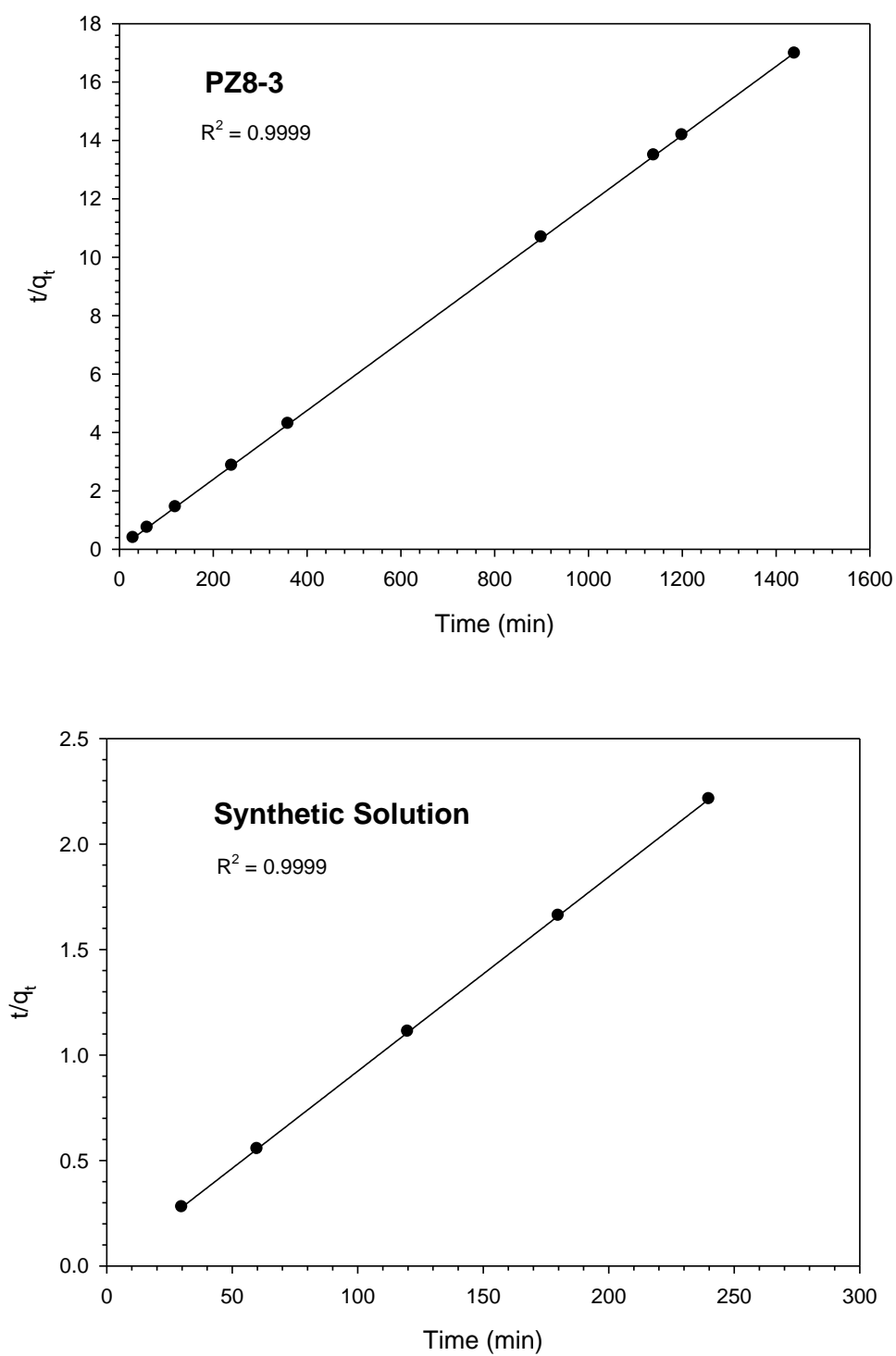


Fig.7. Test of pseudo-second order kinetic model for arsenic adsorption (adsorbent dosage=4 g/L)

Table 5. Kinetic parameters for the adsorption of As(V) by Mn₂O₃

| | | PZ8-3 | Synthetic Solution |
|--------------|------------------|--------------------------------------|--------------------------------------|
| | | $q_{\text{exp}}=84.83 \text{ mg/kg}$ | $q_{\text{exp}}=107.2 \text{ mg/kg}$ |
| First Order | | | |
| | R^2 | 0.82 | 0.4889 |
| | K_1 | 0.0021 | 0.0032 |
| | q_{cal} | 2.77 | 30.15 |
| | | | |
| Second Order | | | |
| | R^2 | 0.9999 | 0.9999 |
| | K_2 | 0.0041 | 0.0368 |
| | q_{cal} | 84.75 | 108.7 |

3.6. Adsorption isotherm experiments

Adsorption isotherm models can be extended to describe experimental isotherm data and identify the mechanism of the adsorption process. Isotherm models with two parameters were therefore considered to establish the relationship between the amounts of arsenic adsorbed onto the Mn₂O₃ and its equilibrium concentration in the leachates and the synthetic solution containing arsenic.

The data from the adsorption isotherm experiments are presented in Fig.8 for As(V) adsorption onto Mn₂O₃ for three different ash leachates and the synthetic solution. From Fig.8, the increase in arsenic removal efficiency for lesser masses of sorbent is indicative of the accessible sites on the surface of Mn₂O₃ for adsorption. By increasing the arsenic concentration, site saturation of Mn₂O₃ surface occurred and a plateau was reached, representing that all active adsorption sites in Mn₂O₃ surface were occupied. As shown in Fig.8, a higher maximum adsorption capacity was observed in the synthetic solution.

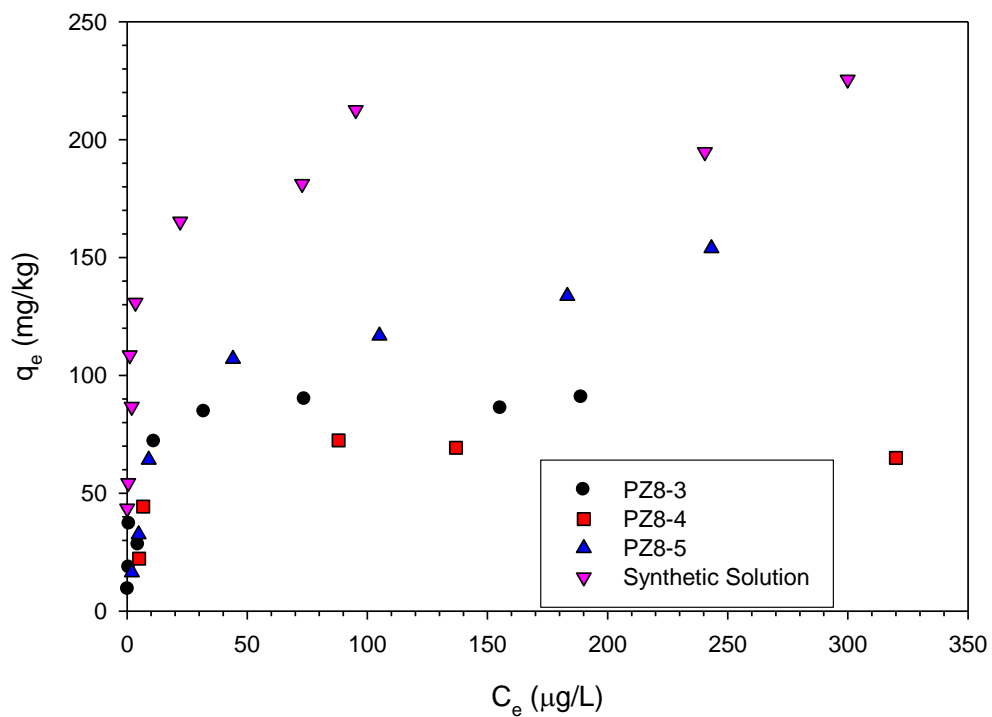


Fig. 8. Adsorption equilibrium isotherm data for the adsorption of arsenate onto Mn_2O_3

The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) adsorption models in the equilibrium and linearized forms (Table 6) were used to analyze the adsorption and rate data.

Table 6. Isotherm model equations.

| Isotherm model | Equilibrium | Linearized |
|----------------|---|---|
| Langmuir | $q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ | $\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$ |
| Freundlich | $q_e = K_F C_e^{1/n}$ | $\log q_e = \log K_F + (1/n) \log C_e$ |
| Temkin | $q_e = \left(\frac{RT}{b}\right) \ln(AC_e)$ | $q_e = \left(\frac{RT}{b}\right) \ln(A) + \left(\frac{RT}{b}\right) \ln(C_e)$ |
| D-R | $q_e = q_m \exp(-K_{DR} \varepsilon^2)$ | $\ln q_e = \ln q_m - K_{DR} E^2$ |

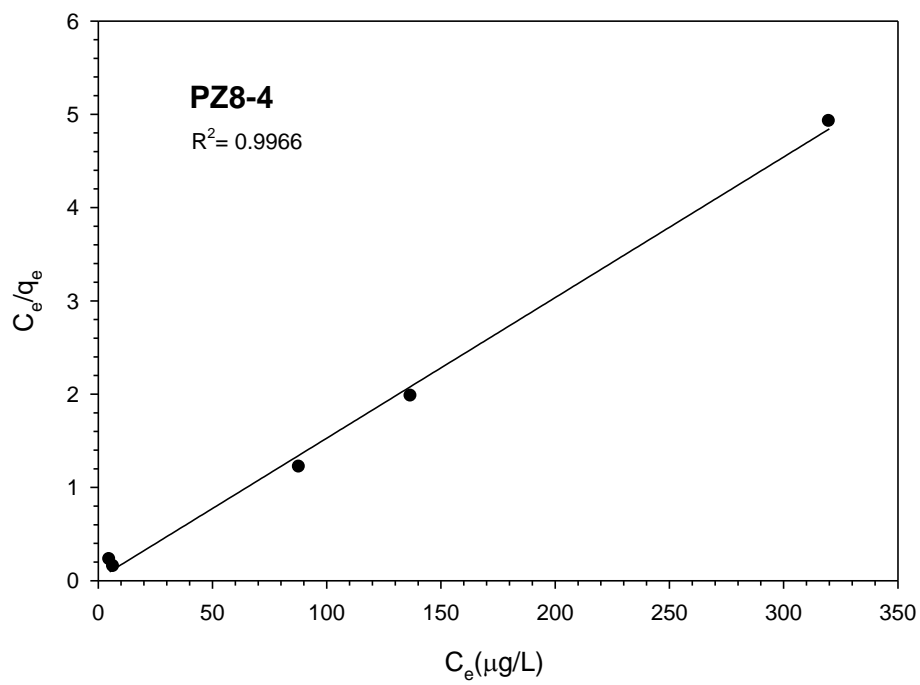
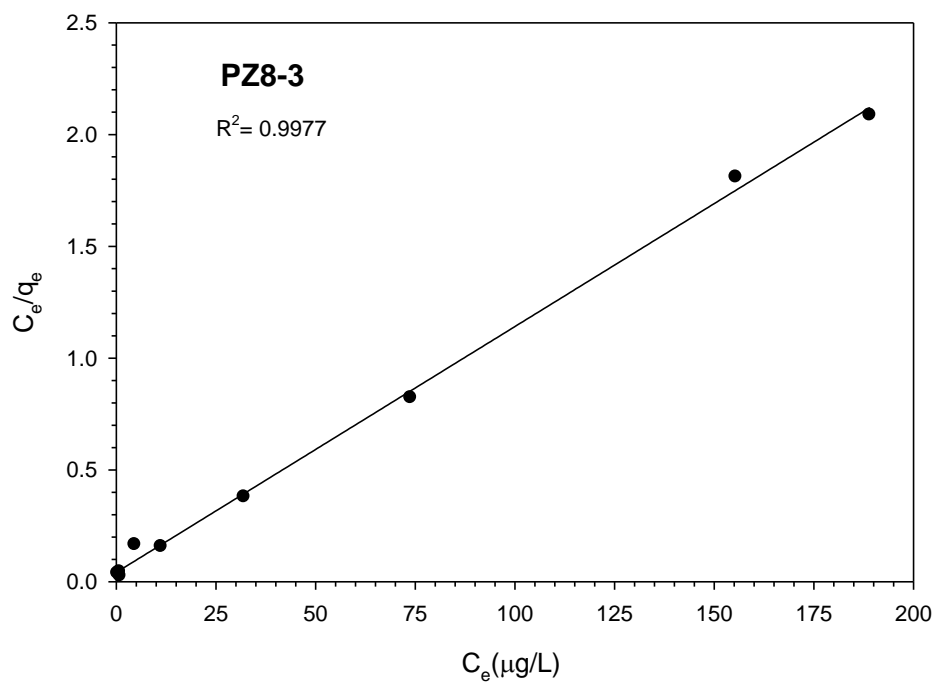
The q_e is the amount of arsenic adsorbed per unit weight of adsorbent (mg/kg) and C_e is the concentration of adsorbate in solution at equilibrium ($\mu\text{g/L}$). In Langmuir isotherm, q_m is maximum arsenic adsorbed (mg/kg) corresponding to complete coverage of available sites and K_L is Langmuir constant related to the free energy or net enthalpy of adsorption. The q_m and K_L can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e or $1/q_e$ versus $1/C_e$ (Fig.9). For Freundlich isotherm model, K_F is the Freundlich constant indicating the adsorption capacity and $1/n$ is a constant that shows the adsorption intensity or strength such that $1/n$ values less than one shows good adsorption intensity. The K_F and $1/n$ can be calculated from the intercept and slope of the plot of $\log q_e$ against $\log C_e$ (Fig.10).

In Temkin isotherm model, A (L/g) is the equilibrium binding constant relating to the maximum binding energy and determines the Temkin adsorption potential, b (J/mol) is corresponded to the

heat of adsorption, and T and R are the temperature (K) and gas constant (8.314 J/mol.K), respectively. Temkin isotherm can be applied with assumption of uniform distribution of binding energies up to some maximum binding energy. The Temkin isotherm constants (b and A) can be determined from the slope and intercept of a plot of q_e versus $\ln C_e$ as shown in Fig.11. In D-R [28] adsorption isotherm, q_m is the D–R constant, ε (Polanyi potential) is $RT \ln(1 + 1/C_e)$ and K_{DR} is a constant related to adsorption energy (mol². kJ²)⁻¹. The q_m and K_{DR} can be determined from the intercept and slope of the plot $\ln q_e$ versus ε^2 , respectively as shown in Fig. 12. The type of adsorption such as physisorption or chemisorption can be determined by calculating the mean free energy (E) in the system using the following equation [29] :

$$E = \frac{1}{\sqrt{(2K_{DR})}} \quad (13)$$

If the magnitude of E is less than 8 kJ/mol the sorption process is of physical sorption, while if E is in the range of 8 to 16 kJ /mol, the sorption is supposed to proceed via chemisorption. The adsorption parameters obtained from the isotherm plots are listed in Table 7.



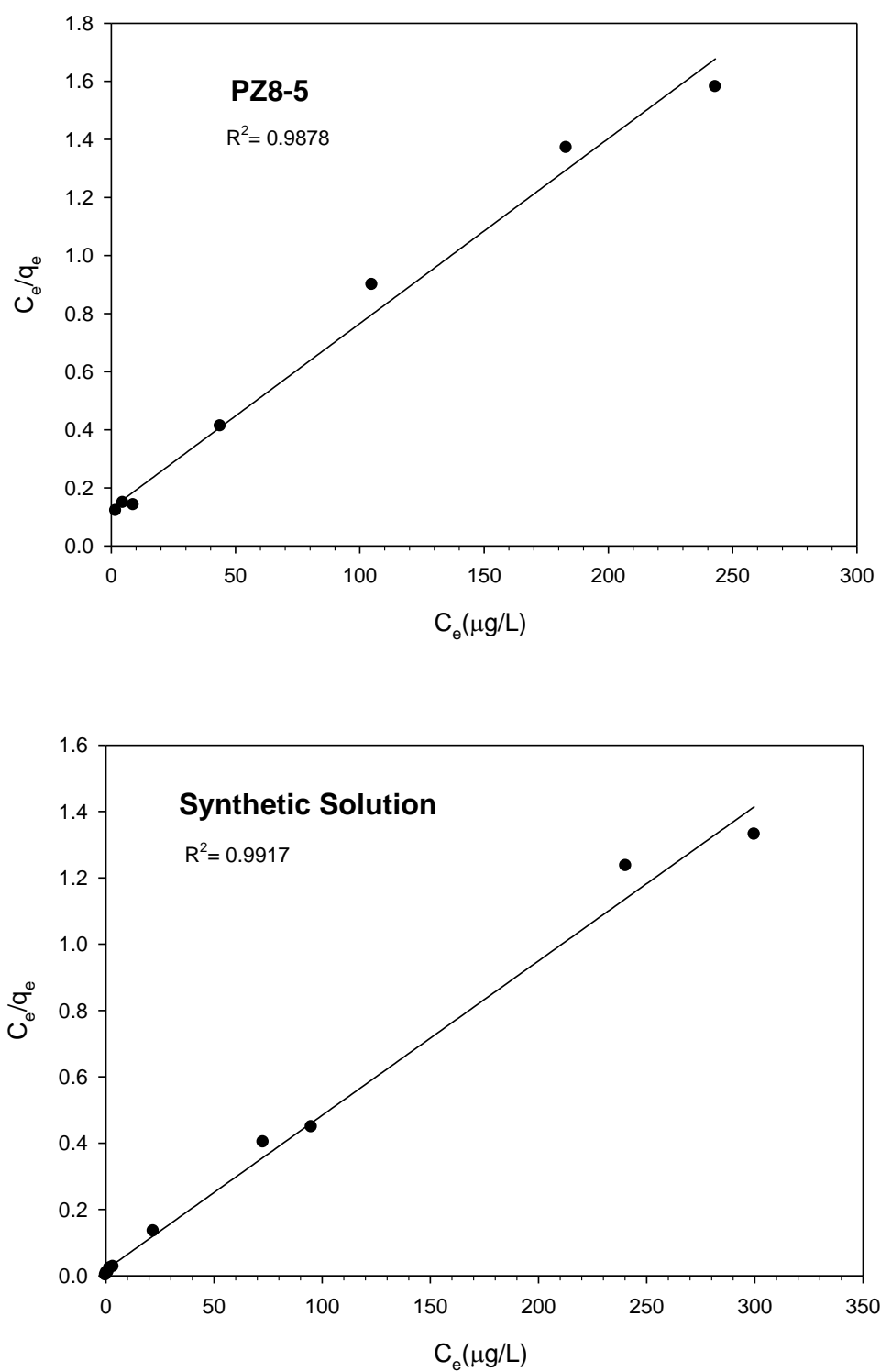
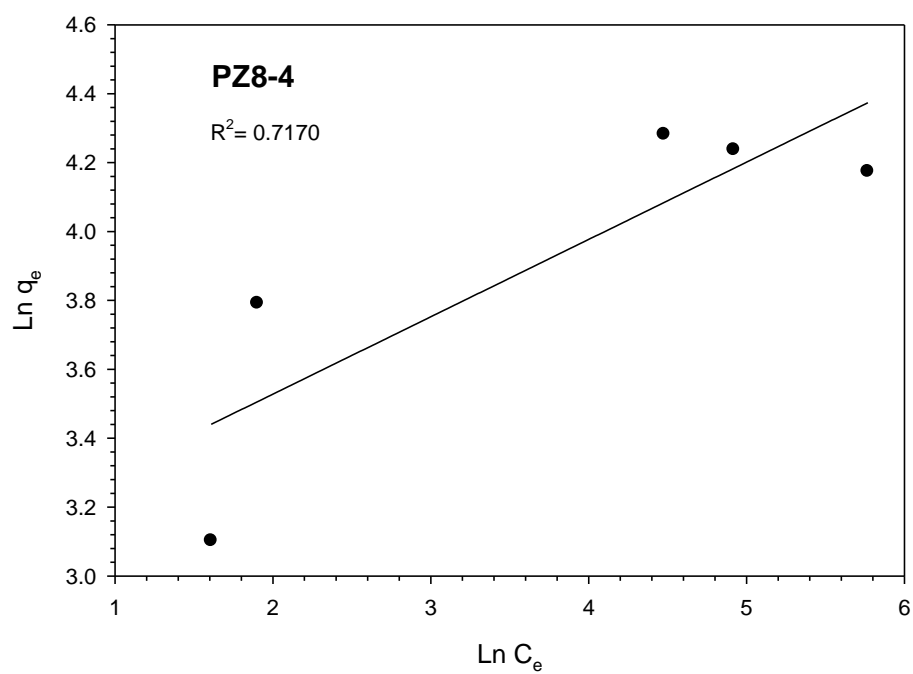
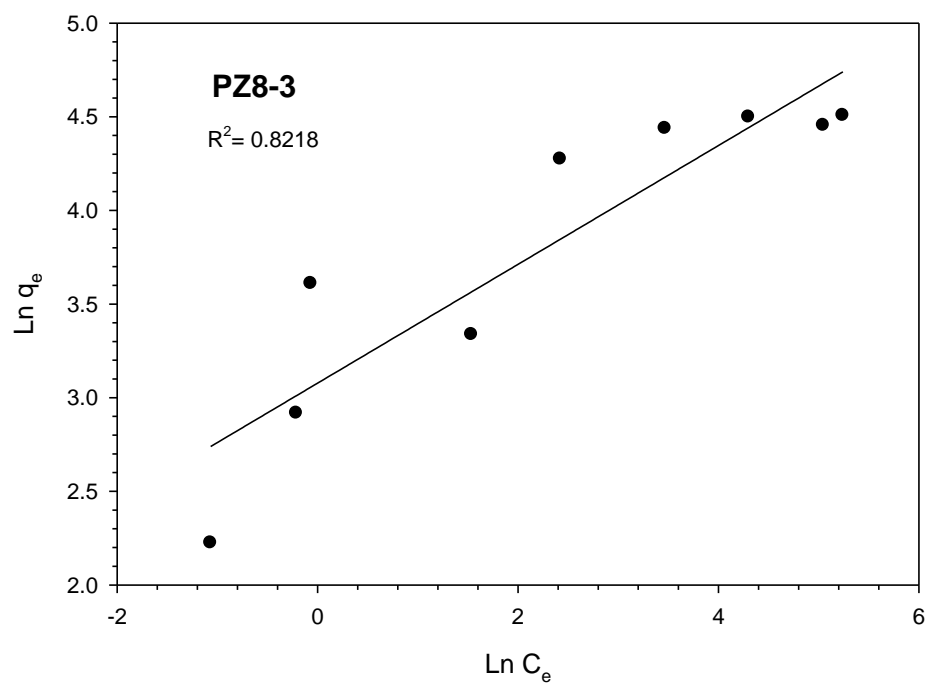


Fig.9. Langmuir adsorption isotherms of As(V) by Mn_2O_3



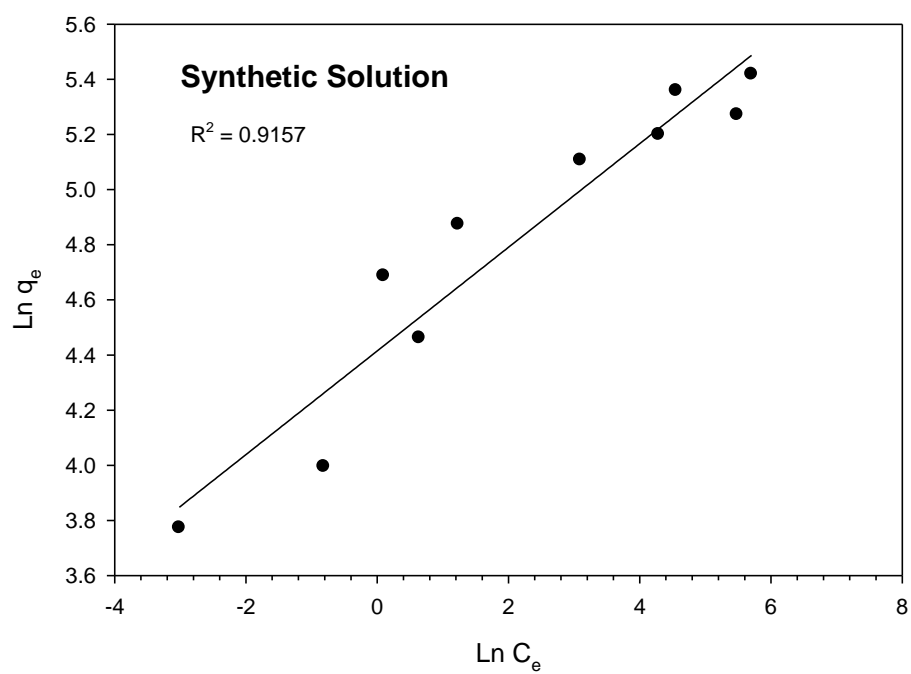
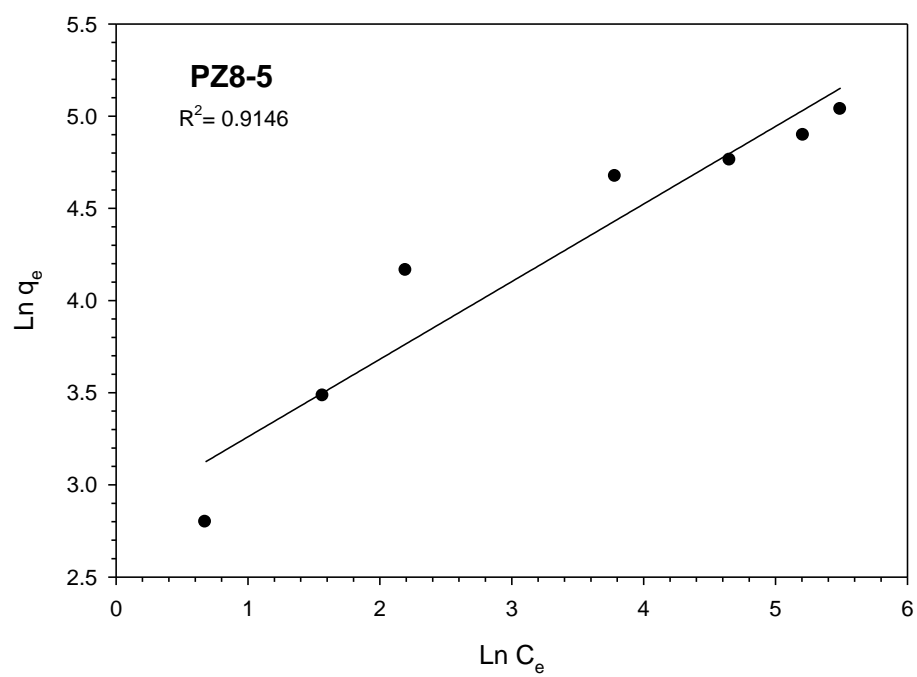
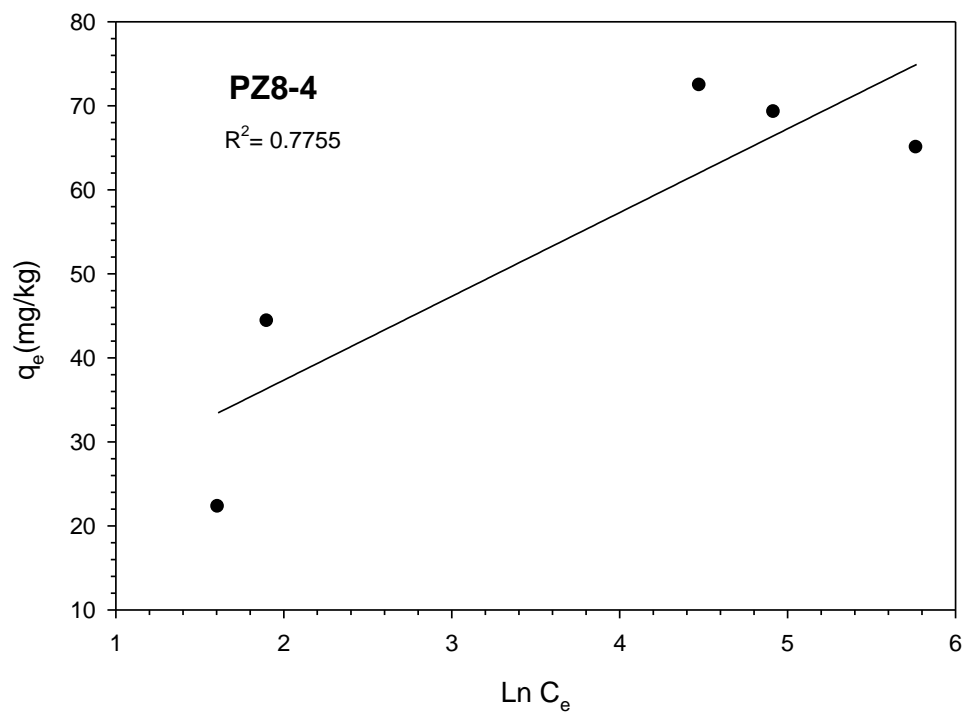
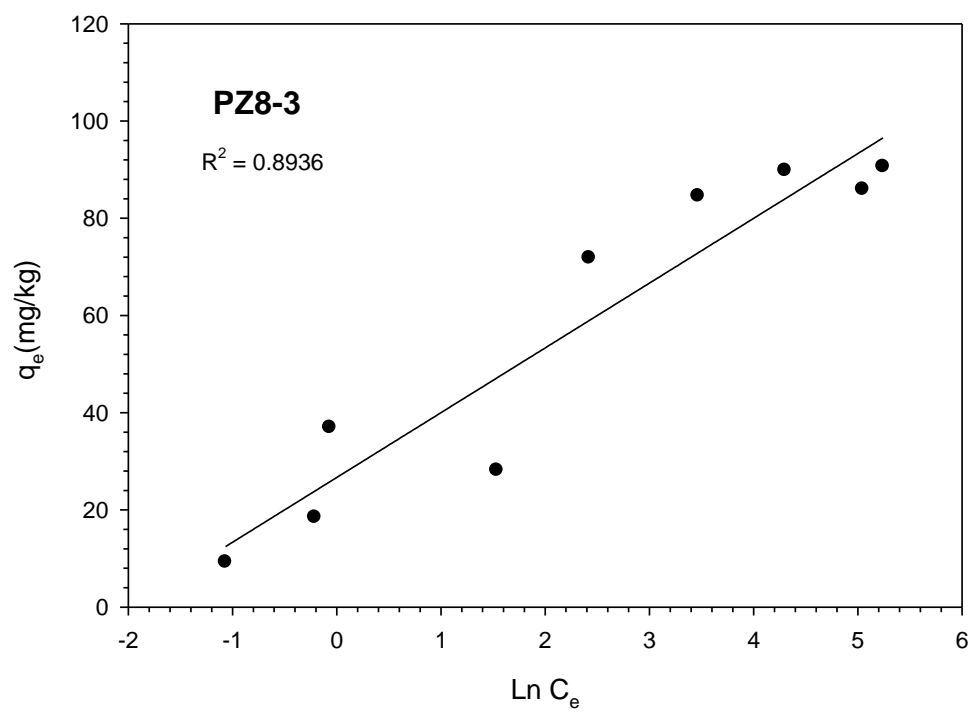


Fig. 10. Freundlich adsorption isotherms of As(V) by Mn_2O_3



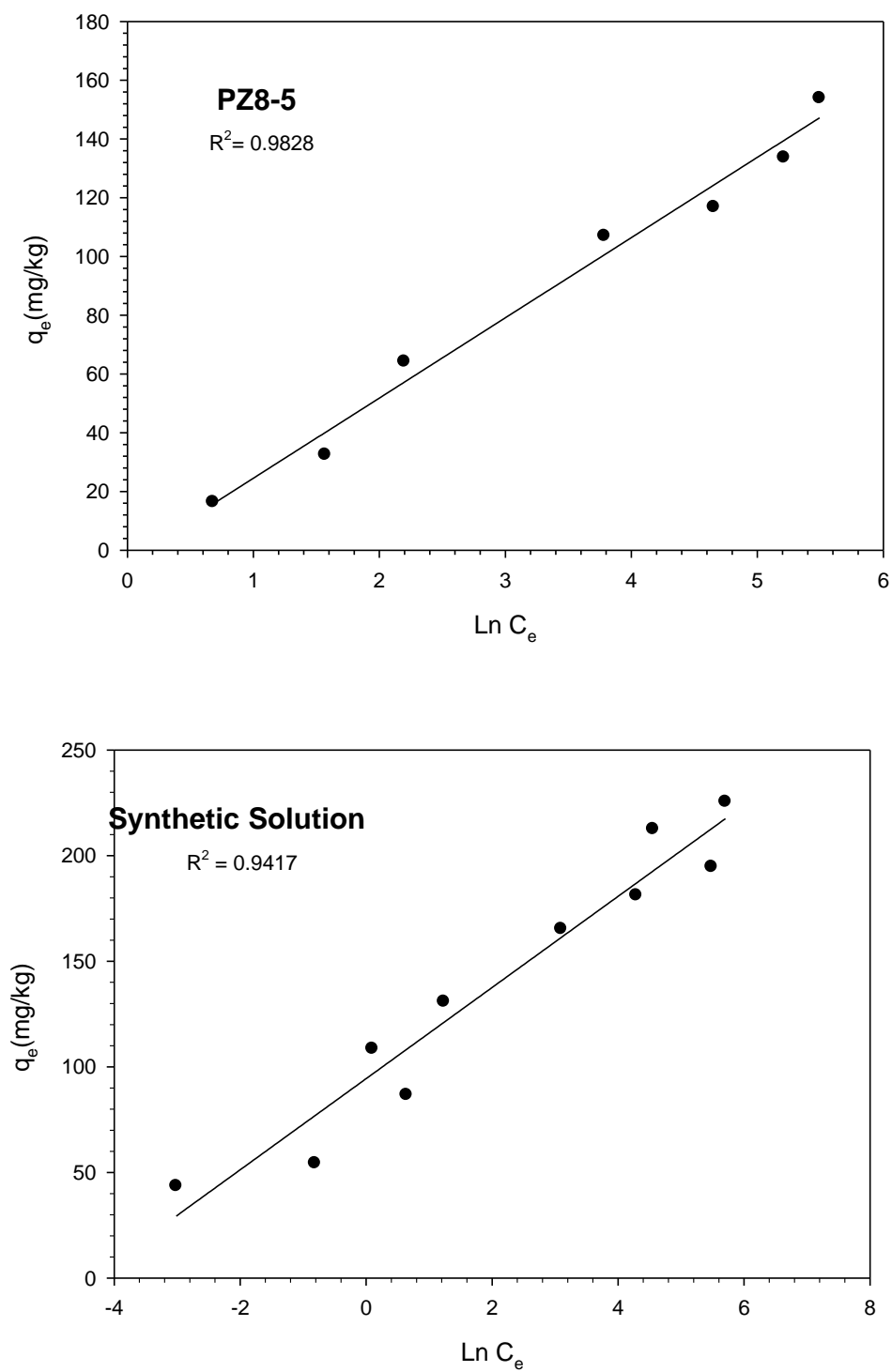
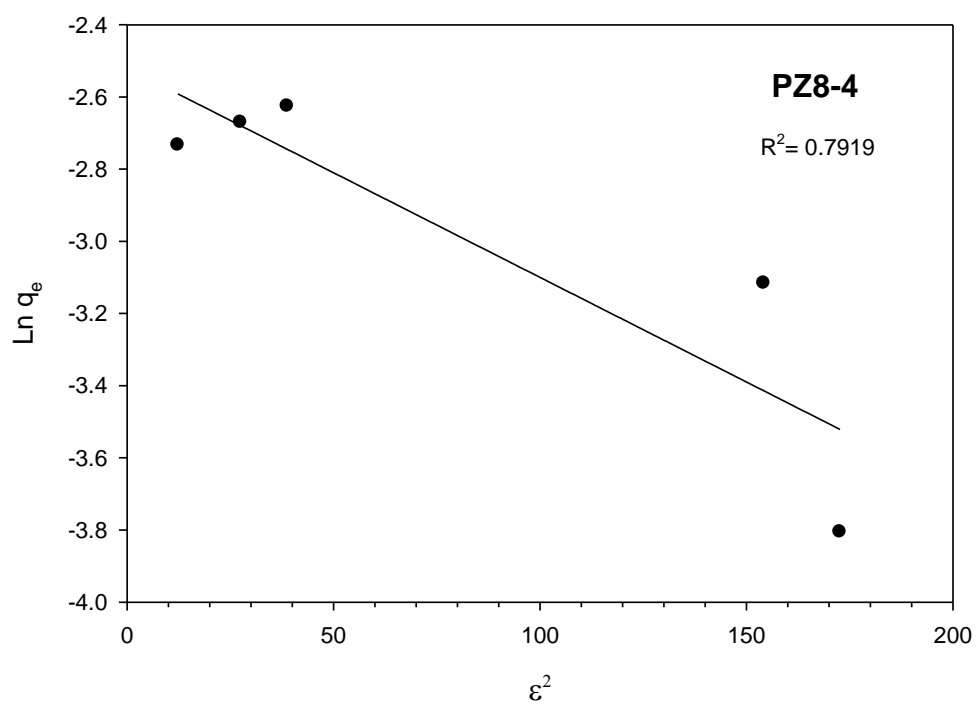
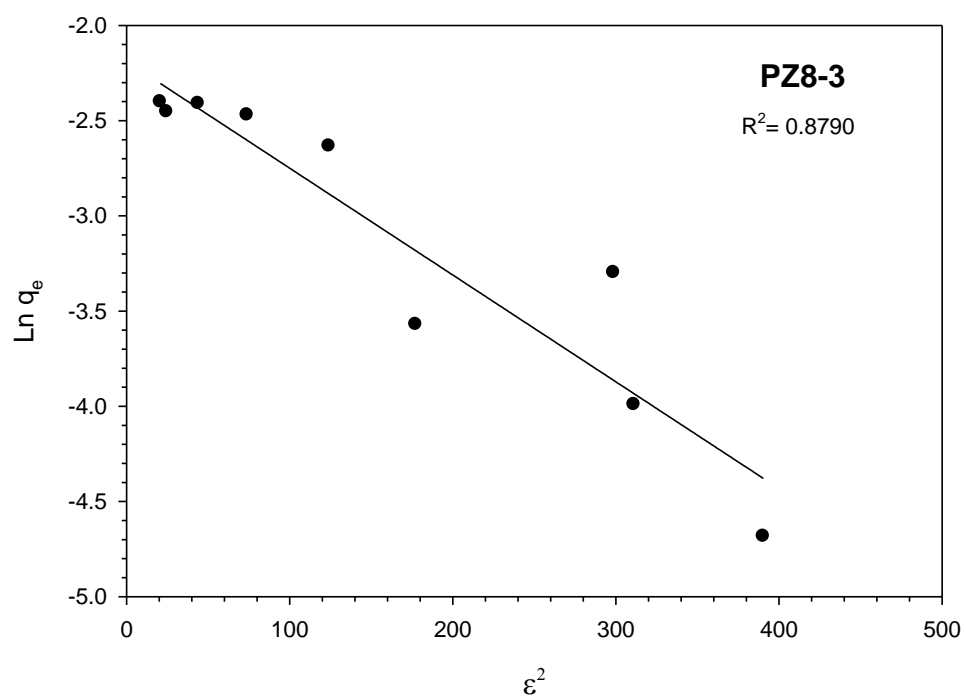


Fig. 11. Temkin adsorption isotherms of As(V) by Mn_2O_3



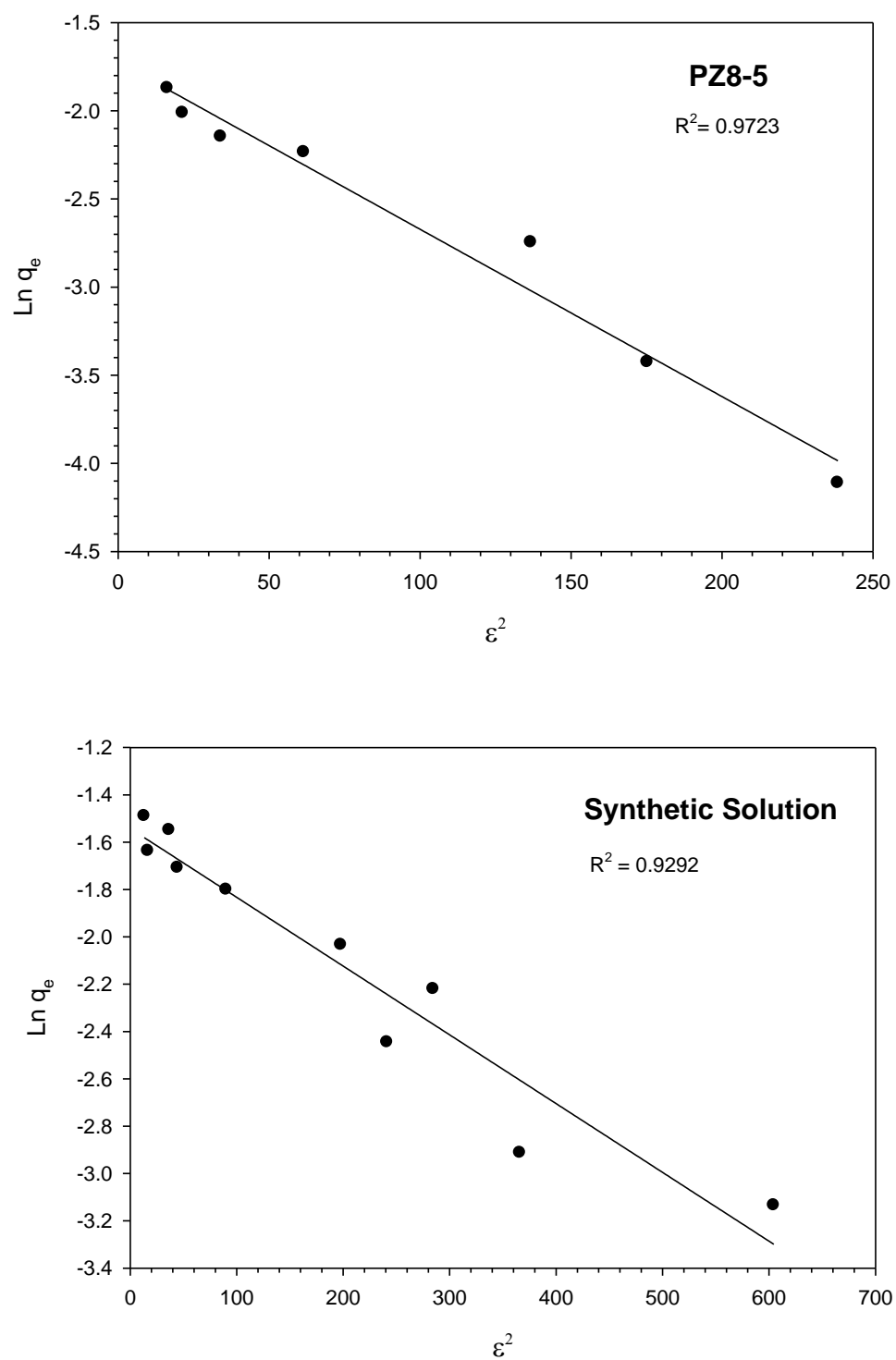


Fig. 12. D-R adsorption isotherms of As(V) by Mn_2O_3

Table 7. Isotherm parameters

| | | PZ83 | PZ84 | PZ85 | Synthetic Solution |
|------------|--------------------|--------|--------|--------|--------------------|
| Langmuir | | | | | |
| | q_m (mg/kg) | 90.91 | 66.23 | 156.25 | 212.77 |
| | K_L (L/ μ g) | 0.26 | 0.74 | 0.05 | 0.26 |
| | R^2 | 0.9977 | 0.9966 | 0.9878 | 0.9917 |
| | | | | | |
| Freundlich | | | | | |
| | 1/n | 0.32 | 0.22 | 0.42 | 0.19 |
| | K_F | 21.71 | 21.74 | 17.11 | 82.67 |
| | R^2 | 0.8218 | 0.717 | 0.9146 | 0.9157 |
| | | | | | |
| Temkin | | | | | |
| | b(kJ/mol) | 0.19 | 0.25 | 0.09 | 0.11 |
| | A(L/ μ g) | 7.40 | 5.72 | 0.90 | 79.49 |
| | R^2 | 0.8936 | 0.7755 | 0.9828 | 0.9417 |
| | | | | | |
| D-R | | | | | |
| | E | 9.45 | 9.28 | 7.25 | 13.13 |
| | R^2 | 0.879 | 0.7919 | 0.9723 | 0.9292 |

The well-matching correlation coefficient of Langmuir isotherm indicates the possibility of monolayer sorption of active sites on the surface of the sorbent in all leachates. The maximum adsorption capacity of the sorbent calculated by the Langmuir isotherm model in PZ8-3, PZ8-4 and PZ8-5 were found to be 90.91, 66.23 and 156.25 mg/kg, respectively which were lower than the maximum adsorption capacity of the sorbent in the synthetic solution. The larger K_L values for As(V) adsorption onto the sorbent in PZ83 and PZ84 versus PZ85 leachate are indicative of stronger binding of arsenic to Mn_2O_3 in PZ83 and PZ84 leachates.

The values of the Freundlich parameter $1/n$ for arsenate adsorption from the leachates and the synthetic solution are indicative of good adsorption intensity. The very large Temkin constant (A) for the synthetic solution indicate the higher arsenic adsorption potential of the sorbent in the synthetic solution versus the leachates. Also, the higher arsenic adsorption potential was obtained from PZ8-3 and PZ8-5 leachate solution versus PZ8-4 leachate. The high R^2 values of Temkin isotherm model in PZ8-5 leachate and the synthetic solution showed that the Temkin adsorption isotherm can relatively describe the arsenic adsorption data for the in PZ8-5 leachate and synthetic solution which may be due to the linear dependence of heat of adsorption at low or medium surface coverage of the sorbent in PZ8-5 leachate and synthetic solution. The b value in Temkin isotherm model is related to the heat of adsorption. The positive values of the constant B ($B=RT/b$) for arsenate adsorption represents an exothermic process.

Fit of D-R equation to the adsorption data of arsenic onto Mn_2O_3 in PZ8-3 , PZ8-4 leachates and the synthetic solution resulted in a mean sorption energy of 9.45 and 9.28 and 13.13 $kJmol^{-1}$, respectively, indicating that chemical adsorption governs the adsorption of arsenic onto the surface of Mn_2O_3 . The mean sorption energy of arsenic adsorption onto Mn_2O_3 in PZ8-5 leachate was calculated as 7.25 kJ/mol indicating that the combination of physisorption and chemisorption and with the dominant former one governs the arsenic adsorption.

4. CONCLUSION

In this chapter the removal of arsenic from the different coal fly ash leachates (PZ8-3,PZ8-4 and PZ8-5) by manganese(III) oxide sorbent was investigated and was compared with arsenic adsorption from a synthetic solution.

The surface analysis of ash particles by TEM, SEM and XEDS showed that the ash sample was heterogeneous and amorphous alumina was present in ash. Also, the ash surface contained mostly oxygen and carbon and appreciable amounts of aluminum and silicon, in addition to calcium and iron. Raman spectroscopy revealed the presence of amorphous inorganic carbon in the ash. The XRD results confirmed the presence of crystalline iron (III) oxide and silica in the ash.

The physical properties of the ash samples showed that all three ash samples were alkaline in nature with pH of more than 7. The chemical content of the ash samples indicated that the arsenic content of ash PZ8-3, PZ8-4 and PZ8-5 were much less than calcium and iron content. The analysis showed that the generated ash leachates contained only As (V).

The Mn_2O_3 sorbent reduced the arsenic concentration from ash leachates below the EPA standard limit in 60 min of contact time. The kinetics experiment showed that adsorption of arsenic was rapid and followed pseudo-second-order kinetics.

The Langmuir, Freundlich and D-R adsorption equations were applied to equilibrium adsorption isotherm data. The adsorption isotherm data were best fitted to the Langmuir isotherm indicating monolayer adsorption process. Based on the Langmuir isotherm model, both As(V) affinity to bind with Mn_2O_3 in PZ83 and PZ84 leachate was higher than PZ85 leachate.

The values of the Freundlich parameter $1/n$ for arsenate adsorption from the leachates and the synthetic solution were indicative of good adsorption intensity. The very large Temkin constant (A) for the synthetic solution indicated the higher arsenic adsorption potential of the sorbent in the synthetic solution versus the leachates.

The results of D-R isotherm model for the As(V) adsorption onto Mn_2O_3 in PZ8-3 , PZ8-4 leachates and synthetic solution indicated that chemical adsorption governed the adsorption of arsenic onto the surface of Mn_2O_3 while in PZ8-5 leachate, the combination of chemisorption and physisorption with the dominant former one governed the arsenic adsorption.

A 10 g/L of Mn_2O_3 sorbent was able to remove greater than 98% of arsenic from ash leachates. In general, the results obtained from the present study showed Mn_2O_3 has potential as adsorbent for uptake and removal of arsenic from ash leachates containing arsenic.

5. REFERENCES

- [1] Pandey,V.C. , Singh ,J.S., Singh,R.P., Singh, N. and Yunus, M.: Arsenic hazards in coal fly ash and its fate in Indian scenario. *Resources, Conservation and Recycling.*, 55:819–835, 2011.
- [2] Neupane,G. and Donahoe,RJ.: Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests. *Fuel*, 104:758–770,2013.
- [3] WWCCPN, 2011. World-Wide Coal Combustion Products Network.See <http://www.wwccpn.org/2011>Last access: 2011.
- [4] American Coal Ash Association, Coal Combustion Product (CCP) Production & Use Survey Results, American Coal Ash Association, 2011, p. 1.See <http://www.acaa-usa.org>.
- [5] Jones, D.R., 1995. The leaching of major and trace elements from coal ash. In *Environmental Aspects of Trace Elements in Coal*: Swaine, D.J.,Goodarzi, F. (Eds.), . Springer.

- [6] Izquierdo, M. and Querol, X.: Leaching behaviour of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology* ., 94:54–66, 2012.
- [7] Khodadoust, A.P., Naithani, P., Theis, T. L., and Murarka, I.P.: Leaching Characteristics of Arsenic from Aged Alkaline Coal Fly Ash Using Column and Sequential Batch Leaching. *Ind. Eng. Chem. Res.*, 50:2204–2213, 2011.
- [8] Zhao, F., Peng, P., Zheng, B., Tang, Y., Cong, Z. and Ren, D.: The Leaching Behavior of Cadmium, Arsenic, Zinc, and Chlorine in Coal and Its Ash from Coal-Fired Power Plant. *Environ. Eng. Sci.*, 23:68-76, 2006.
- [9] Wadge, A., Hutton, M. and Peterson, P.J.: The concentrations and particle size relationships of selected trace elements in fly ashes from U.K. coal-fired power plants and a refuse incinerator. *Sci. Total Environ.*, 54:13-27, 1986.
- [10] Finkelman, R.B., 1995. Modes of occurrence of environmentally-sensitive trace elements in coal. In: Swaine, D.J., Goodarzi, F. (Eds.), *Environmental Aspects of Trace Elements in Coal*. Springer.
- [11] YaE, Y. and Ketris, M.P.: Arsenic in coal: a review. *International Journal of Coal Geology*., 61:141–196, 2005.
- [12] Huffman, G.P., Huggins F.E., Shah N. and Zhao, J.: Speciation of arsenic and chromium in coal and combustion ash by XAFS spectroscopy. *Fuel Processing Technology*. 39:47–62, 1994.
- [13] Huggins, F.E., Shah, N., Huffman, G.P. and Robertson, J.D.: XAFS spectroscopic characterization of elements in combustion ash and fine particulate matter. *Fuel Processing Technology*, 65–66:203–218, 2000.
- [14] Huggins, F.E. and Huffman, G.P.: X-ray Absorption Fine Structure (XAFS) Spectroscopic Characterization of Emissions from Combustion of Fossil Fuels. *International Journal of the Society of Materials Engineering for Resources*., 10, 1–13. 2002.
- [15] World Health Organization, 2008. Guidelines for Drinking-water Quality, third ed.
- [16] USEPA. (US. Environmental Protection Agency), 1997. IRIS (Integrated Risk Information System) On-line Database Maintained in Toxicology Data Network (TOXNET) by the National Library of Medicine. USEPA, Bethesda, MD.
- [17] Wang, Y. and Reardon, E.J.: A siderite/limestone reactor to remove arsenic and cadmium from wastewater, *Appl Geochem* ., 16:1241 –1249, 2001.
- [18] Meng, X., Korfiatis, G.P., Bang, S. and Bang, K.W.: Combined effects of anions on arsenic removal by iron hydroxide. *Toxicol Lett.*, 133: 103 –111, 2002.
- [19] Sancha, A.M., O’Ryan, R. and Perez, O.: The removal of arsenic from drinking water and associated costs: The Chilean case. Interdisciplinary perspectives on drinking water risk

assessment and management Proceedings of the Santiago Symposium, September 1998, IAHS publ.260 2000, pp.17–25.

[20] Clifford, D. and Lin, CC.: Arsenic (III) and arsenic (V) removal from drinking water in San Ysidro, New Mexico, EPAy 600yS2-91y011, US EPA, Cincinnati 199.

[21] Pattanayak, J., Mondal, K., Mathew, S. and Lalvani, SB.: A parametric evaluation of the removal of As (V) and As (III) by carbon based adsorbents. *Carbon*, 38: 589 –596, 2000.

[22] Dambies, L., Vincent, T., E. Guibal.: Treatment of arsenic-containing solutions using chitosan derivatives: uptake mechanism and sorption performances. *Water Res.*, 36:3699–3710, 2002.

[23] Smedley, PL. and Kinniburgh, DG.: A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17(5):517-568, 2002.

[24] Dias, A., Sa, RG., Spitale, MC., Athayde, M. and Ciminelli, VST.: Microwave-hydrothermal synthesis of nanostructured Na-birnessites and phase transformation by arsenic(III) oxidation. *Materials Research Bulletin*. 43:1528-1538, 2008.

[25] Oscarson, D. W., Huang, P. M., Defosse, C. and Herbillon, A.: Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature*, 291:50 – 51, 1981.

[26] Lagergren, S. : Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens. *Handlingar*, Band 24:1-39, 1898.

[27] Ho, Y.-S. and McKay, G.: Pseudo-second order model for sorption processes. *Process Biochem*, 34:451–465, 1999.

[28] Dubinin, M.M. and Radushkevich, L.V.: Equation of the characteristic curve of activated charcoal. *Chem. Zentr.*, 1 :875.1947.

[29] Islam, M., Mishra, P.C. and Patel, R.: Fluoride adsorption from aqueous solution by a hybrid thorium phosphate composite. *Chem. Eng. J.* , 166(3):978-985, 2011.

Chapter (VI)

VI. Development of manganese coated sand (mcs)

1. INTRODUCTION

Based on the evidence of oxidation of As(III) to As(V) by some manganese oxides like MnO_2 [1,2] and their As(V) adsorption capacity in the presence of divalent cations [3], it appears that manganese oxides would be an effective medium for removing arsenic from aqueous solution.

Bajpai and Chaudhuri [4] applied manganese dioxide-coated sand (MDCS), prepared by reacting potassium permanganate with manganese chloride under an alkaline condition and in the presence of sand and reported that the promising ability of the sorbent as a medium for use in small systems or home-treatment units in developing areas of the world, for removing arsenic (III) and arsenic(V) from ground water. However, the effects of some important parameters like water pH, concentration and type of competing anions, and cations on the process was not carried out in the study.

However and as mentioned in previous chapters, manganese oxides have usually been used in a combination with other metals like iron to remove contaminants. Chang et al. [5] investigated the applicability of manganese-coated sand (MCS) and iron-coated sand (ICS) for the treatment of As(III) via oxidation and adsorption processes. They found that in the batch adsorption, the adsorption rate of As(V) onto ICS was greater than that of As(III), and ICS showed a greater adsorption capacity for the removal of As(V) than As(III). From a bench-scale column test, a

column reactor packed with both MCS and ICS was found to be the best system for the treatment of As(III) due to the promising oxidation efficiency of As(III) to As(V) by MCS and adsorption of As(V) by both MCS and ICS. Viraraghavan et al. [6] examined manganese greensand and iron oxide-coated sand for arsenic remediation from drinking water. Manganese greensand was effective for removing arsenic to $<25 \mu\text{g/L}$. Iron addition was necessary to achieve an effluent arsenic level of $25 \mu\text{g/L}$ in the manganese greensand filtration system [7].

Aluminum oxide has also been reported as a good adsorption media for As(V) [8]. The other adsorbents based on aluminium include activated alumina, aluminium hydroxide precipitated from aluminium salts, gibbsite (mineral $\text{Al}(\text{OH})_3$) and layered double hydroxides. Manganese supported on activated alumina (MAA), prepared by calcining (400°C) manganese acetate-impregnated activated alumina, has been reported as a more effective medium for As(III) and As(V) removal from groundwater than activated alumina (AA) [9]. In general, the As(V) has long been known to be strongly adsorbed by aluminium hydroxides, whereas arsenic(III) is considerably less readily adsorbed [10,11,12].

Conceivably, oxidation/ adsorption by Mn-Al combination is an effective process for removing arsenite and arsenate from water, and a matrix, such as sand, coated with manganese and aluminum oxide would be an effective medium for removing arsenic(III) and arsenic(V) from water. In this chapter the development of a manganese-aluminum coated sand will be investigated and its ability to remove As(V) and As(III) from aqueous solution will be studied.

2. MATERIALS AND METHODS

2.1. Manganese-aluminum -coated sand preparation

In the preparation of Manganese oxides coated sand (MCS) and before the coating, the sand was first washed and soaked in 0.1M HCl solution for 3h, and then subsequently rinsed with de-ionized water until the pH of the washing water is close to 7.0. After that, it was dried in an oven at 110 °C to prepare for coating. Then, a high concentrated small volume of manganese and aluminum source solution with the optimized combination percentages, which has previously adjusted to pH 7 with 6 N NaOH solution or without pH adjustment, was mixed with the sand (80 g) in a flask for the optimized time period. Then, the residual coating solution was poured, and the sand was air dried for 12 h followed by heating in the oven (110 °C) for certain times. This is the first step for the whole coating process. Then, the sand was introduced into a furnace to finish coating of metal oxides on the sand. This process was performed at 550 °C for certain times as the second coating step. Finally, the coated sand was stored in airtight containers for further use.

2.2. Adsorbent Characterization

The optimized MCS was characterized by SEM/EDX and XPS. Photomicrography of the exterior MCS surface was obtained by SEM (TOPCON ABT-150S). The imaging and XEDS carried out at 10kV in variable pressure mode at 10Pa. Images acquired using Backscattered Electron Detector in Atomic number contrast (Z). Samples for EDAX (JXA 840, Japanese) analysis were coated with thin carbon film in order to avoid influence of charge effect during the SEM operation.

An X-ray photoelectron spectrometer (XPS; Kratos AXIS-165) equipped with a monochromatic Al K α (1486.6 eV) X-ray source operating at 15 kV and 10 mA was used to investigate the oxidation state of the manganese and aluminum on the surface of MCS. High-resolution spectra of O 1s and C 1s were collected using a step size of 0.1 eV, pass energy of 20 eV and dwell time of 200 ms. Semi-quantitative analysis of peak intensities was performed through spectral peak-fitting, where peaks were subtracted from Shirley-typed backgrounds and deconvoluted using Gaussian–Lorentzian peak shape functions. The binding energy scales of all XPS spectra were calibrated with reference to the adventitious carbon 1s position at 285 eV.

The BET surface area of the MCS was measured with an Accelerated Surface Area and Porosimetry system, ASAP 2010 (Micromeritics Instrument Corporation, Norcross, GA), using nitrogen adsorption/desorption isotherms.

3. RESULTS AND DISCUSSION

3.1. Development of manganese-aluminum -coated sand

The final procedure of synthesizing the manganese-aluminum coated sand adsorbent was obtained by optimizing the source of manganese, the mixing time, combination percentage of aluminum manganese coated sand, pH adjustment versus no pH adjustment process and calcination time in furnace.

The manganese (II) chloride (MnCl₂) and manganese (II) sulfate (MnSO₄) were initially used as the source of manganese for coating according to the literatures [13, 14]. Aluminum chloride was selected as the source of aluminum for coating [15,16]. First the sand was just coated with

manganese using 1 M of MnCl_2 and 1M of MnSO_4 as the sources of manganese and the removal efficiency of arsenic by the coated sand and the amount of manganese coated on the sand was determined. Table 1 shows the results. The MnCl_2 was found to be a superior source for manganese in removing both As(III) and As(V) versus MnSO_4 . The less amount of manganese from MnCl_2 was able to remove more arsenic than MnSO_4 . It should be noted that the mixing and calcination time was set for 3hr and 1 hr, respectively to only compare the adsorption efficiency of two sorbents with two different manganese sources. The arsenic removal efficiency will be improved by optimizing the other effective factors which will be discussed later in this chapter. The pH of the adsorbents with MnSO_4 and MnCl_2 manganese source was found to be 4.95 and 6.102, respectively.

Table 1. Adsorption efficiency and manganese content of MnSO_4 and MnCl_2 manganese source.

| Manganese Source | Removal (%) | Removal (%) | Manganese content (mg/g) |
|------------------|---------------------|-------------------|--------------------------|
| | As(III)+DI solution | As(V)+DI solution | |
| MnCl_2 | 12.24 | 10.01 | 0.649 |
| MnSO_4 | 5.99 | 4.40 | 2.666 |

After selecting the manganese source, the preliminary analysis was carried out to delineate the effect of mixing time on the arsenic removal efficiency. The time that the sand was exposed to MnCl_2 was increased to maximum 24 hr, due to the practical stand point, and the resulted arsenic removal percentage was compared to the sand coated by MnCl_2 for 3hr. The arsenic removal

efficiency for As(V) and As(III) increased from 10.01 % and 12.24 % to 13.2 % and 31.5 % ,respectively indicating a higher arsenic removal can be obtained by increasing the mixing time.

As mentioned before, aluminum oxide has also been reported as a good adsorption media for arsenic. The presence of aluminum along with manganese in the coating procedure was considered in this study. Different combinations of manganese-aluminum coated sand were tested to optimize the coating process which results the maximum arsenic removal efficiency. Five different scenarios were considered: 100% MnCl_2 , 75% MnCl_2 +25% AlCl_3 , 50% MnCl_2 +50% AlCl_3 , 25% MnCl_2 +75% AlCl_3 and 100% AlCl_3 . The calcination time was fixed at 1 hr. The results are shown in Table 2. As the results show, the presence of both aluminum and manganese enhanced the arsenic removal efficiency, specially for the As(III) removal. The MCS by 50% MnCl_2 +50% AlCl_3 was found to be the most effective sorbent and was used for the subsequent studies. The MCS by just AlCl_3 and MnCl_2 was able to remove only 62% and 30% of As (III) and 93% and 13% of As(V),respectively. The higher arsenic removal efficiency by manganese-aluminum MCS versus manganese MCS and aluminum MCS might be due to the lower pH of the manganese-aluminum MCS versus manganese MCS and aluminum MCS (6-6.4 for manganese-aluminum MCSs versus pH>7 for manganese-MCS and aluminum-MCS) which may favor the arsenic adsorption.

Table2. Combinations of manganese-aluminum coated sand-20g/L sorbent-24hr mixing-calcination time: 1hr

| Scenario | Removal (%) | Removal (%) |
|--|---------------------|-------------------|
| | As(III)+DI solution | As(V)+DI solution |
| MCS MnCl_2 100% | 31.5 | 13.2 |
| MCS MnCl_2 75%+ AlCl_3 25% | 99.3 | 99.6 |
| MCS MnCl_2 50%+ AlCl_3 50% | 99.5 | 99.7 |
| MCS MnCl_2 25%+ AlCl_3 75% | 99.5 | 99.6 |
| MCS AlCl_3 100% | 61.5 | 93.1 |

In order to determine the effect of adjusting the pH of the coating solution on the arsenic removal efficiency, the coating procedure was also carried out without adjusting the pH of the aluminum-manganese mixing solution and the results were compared to the adsorption capacity of MCS prepared by the pH adjusted coating solution. Fig.1 shows the results for As(III) and As(V) removal efficiency where three different MCSs were applied for arsenic removal.

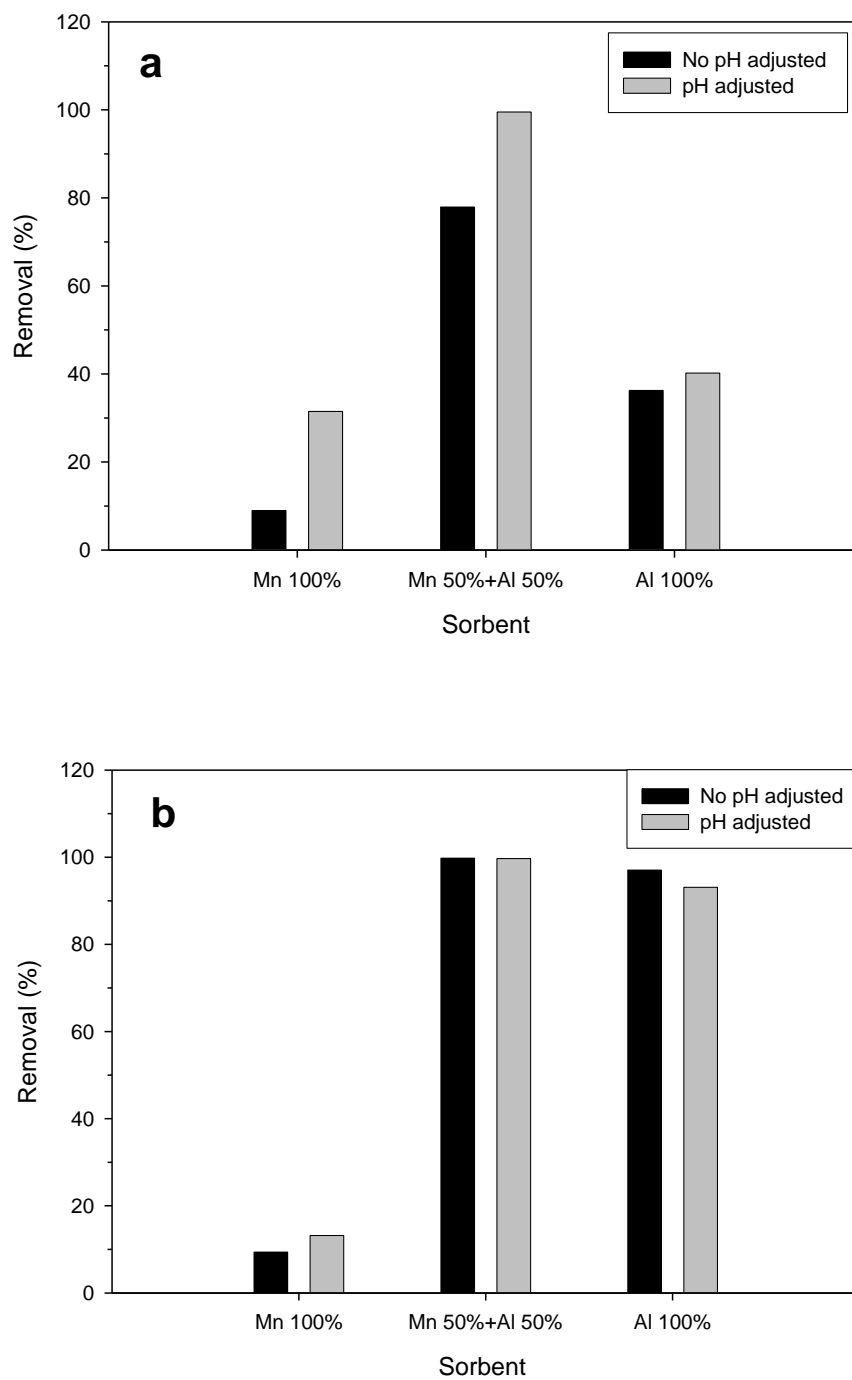


Fig1. Comparison of pH adjusted MCS versus no pH adjusted MCS on the removal a) As(III)

b)As(V)

The results from Fig.1 show that adjusting the pH of the coating solution will improve the arsenite adsorption onto the sorbent while a comparable results were obtained for arsenate adsorption. The higher adsorption of arsenite might be due to the formation of aluminum hydroxide and manganese hydroxide on the surface of the sorbent which can itself increase the active sites on MCS. It should be noted that the MCS by 50% MnCl_2 +50% AlCl_3 solution was able to remove greater than 99.5 % of arsenate with and without the adjustment of the coating solution. Based on the results derived from Fig 1, the pH adjusted MCS with the 50% MnCl_2 +50% AlCl_3 coating solution was found to be the most effective sorbent.

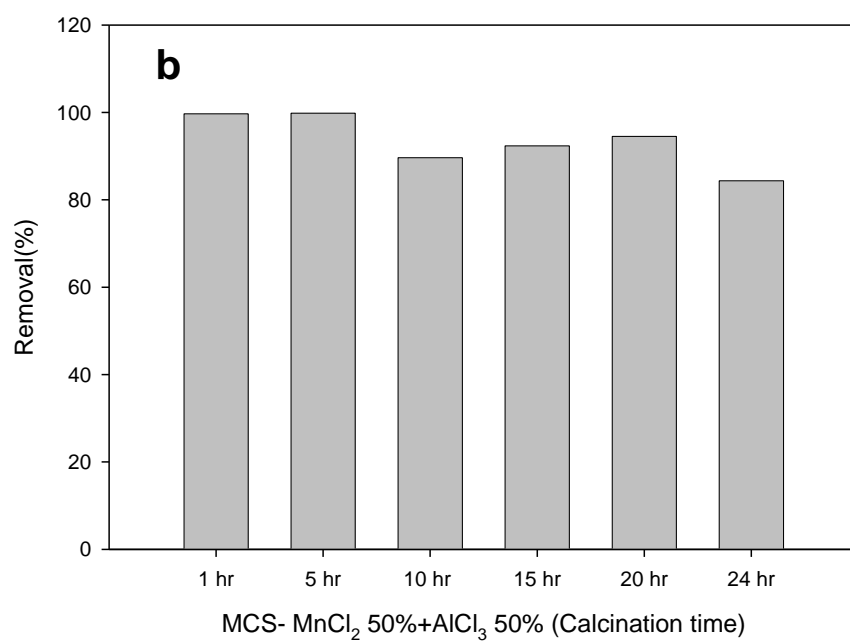
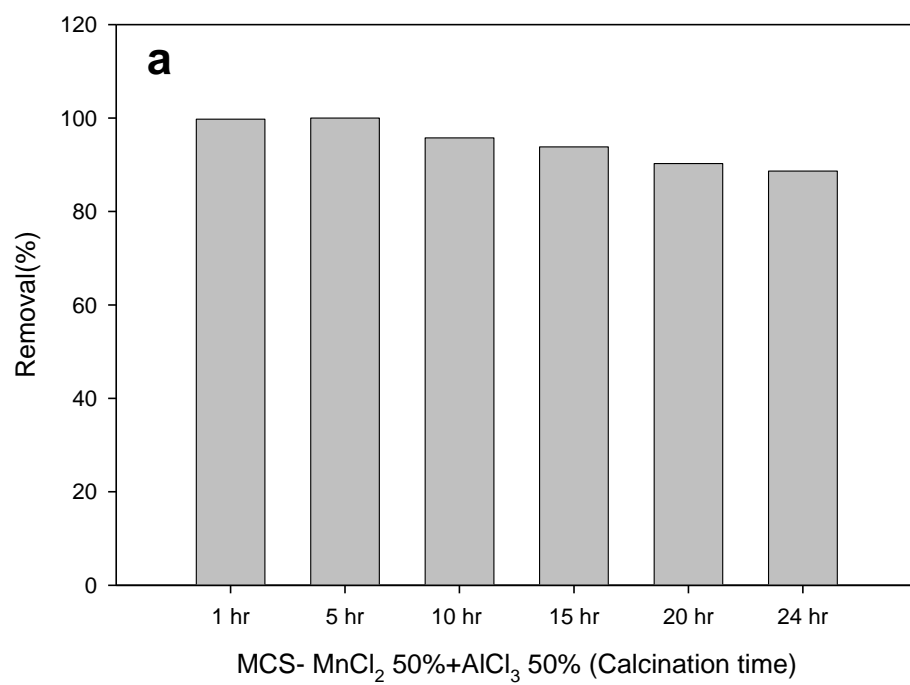
The last step in coating procedure is introducing the sand into a furnace at 550 °C to finish coating of metal oxides on the sand. The effect of calcination time on the arsenic removal efficiency was determined by exposing the coated sand into a furnace at different time of 1, 5,10,15,20 and 24 hr. Fig. 2 (a-d) shows the effect of calcination time on the removal efficiency of arsenite and arsenate from the solutions with and without the presence of the other ions. In general, the longer coated sand exposure to the furnace did not significantly change the arsenic removal efficiency. In DI solution, increasing the calcination time to more than 5 hr slightly decreased both As(III) and As(V) removal efficiency (Fig2.a-b) while in solutions with ionic background, the arsenic adsorption was not effected at longer calcination time (Fig2.c-d). Based on the results, the calcination time of 5 hr was found to be the most effective time resulting the highest arsenic removal efficiency both from DI and synthetic solution and was considered for subsequent experiments.

Increasing the calcination time would help sticking manganese and aluminum compounds on the surface and preventing their leaching when the sorbent comes in contact with solutions. Due to

comparable arsenic removal efficiency with the 5hr furnace exposed MCS specially in more practical solution (synthetic solution), the pH adjusted MCS with maximum calcination time ,24 hr furnace exposure, was also considered as promising sorbent for the subsequent experiments. The As(III) and As(V) adsorption ability of the pH adjusted 5hr and 24 hr furnace exposed MCS with MnCl_2 and AlCl_3 as the sources of manganese and aluminum will be compared and discussed later in the next chapter.

The BET surface area of the clean uncoated sand, 5hr MCS and 24hr MCS were found to be $0.04 \text{ m}^2/\text{g}$, $2.04 \text{ m}^2/\text{g}$ and $1.69 \text{ m}^2/\text{g}$, respectively indicating that coating the sand significantly increases the surface area of the clean sand. The higher arsenic adsorption ability of 5hr MCS versus 24hr MCS can be explained by the higher surface area of 5hr MCS versus the 24hr MCS.

The results of MCSs acid digestions showed that the manganese and aluminum content of 5hr MCS was greater than 24hr MCS helping 5hr MCS to adsorb more arsenic versus the 24hr MCS. The manganese content of 5hr and 24hr MCS was found to be 17.09 mg/g and 15.53 mg/g ,respectively while the aluminum content of 5hr and 24hr MCS was resulted as 13.1 mg/g and 12.0 mg/g ,respectively.



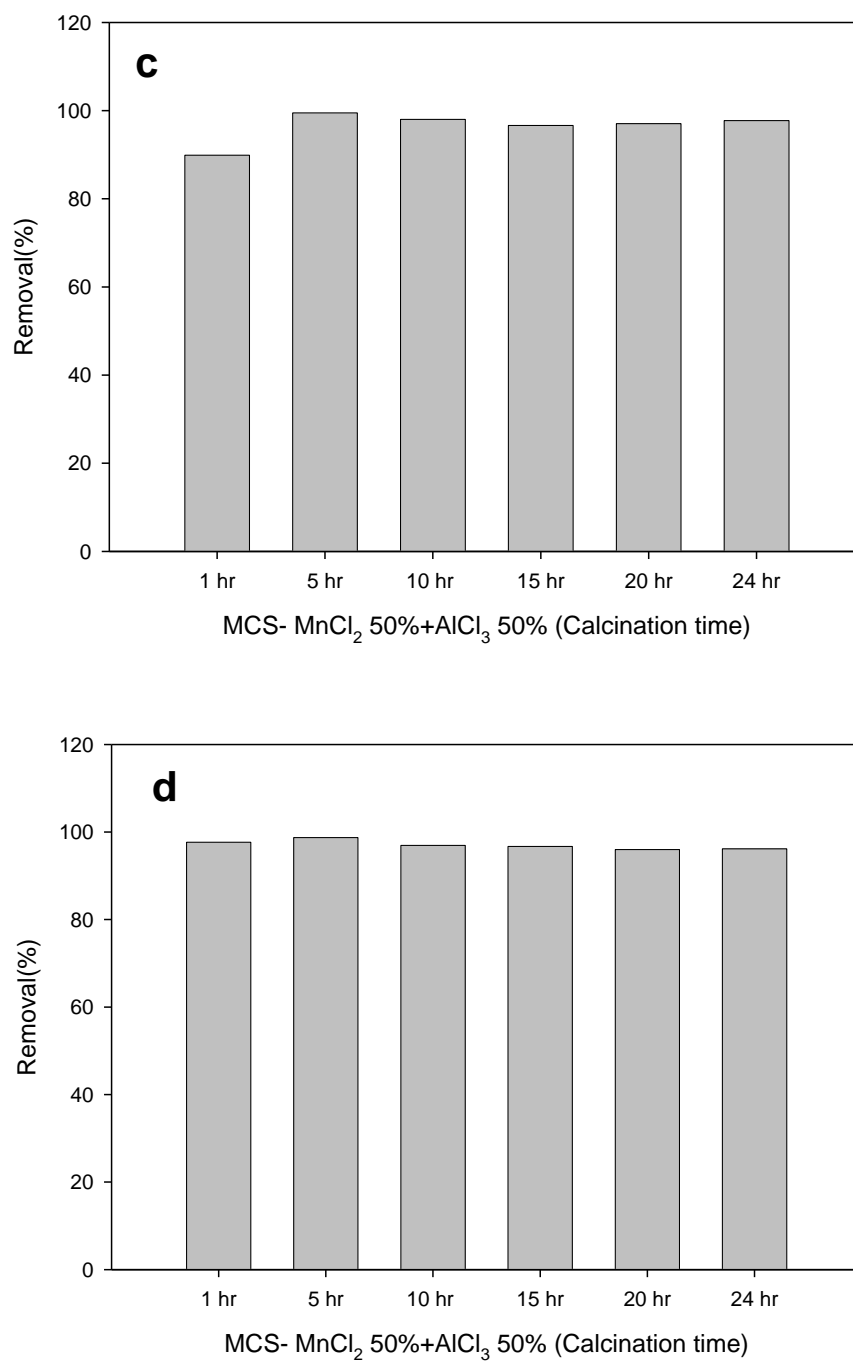


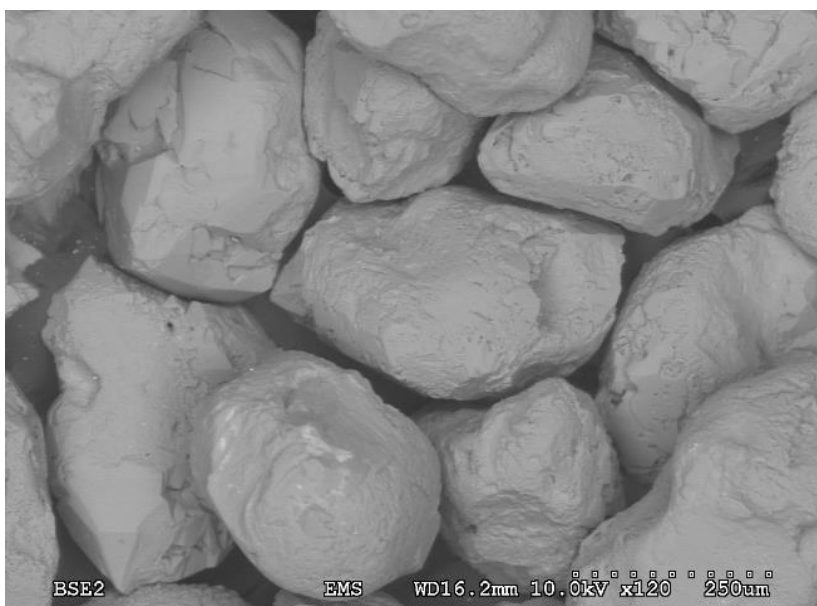
Fig 2. Effect of MCS calcination time on the removal of a) As(III) from DI solution b) As(V) from DI solution c) As(III) from synthetic solution d) As(V) from synthetic solution

3.2. The MCS characterization

The optimized 5hr and 24hr furnace exposed MCS were characterized by SEM/EDX and XPS.

3.2.1. SEM/EDX

The SEM photographs were taken to observe the surface morphology of the uncoated sand, 5hr and 24 furnace exposed MCS. Fig.3 shows the virgin sand had a relatively uniform surface and small cracks and lightly roughness could be found on the sand surface. Also, the particles of the uncoated sands are irregular in shape and lack a definite morphology. The EDX analyses showed that the uncoated sand has high silicon content at its surface which indicates as expected that the sand is essentially silica before the coating.



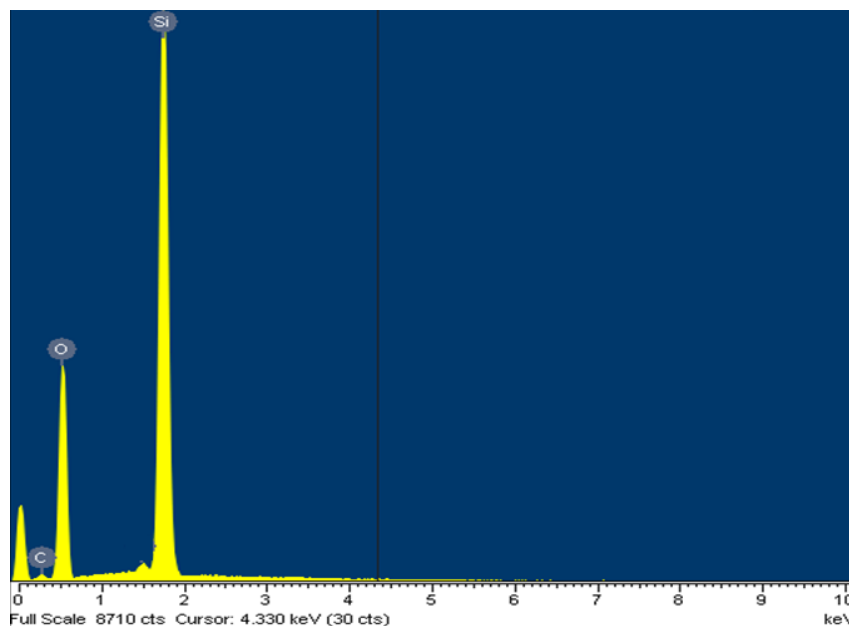
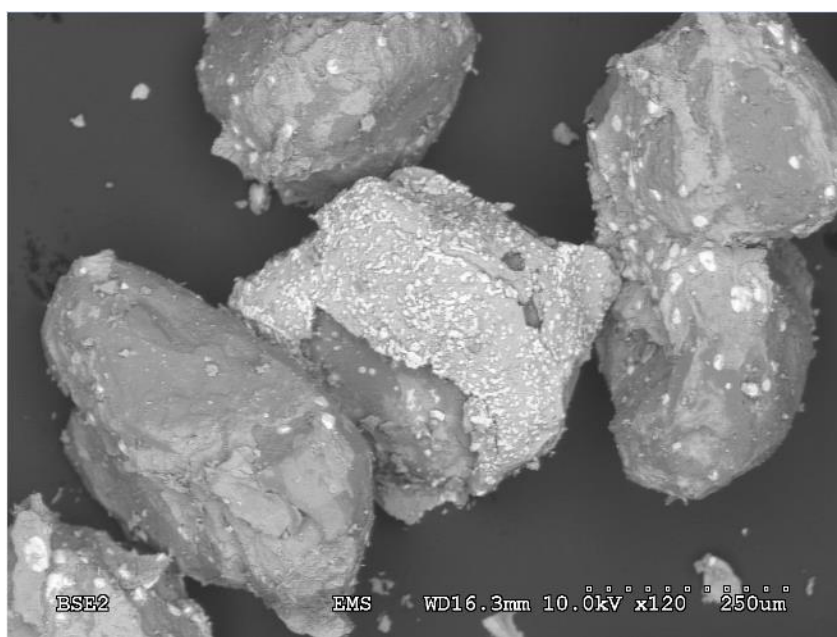


Fig. 3. SEM images and EDX spectrum of manganese uncoated sand

The SEM images of the 5hr and 24hr furnace exposed MCS are shown in Fig.4. The coated sands in Fig.4 appeared as a rough coated surface. No uniform coating was visible. Fig. 4 also shows that aluminum and manganese oxides formed in clusters on the surfaces.

The EDX mapping can provide an indication of the qualitative abundance of mapping elements. The elemental distribution mapping of EDX for the sample of 5hr furnace exposed MCS and 24hr furnace exposed MCS is indicated in Fig. 5 and Fig.6. The bright points represented the single of the element from the solid sample. Based on the EDX mapping analysis of different elements for MCS adsorbents (Fig.5 and Fig.6), the surface of the sorbents included the areas where the silica was coated with aluminum, manganese and sodium chloride and there were areas where the silica was exposed.

The qualitative EDX spectra for MCS (Fig.7) indicated that Mn, Al, C, O, Si, Na and Cl are the main constituents. It should be noted that the peak of Si occurred in EDX showed that the manganese/aluminum oxides didn't not cover a full surface of the MCS. Based on Fig.7, the 5hr furnace exposed MCS and 24hr furnace exposed MCS gave basically similar spectrum however a higher manganese content was observed on 5hr furnace exposed MCS versus the 24hr furnace exposed MCS which is in good agreement with the results obtained from acid digestion.



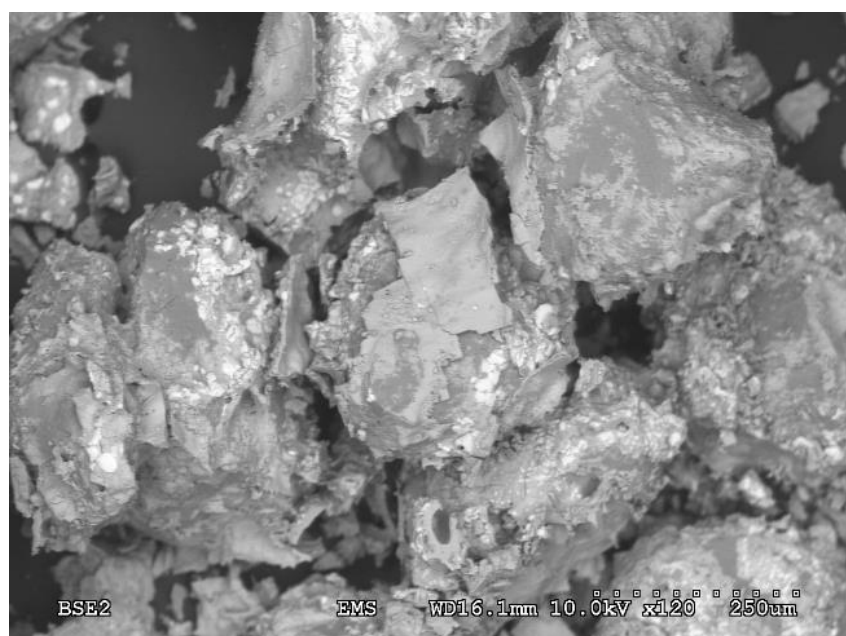


Fig. 4. SEM images of the 5hr (top) and 24hr (bottom) furnace exposed MCS

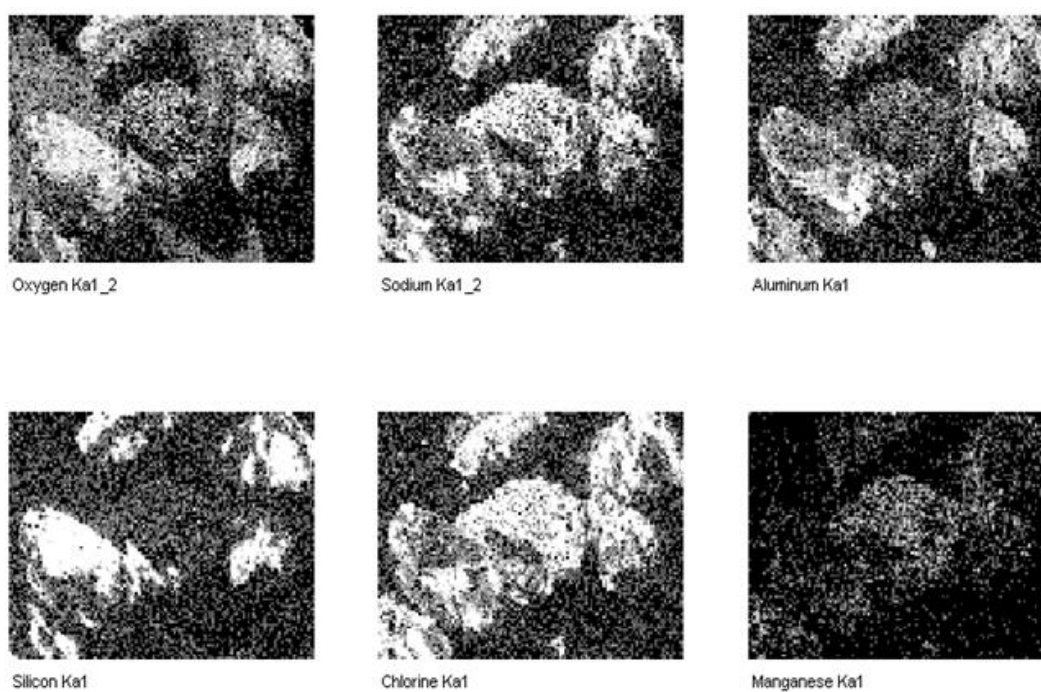


Fig. 5. EDX mapping analysis of different element for 5hr furnace exposed MCS.

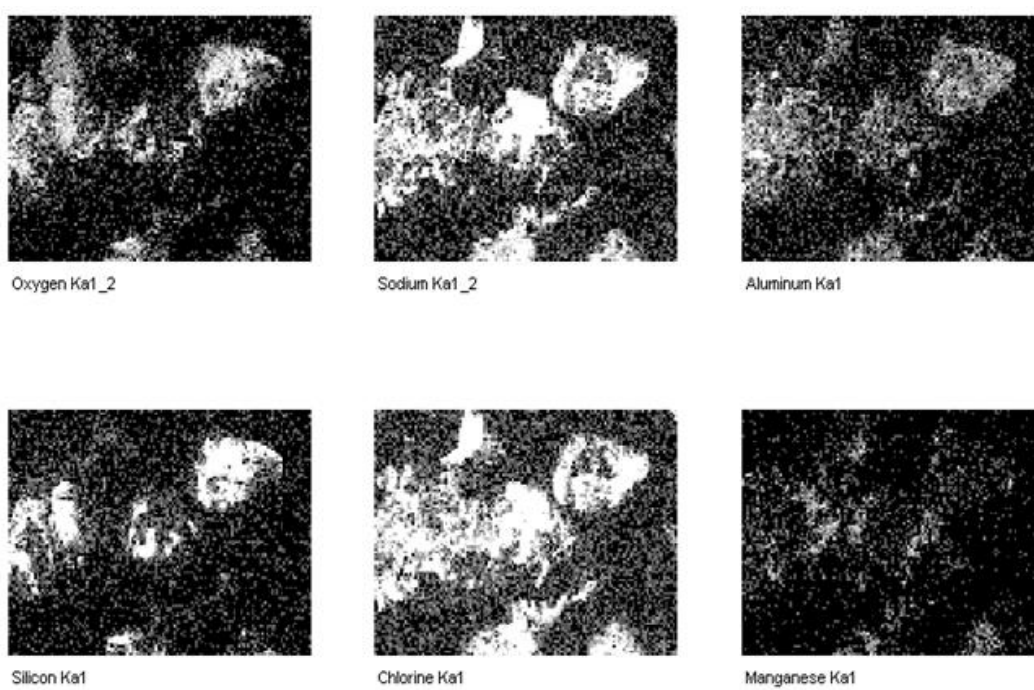
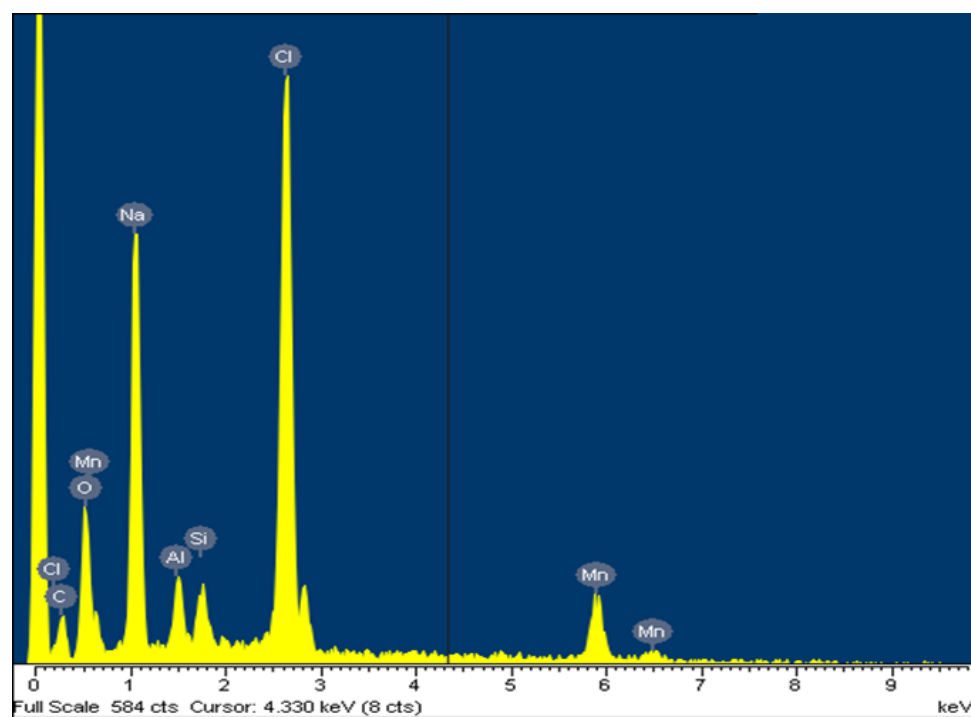


Fig. 6. EDX mapping analysis of different element for 24hr furnace exposed MCS.



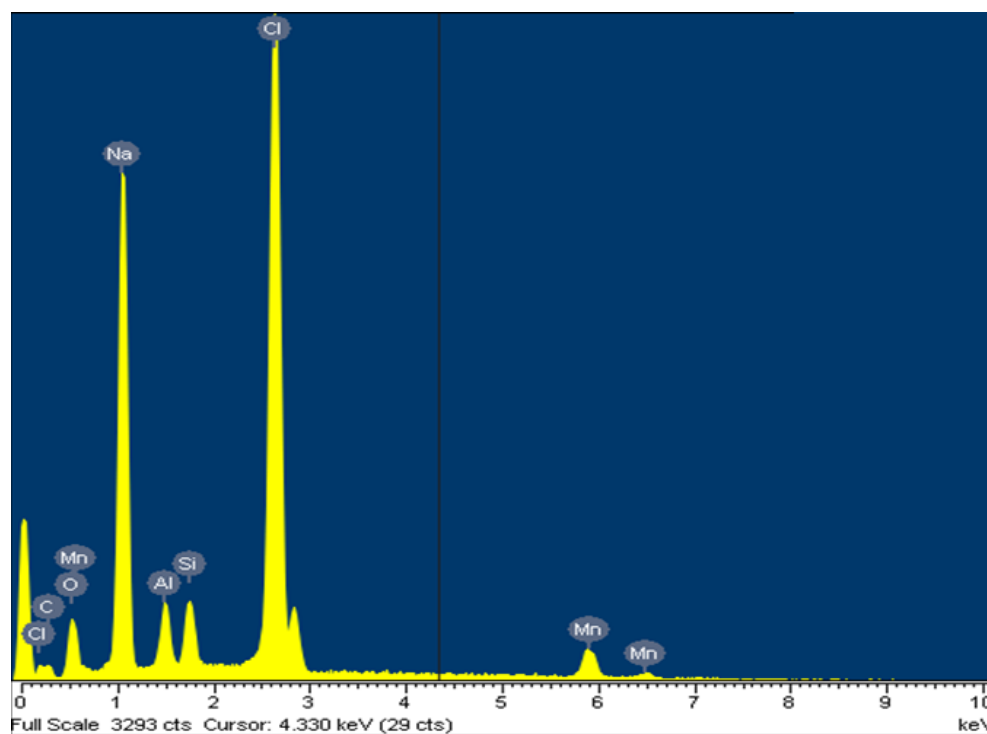


Fig.7. EDX spectrum of the 5hr (top) and 24hr (bottom) furnace exposed MCS

3.2.2. XPS

XPS wide scan spectra of the 5hr and 24hr furnace exposed coated sand are illustrated in Figure 8. Eleven major peaks at different binding energies, designated for the Na 1s, Mn 2p, O 1s, C 1s, Cl 2s, Cl 2p, Si 2s, Al 2s, Si 2p, and Al 2p, respectively, were observed for the both applied sorbents (Fig.8). No Significant changes were found in Figure 8 between 5hr and 24hr furnace exposed MCS.

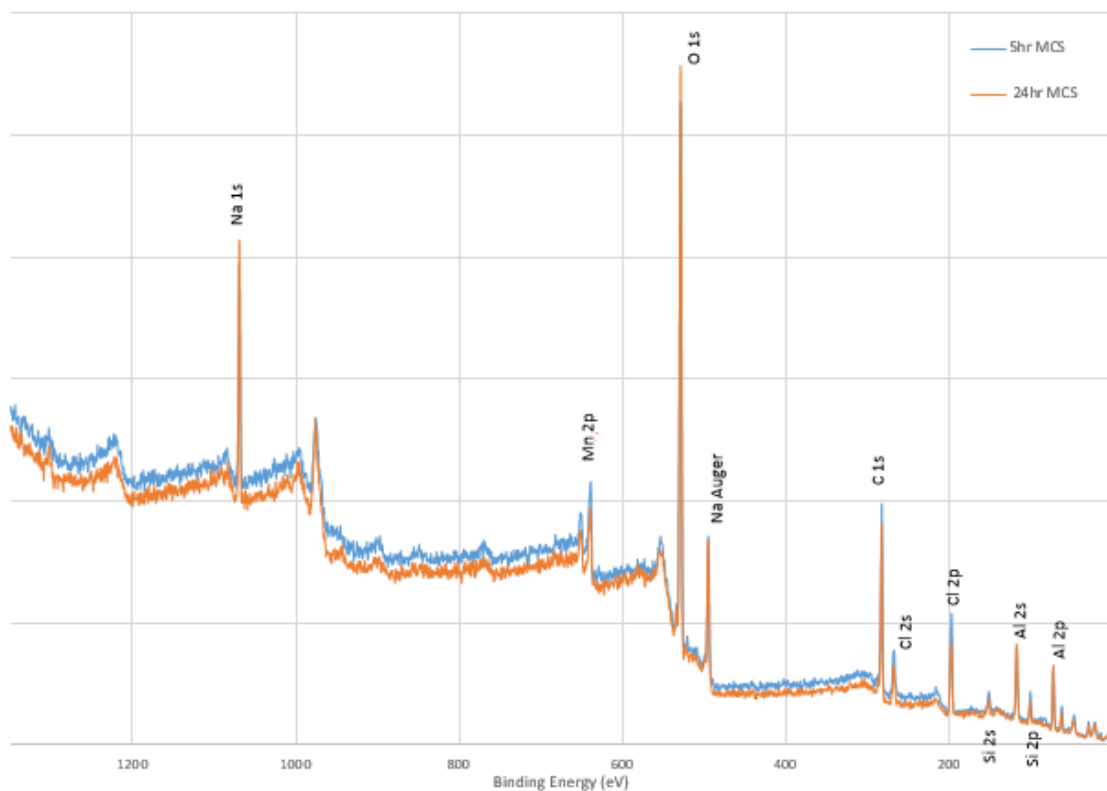
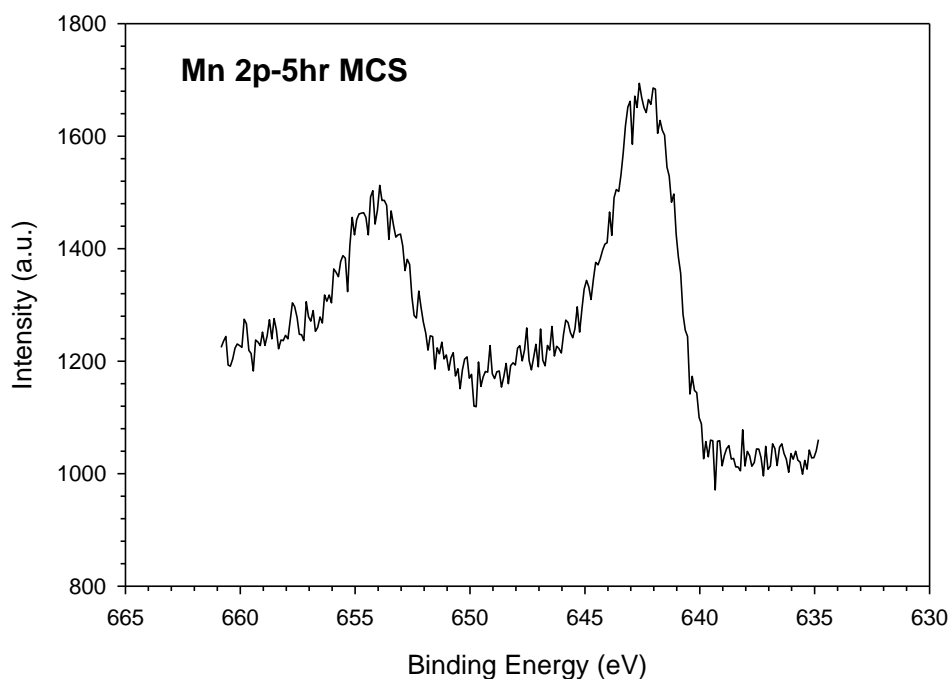


Fig.8. XPS wide scan spectra of the 5hr and 24hr furnace exposed MCS sorbents.

The chemical formula of manganese oxides are generally expressed as MnO_x , due to the multiple valence states exhibited by Mn. Hence, it is reasonable to measure the average oxidation state for a manganese mineral [17]. The observation of the Mn 2p_{3/2} peak at 642.6 eV for both adsorbent (Fig.9 and Fig.10) and the Mn 2p_{1/2} peak at 653.9 eV for 5hr furnace exposed MCS and 654.1 eV for 24hr furnace exposed MCS indicates the manganese exhibited oxidation between Mn^{3+} and Mn^{4+} as shown from the auger plot, but it can be seen to show Mn^{3+} predominantly from the Mn 2p_{3/2} peaks [18, 19].

The large peak in Fig.11 at 531.8 eV and 531.4 eV for 5hr furnace exposed MCS and 24hr furnace exposed MCS ,respectively can be assigned to O 1s which is generally accepted as lattice oxygen in the form of O^{2-} (metal oxygen bond). This peak is characteristic of the oxygen in manganese oxides [20, 21].

Figure 9 and 10 also include Al 2p core spectra of the 5hr and 24hr furnace exposed MCS. This spectrum could not be deconvoluted into more than one symmetric peak at 74.8 eV corresponding to Al^{3+} . This indicates that the both MCSs mainly consist of Al_2O_3 [22].



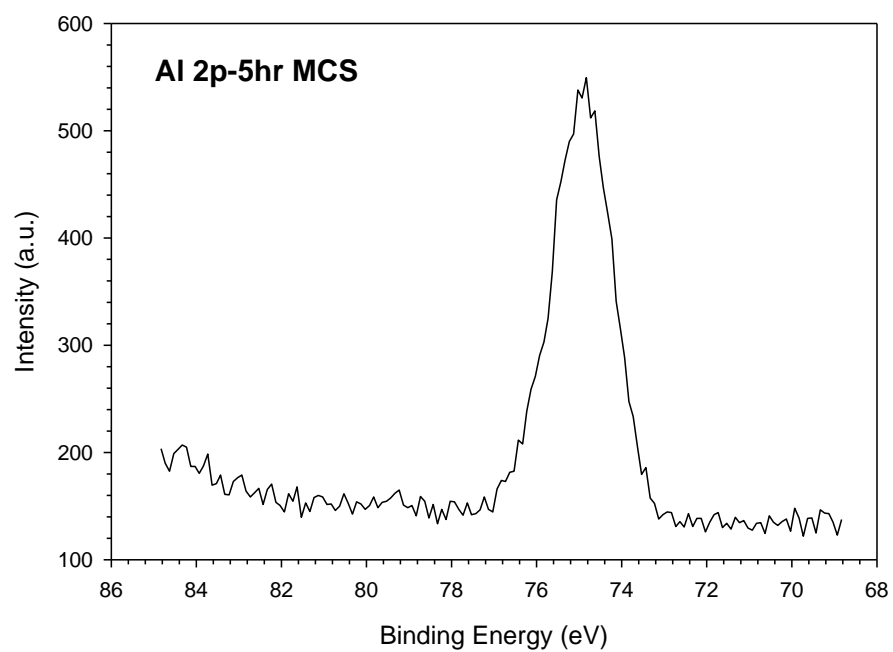


Fig.9. XPS detailed spectrum for Mn and Al for 5hr furnace exposed MCS

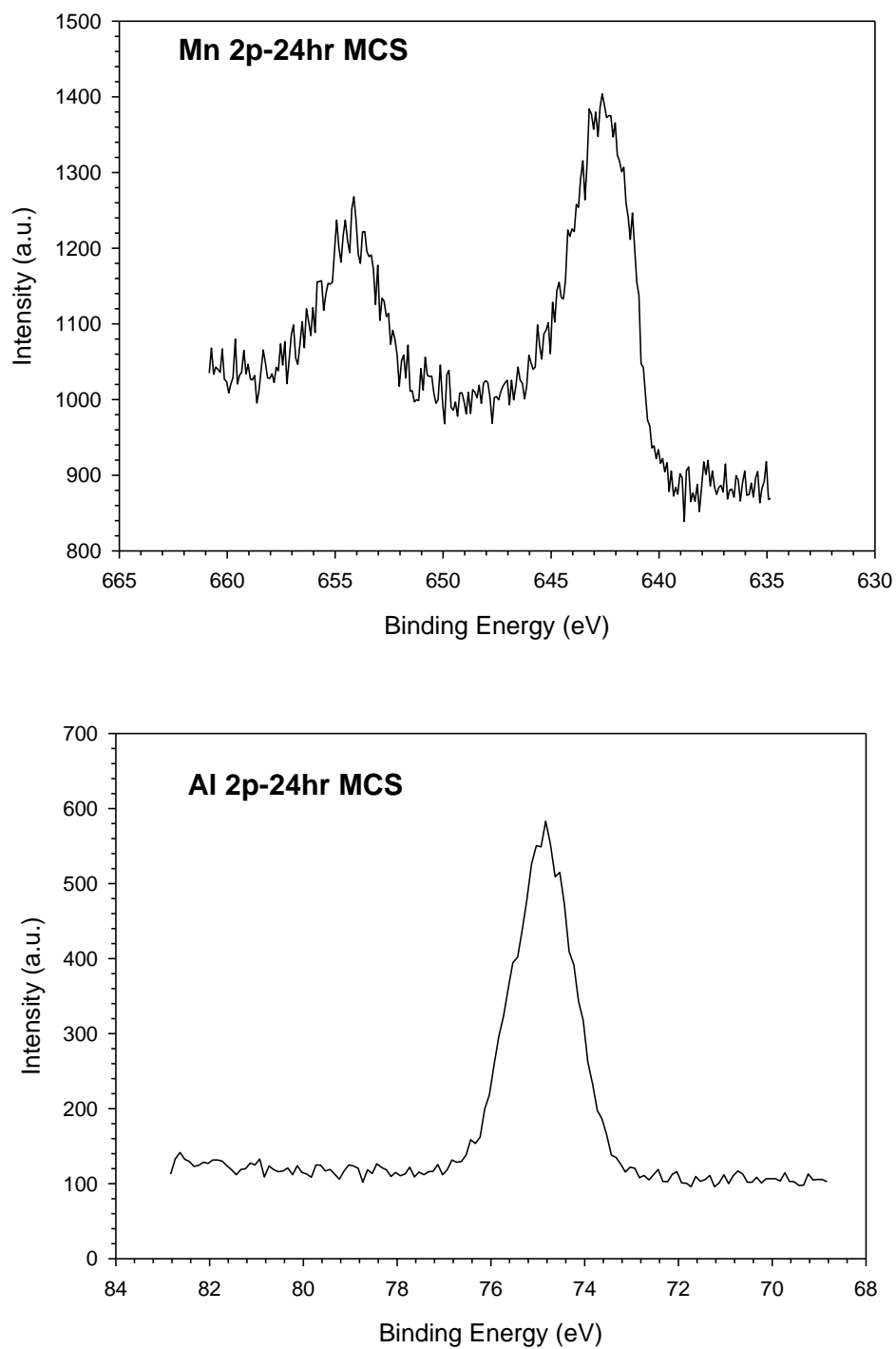


Fig.10. XPS detailed spectrum for Mn and Al for 24hr furnace exposed MCS

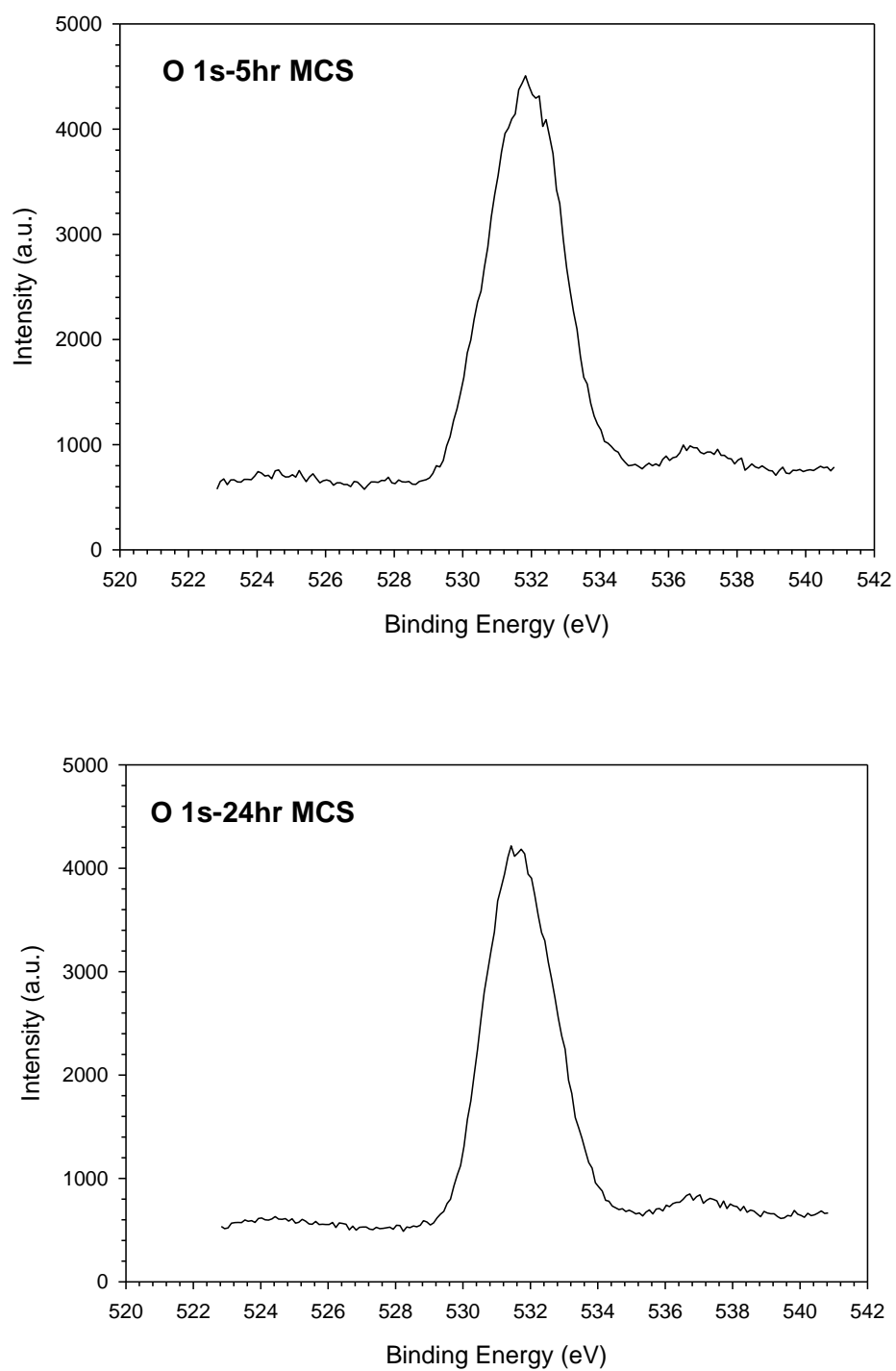


Fig.11. XPS detailed spectrum for O 1s for 5hr and 24hr furnace exposed MCS

4. CONCLUSION

In this chapter the development of a manganese-aluminum coated sand was investigated and its ability to remove As(V) and As(III) from aqueous solution was studied. In order to synthesize the most efficient Manganese-aluminum Coated Sand (MCS) adsorbent, the source of manganese, the mixing time, combination percentage of aluminum manganese coated sand, pH adjustment versus no pH adjustment coating process and the sorbent calcination time in furnace was optimized.

The MnCl_2 and AlCl_3 were found to be the superior sources for manganese and aluminum in removing both As(III) and As(V) from aqueous solution. A higher arsenic removal was obtained by increasing the mixing time from 1hr to 24hr. For different combinations of manganese-aluminum coated, the MCS by 50% MnCl_2 +50% AlCl_3 was found to be the most effective sorbent. Adjusting the pH of the coating solution improved the arsenite adsorption onto the MCS in general while a comparable results with no pH adjustment process were obtained for arsenate adsorption. In general, the longer coated sand exposure to the furnace did not significantly change the arsenic removal efficiency. However, the calcination time of 5 hr was found to be the most effective time resulting the highest arsenic removal efficiency in DI solution and the solution with the ionic background. Due to comparable arsenic removal efficiency with the 5hr furnace exposed MCS specially in the more practical solution, solution with the ionic background, the pH adjusted MCS with maximum calcination time, 24 hr furnace exposure, was also considered as promising sorbent for the subsequent experiments.

Therefore, the 5hr and 24hr furnace exposed MCS obtained from pH adjusted coated solution with MnCl_2 and AlCl_3 as their sources of manganese and aluminum, respectively was developed as the

most efficient sorbents for the As(III) and As(V) removal from aqueous solution. The effect of different factors on the arsenic adsorption ability of these two developed sorbents will be discussed in the next chapter.

The optimized 5hr and 24hr furnace exposed MCS were characterized by SEM/EDX and XPS. The EDX analyses showed that the uncoated sand has high silicon content at its surface indicating that the sand is essentially silica before the coating. The SEM images of the 5hr and 24hr furnace exposed MCS indicated the coated sands as a rough coated surface where no uniform coating was visible. It also showed that aluminum and manganese oxides formed in clusters on the surfaces. Based on the EDX mapping analysis of different elements for MCS adsorbents, the surface of the sorbents included the areas where the silica was coated with aluminum, manganese and sodium chloride and there were areas where the silica was exposed.

The Eanalysis of different element on the MCS revealed that Mn, Al,C,O, Si, Na and Cl are the main constituents. Also the 5hr furnace exposed MCS and 24hr furnace exposed MCS gave basically similar spectrum however a higher manganese content was observed on 5hr furnace exposed MCS versus the 24hr furnace exposed MCS.

The XPS analysis of Mn 2p resulted that the manganese exhibited oxidation between Mn^{3+} and Mn^{4+} with the predominant Mn^{3+} . The analysis of O 1s spectra indicate the presence of oxygen as lattice oxygen in the form of O^{2-} . Also the analysis of Al 2p core spectra of the 5hr and 24hr furnace exposed MCS indicated that the resulted spectrum could not be deconvoluted into more than one symmetric peak at 74.8 eV corresponding to Al_3^+ . This indicated that the presence of aluminum as Al_2O_3 on both MCSs.

5. REFERENCES

- [1] Driehaus, W., Seith, R., and Jekel, M.: Oxidation of arsenic(III) with manganese oxides in water treatment. *Water Res.*, 29(1):297–305, 1995.
- [2] Scott, M. J., and Morgan, J. J.: Reactions at oxide surfaces. 1. Oxidation of As(III) by synthetic birnessite.” *Environ. Sci. Technol.*, 29(8):1898–1905, 1995.
- [3] Takamatsu, T., Kawashima, M. and Koyama, M.: The role of Mn^{2+} -rich hydrous manganese oxide in the accumulation of arsenic in lake sediments. *Wat. Res.*, 19(8):1029-1032, 1985.
- [4] Bajpai, S. V., and Chaudhuri, M.: Removal of arsenic from ground water by manganese dioxide-coated sand. *J. Environ. Eng.*, 125(8):782–784, 1999.
- [5] Chang, Y. Y., Song, K. H. and Yang, J. K.: Removal of As(III) in a column reactor packed with iron-coated sand and manganese-coated sand. *Journal of Hazardous Materials*. 150(3): 565–572, 2008.
- [6] Viraraghavan, T., Subramanian, K. S. and Aruldoss, J. A.: Arsenic in drinking water—problems and solutions, *Water Sci. Technol.*, 40 (2):69–76, 1999.
- [7] Thirunavukkarasu, O. S., Viraraghavan, T., Subramanian, K. S., Chaalal, O. and Islam. M. R., Arsenic removal in drinking water—impacts and novel removal technologies. *Energy Sources*, 27:209–219, 2005.
- [8] Jeong Y., Fan M. and Li N., 2005. The adsorption of arsenic (V) by iron and aluminum oxides[D]. Ph. D Dissertation, Iowa State University, USA.
- [9] Kunzru, S. and Chaudhuri, M., Manganese amended activated alumina for adsorption/oxidation of arsenic. *J. Environ. Eng.* 131(9):1350–1353, 2005.
- [11] Hering, J. G. and Dixit, S.: Contrasting Sorption Behavior of Arsenic(III) and Arsenic(V) in Suspensions of Iron and Aluminum Oxyhydroxides . *ACS Symp. Ser.*, 915:8–24, 2005.
- [12] Giles, D. E., Mohapatra, M., Issa, T. B., Ananda, S., Singh, P.: Iron and aluminium based adsorption strategies for removing arsenic from water.” *Journal of Environmental Management*. 92(12):3011–3022, 2011.
- [13] Maliyekkal, S. M., Sharma, A. K and Phili, L.: Manganese-oxide-coated alumina: A promising sorbent for defluoridation of water. *Water Res.*, 40:3497–3506, 2006.
- [14] Naidu, R., Smith, E., Owens, G., Bhattacharya, P., Nadebaum. 2006. Managing Arsenic in the Environment: From soil to human health. CSIRO.

- [15] Min, S.Y., Kim, B.K., Park, S.J., Chang, Y.Y., and Yang, J.K., Removal Efficiency of Arsenic by Adsorbents having Different Type of Metal Oxides. *Environ. Eng. Res.*, 14(2):134-139, 2009.
- [16] Basu, T., Gupta, K., Ghosh, U.C.: Performances of As(V) adsorption of calcined (250 °C) synthetic iron(III)–aluminum(III) mixed oxide in the presence of some groundwater occurring ions. *Chem. Eng. J.*, 183(15):303–314, 2012.
- [17] Katsoyiannis, I.A. and Zouboulis, A.I.: Biological treatment of Mn(II) and Fe(II) containing groundwater: kinetic considerations and product characterization. *Water Res.* 38:1922–1932, 2004.
- [18] Ansell, R.O., Dickinson, T. and Povey, A.F.: An X-ray photo-electron spectroscopic study of the films on coloured stainless steel and coloured ‘Nilomag’ alloy 771. *Corros. Sci.*, 18, 245-256, (1978).
- [19] Umezawa, Y. and Reilley, C.N.: Effect of Argon Bombardment of Metal Complexes and Oxides Studied by X-Ray Photoelectron Spectroscopy. *Anal. Chem.* 50:1290-1295, 1978.
- [20] Wagner, C.D., Riggs, W.M., Davis, L.E., Moulder, J.F. and Muilenberg, G.E., Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden Prairie, USA, 1979.
- [21] Liu, J-S. and Hu, Y.: Characterization of Manganese Oxides/Au Nanocomposite Thin Films for Supercapacitor. *Int. J. Electrochem. Sci.*, 8:9231–9241, 2013.
- [22] Tan, B.J., Klabunde, K.J. and Sherwood P.M.A.: XPS studies of solvated metal atom dispersed catalysts - evidence for cobalt-manganese particles on alumina and silica. *J. Am. Chem. Soc.* 113:855-861, 1991.

Chapter (VII)

VII. ADSORPTION OF ARSENIC ONTO MANGANESE COATED SAND: BATCH STUDY

1. INTRODUCTION

As mentioned in previous chapters, arsenic-enriched drinking water is a major health problem. The limit for arsenic concentration is set as low as 10 µg/L.

Among the conventional water treatment processes and the advanced water treatment techniques to remove arsenic ions, adsorption currently appears to have the best potential for overall treatment, and it can be expected to be useful for a wide range of compounds. [1]. The most common option used was reported as sorption onto the oxides of aluminum (Al) and iron (Fe). [2,3]. Sorptive filtration by iron or aluminum oxide coated sands was reported as an innovative technology for treating drinking water contaminated by toxic metal pollutants.

Aluminum oxides coated sand has been reported as an excellent sorbent with combination with iron for construction of an arsenic removal system for waste waters. [4]. On the other hand, manganese-coated sand (MCS), as one of the promising media, had much attention and has been widely applied for the treatment of dissolved elements such as As(III) and As(V) [5,6]. Manganese in combination with other elements such as iron has been reported to have a good oxidation capacity for As(III) and a high adsorption capacity for As(V). [7,8,9].

Considering this phenomena, we were interested in the preparation of manganese-aluminum coated sand (MCS) which has multi-functionality such as oxidation of As(III) by manganese oxide

as well as adsorption of several arsenic ions on aluminum oxides. Hence, two different MCSs were developed and the optimized synthesizing procedure was introduced in the previous chapter.

For this chapter, the primary focus was aimed to explore the feasibility of arsenic removal by the synthesized MCS. In particular, attempt was made to investigate the effects of initial solution pH, adsorbent dosage, contact time and co-existing ions on the arsenic removal efficiency.

2. MATERIALS AND METHODS

2.1. Chemical and Reagents

All chemicals were of analytical reagent grade and no further purification was carried out. All solutions were prepared with de-ionized (DI) water made in the laboratory with a resistance greater than 18 MΩ. Sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 99% purity, ACS grade) and sodium meta-arsenite (NaAsSO_2 , 95% purity, ACS grade) were purchased from Sigma-Aldrich. The other chemicals were obtained from Fisher scientific (Fair Lawn, NJ).

2.2. Preparation of MCS

The preparation procedure of Manganese-aluminum Coated Sand(MCS) was reported in general in chapter 6. The optimized procedure for synthesis of MCS is as follow:

First and before the coating process, the sand was first washed and soaked in 0.1M HCl solution for 3h, and then subsequently rinsed with de-ionized water until the pH of the washing water is close to 7.0. After that, it was dried in an oven at 110 °C to prepare for coating. Then, 50 mL of a high concentrated MnCl_2 (1M) was mixed with 50 mL of high concentrated AlCl_3 (1 M) solution and

the solution pH was adjusted to pH about 7 with 6 N NaOH. Then the coating solution was mixed with the sand (80 g) in a flask for 24hr. Then, the residual coating solution was poured, and the sand was air dried for 12 h followed by heating in the oven (110 °C) for 4hr .This is the first step for the whole coating process. Then, the sand was introduced into a furnace to finish coating of metal oxides on the sand. This process was performed at 550 °C for 5hr and 24hr as the second coating step. Finally, the coated sand was stored in airtight containers for further use.

2.3. Arsenic removal experiments

2.3.1. Equipments

Arsenic concentrations were determined by atomic absorption spectroscopy-graphite furnace using a Perkin Elmer AAnalyst 800 instrument. All measurements for arsenic analysis, were carried out using an electrodeless lamp (EDL) at 193.7 nm and the modifier used was palladium-magnesium modifier. The atomization and pre-treatment temperature were 2000 and 1200°C, respectively. The detection limit of arsenic was estimated to be 1 µg/L. The zeta potential of the sorbent was measured by a Zeta-meter system 3.0(Zeta meter Inc,VA).

2.3.2. Preparation of synthetic solution

The 1 mM calcium chloride (CaCl_2 , 98.8% purity, ACS grade), 0.5 mM sodium sulfate (Na_2SO_4 , 99.3% purity, ACS grade) and 2.5 mM sodium bicarbonate (NaHCO_3 , 100% purity, ACS grade) were used to prepare a solution, referred to as synthetic solution, representative of natural waters containing bicarbonate alkalinity and considering the effect of other co-existing ions. The As (III)

and As (V) stock solution was prepared with sodium arsenite and sodium arsenate, respectively in DI solution and synthetic solution.

2.4. Batch studies

The adsorption of arsenic ions were analyzed in a batch system at room temperature. A 1 mg/L solution of As(III) and a 1 mg/L solution of As(V) were prepared. The experiments were conducted with dry sorbent suspension of different concentrations in DI water and synthetic solution. In order to avoid the formation of precipitation and converting of ions in acid conditions, the solution pH was not adjusted. The experiments were carried out in high density polyethylene (HDPE) bottles, where different dosages of the sorbent were placed in the bottles and 50 mL of solution was added to the sorbent. The bottles were capped and shaken by hand to mix the slurry of sorbent and water before placing the bottles inside a rotating tumbler. The bottles were shaken in the tumbler at 16 rpm for 24 h and at 25 °C. After shaking, the bottles were removed from the tumbler, the contents of the bottles were then centrifuged at 9,500 rpm to separate the aqueous phase from the sorbent. The supernatant were filtered with a 0.45 µm cellulose acetate filter (Magna, MA) and the concentration of arsenic in the filtrate was analyzed using atomic absorption (AA).

The effects of contact time is one of the main parameters in the adsorption of arsenic ions in aqueous solution. This study determines the capacity of MCS to remove specific metal ions in the solution at the equilibrium time. Also, the adsorption kinetics of As (III) and As(V) for adsorption onto the sorbent was investigated using several time intervals. For the kinetics study, 1 g of MCS was mixed with 50 mL of 1 mg/L arsenic solution at 25 °C for 24 hr.

In order to determine the adsorption capacity of the MCS sorbent, different dosages of the sorbent were mixed in HDPE bottles with 50 mL of the DI and synthetic solution. The initial concentration of arsenic was fixed at 1 mg/L. The bottles were shaken in a tumbler in the dark at 16 rpm for a period of time required for the adsorption equilibrium determined from the adsorption kinetics experiment. Afterwards, the bottles were removed from the tumbler and the samples were analyzed similar to the batch adsorption tests.

The effect of pH on the adsorption of As(III) and As(V) was analyzed by determining the adsorption and removal of arsenic from water over a broad range of solution pH. For the pH experiments, 1 g of the MCS sorbent was mixed with 50 mL of 1 mg/L As(III) or 1 mg/L As(V) solution. The initial pH of the solution in DI water was adjusted to a pH of 2-12 using 0.1 M HCl and 0.1 M NaOH solutions.

The surface charge of the sorbents were analyzed by zeta potential measurements. The 5g/L of the MCS solution was prepared in DI solution and the zeta potential of the sorbent was measured by a Zeta-meter system 3.0 at pH range of 2-12. A high concentration of MCS sorbents were applied due to the settling problems of MCS particles and the Zeta-meter cell limitation.

Different concentrations of the four different ions (calcium, sulfate, phosphate and bicarbonate) were prepared to study the effect of co-existing ions on the removal efficiency of As (III) and As(V) by the MCS sorbent. For this purpose, a 50 mL volume of each solution with an initial arsenic concentration of 1 mg/L was mixed with 1g MCS.

Five consecutive adsorption- cycles were performed to test the reusability of MCS adsorbents. For the first adsorption cycle, 1 g of the sorbent was mixed with 50 mL of the synthetic solution of 1

mg/L of As (III) or 1 mg/L As(V) for 24 hr. For the second adsorption cycle, the same mass of the used sorbent from the first adsorption cycle was exposed to a fresh batch of arsenic solution. The adsorption processes were carried out according to the same procedures as in the batch experiment for 24 h. The residual concentration and the removal of arsenic were determined for each adsorption cycle.

3. RESULTS AND DISCUSSION

3.1. Effect of contact time and kinetic modeling on As(III) and As(V) adsorption

The effect of contact time on the adsorption of the As(III) and As(V) on MCS in solutions with ionic background is illustrated in Fig. 1(a and b). The results show that MCS removes As(V) faster than As(III).

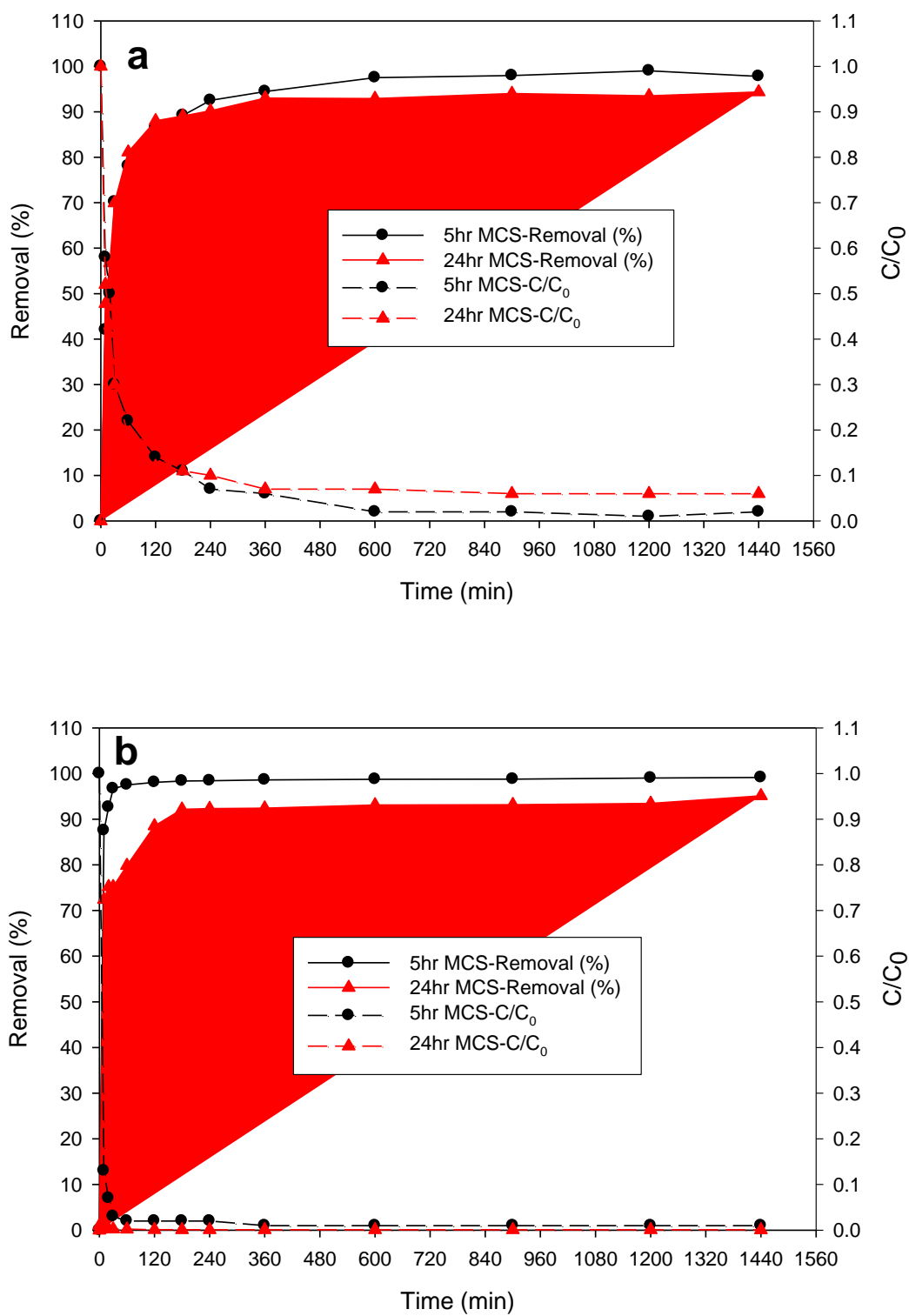


Fig.1. Effect of contact time on a) As(III) adsorption b) As(V) adsorption

The shapes of the curves representing arsenic removal versus time suggest that a two-step mechanism occurs. The first portion indicates that a rapid adsorption occurs during the first 60 min after which equilibrium is slowly achieved. The higher initial sorption rate may be due to the great number of vacant adsorption sites available at the initial stage of the adsorption process, resulting a large concentration gradient between the solute on the adsorbent surface and the solute in solution. With increasing contact time, the concentration gradient is reduced due to the accumulation of arsenic on the vacant adsorption sites leading to a decreased adsorption rate of arsenic at the later stages of adsorption.

For As(III) adsorption by 5hr and 24hr furnace exposed MCS and As(V) adsorption by 24hr furnace exposed MCS, almost 80% of total removal occurred within 60 min. For As(V) adsorption by the 5hr furnace exposed MCS, 97.5% of the total arsenic removal occurred within an hour of contact time.

In order to consider the maximum removal of As(III) and As(V) , the equilibrium time of 24hr were considered for all different situations. As a consequence, 24 hr was selected as the reaction time required to reaching pseudo-equilibrium in the present equilibrium adsorption experiments. In general and based on Fig.1 (a-b), a higher arsenic removal was obtained by 5hr furnace exposed MCS.

The kinetics models are important in water treatment process design. The models of adsorption kinetics were correlated with the solution uptake rate. In order to investigate the adsorption kinetics of MCS, three kinetic models including the pseudo-first-order equation, the pseudo-second-order equation and intraparticle diffusion model were applied to the experimental data obtained from batch experiments. These three models were explained in previous chapters.

Fig 2-7 show the plots of linearized form of three models for adsorption of As(III) and As(V) by 5hr and 24 hr furnace exposed MCS. The straight-line plots of $\ln(q_e - q_t)$ versus t , t/q_t versus t , and q_t versus $t^{1/2}$ for these kinetic reaction for adsorption of As(III) and As(V) onto MCS have also been tested to obtain the rate parameters according to the kinetic model equations mentioned in previous chapters. Kinetic parameters for all three kinetic models and correlation coefficients of As(III) and As(V) adsorption were calculated from these plots and listed in Table 1.

Based on the results in Table 1 and Fig 2-7, a good agreement of dynamical data with pseudo second-order kinetic model were observed. As shown in Table 1, the correlation coefficient values of R^2 of pseudo second-order kinetic model for As(III) and As(V) were found to be almost 1. The pseudo first-order kinetic model was not able to predict the experimental data well and the equilibrium sorption capacities of pseudo first-order were found to be lower than experimental results. On the other hand, the equilibrium sorption capacities for second-order correlation were much more reasonable and the calculated arsenic uptake agreed perfectly with the experimental values. These suggest that the sorption systems do not follow a pseudo first-order reaction and the pseudo second-order sorption mechanism be predominant.

The pseudo-second order kinetic model rates show that the As(V) adsorption by 5hr furnace exposed MCS is faster than As(III) adsorption by the same sorbent while a comparable adsorption rate of As(III) and As(V) adsorption was achieved for the arsenic adsorption on 24 hr furnace exposed MCS. Increasing the calcination time did not significantly effect the As(III) adsorption rate while it decreased the rate of As(V) adsorption process.

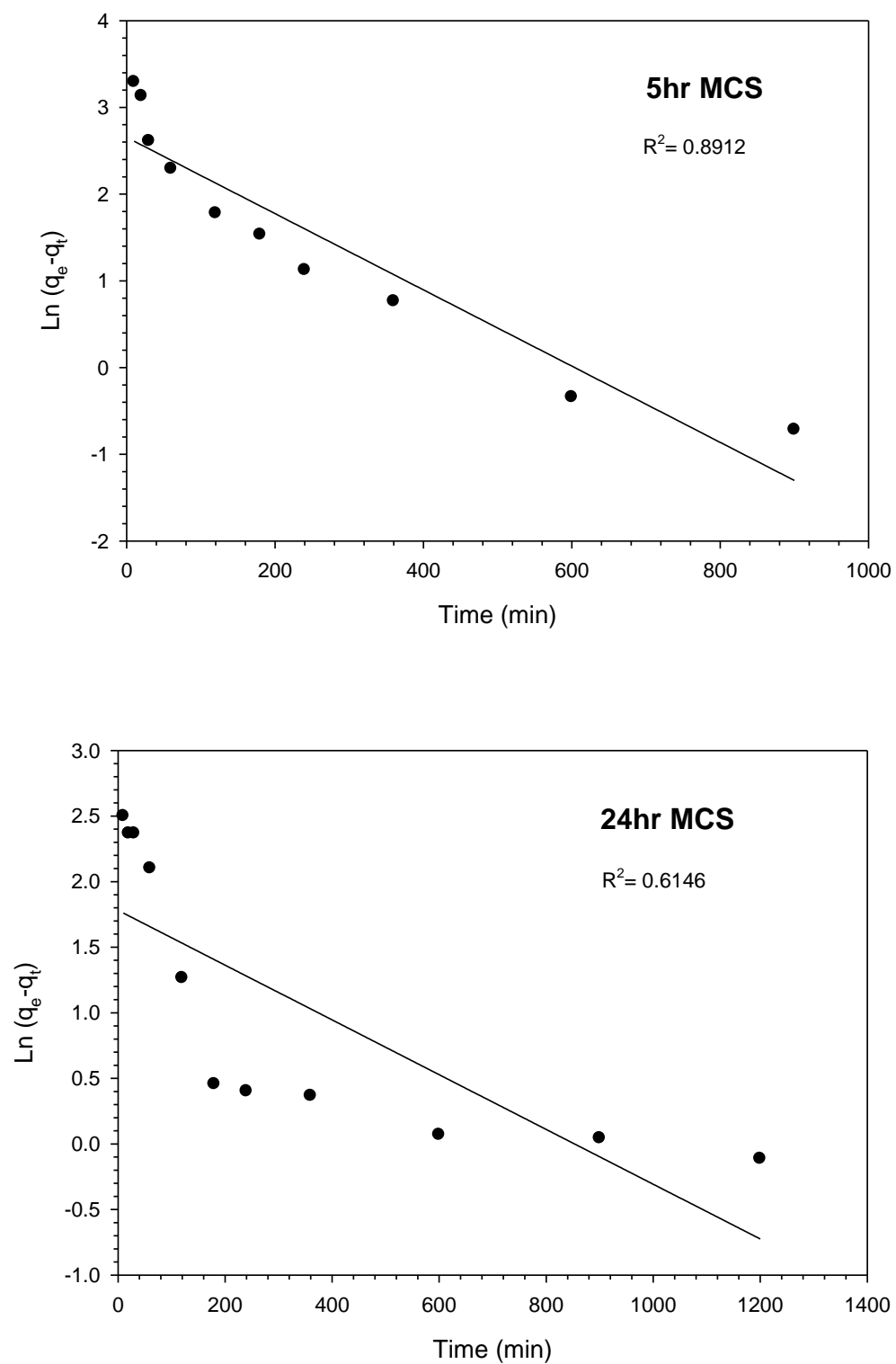


Fig.2. Kinetic Study-First Order kinetic model for As(III) adsorption onto MCS

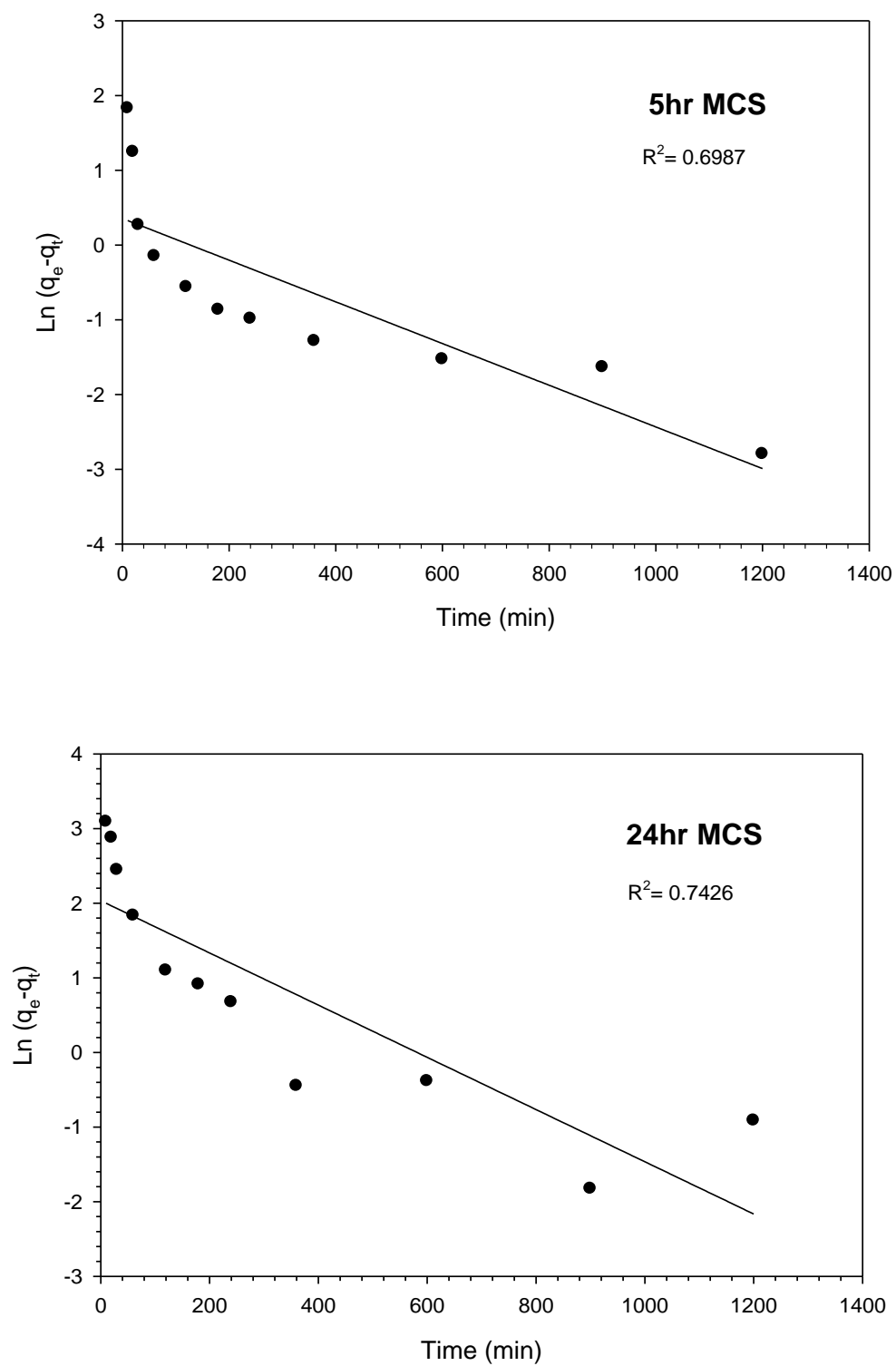


Fig.3. Kinetic Study-First Order kinetic model for As(V) adsorption onto MCS

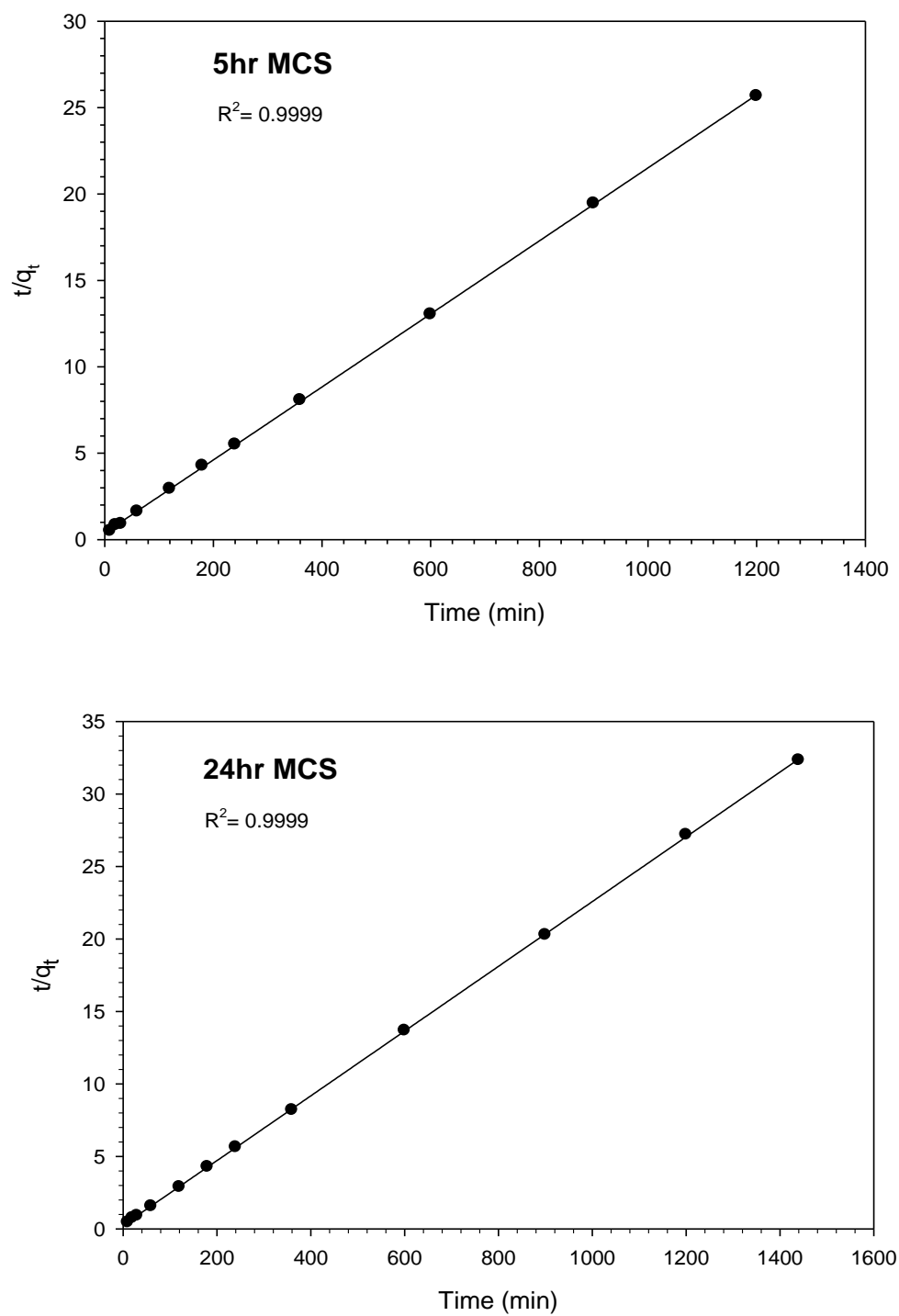


Fig.4. Kinetic Study-Second Order kinetic model for As(III) adsorption onto MCS

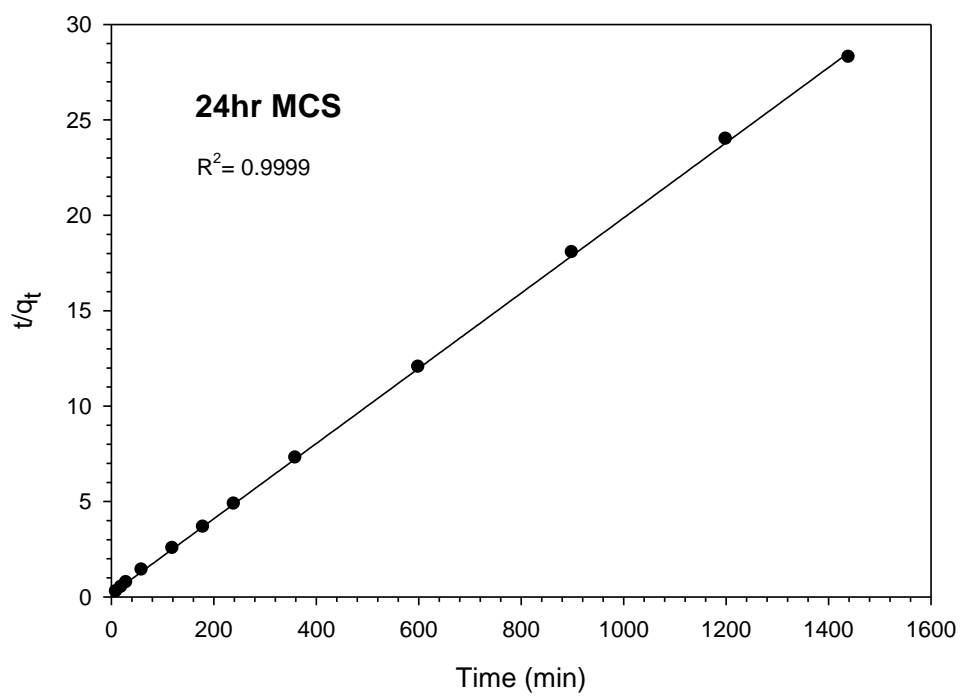
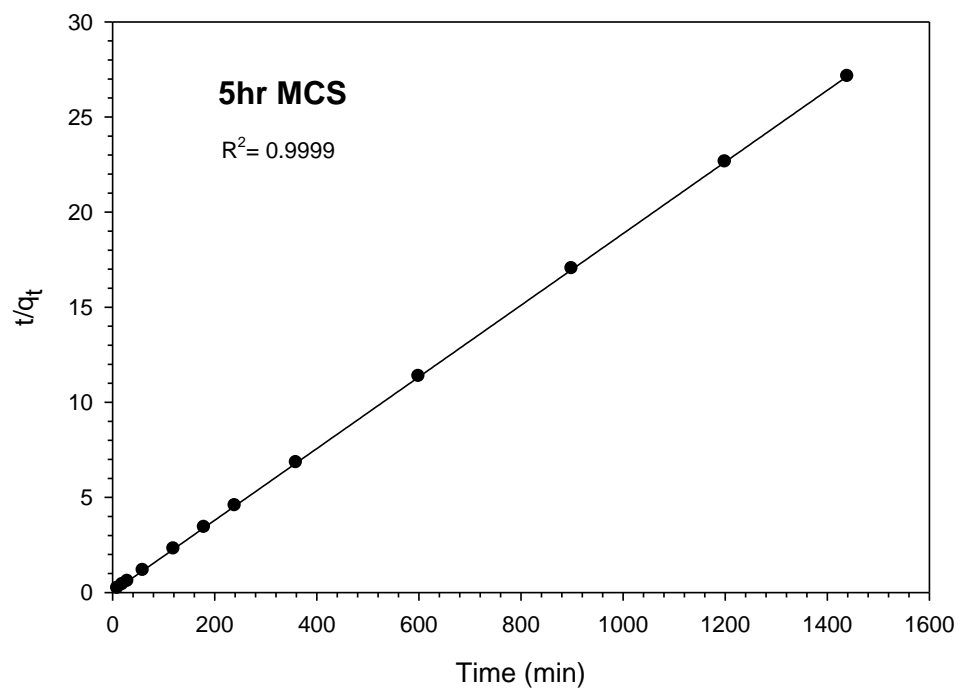


Fig.5. Kinetic Study-Second Order kinetic model for As(V) adsorption onto MCS

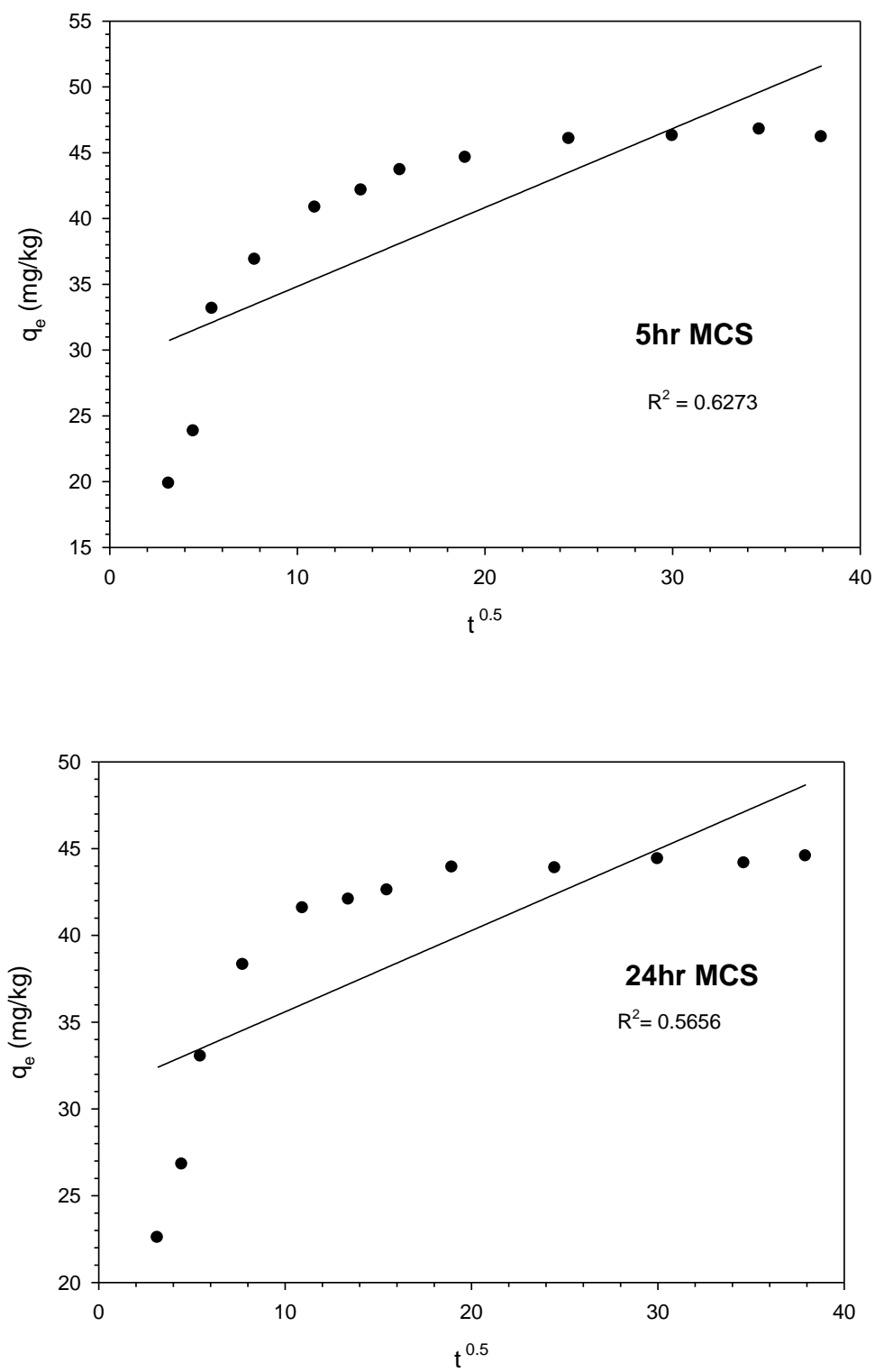


Fig.6. Kinetic Study-Intraparticle diffusion model for As(III) adsorption onto MCS

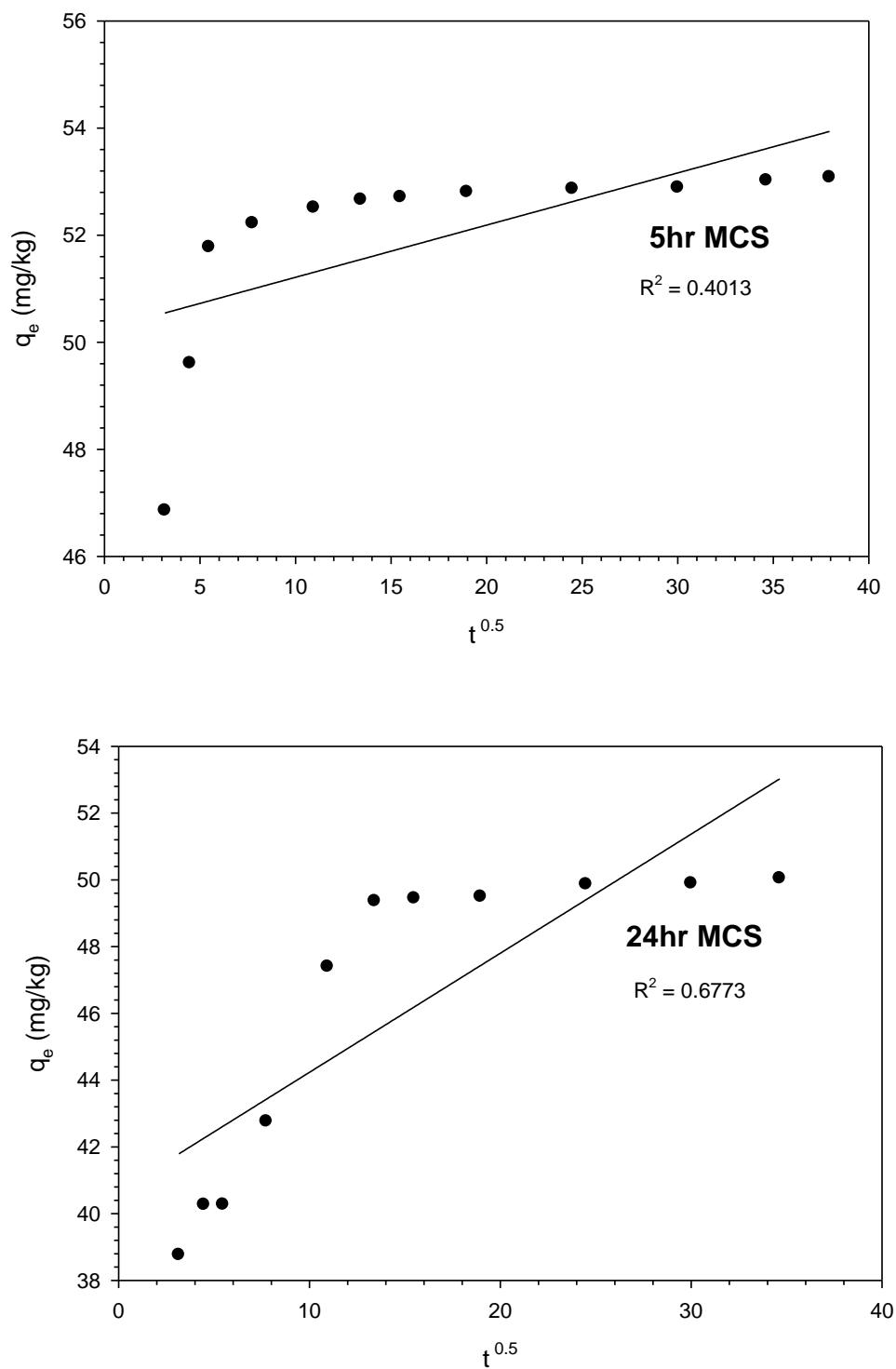


Fig.7. Kinetic Study-Intraparticle diffusion model for As(V) adsorption onto MCS

Table 1. Kinetic parameters for the adsorption of As(III) and As(V) by MCS

| | | As(III)+ synthetic solution | | As(V)+synthetic solution | |
|-------------------------|-----------|-----------------------------|-------------------------|--------------------------|-------------------------|
| | | 5hr $q_{exp}=46.75$ | 24hr $q_{exp}=44.51$ | 5hr $q_{exp}=53.08$ | 24hr $q_{exp}=50.93$ |
| First Order | | | | | |
| | R^2 | 0.8912 | 0.5722 | 0.6987 | 0.539 |
| | K_1 | 0.0044 | 0.0016 | 0.0028 | 0.0012 |
| | q_{cal} | 14.22 | 10.06 | 1.43 | 8.52 |
| | | | | | |
| Second Order | | | | | |
| | R^2 | 0.9999 | 0.9999 | 0.9999 | 0.9999 |
| | K_2 | 0.0012 | 0.0021 | 0.0126 | 0.0025 |
| | q_{cal} | 47.39 | 44.84 | 53.19 | 50.76 |
| | | | | | |
| Intraparticle Diffusion | | | | | |
| | R^2 | 0.6273 | 0.5656 | 0.4013 | 0.6773 |
| | K_{id} | 0.06 | 0.468 | 0.0975 | 0.3568 |
| | C | 28.84 | 30.92 | 50.24 | 40.67 |

3.2. Effect of MCS dose

The effect of adsorbent dosage on As(III) and As(V) adsorption was studied and the results are shown in Fig.8 and Fig.9. It was observed that the removal percent of As(III) and As(V) increased with increasing adsorbent load. This might be due to the availability of more and more binding sites for complexation of arsenic ions.

The plot of arsenic adsorption per unit of adsorbent versus adsorbent dose indicated that the unit adsorption capacity was high at low doses and reduced at high dose. The most important reason for

this is that adsorption sites remain unsaturated during the adsorption reaction. This is due to the fact that as the dosage of adsorbent is increased, there is less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent. [10].

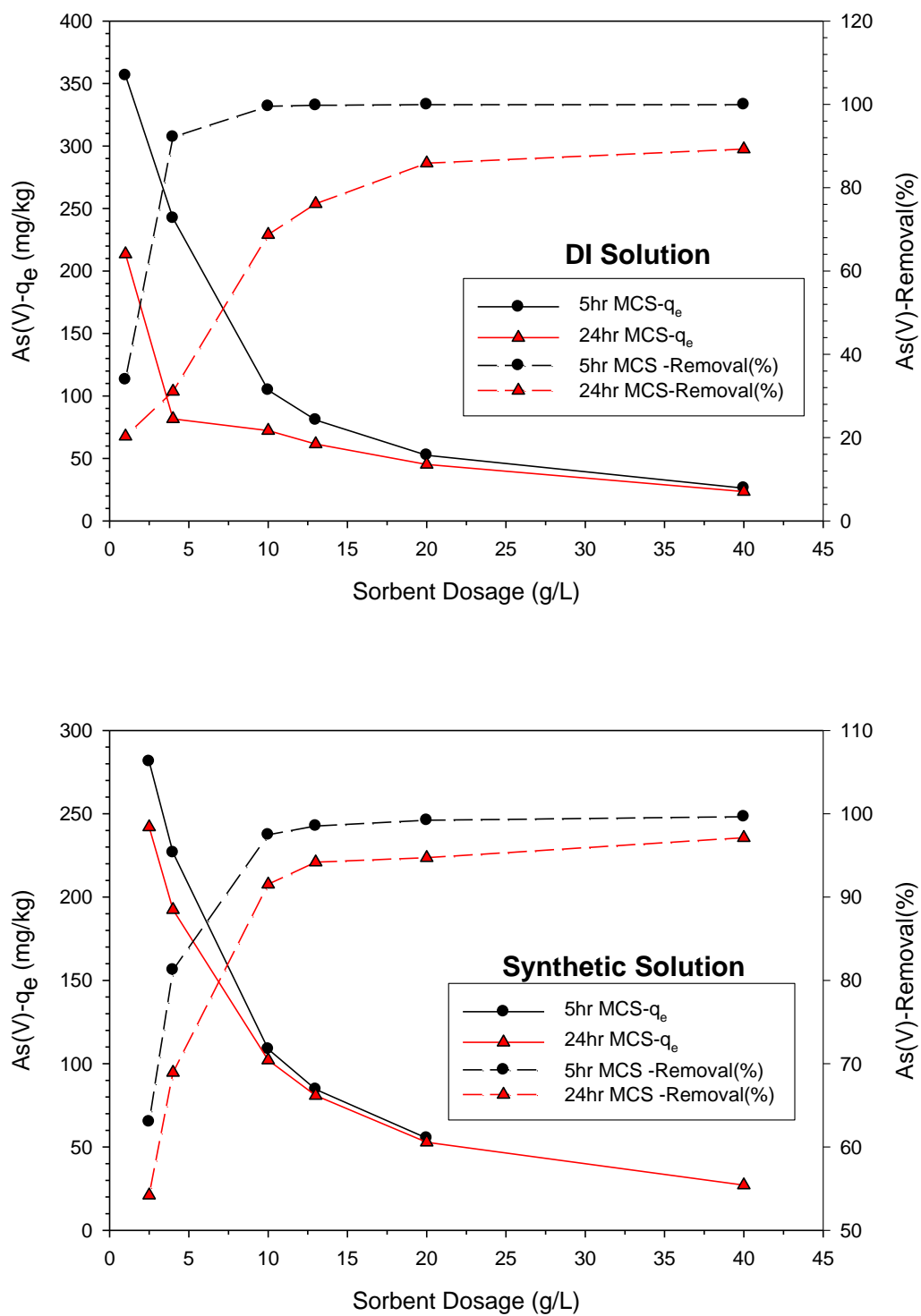


Fig.8. Effect of dosage of MCS on As(V) removal.

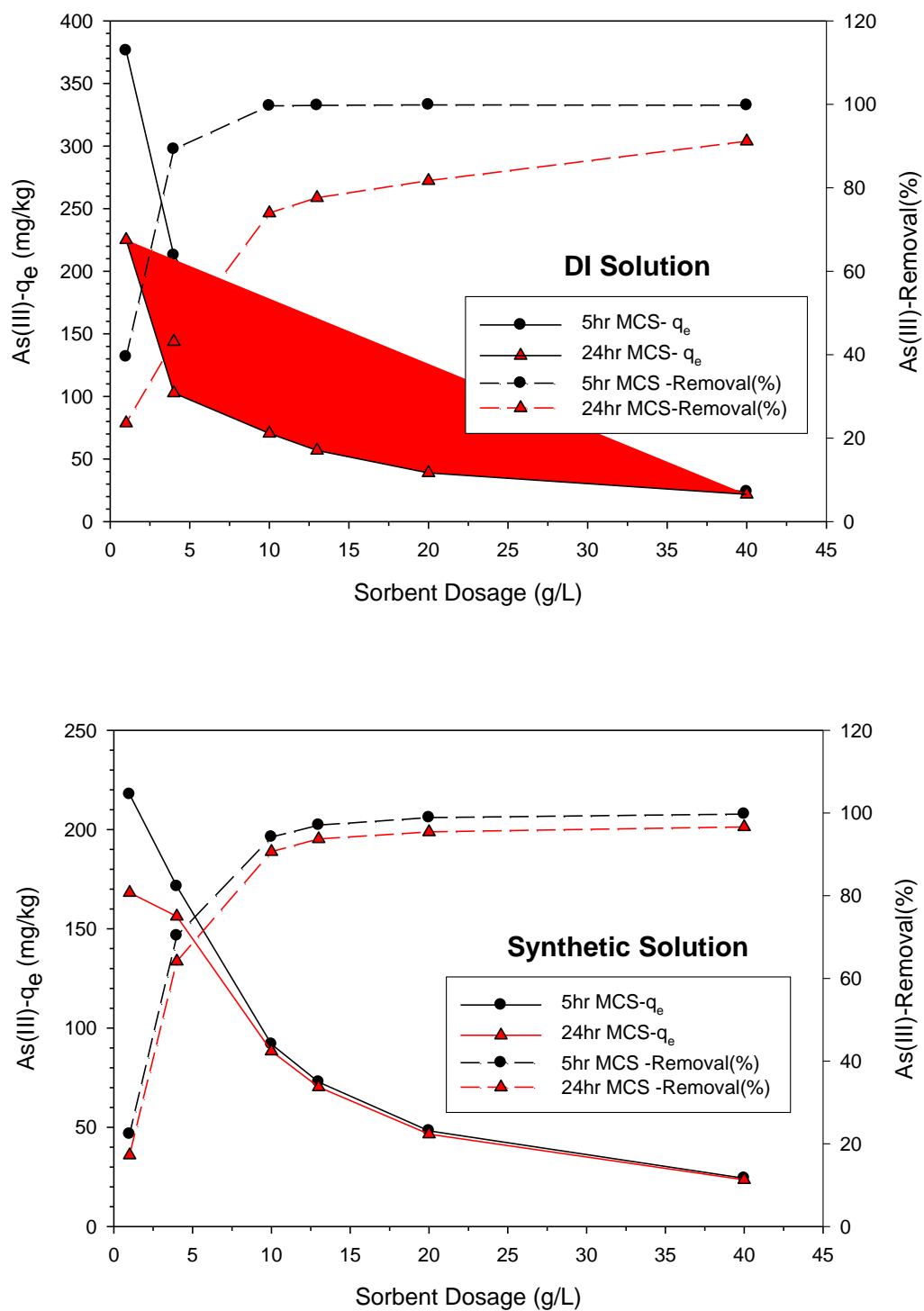


Fig.9. Effect of dosage of MCS on As(III) removal.

As seen from Fig.8, a comparable adsorption of As(V) by 5hr furnace exposed MCS was observed in both DI solution and the solution with ionic background. A higher As(V) adsorption onto the 24hr furnace exposed MCS was achieved in solution with ionic background versus in DI solution. The same trend was obtained for As(III) adsorption(Fig.9). Both 5hr and 24hr 5hr furnace exposed MCS were able to remove comparable amount of As(III) versus As(V) showing their promising potential to remove the more toxic form of inorganic arsenic.

3.3. Isotherm Study

In order to optimize the design of an adsorption system to remove As(III) and As(V) from both DI solution and the solution with ionic background, it is important to establish the most appropriate correlation for the equilibrium curves. In this chapter, four different adsorption models, such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), were used to represent the equilibrium between the arsenic ions in DI solution and solution with ionic background and the adsorbed arsenic ions on MCS. The resulted parameters of the mentioned equilibrium models often provide some insight into the sorption mechanisms and affinities of the adsorbent. All of these four isotherm models were introduced in previous chapters.

The capacity of the 5hr furnace exposed and 24hr furnace exposed MCS at different residual concentration of arsenic in DI solution and synthetic solution is shown in Fig 10-13. The similar adsorption pattern was achieved for As(III) and As(V) adsorption by 5hr and 24hr furnace exposed MCS in different solutions. Based on the results, first the arsenic uptake increased sharply which is indicative of the accessible sites on the surface of 5hr furnace exposed and 24hr furnace exposed

MCS for As(III) and As(V) adsorption. A plateau was obtained by increasing the arsenic concentration indicating that all active adsorption sites on the sorbents' surface were occupied. The resulted pattern for the adsorption process by MCS sorbents is indicative of a favorable As(III) and As(V) adsorption onto 5hr and 24hr furnace exposed MCS in different solutions.

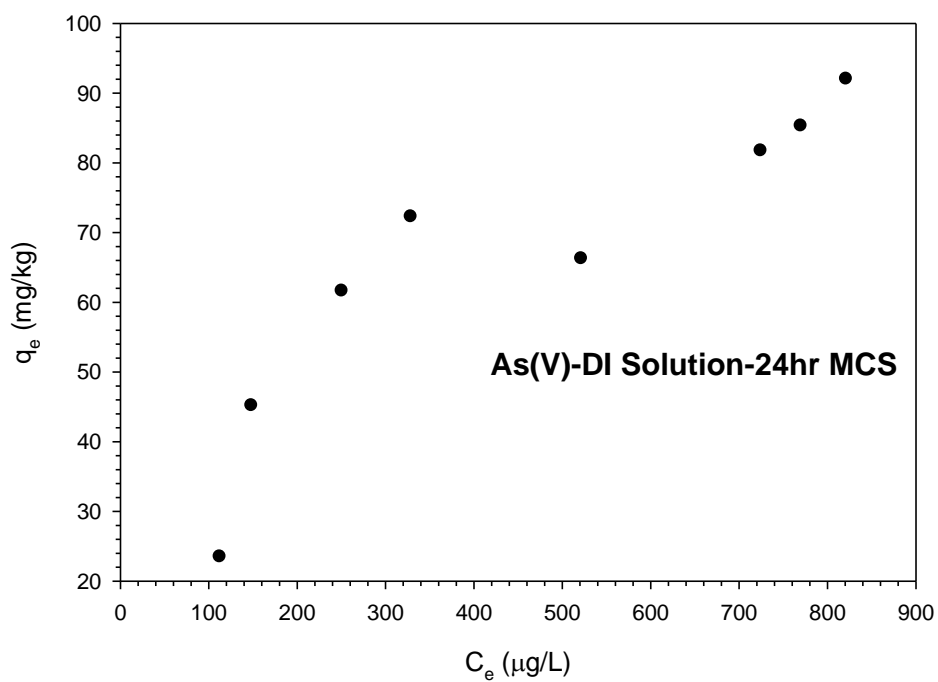
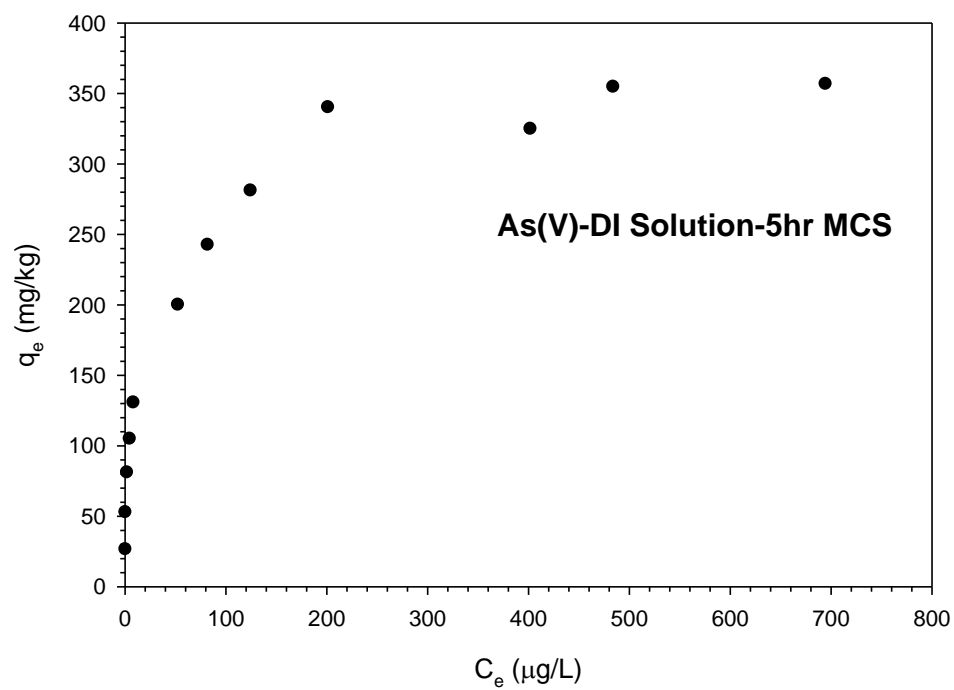


Fig.10. As(V) Adsorption capacity of the 5hr and 24hr furnace exposed MCS in DI

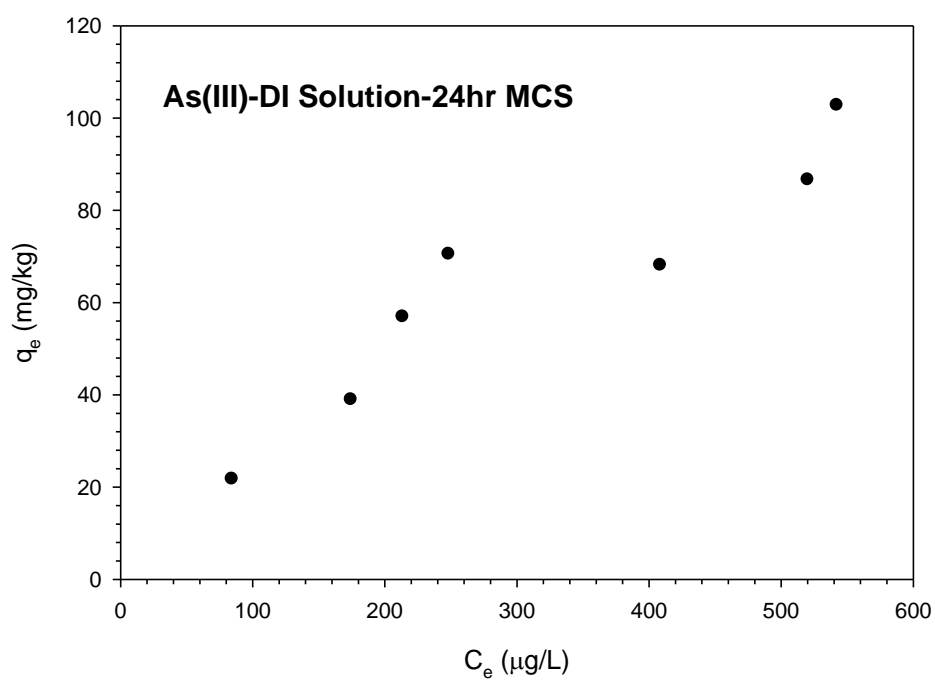
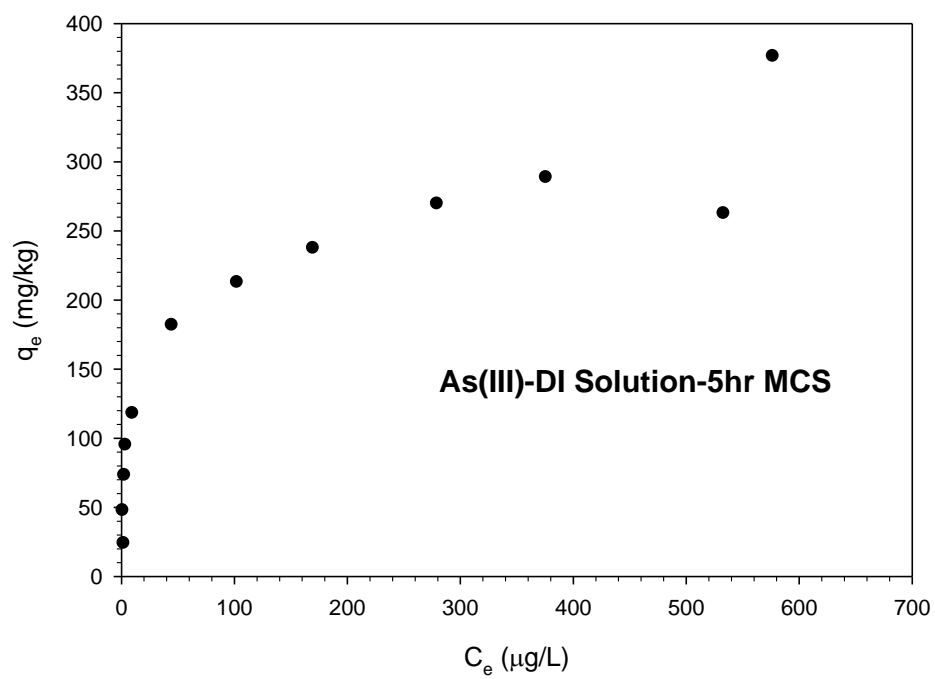


Fig.11. As(III) Adsorption capacity of the 5hr and 24hr furnace exposed MCS in DI

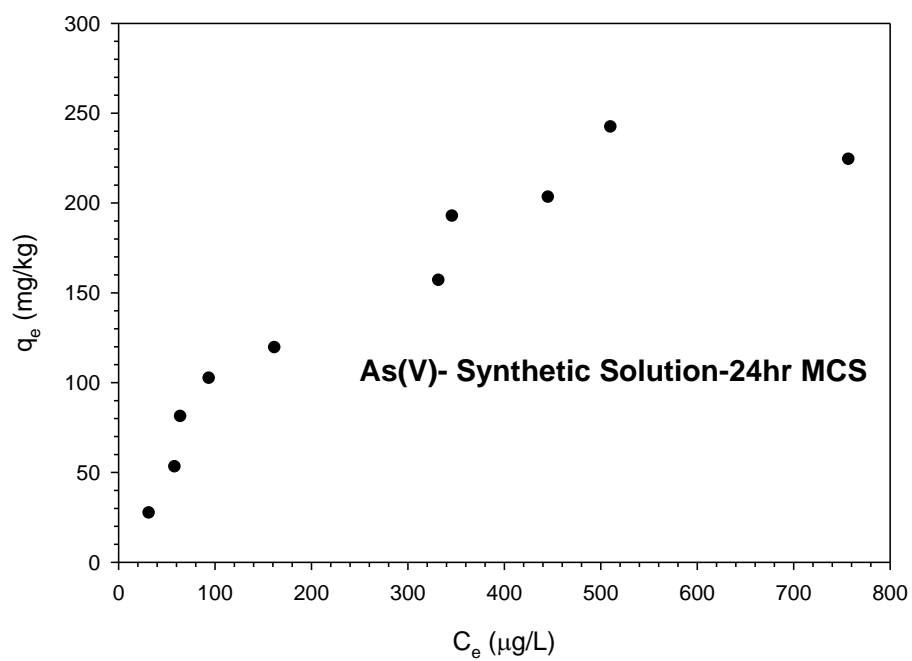
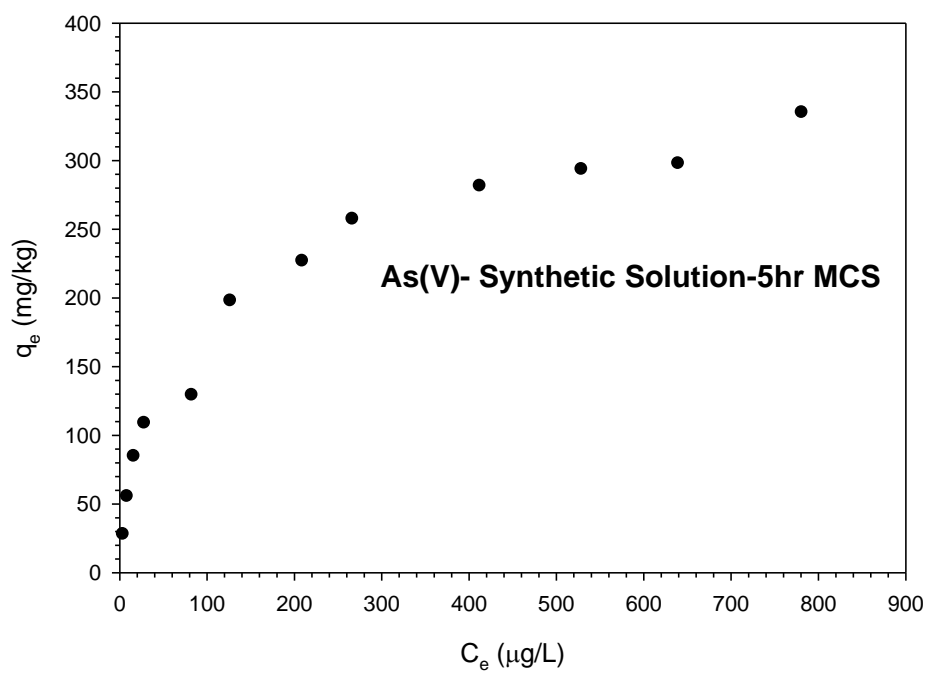


Fig.12. As(V) Adsorption capacity of the 5hr and 24hr furnace exposed MCS in synthetic solution

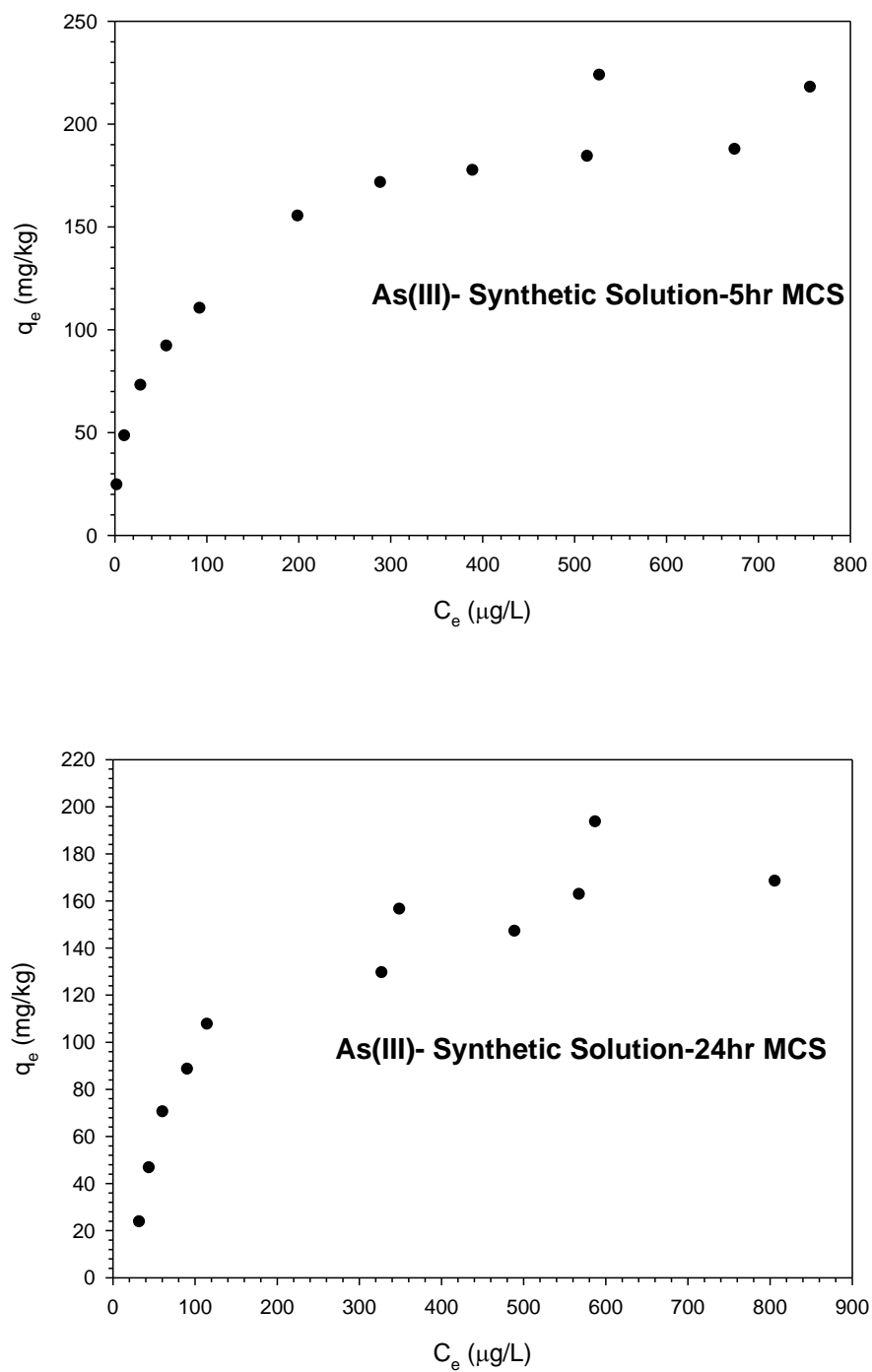
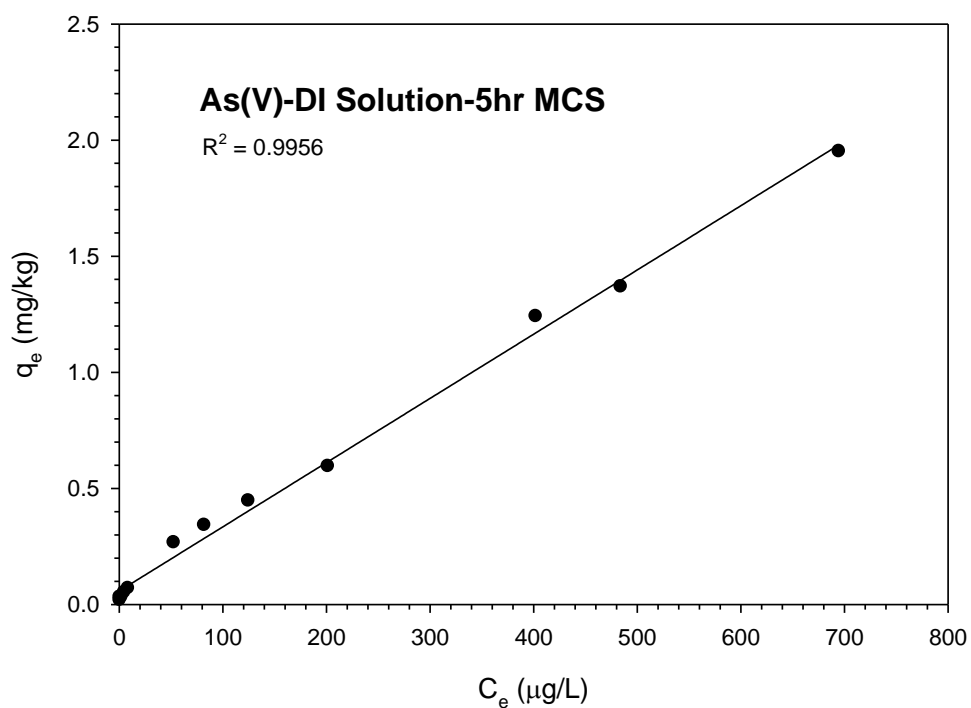
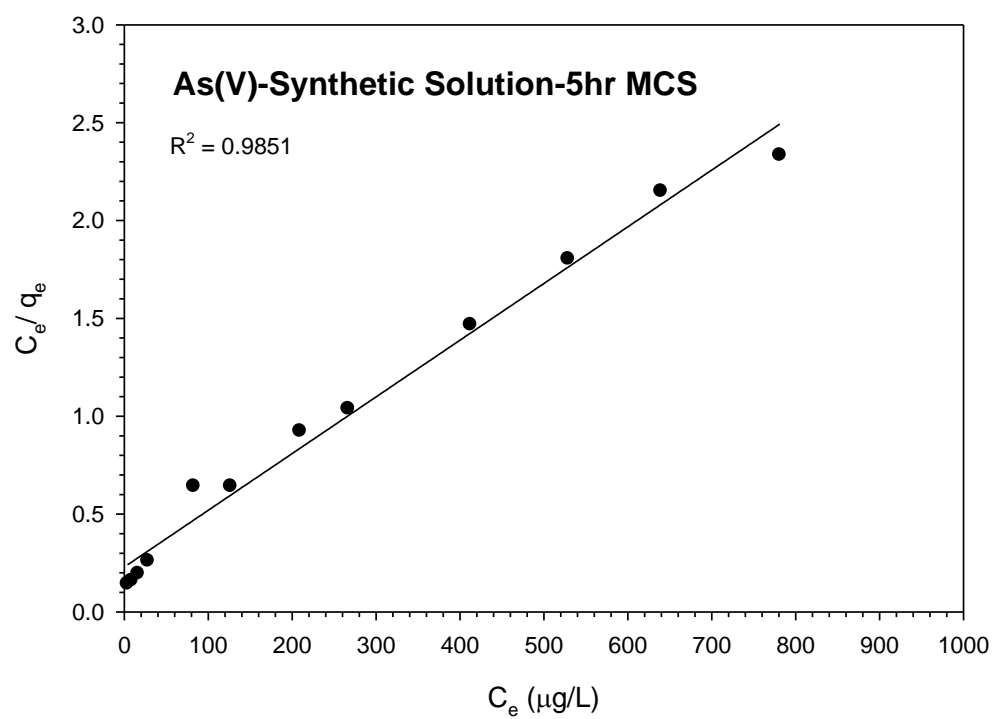
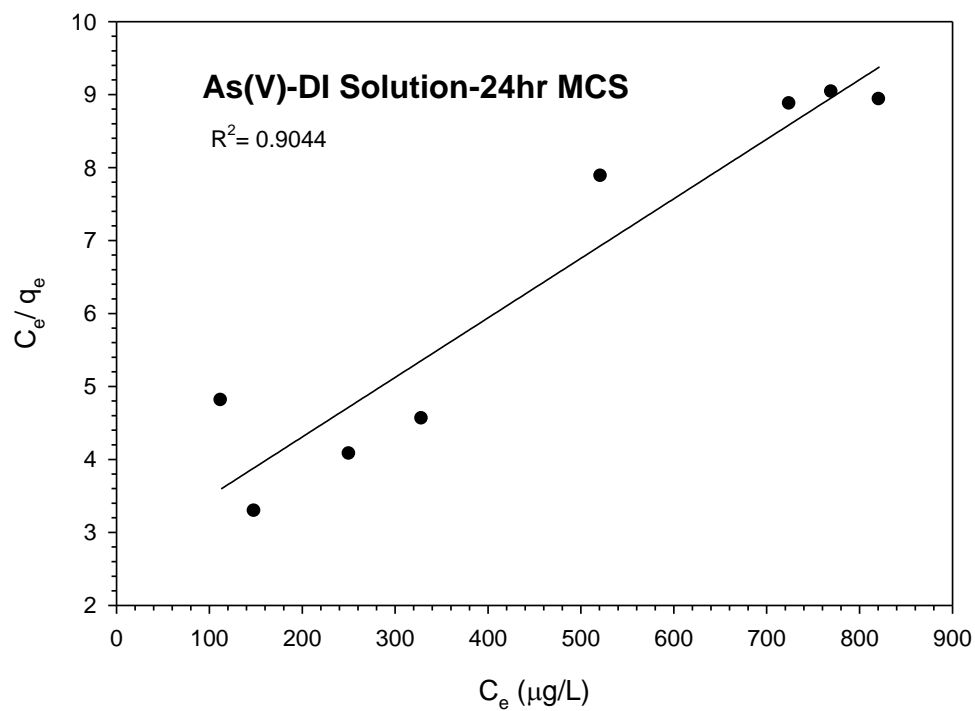
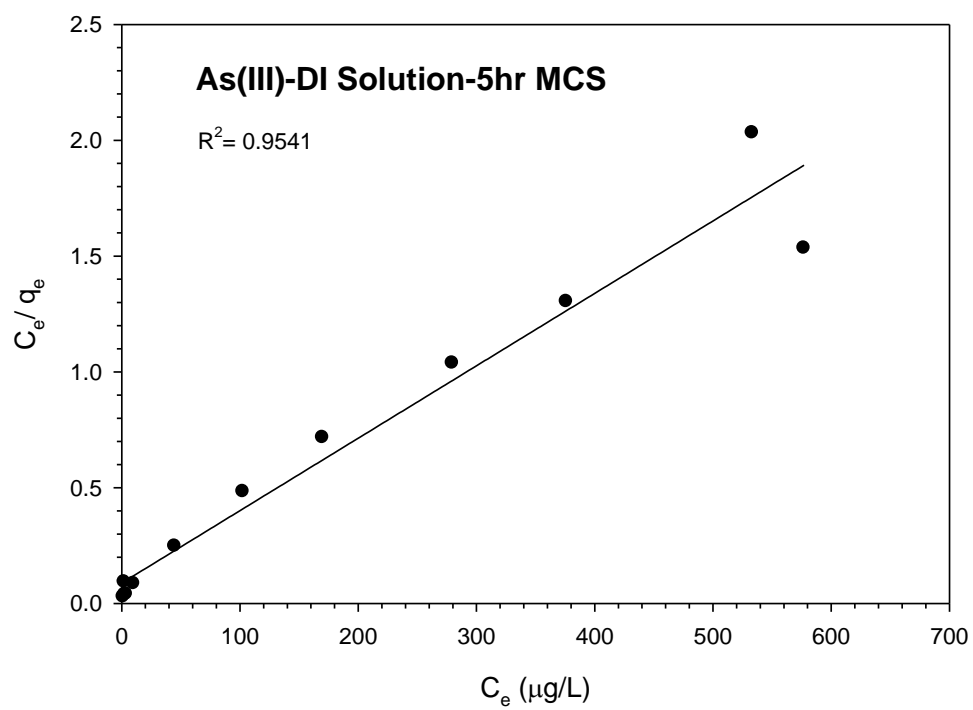
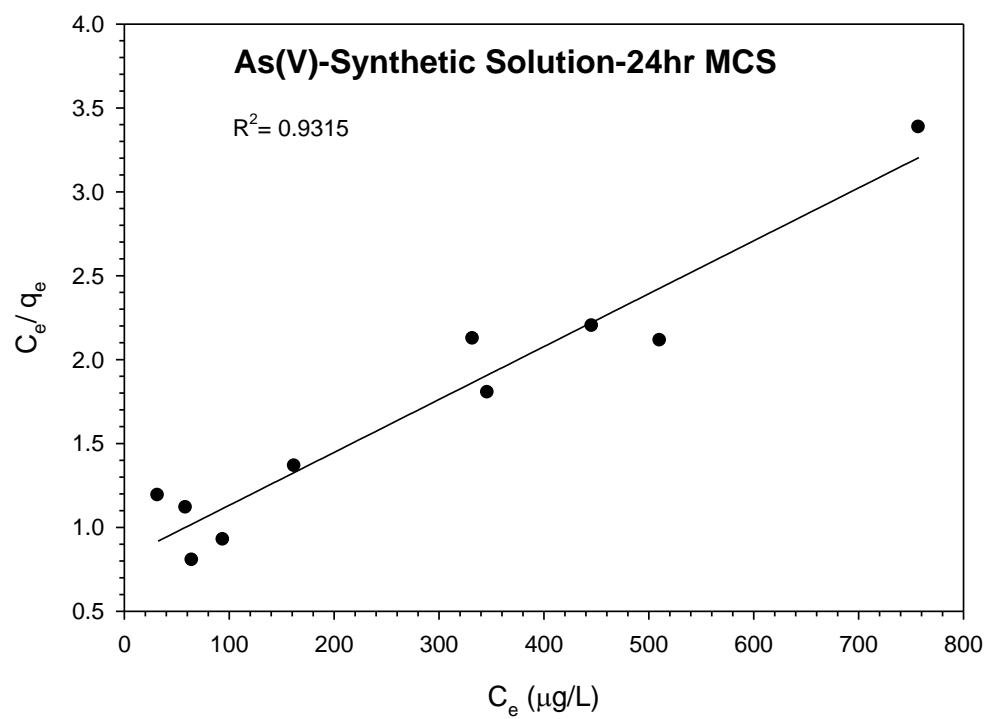


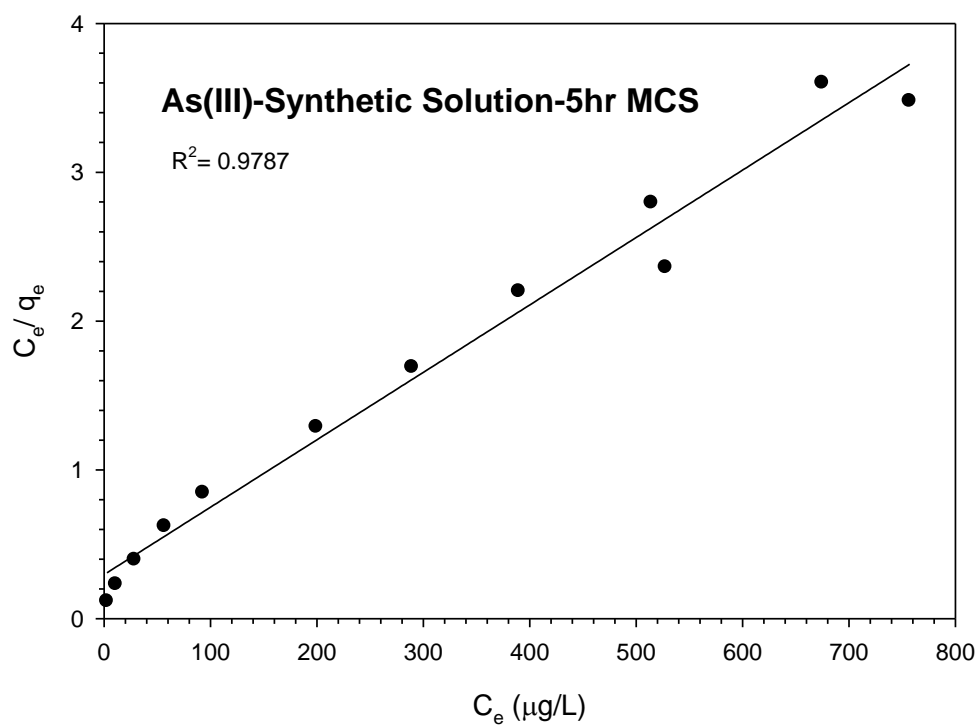
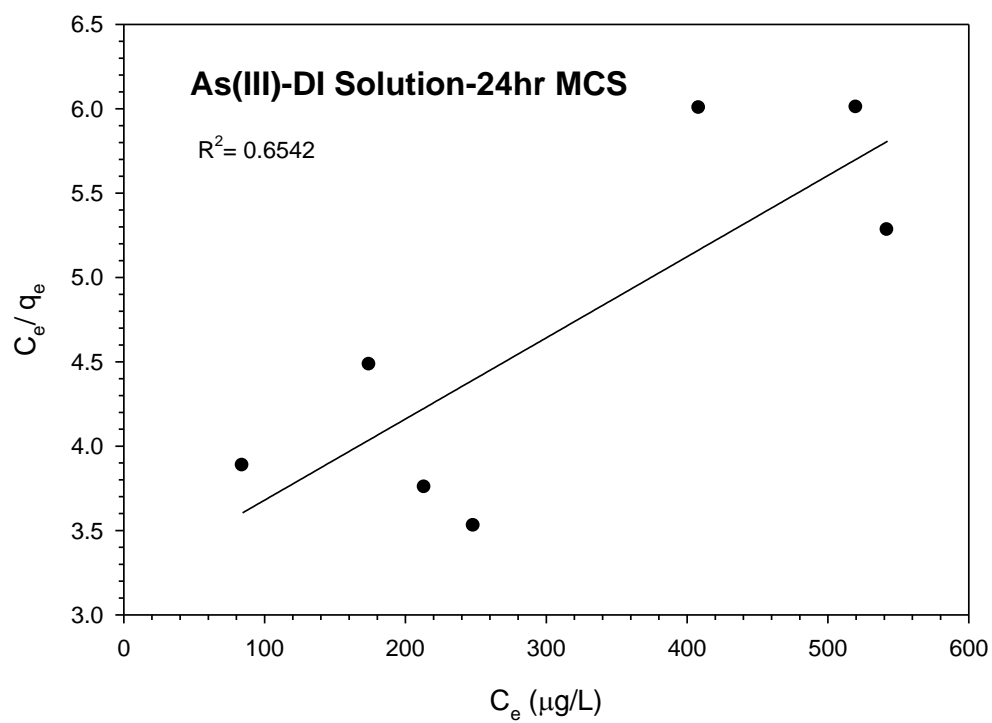
Fig.13. As(III) Adsorption capacity of the 5hr and 24hr furnace exposed MCS in synthetic solution

The linearized form of Langmuir, Freundlich, Temkin and D-R adsorption isotherms for 5hr furnace exposed MCS and 24hr furnace exposed MCS and in both DI and synthetic solution at the temperatures of 298 K are given in Fig. 14, Fig. 15, Fig. 16 and Fig. 17, respectively, whereas Table 2 presents the correspondent constants along with the correlation coefficients.









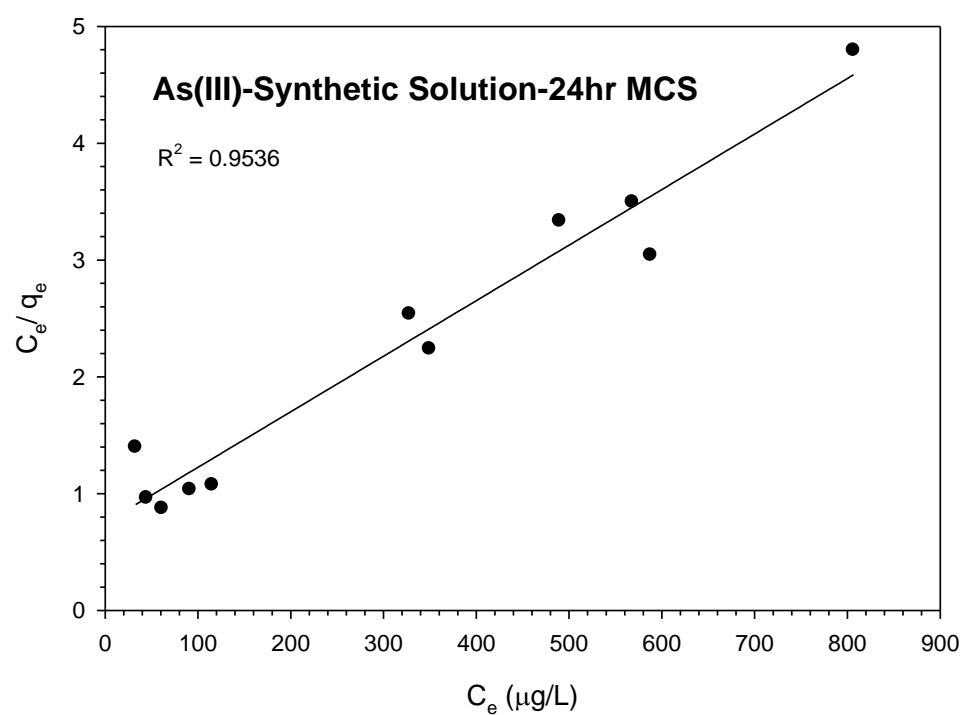
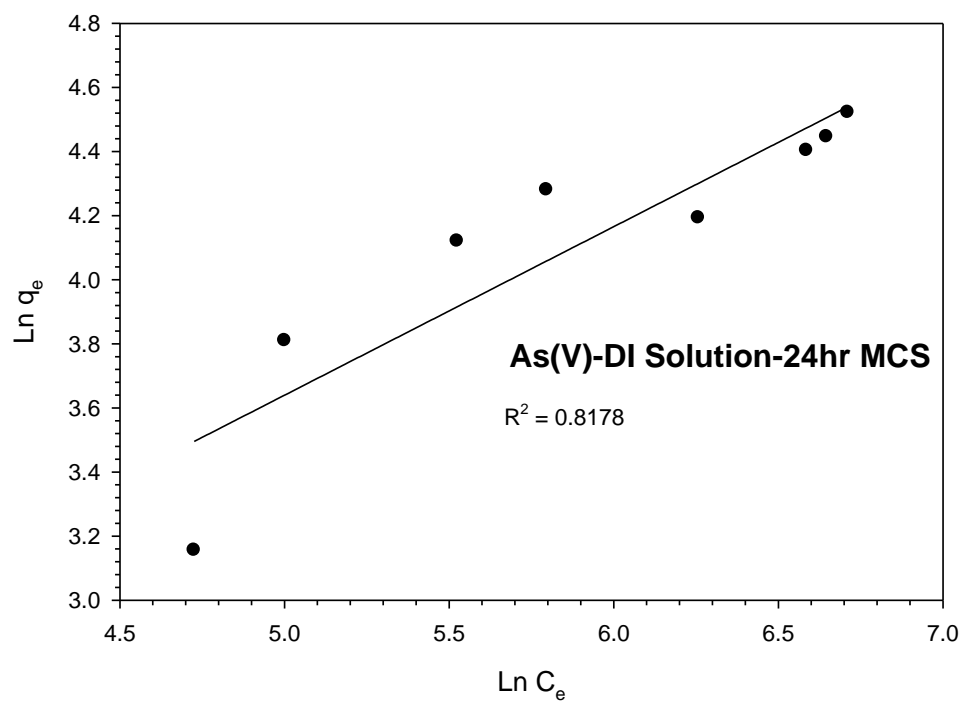
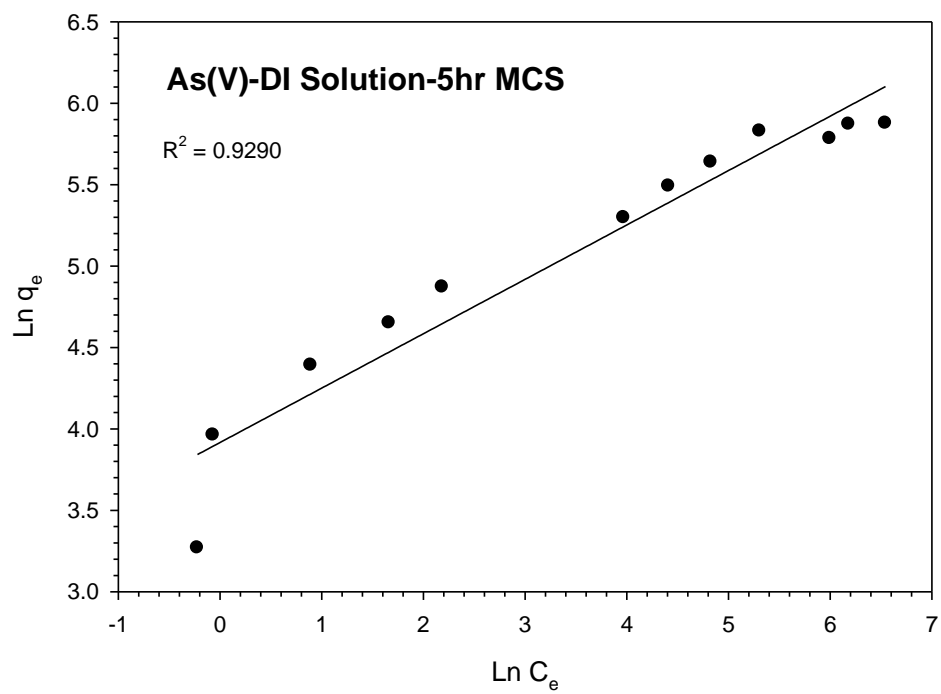
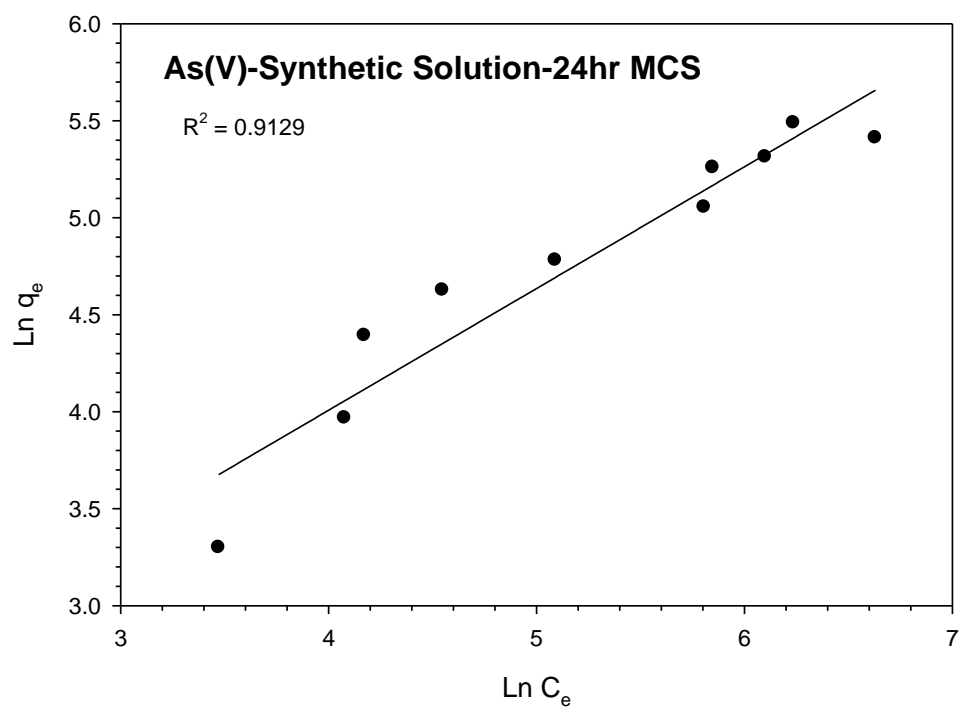
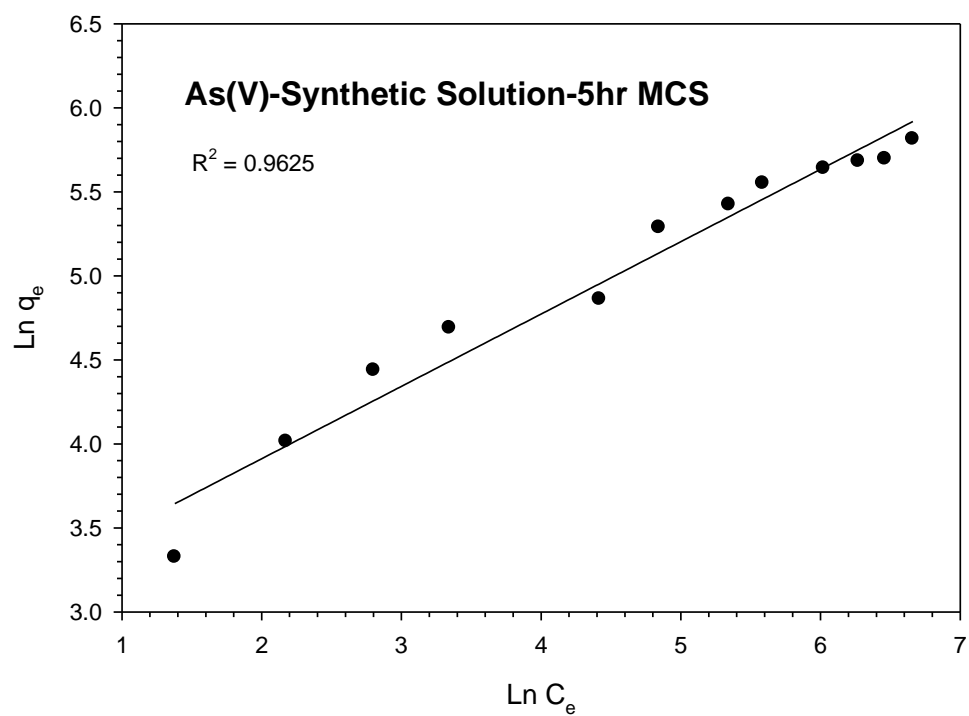
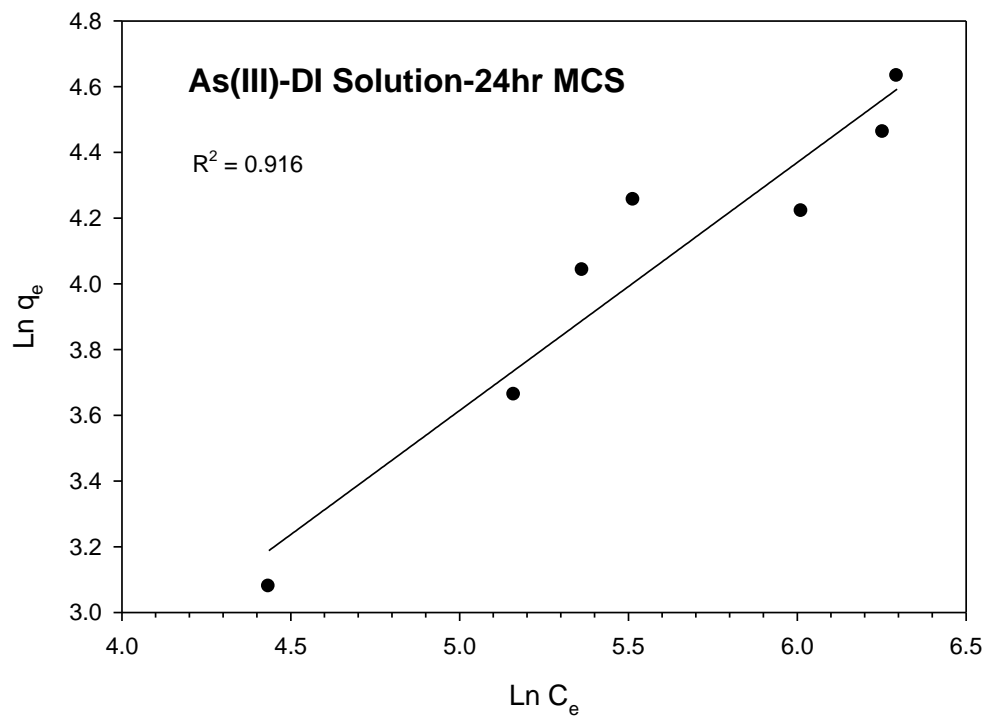
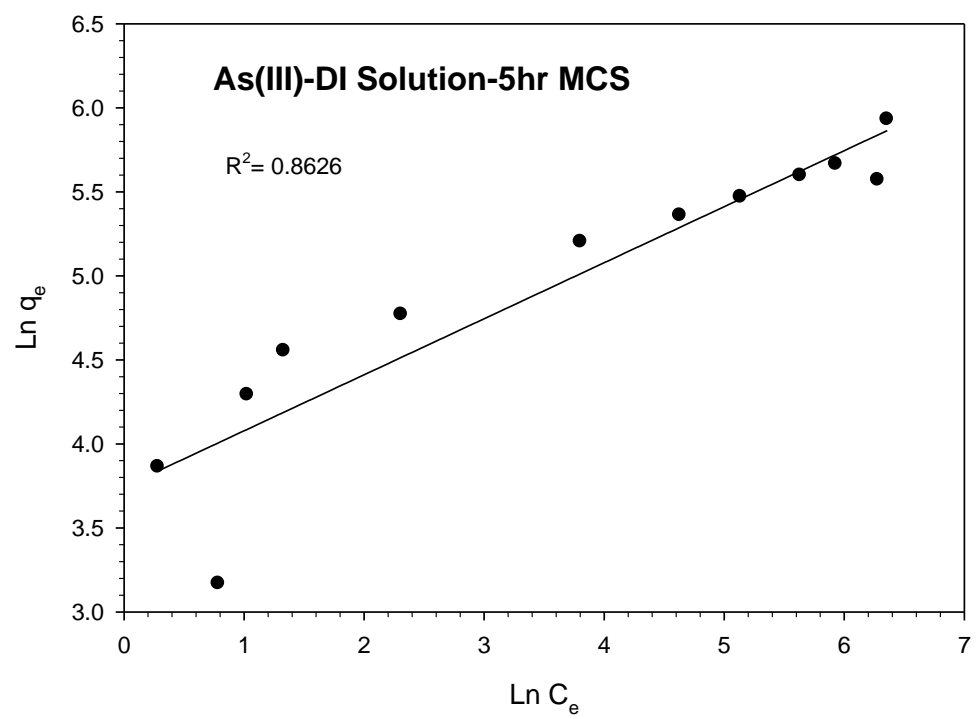


Fig. 14. Langmuir adsorption isotherms of As(III) and As(V) by MCS







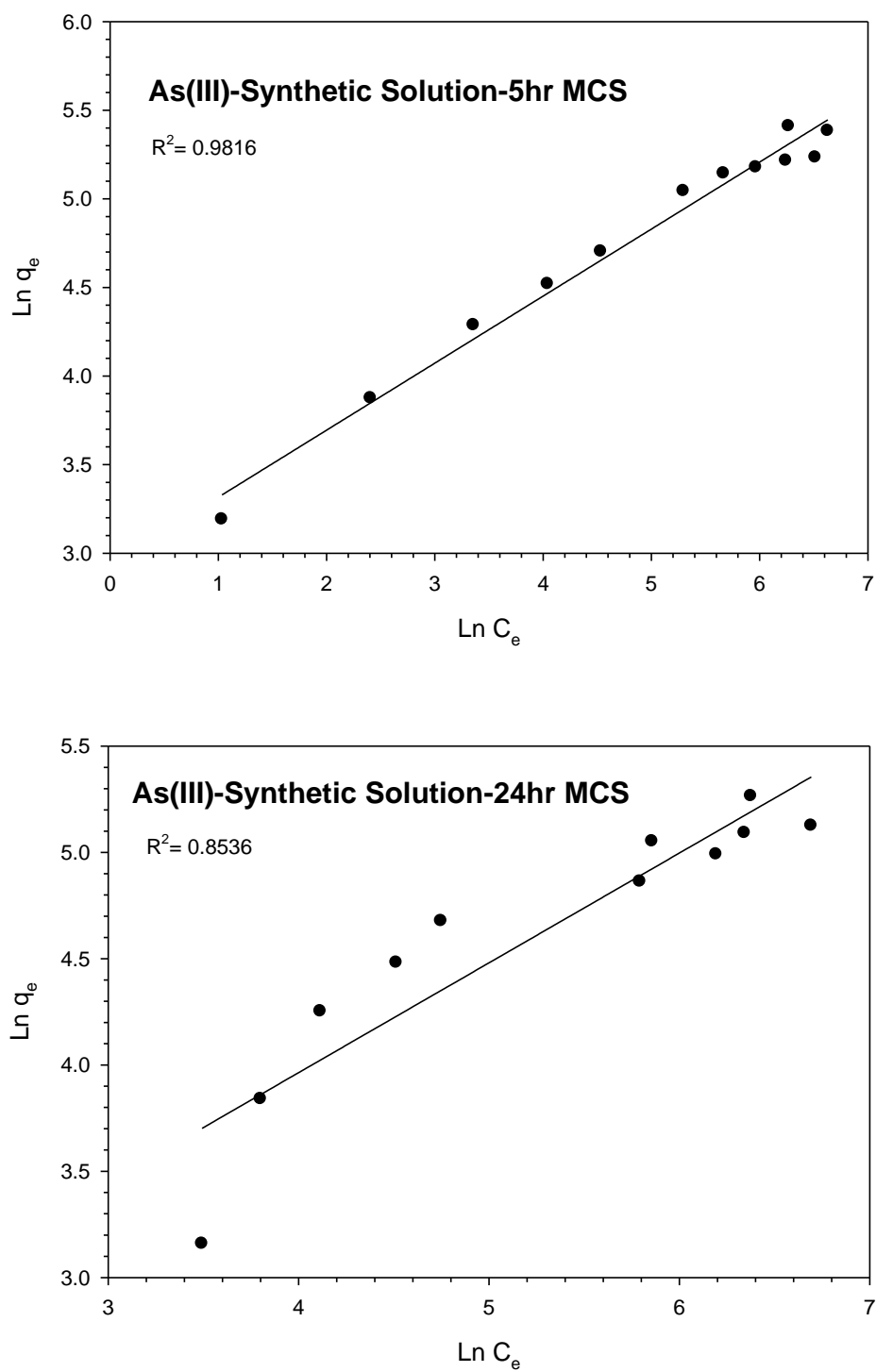
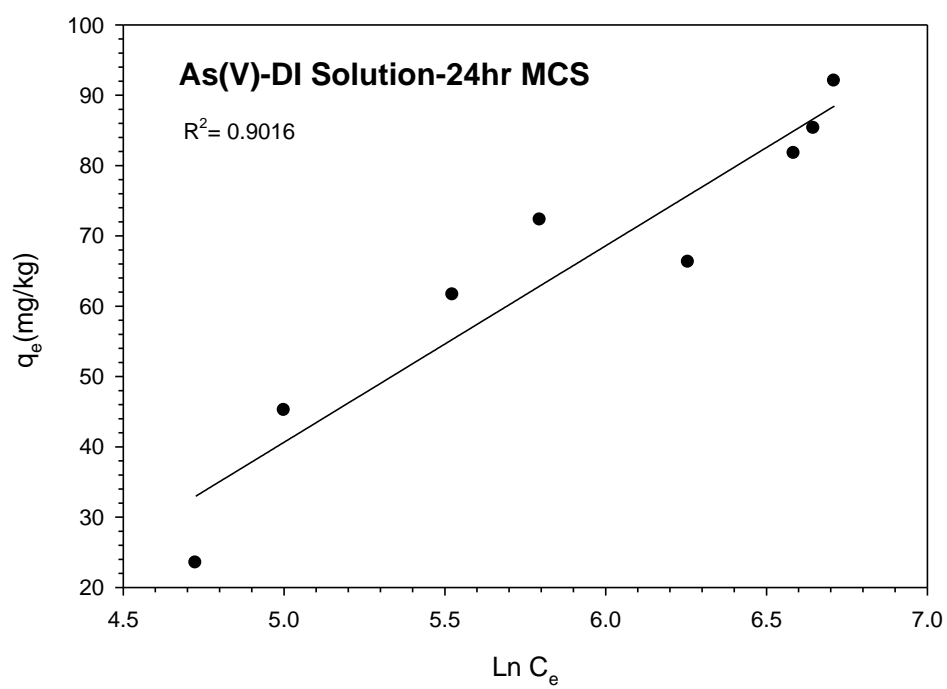
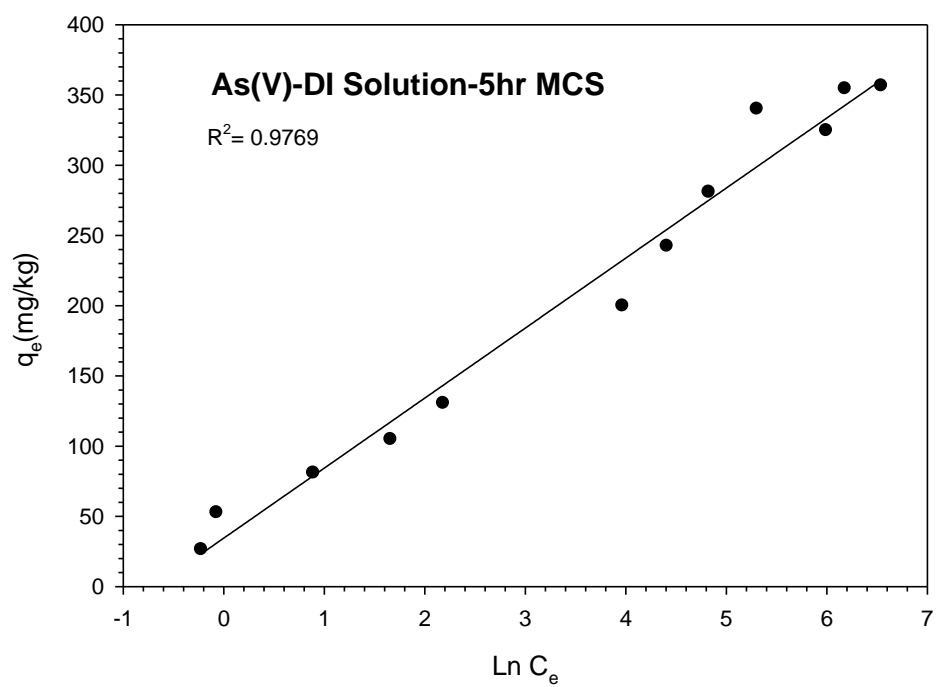
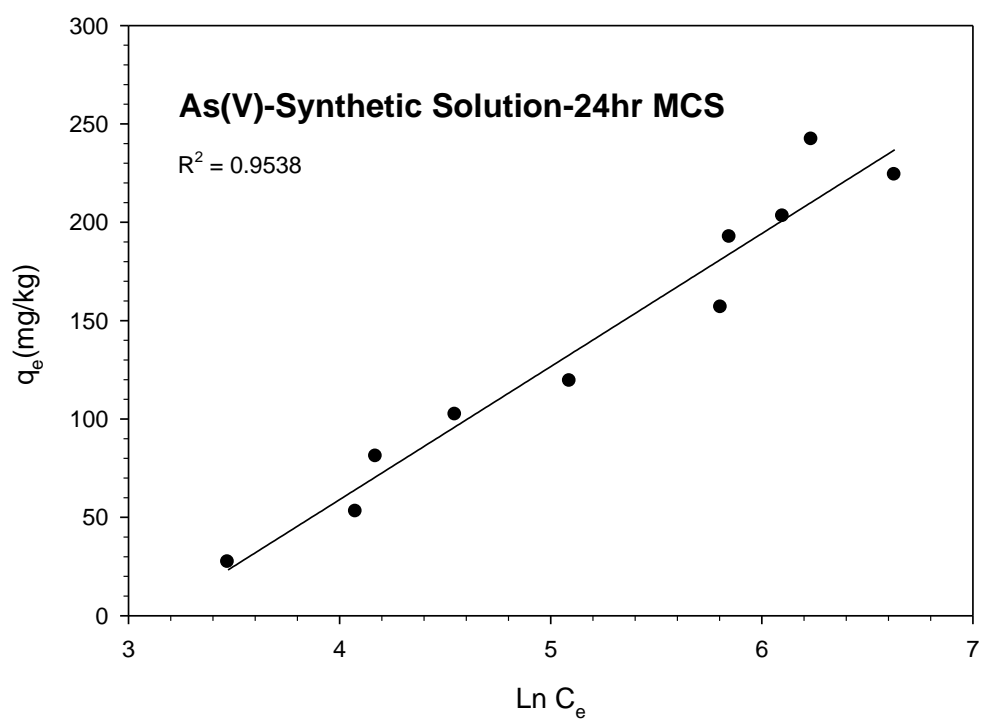
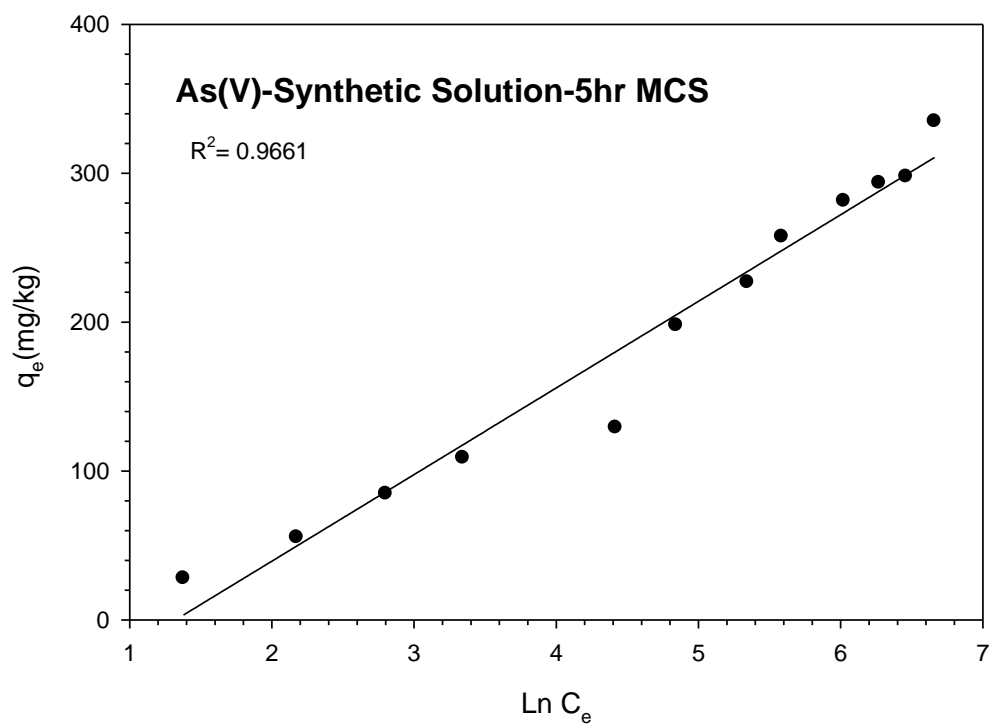
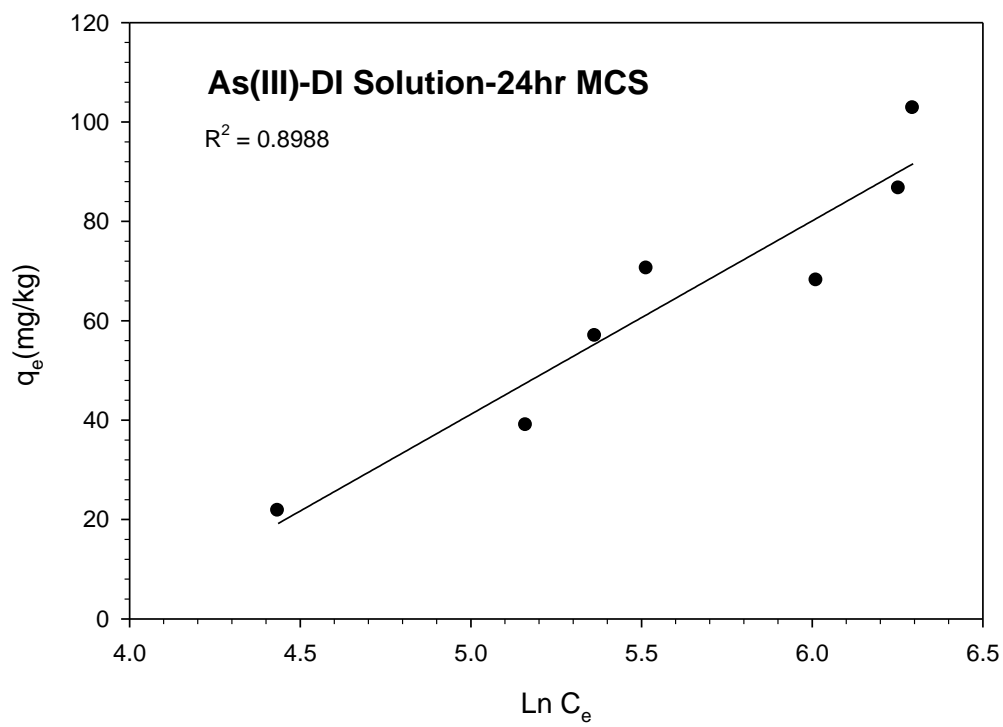
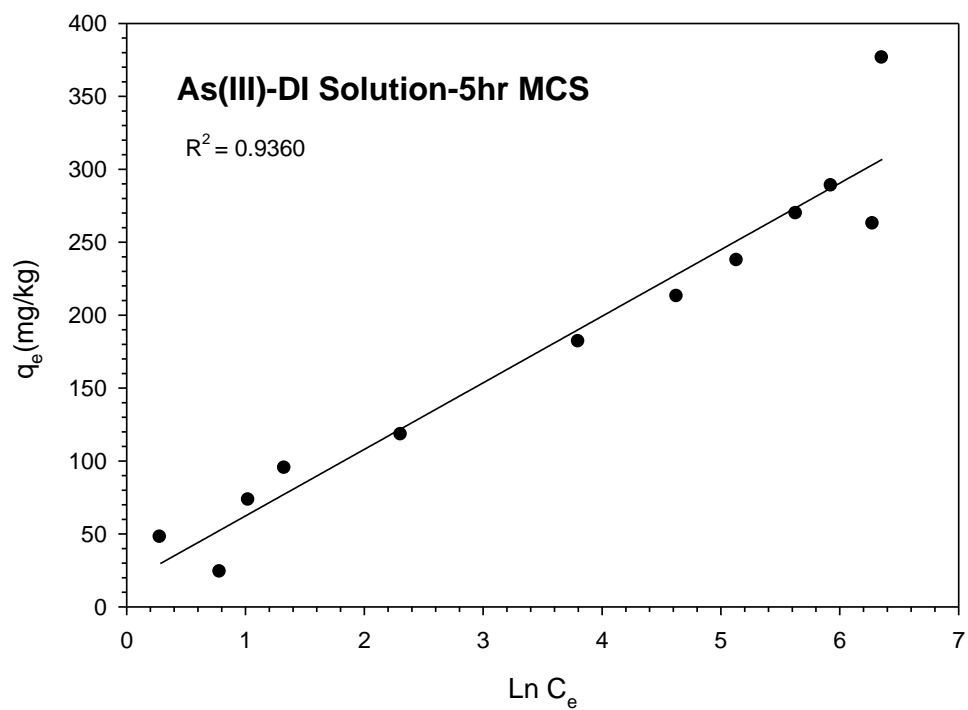


Fig. 15. Freundlich adsorption isotherms of As(III) and As(V) by MCS







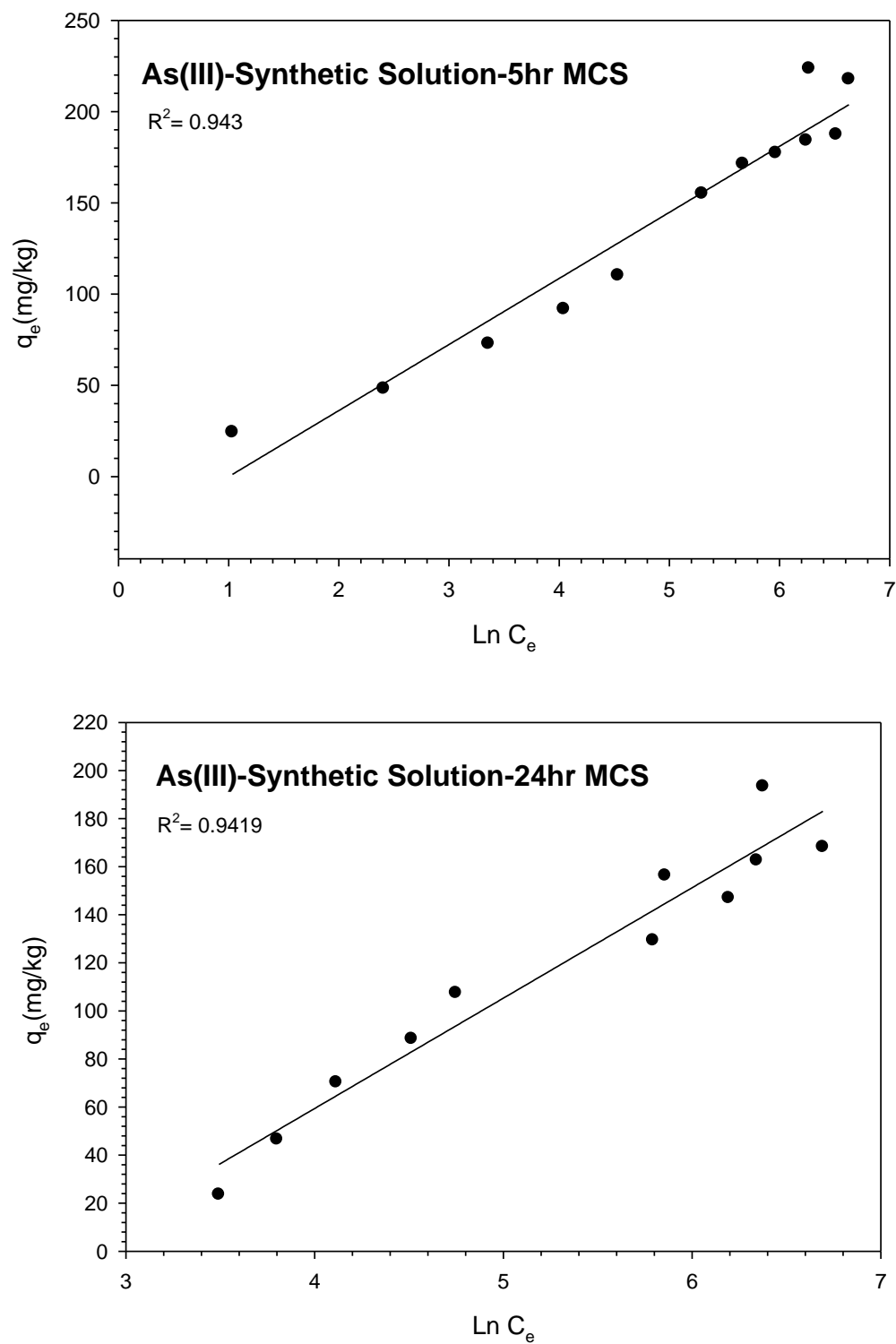
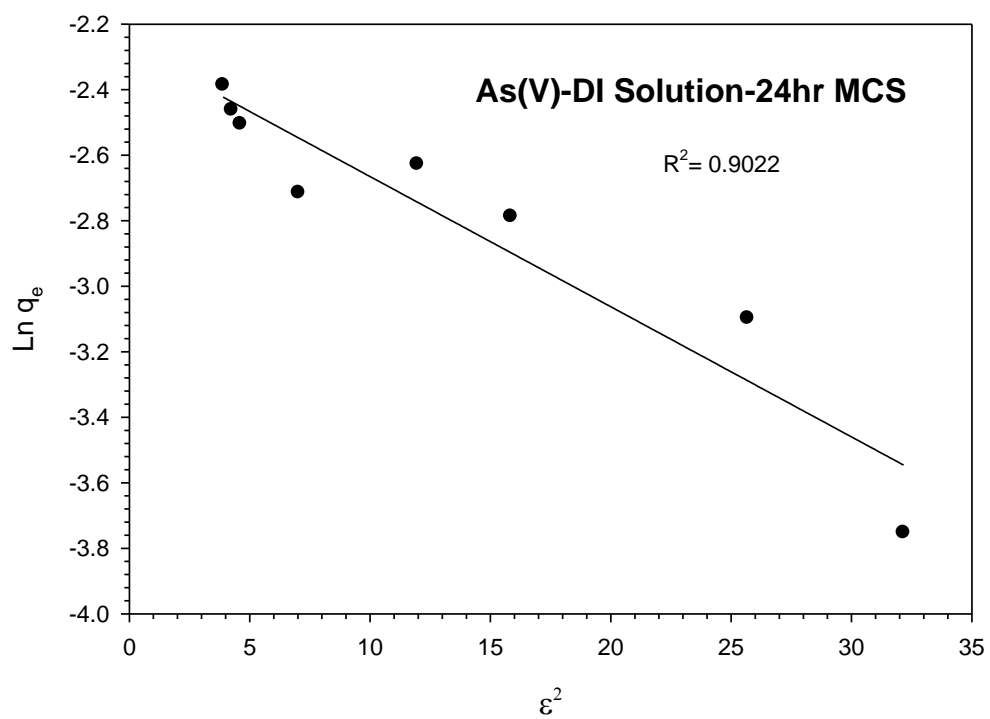
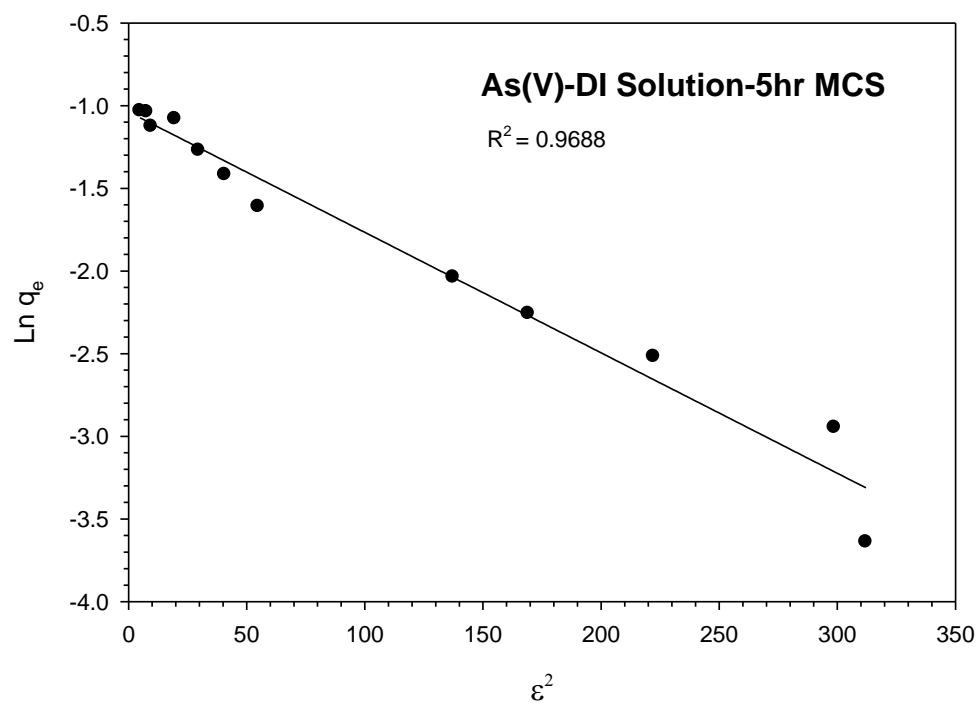
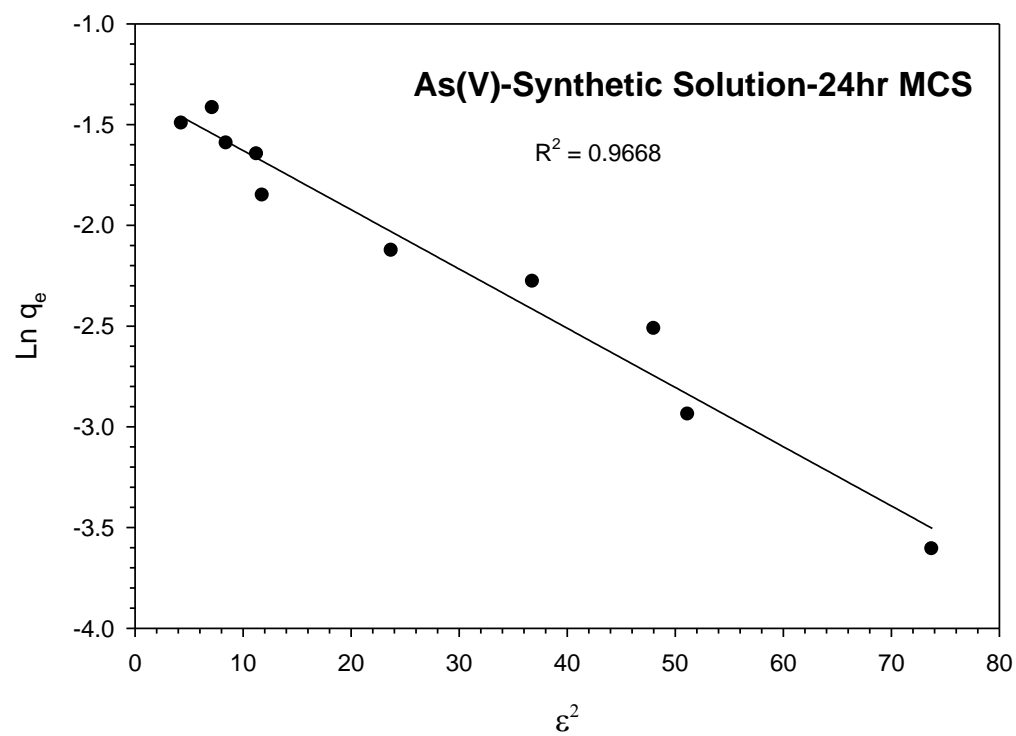
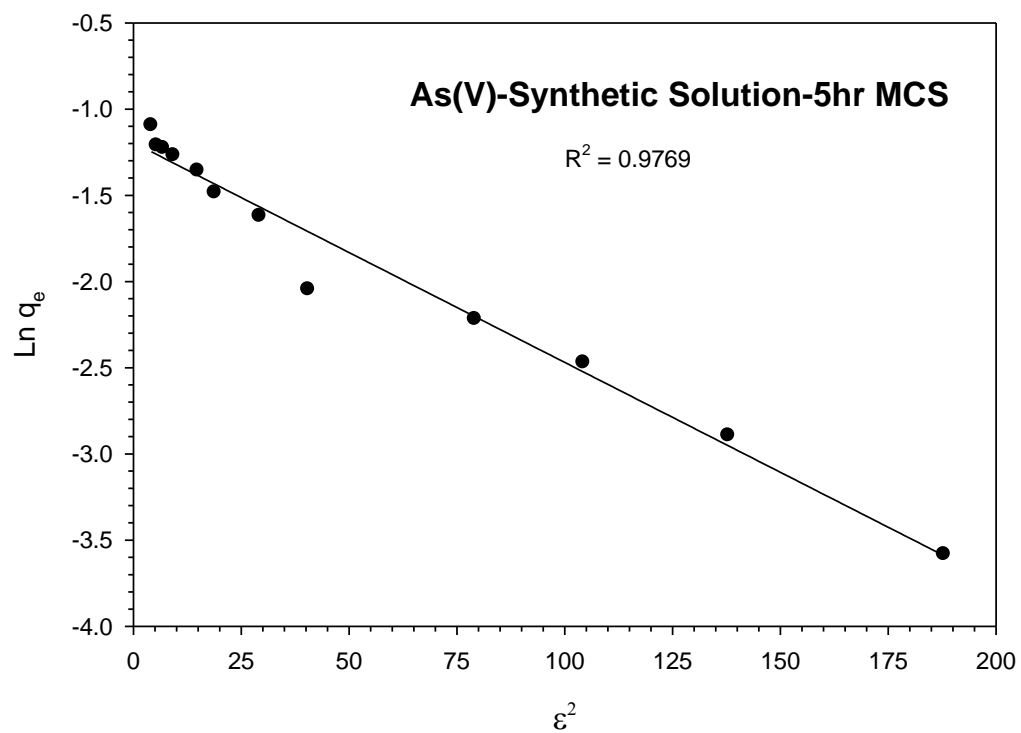
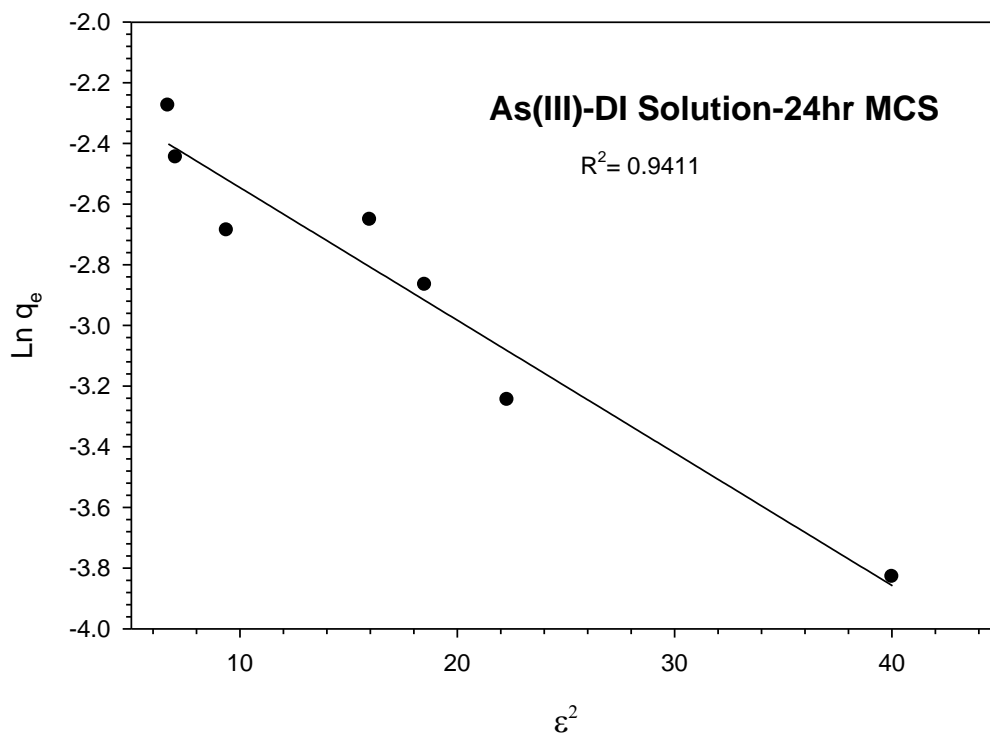
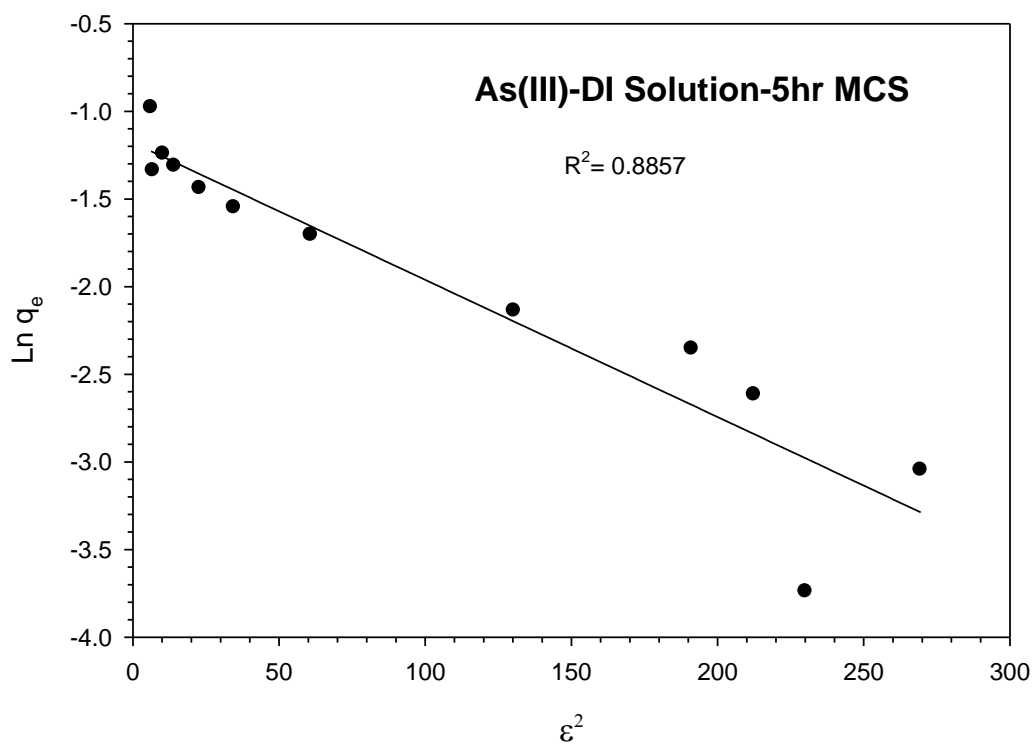


Fig. 16. Temkin adsorption isotherms of As(III) and As(V) by MCS







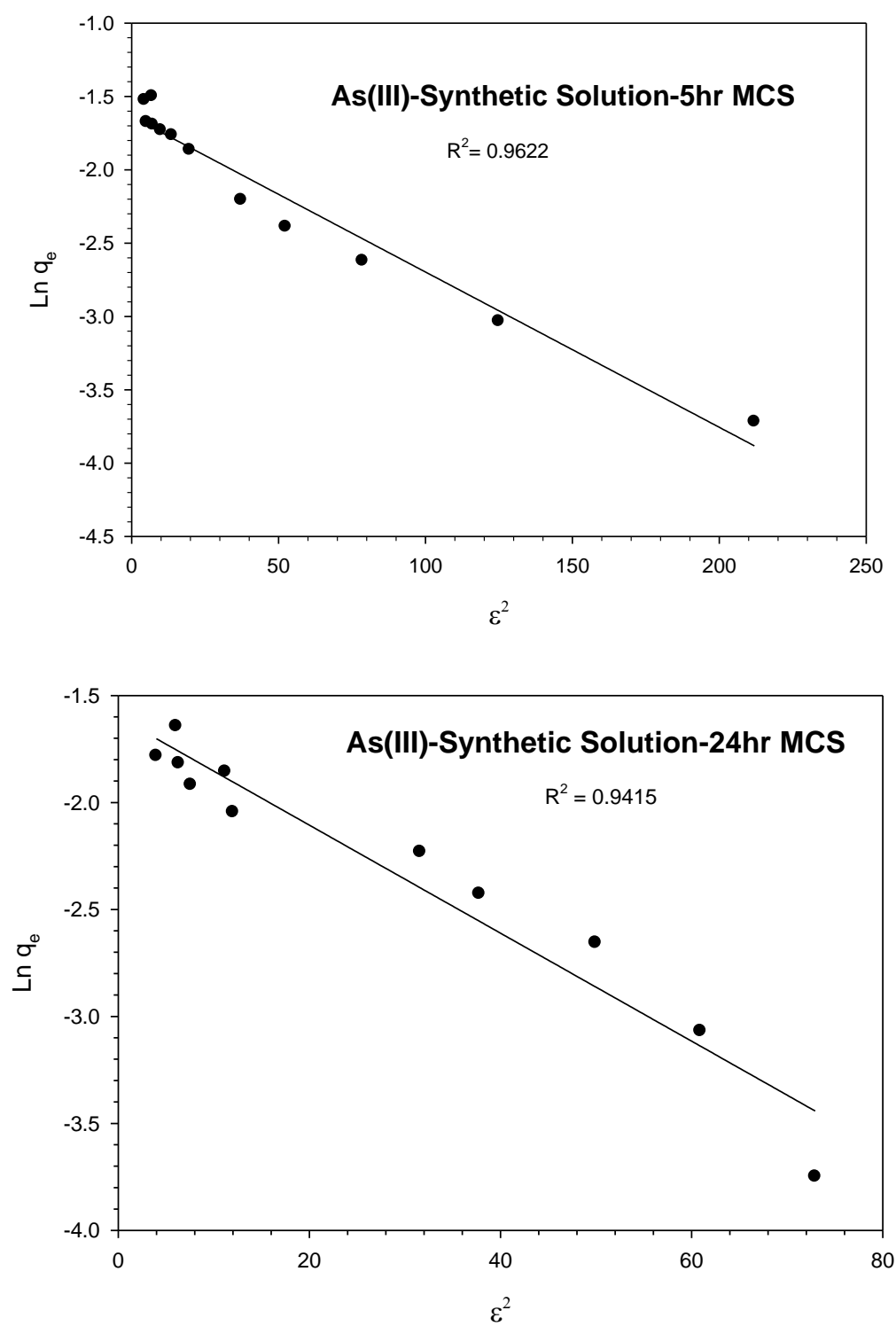


Fig. 17. D-R adsorption isotherms of As(III) and As(V) by MCS

Table 2. Langmuir, Freundlich, Temkin and D-R parameters for adsorption of As(III) and As(V) onto MCS

| | | As(III)+DI | | As(V)+DI | | | As(III)+synthetic solution | | As(V)+synthetic solution | | |
|------------|------------------------|------------|--------|----------|--------|--|----------------------------|--------|--------------------------|--------|--------|
| | | 5hr | 24 hr | 5hr | 24 hr | | 5hr | 24 hr | 5hr | 24 hr | |
| Langmuir | | | | | | | | | | | |
| | q _m (mg/kg) | 322.58 | 208.33 | 357.14 | 121.95 | | 222.22 | 208.33 | 344.83 | 312.5 | |
| | K _L (L/μg) | 0.0351 | 0.0015 | 0.0484 | 0.0031 | | 0.0152 | 0.0064 | 0.0126 | 0.0039 | |
| | R ² | 0.9541 | 0.6542 | 0.9956 | 0.9044 | | 0.9787 | 0.9536 | 0.9851 | 0.9315 | |
| | | | | | | | | | | | |
| Freundlich | | | | | | | | | | | |
| | 1/n | 0.3334 | 0.755 | 0.334 | 0.526 | | | 0.3782 | 0.5164 | 0.4305 | 0.6276 |
| | K _F | 42.28 | 1.17 | 50.21 | 2.75 | | | 18.88 | 6.67 | 21.13 | 4.47 |
| | R ² | 0.8626 | 0.916 | 0.929 | 0.8178 | | | 0.9816 | 0.8536 | 0.9625 | 0.9129 |
| | | | | | | | | | | | |
| Temkin | | | | | | | | | | | |
| | b(kJ/mol) | 0.0543 | 0.0621 | 0.0497 | 0.0887 | | | 0.0684 | 0.0577 | 0.0426 | 0.0366 |
| | A(L/μg) | 1.442 | 0.0214 | 1.9968 | 0.0289 | | | 2.7187 | 0.0552 | 0.2666 | 0.0438 |
| | R ² | 0.936 | 0.8988 | 0.9769 | 0.9016 | | | 0.943 | 0.9419 | 0.9661 | 0.9538 |
| | | | | | | | | | | | |
| D-R | | | | | | | | | | | |
| | q _m (mg/kg) | 307.61 | 121.48 | 354.27 | 103.56 | | | 282.04 | 201.71 | 302.89 | 263.32 |
| | E | 8.01 | 3.38 | 8.28 | 3.55 | | | 6.87 | 4.45 | 6.27 | 4.12 |
| | R ² | 0.8857 | 0.9411 | 0.9688 | 0.9022 | | | 0.9622 | 0.9415 | 0.9769 | 0.9668 |

The Langmuir isotherm model described the arsenic adsorption data for 5hr furnace exposed MCS better than 24hr 5hr furnace exposed MCS. From Table 2 and based on the K_L constant in Langmuir isotherm, both As(V) and As(III) affinity to bind with the 5hr furnace exposed MCS in both DI and synthetic solution was higher than the 24hr furnace exposed MCS. The applied sorbents showed comparable affinity to adsorb As(III) versus As(V). Also, the presence of other ions in synthetic solution decreased the arsenic affinity to adsorb onto the 5hr furnace exposed MCS while a comparable arsenic adsorption affinity was achieved by 24hr furnace exposed MCS in solutions with and without the presence of other ions. The maximum adsorption capacity of the 5hr furnace exposed MCS was also found to be higher than the 24hr furnace exposed MCS in both DI and synthetic solution.

Despite well-fit of adsorption data with Langmuir isotherm model, yet it can't highlight the mechanistic implications. However, the dimensionless constant separation (R_L), obtained from Langmuir isotherm and introduced in previous chapters, can predict whether the adsorption is favorable or unfavorable. The value of R_L between 0 to 1 indicate the favorable type of the system. The R_L values of the arsenic adsorption onto MCS was calculated based on the K_L values in Table.2 and they were found to be in the range of 0.014 to 0.4 indicating the favorable adsorption system on the applied sorbents. The R_L values for As(III) were found comparable to those for As(V) suggested the comparable adsorption favorability of the reduced arsenic compared to that of the oxidized species.

The Freundlich expression is an exponential equation that assumes the increase in concentration of adsorbate on the adsorbent surface with increasing adsorbate concentration in the solution. Freundlich values of $1/n$ show the favorability of adsorption of As(V) and As(III) onto the

sorbents. The relative adsorption capacity of 24hr furnace exposed MCS was found to be lower than the other sorbent which can be due to the lower affinity of this sorbent to arsenic according to the langmuir K_L constants. These results are in good agreement with the results obtained from Fig.8 and Fig.9.

The Temkin isotherm is based on the supposition that the decline of the heat of sorption as a function of temperature is linear rather than logarithmic, as entailed in the Freundlich equation. The relatively high correlation coefficient resulted from Temkin isotherm for the As(V) and As(III) adsorption onto the applied sorbents may be due to the linear dependence of heat of adsorption at low or medium coverage. As mentioned before in previous chapters, the Temkin constant (A) is indicative of the adsorption potential of the sorbent. The results from Table 2 indicates a higher adsorption potential of 5hr furnace exposed MCS versus the 24hr furnace exposed MCS in both DI and synthetic solution. The results are in good agreement with the Langmuir isotherm results. The b constant in Temkin isotherm is related to the heat of adsorption. The resulted positive value of the constant B($B=RT/b$) for all different sorbents in DI and synthetic represents an exothermic process.

The adsorption data was also applied to the D-R model, which was introduced in previous chapters, in order to evaluate the nature of the sorption distinguishing between physical and chemical adsorption. The mean free energy of As(III) and As(V) adsorption onto 5hr furnace exposed MCS in DI solution (obtained from the D-R adsorption equation) was found to be about 8 kJ/mol indicating that the combination of chemisorption and physisorption with the dominant former one governs the arsenic adsorption. However, the low values of mean free energy(<8 kJ/mol) of As(III) and As(V) adsorption onto 5hr furnace exposed MCS in synthetic solution and

24hr furnace exposed MCS in DI and synthetic solution is indicative of physisorption nature of arsenic adsorption process by the sorbents. Since physical adsorption is prevailing phenomena with 5hr furnace exposed MCS in synthetic solution and 24hr furnace exposed MCS in DI and synthetic solution, it also indicates possibility of better regeneration of the used sorbents specially in synthetic solution.

3.4. Effect of pH on the sorption of As(III) and As(V) by MCS

It is well known that the pH of the system is an important variable in the adsorption process. The charge of the adsorbate and the adsorbent often depends on the pH of the solution. The manganese oxide surface charge is also dependent on the solution pH due to exchange of H^+ ions. The surface groups of manganese oxide are amphoteric and can function as an acid or a base [11]. The oxide surface can undergo protonation and deprotonation in response to changes in solution pH. Fig 18 and Fig.19 show the percentage of arsenic removed as a function of equilibrium pH.

As shown in Fig. 18, the uptake of As(III) and As(V) depends on pH. As can be seen, the maximum adsorption of arsenic was obtained in the pH range from 3.0 to 10.0 and the arsenic removal was not significantly affected within the pH range of 2-10. Above the pH=10, the adsorption curves started decreasing with a significant drop at pH =12. At very high pH, As(III) and As(V) removal were inhibited possibly as result of a competition between hydroxyl and arsenic ions on the sorption sites, with an apparent preponderance of hydroxyl ions.

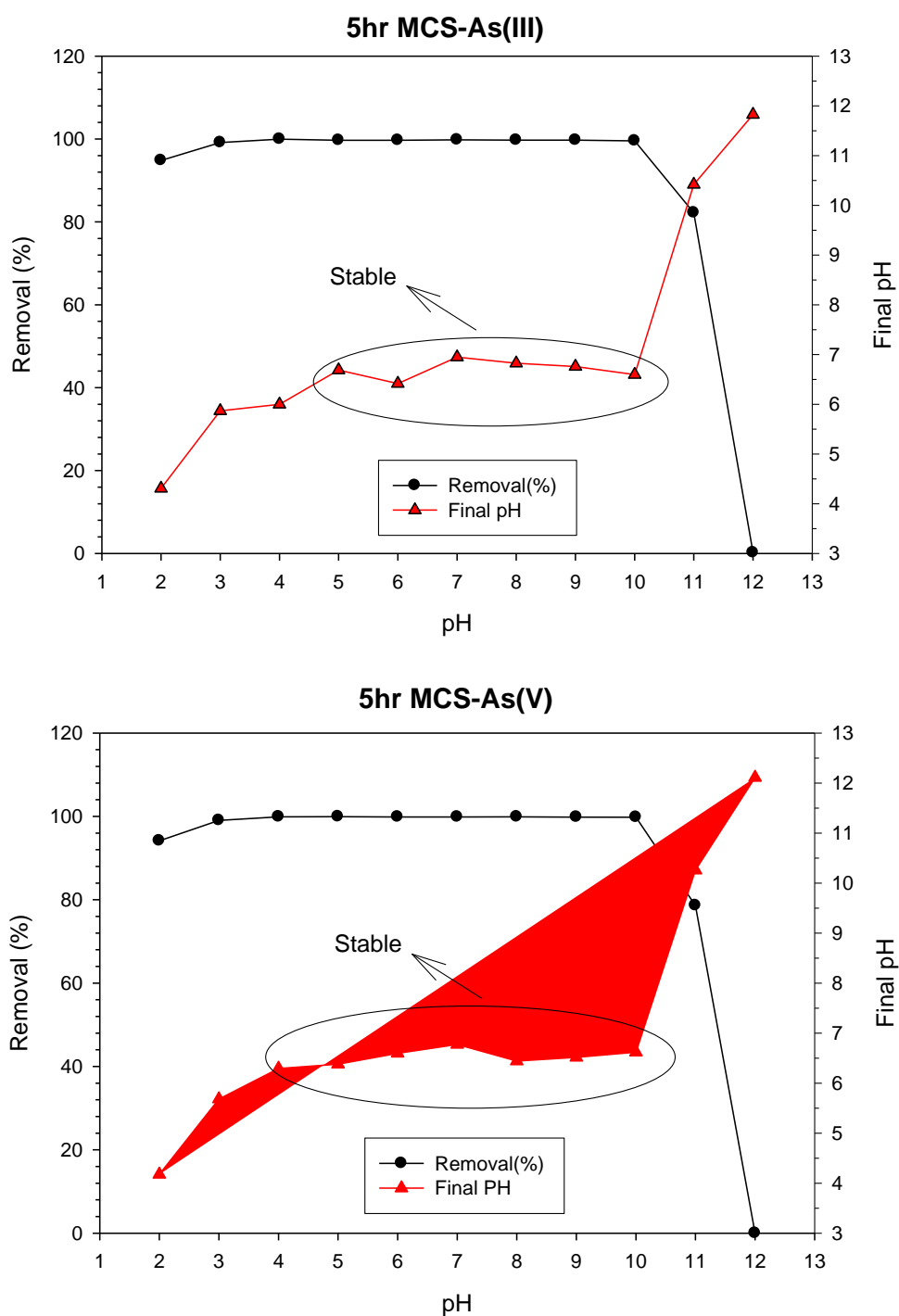


Fig.18. Effect of pH on adsorption of As(V) and As(III) onto 5hr MCS (20 g/L sorbent dosage)
from a 1 mg/L solution of arsenic

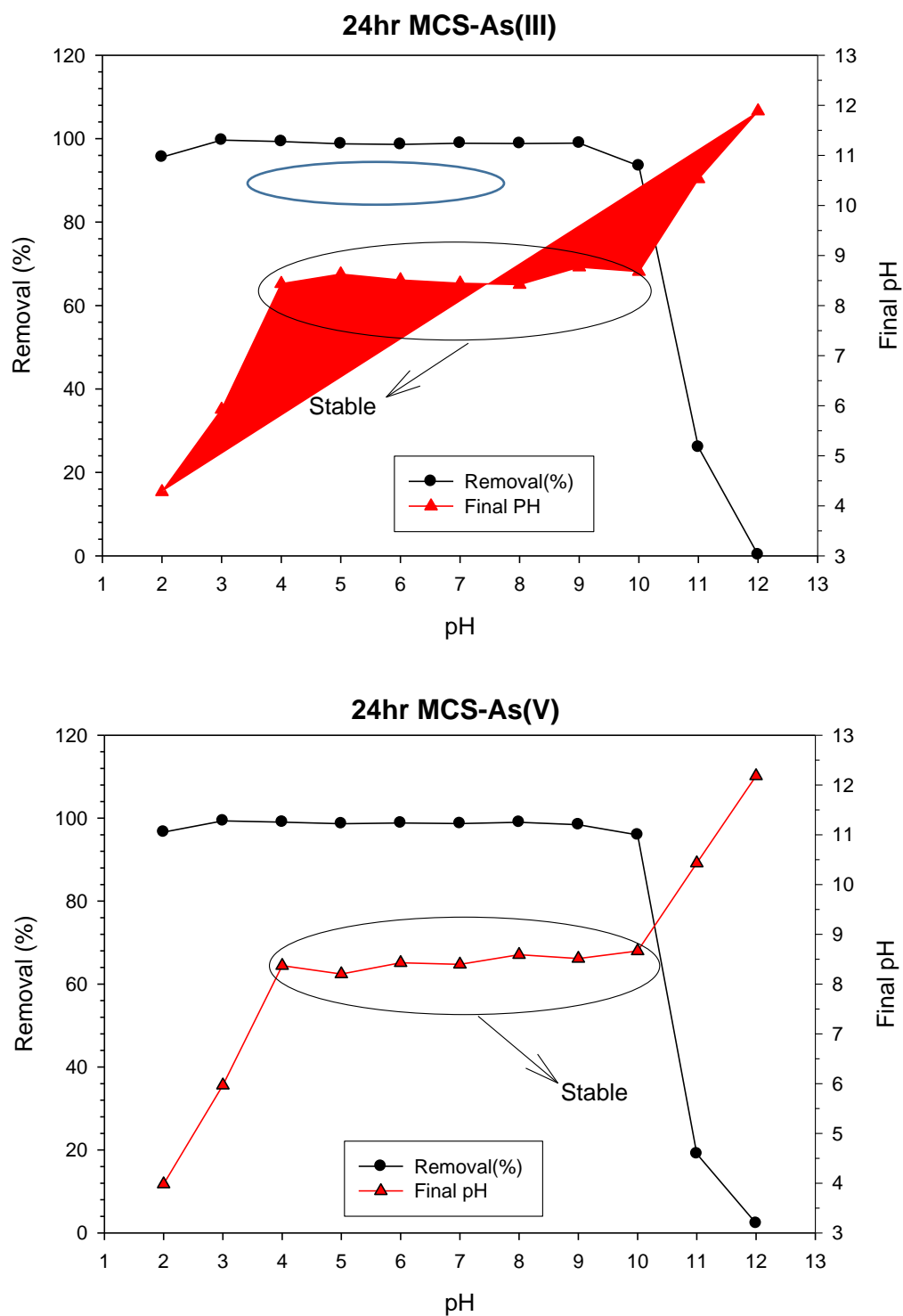


Fig.19. Effect of pH on adsorption of As(V) and As(III) onto 24hr MCS (20 g/L sorbent dosage) from a 1 mg/L solution of arsenic.

The results also show that at the initial pH 3–10, after addition of the sorbent, the pH changed to about 6–7 for arsenic adsorption onto 5hr furnace exposed MCS and 8-9 for arsenic adsorption onto 24hr furnace exposed MCS. This implies H^+/Cl^- and OH^-/Cl^- ion-exchange occurs to a certain extent during the arsenic adsorption onto 5hr furnace exposed MCS and 24hr furnace exposed MCS adsorption, respectively.

The relationship between the initial and equilibrium pH of As(III) and As(V) adsorption onto MCS is also shown in Fig.18 and 19. At an initial pH of around 4.0–10.0, a stable pH zone was observed, where the equilibrium pH was in the range of 5.8–6.9 for 5hr furnace exposed MCS and 6-8.8 for 24hr furnace exposed MCS and the adsorption capacities were stable. This may be due to continuous protonation under acidic conditions for 5hr furnace exposed MCS and continuous deprotonation under basic conditions for 24hr furnace exposed MCS.

Nevertheless, the optimum arsenic removal was found to be over a wide pH range of 4–10, suggesting that the MCS can be successfully utilized in drinking water processes and the pH does not need adjustment.

The higher uptake of arsenic in the $pH < 10$ may also be explained by the effect of pH on the charge of the adsorbent surface by measuring the zeta potential of the solution at different pH.

The zeta potentials of the quartz clean sand, 5hr furnace exposed MCS and 24hr furnace exposed at different pHs are shown in Fig.20. In the pH range of 2.5–12, the zeta potentials of the clean quartz sand were negative. The negative values of the zeta potential of the quartz clean sand at all pHs suggests that the surfaces of the clean uncoated sand is negatively charged. The amount of negative charges increased with increasing pH. Thus, removal of the arsenic anions by

adsorption onto the quartz sand is difficult because of electrostatic repulsion between the arsenic anions and the sand media surface.

As seen from Fig.20, coating the quartz sand increases the zeta potential of the sand and makes the surface more electropositive at approximate pH range of 2-10 for 5hr furnace exposed MCS and pH range of 2-8 for 24hr furnace exposed MCS. The increase of zeta potential of the quartz sand by MCS could be due to the manganese and aluminum oxide deposition on the surface of the clean sand. This increase in zeta potential facilitates a greater attraction between the arsenic anion and sorbent (i.e. increases the sorbent's adsorption affinity for arsenic anions), thereby enhancing removal efficiency.

The PZC of 5hr and 24hr furnace exposed MCS was found to be 9.8 and 8.3, respectively. At $\text{pH} > \text{PZC}$ the MCS surface will attract cations to the surface, conversely at $\text{pH} < \text{PZC}$ it will attract anions. Hence, the adsorption of the arsenic anion would be favored at $\text{pH} < \text{PZC}$ regions where the surface is more positive. On the other hand, at higher solution $\text{pH} > \text{PZC}$, the negative charge of the surface prevented the sorbent from adsorbing arsenic, resulting in the lower adsorption of arsenic. The greater arsenic adsorption in $\text{pH} < 10$ for 5hr furnace exposed MCS and $\text{pH} < 9$ for 24hr furnace exposed MCS and the decrease in the uptake of arsenic at very high pH shown in Fig.18 and Fig.19 are in good agreement with the results obtained from the zeta potential measurements. Also, a higher zeta potential of the 5hr furnace exposed MCS was obtained than the 24hr furnace exposed MCS at most pHs. which can be one of the reasons for the higher arsenic adsorption onto 5hr furnace exposed MCS than 24hr furnace exposed MCS.

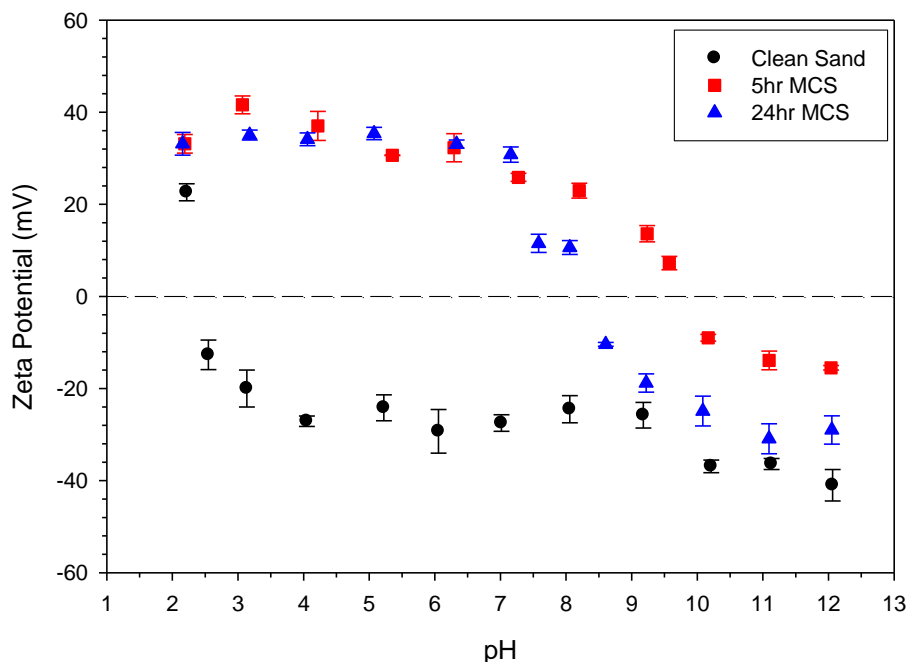


Fig.20. Zeta potential measurement of clean sand and MCS. 5g/L sorbent.

The adsorption of cations and anions may occur onto the surface through the formation of outer-sphere complexes via van der Waals forces at the PZC or pH_{pzc} . The specific adsorption of ions onto the surface (i.e., inner-sphere complexation) can change the PZC of the surface.

The results of surface charge analysis of both 5hr and 24hr furnace exposed MCS with the presence of 1 mg/L As(V) and 1 mg/L As(III) are presented in Fig.21 and Fig.22. Based on the data from Fig. 21 the PZC of 5g/L of 5hr and 24hr furnace exposed MCS in the solution with the presence of 1mg/L As(V) was found to be 9.33 and 7.75, respectively. For solutions with the presence of 1mg/L As(III) (Fig.22), the PZC of the 5hr and 24hr furnace exposed MCS was obtained as 9.42 and 8.23, respectively. As mentioned in chapter 4, the surface charge of the sorbent can not be altered in the outer-sphere complexes where no certain chemical reaction

occurs between the sorbent and adsorbate to change the sorbent surface charge. Hence, the lower PZC value of the applied MCSs with the presence of the As(III) and As(V) in the solution versus with absence of these species was is indicative of the mainly due to the formation of inner-sphere complexes by arsenate at the surface of MCSs. The decrease in the PZC of the sorbent indicates the adsorption of arsenic onto the surface of MCSs or shows that the arsenic forms inner-sphere complexes at the surface of MCSs.

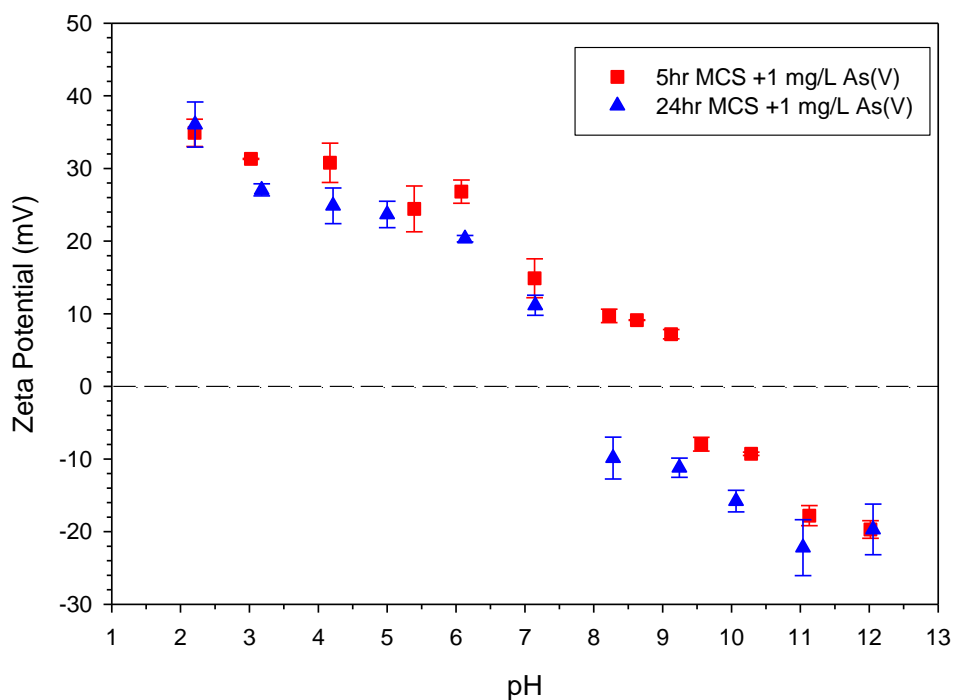


Fig.21. Zeta potential measurement of MCSs with the presence of 1 mg/L As(V) . 5g/L sorbent.

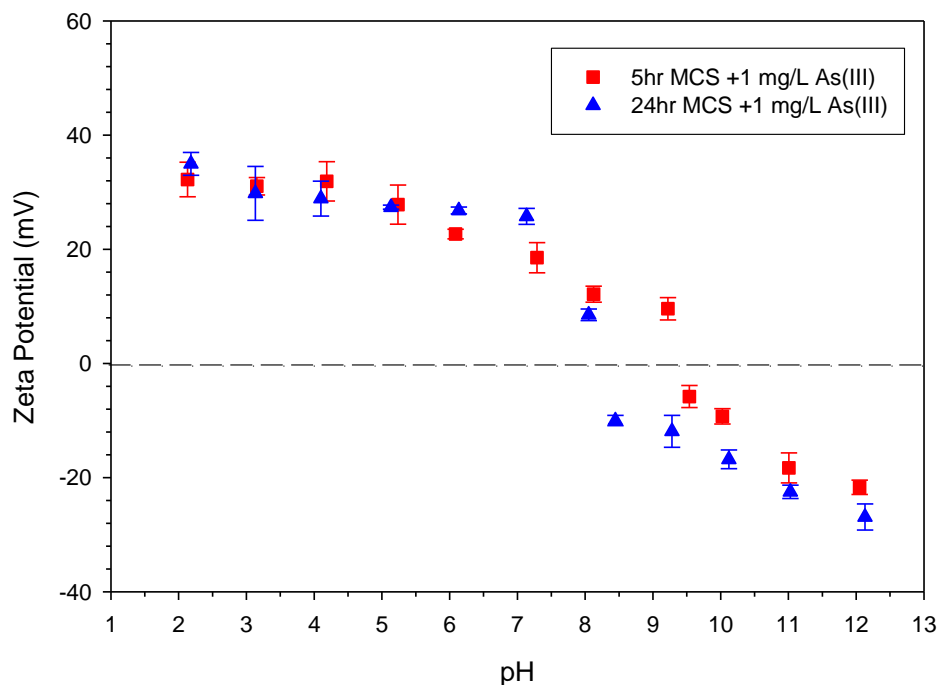


Fig.22. Zeta potential measurement of MCSs with the presence of 1 mg/L As(III) . 5g/L sorbent.

3.5. Effect of Competing ions

The effect of co-existing ions on arsenic adsorption onto the MCSs was investigated. For this study, the effect of bicarbonate, sulfate, calcium and phosphate on the removal of As(III) and As(V) were tested . The 1 mg/L of initial As(V) and As(III) solution was used in all solutions and a constant mass of the sorbent(20 g/L) was used and the sorbent was exposed to each solution for 24 h. the corresponding results are summarized in Fig.23.

The calcium, bicarbonate and sulfate did not inhibit both As(III) and As(V) adsorption process even though they coexisted at very high concentration suggesting that they had low affinity

toward the adsorbent. Phosphate anions exerted the highest negative effect. Phosphate and arsenic ion always compete with each other in aqueous system (in this case for sorption sites on the MCSs surface) due to this fact that they belong to the same group in the periodic table therefore having similar chemical properties and atomic structure resemblance. In addition, arsenate and phosphate are all tetrahedral anions which compete with each other for active adsorption sites on the adsorbent surface resulting in a decreased of equilibrium adsorption capacity. The results from Fig.23 shows that incomplete arsenic removal is more pronounced in case of arsenate than arsenite when phosphate anions are present at very high concentration. In order to ensure complete removal of As(III) and As(V) in the presence of competing ions specially phosphate, excess MCSs should be used. Also, the arsenic adsorption capacity of 5hr furnace exposed MCS was found to be less effective to the presence of phosphate ions versus the 24hr furnace exposed MCS.

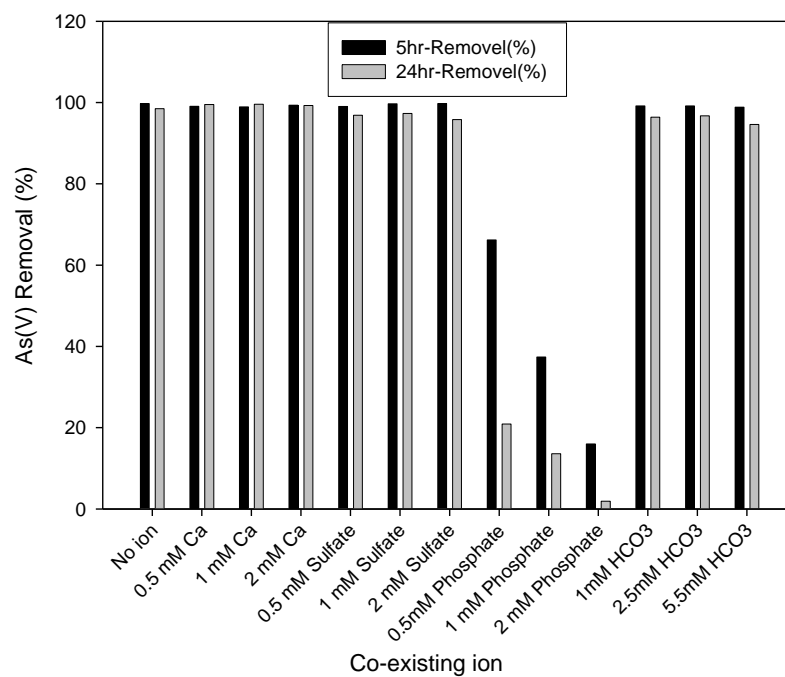
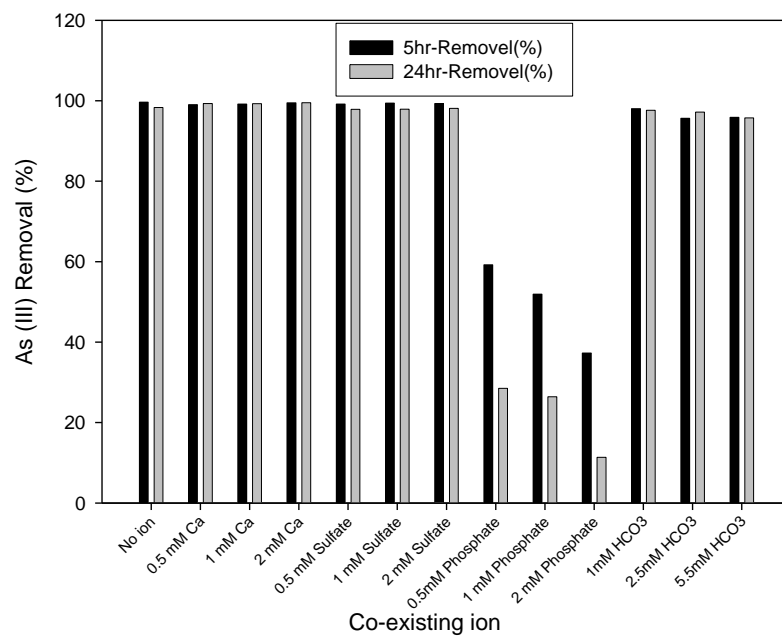


Fig.23. Effect of co-existing ions on the As (III) and As(V) adsorption

3.6. Sorbent Reuse

In order for the sorption process to be viable, the MCS has to be amenable to efficient reuse. To this end, the adsorption cycles were carried out up to five times in which 1 g of the sorbent was exposed to 50 ml of 1 mg/L arsenic in synthetic solution. Fig.24 demonstrates the As(V) and As(III) removal percentage of the reused 5hr and 24hr furnace exposed MCS on synthetic solution for 5 times.

Based on Fig.24, the last three cycles of adsorption corresponded to more than 50% of the total combined arsenic uptake (100%) achieved during the five cycles of adsorption, showing that almost half of the total uptake of As(V) and As(III) was achieved during the last three cycles of adsorption. A comparable adsorption of As(III) and As(V) was achieved for each cycle. Also, the adsorption capability of 20 g/L of 24hr furnace exposed MCS was comparable to the 5hr furnace exposed MCS in different cycles. The results also showed that after being reused for four times, the adsorbents could still keep more than 50% of its arsenic removal capability, which is desirable for its potential applications in real practice to reduce the operation cost.

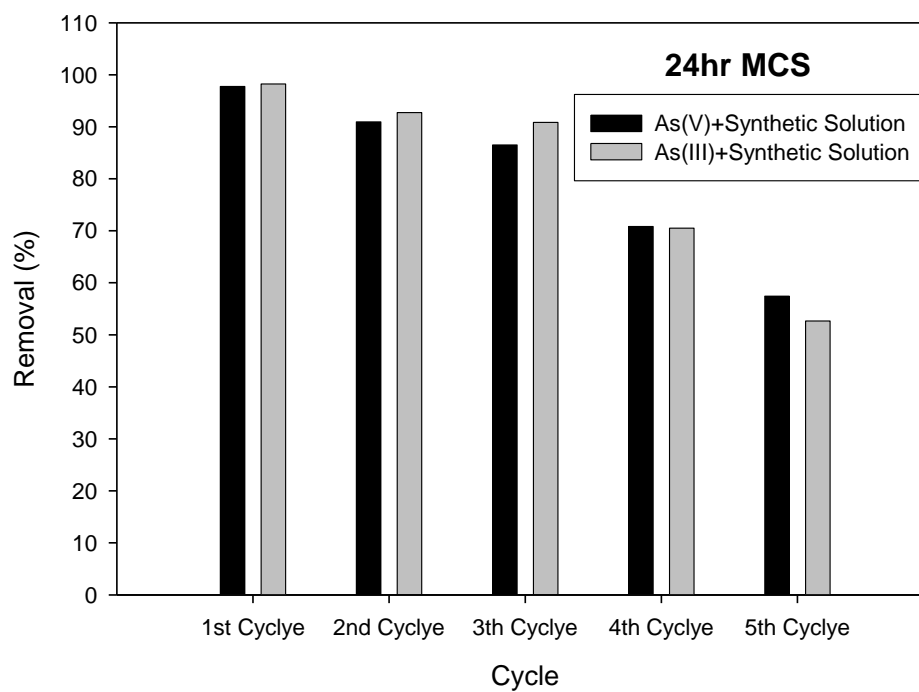
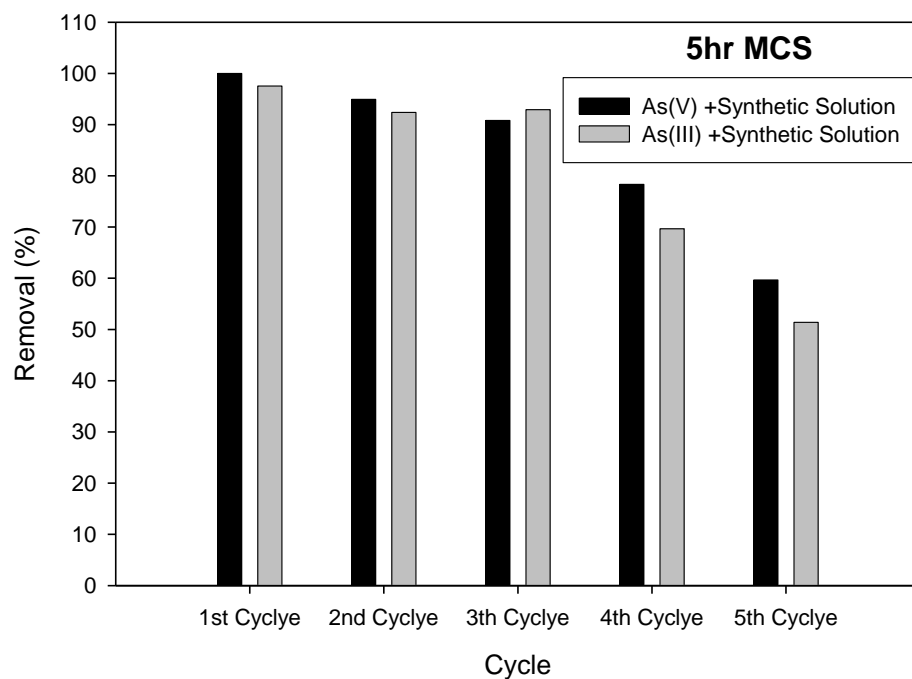


Fig.24. Reusability of the MCS, dose 20g/L, contact time: 24hr, temperature: 25°C

4. CONCLUSION

The feasibility of arsenic removal by the two different developed MCS, 5 hr and 24 hr furnace exposed MCS, was studied. The effects of initial solution pH, adsorbent dosage, contact time and co-existing ions on the arsenic removal efficiency by MCSs was investigated.

After developing the MCS sorbent, it was characterized by SEM/EDX and XPS. The SEM images showed that the coated sands appeared as a rough coated surface with no uniform coating. The aluminum and manganese oxides formed in clusters on the surfaces.

Based on EDX results, the 5hr furnace exposed MCS and 24hr furnace exposed MCS gave basically similar spectrum however a higher manganese content was observed on 5hr furnace exposed MCS versus the 24hr furnace exposed MCS which were in good agreement with the results obtained from acid digestion in previous chapter.

The kinetics experiment showed that for the adsorption of arsenic onto MCS, a two-step mechanism occurs. First a rapid adsorption occurs during the first 60 min after which equilibrium is slowly achieved. The kinetics data followed a pseudo-second order kinetics model.

The Langmuir, Freundlich, Temkin, and D-R adsorption equations were applied to equilibrium adsorption isotherm data. Based on the Langmuir isotherm model, both As(V) and As(III) affinity to bind with the 5hr furnace exposed MCS in both DI and synthetic solution was higher than the 24hr furnace exposed MCS. The applied sorbents showed comparable affinity to adsorb As(III) versus As(V). Also, the presence of other ions in synthetic solution decreased the arsenic

affinity to adsorb onto the 5hr furnace exposed MCS while a comparable arsenic adsorption affinity was achieved by 24hr furnace exposed MCS in solutions with and without the presence of other ions. Freundlich model data indicated the favorability of adsorption of As(V) and As(III) onto the sorbents. The arsenic adsorption process was found to be an exothermic process according to the Temkin isotherm model. The results of D-R isotherm model for the As(III) and As(V) adsorption onto 5hr furnace exposed MCS in DI solution indicated that the combination of chemisorption and physisorption with the dominant former one governs the arsenic adsorption. However, the nature arsenic adsorption process onto 5hr furnace exposed MCS in DI solution and 24hr furnace exposed MCS in DI and synthetic solution was found to be physisorption.

The maximum adsorption of arsenic was obtained in the pH range from 3.0 to 10.0 suggesting that the MCS can be successfully utilized in drinking water processes and the pH does not need adjustment. The surface charge analysis of the sorbents were used to explain the lower adsorption of arsenic at higher pH. The zeta potential measurements proves the adsorption of arsenic onto the surface of MCSs and formation of inner-sphere complexes at the surface of MCSs.

According to the co-existing ion effect study, calcium, bicarbonate and sulfate did not inhibit both As(III) and As(V) adsorption process even though they coexisted at very high concentration while phosphate anions exerted the highest negative effect. Based on the sorbent reusing analysis, both 5hr and 24hr furnace exposed MCS showed reused capacity up to 5 cycles of adsorption.

Overall, the developed 5hr and 24hr furnace exposed MCS was an effective and viable sorbent for rapid removal of arsenite and arsenate from natural waters in the pH range of 3-10.

5. REFERENCES

- [1] Gupta, V.K., Saini, V.K. and Jain, N.: Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *Journal of Colloid and Interface Science*. 288(1):55–60, 2005.
- [2] Boddu, V.M., Abburi, K., Talbott, J.L., Smith, E.D. and Haasch, R.: Removal of arsenic(III) and arsenic(V) from aqueous medium using chitosan-coated biosorbent. *Water Res*, 42:633-642, 2008.
- [3] Jimenez-Cedillo, M.J., Olguin, M.T., Fall, Ch. and Colin, A.: Adsorption capacity of iron- or iron-manganese-modified zeolite-rich tuffs for As(III) and As(V) water pollutants. *Appl Clay Sci*, 54:206-216, 2011.
- [4] Arias, M., Astray, G., Fernández-Calviño, D., García-Río, L., Mejuto, J.C., Nóvoa-Muñoz, J.C. and Pérez-Novo, C.: Sorption behavior of arsenic by iron and aluminum oxides coated quartz particles. *Fresenius Environmental Bulletin*. 17(12a), 2008.
- [5] Singh, T. and Pant, K.K.: Experimental and modeling studies on fixed bed adsorption of As(III) ions from aqueous solution. *Separation and purification Technology*, 48 :288–296, 2006.
- [6] Kumpiene, J., Lagerkvist, A. and Maurice, C.: Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments –A review. *Waste Management*, 28:215–225, 2008.
- [7] Zhang, G., Qu, J., Liu, H., Liu, R. and Wu, R.: Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. *Water Res*, 41:1921– 1928, 2007.
- [8] Chang, Y.Y., Song, K.H. and Yang, J.K.: Removal of As(III) in a column reactor packed with iron-coated sand and manganese-coated sand. *J Hazard Mater.*, 150(3):565-72, 2008.
- [9] Lee, S.M., Kim, W.G., Yang, J.K. and Tiwari, D.: Sorption behaviour of manganese-coated calcined-starfish and manganese-coated sand for Mn(II). *Environmental Technology*, 31(4), 2010.
- [10] Han, R., Zou, W., Zhang, Z., Shi, J. and Yang, J.: Removal of copper (II) and lead(II) from aqueous solution by manganese oxide coated sand: I. Characterization and kinetic study. *J Hazard Mater.*, 137(1):384–395, 2006.
- [11] Davies, S.H.R. and Morgan, J.J.: Manganese (II) oxidation kinetics on metal oxide surfaces. *J. Colloid Interf. Sci.* 29:63–77, 1989.

Chapter (VIII)

VIII. COLUMN STUDY

1. INTRODUCTION

The WHO provisional guideline value for arsenic in drinking water is 10 µg/L [1]. Considering the relative risks to life and health there is a growing interest in using low-cost methods and materials to remove arsenic from water before it may cause significant contamination. The requirements for a removal technique of arsenic from drinking water are the safe operation with respect to the maximum contaminant level, effectiveness, simple processing for application in small water facilities and minimal residual mass of arsenic contaminated waste. Among the used removal techniques for arsenic treatment, adsorption is the most widely used process in the view point of removal efficiency as well as operating cost.

The manganese coated sand (MCS) has been applied, as one of the promising techniques, mostly for the oxidation of As(III) [2]. For arsenic adsorption, the MCS has been extensively used in combination with other sorbents such as iron-coated sand (ICS) [2-6]. However, until now,

limited information has been available on the treatment of arsenic by using MCS alone.

As mentioned in previous chapter, we developed a manganese oxide coated sand (MCS) as a simple, cost effective arsenic removal sorbent. The chief constituents of the developed sorbent were SiO_2 , MnO_2 , Mn_2O_3 , Al_2O_3 and NaCl .

The adsorbent was successfully applied for arsenic removal from DI and synthetic solution in batch system. Different important parameters like adsorption isotherm, pH, contact time and reusing of the adsorbent in batch system was studied. In this chapter, a column operation involving MCS as the adsorbent was applied to remove arsenic from the synthetic solution containing bicarbonate. The column studies were performed to actually confirm the results of the batch studies. The pH and TDS values were monitored alongside the removal rates of the target pollutant, in order to explain the factors which must be taken into account when optimizing the adsorption system for arsenic removal in synthetic solution. Also, the performance characteristics of the column was evaluated and simulated based on a plug flow dispersion reactor (PFDR) model.

2. MATERIALS AND METHODS

2.1 Chemicals and Media Used

All chemicals were of analytical reagent grade and no further purification was carried out. All solutions were prepared with de-ionized (DI) water made in the laboratory with a resistance greater than 18 M Ω . Sodium arsenate ($\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$, 99% purity, ACS grade) was purchased

from Sigma-Aldrich. The other chemicals were obtained from Fisher scientific (Fair Lawn, NJ). The calcium chloride (CaCl_2 , 98.8% purity, ACS grade), sodium sulfate (Na_2SO_4 , 99.3% purity, ACS grade) and sodium bicarbonate (NaHCO_3 , 100.1 % purity, ACS grade) were used to synthesize a more realistic solution, called synthetic solution, considering the effect of other co-existing ions.

2.2. Arsenate Solution

The feed solution for column study included the 1mM of CaCl_2 , 2.5 mM NaHCO_3 and 0.5 mM of Na_2SO_4 . The initial concentration of 1 mg/L for As(V) was used in this study.

2.3. MCS Preparation

The sand was first washed and soaked in 0.1M HCl solution for 3h, and then subsequently rinsed with de-ionized water until the pH of the washing water is close to 7.0. After that, it was dried in an oven at 110 °C to prepare for coating. Then, 50 mL of a high concentrated MnCl_2 (1M) was mixed with 50 mL of high concentrated AlCl_3 (1 M) solution and the solution pH was adjusted to pH about 7 with 6 N NaOH. Then the coating solution was mixed with the sand (80 g) in a flask for 24hr. Then, the residual coating solution was poured, and the sand was air dried for 12 h followed by heating in the oven (110 °C) for 4hr .This is the first step for the whole coating process. Then, the sand was introduced into a furnace to finish coating of metal oxides on the

sand. This process was performed at 550 °C for 5hr and 24hr as the second coating step. Finally, the coated sands were stored in airtight containers for column study.

2.4. Experimental Procedure

The duplicate column leaching experiments were conducted in 30 cm long borosilicate glass columns (KONTES CHROMAFLEX TM, 420830-3020) with an inside diameter of 2.5 cm. The pore volume (V_o) in the column packed with MCS was 32.4 cm³ when the porosity (Φ) was assumed to be 0.33. A weight of 150 g of MCS was packed in each glass column occupying 75% of the column volume. For the column experiments, the As(V) solution (1 mg/L) with ionic background (synthetic solution), was pumped downwards through the top of the column, using Masterflex peristaltic pump (Cole Parmer), at a flow rate of 10 mL/min. Once the process started, samples of the arsenic water were collected at suitable time intervals. This process was continued for a long period of time until the material adsorbent was exhausted. The arsenic concentration before the column test and As(V) concentration in the column effluent were measured using the graphite furnace atomic absorption spectroscopy (GFAAS) with Zeeman background correction. The detection limit of arsenic was 1 µg/L. All arsenic concentration measurements were carried out using an electrode-less lamp (EDL) at 193.7 nm and the modifier used was palladium-magnesium modifier. The atomization and pre-treatment temperature were 2000 and 1200 °C, respectively. The effluent was also analyzed for pH (Orion comb. pH 915600), conductivity (Orion cond cell 013005D), TDS (Orion cond cell 013005D) and alkalinity (Schott titronic basic).

Fig. 1 shows a schematic diagram of the apparatus of the column reactor. The detailed specifications of the column reactor and composition of the synthetic solution are represented in Tables 1 and 2, respectively.

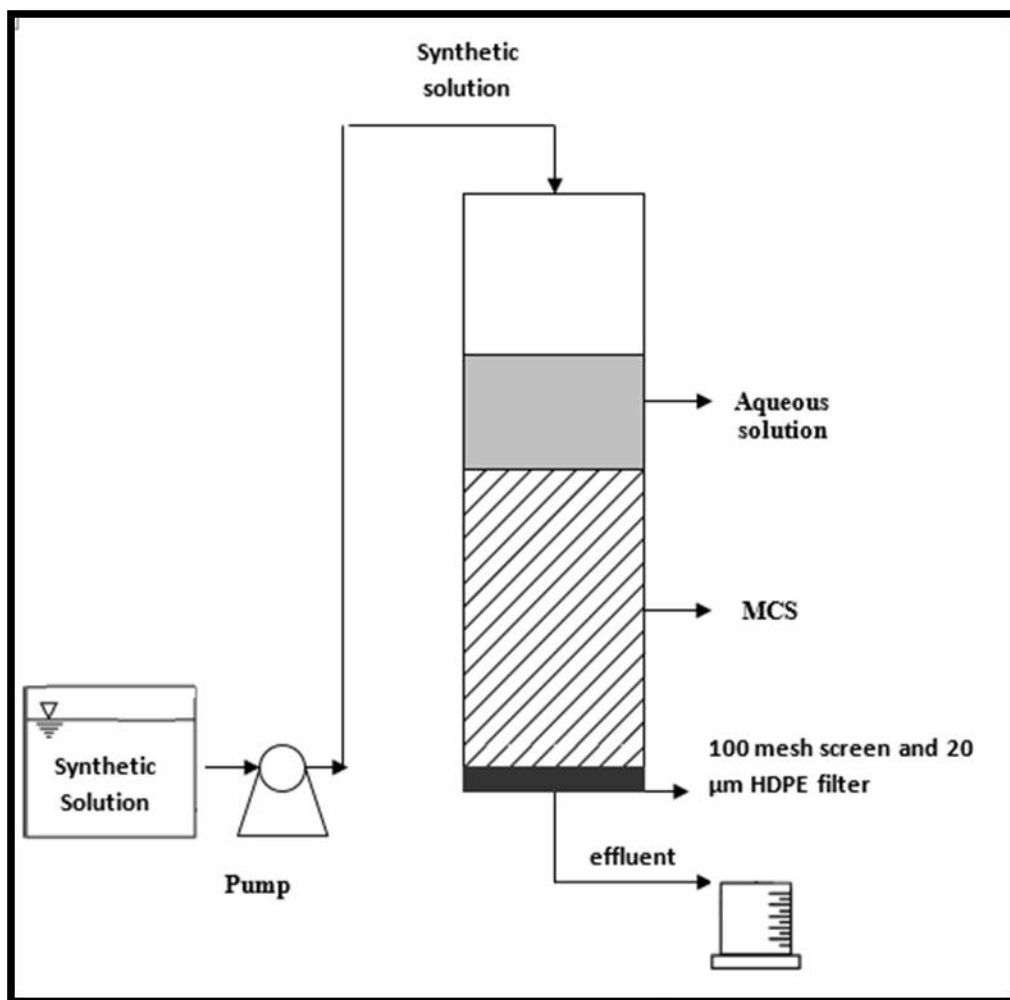


Fig.1. Column study setup.

Table 1. Characteristics of MCS columns

| Specification of MCS column | Operating parameter |
|--|-----------------------|
| Material of reactor | borosilicate glass |
| Reactor height (H) | 30 cm |
| Reactor diameter (D) | 2.5 cm |
| Reactor volume (V_T) | 147.3 cm ³ |
| Reactor pore volume (PV_T) | 48.6 cm ³ |
| Flow rate (Q) | 10 mL/min |
| Linear velocity (v) | 2.04 cm/s |
| MCS bed height (H_{MCS}) | 20 cm |
| MCS bed volume (V_{MCS}) | 98.2 cm ³ |
| MCS bed pore volume (PV_{MCS}) | 32.4 cm ³ |
| Retention time of MCS bed (θ_{MCS}) | 3.2 min |

Table 2. Composition of the synthetic solution

| Ingredient | As(V) | Ca ²⁺ | HCO ₃ ⁻ | SO ₄ ²⁻ | TDS | pH |
|--------------------|--------|------------------|-------------------------------|-------------------------------|-----|------|
| Concentration (mM) | 1 mg/L | 1 | 2.5 | 0.5 | 923 | 7.95 |

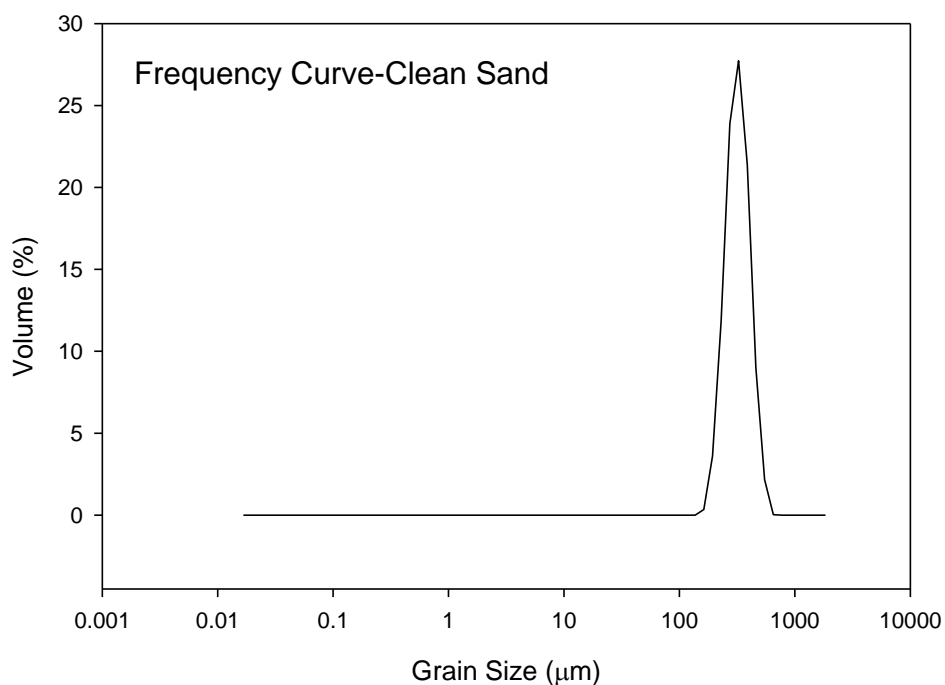
3. RESULTS AND DISCUSSION

3.1. Composition and characterization of MCS

Acid digestion was performed on both 5hr and 24hr MCS for analyzing the manganese and aluminum content of the coated sands. The manganese and aluminum content of the 5hr MCS were found to be 17.1 mg/g and 13.1 mg/g, respectively while the 24hr MCS's manganese and aluminum content were 15.5 mg/g and 12 mg/g, respectively. The lower manganese and aluminum content in 24hr MCS can be the reason for the lower arsenic adsorption by 24hr MCS versus the 5hr MCS. The amount of manganese coated on the sands was found to be almost 30% more than the aluminum content.

The MCS sorbent was characterization by SEM/EDX and XPS and the results were discussed in chapter 6 and 7. As discussed before, the coated sands appeared as a rough coated surface with no uniform coating based on SEM analysis. A similar spectrum was resulted for the 5hr furnace exposed MCS and 24hr furnace exposed MCS based on EDX analysis however a higher manganese content was observed on 5hr furnace exposed MCS versus the 24hr furnace exposed MCS which were in good agreement with the results obtained from acid digestion. The XPS analysis of Mn 2p resulted that the manganese exhibited oxidation between Mn^{3+} and Mn^{4+} with the predominant Mn^{3+} . The analysis of O 1s spectra indicate the presence of oxygen as lattice oxygen in the form of O^{2-} . Also the analysis of Al 2p core spectra of the 5hr and 24hr furnace exposed MCS indicated the presence of aluminum as Al_2O_3 on both MCSs.

Particle size distribution of the MCS was also determined by laser diffraction on Mastersizer 2000 (Malvern Instrument, Worcestershire, UK). This measurement reflected the agglomerate nature of MCS due to particle to particle attraction. The frequency curve of clean (uncoated) sand, 5hr MCS and 24hr MCS is represented in Fig.2. The results represented the volume percentage of the sorbent particles in different grain size. The results proved the presence of 100% of clean sand particles in the sand size category while coating the sand decreased the sand size category of the sorbent particle size down to 90% for 24hr MCS and 85% for 5hr MCS, respectively. The rest of the 5hr (15%) and 24hr (10%) MCS particles size were classified in the silt size category.



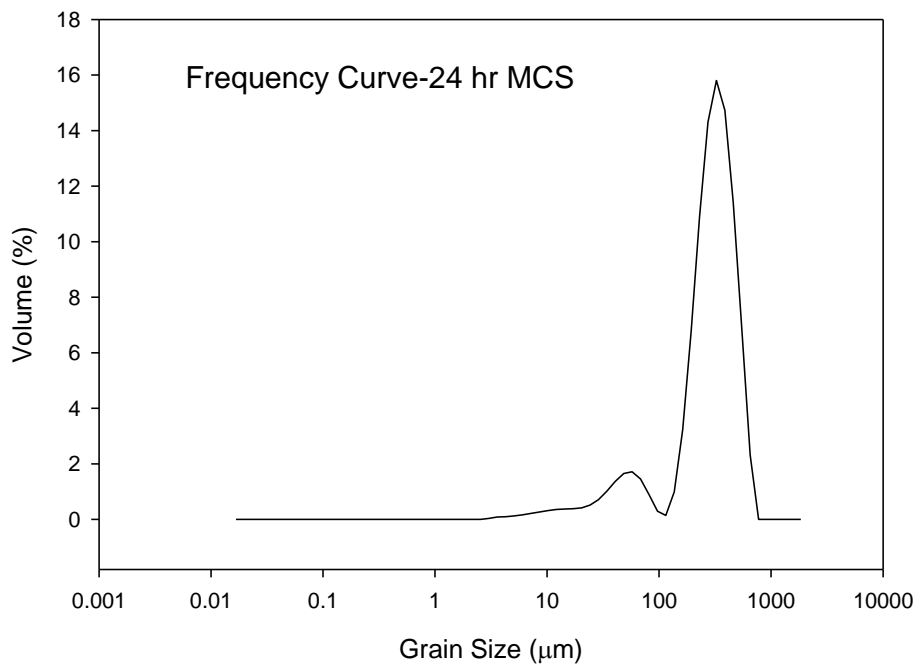
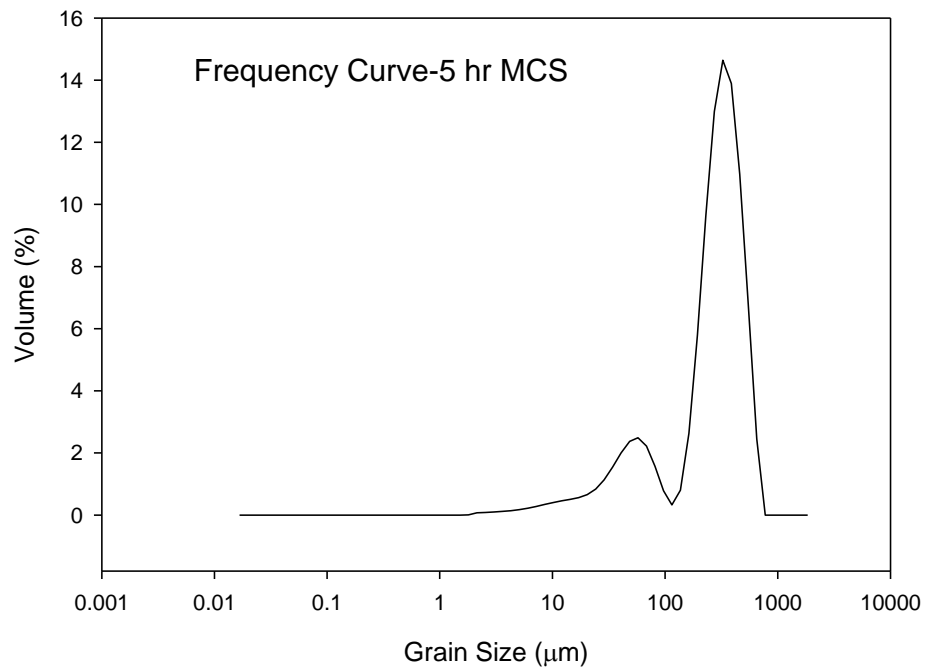


Fig.2. Particle size distribution of clean sand,5hr MCS and 24hr MCS

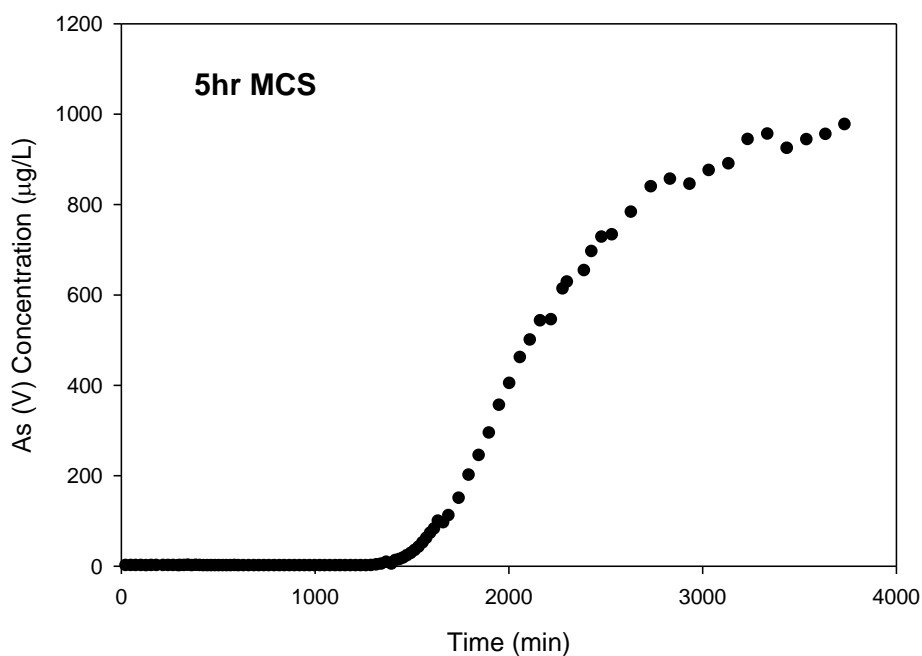
3.2. Adsorption column behavior

The experiment with a laboratory column is a practical way to design an adsorption column. At first, the adsorbent (here MCS) is fresh with all its adsorption sites and none of the material to be removed escapes from the column. The first layers of the MCS are in contact with the feed solution (here synthetic solution) at its highest concentration level which is basically the initial concentration of arsenic taken (C_0). As the synthetic solution continues to flow into the column, the top part of the MCS becomes practically saturated with solute and becomes less effective for further adsorption. Thus the primary adsorption zone moves downward through the column to regions of fresher adsorbent. As the zone moves upward, more and more solute tends to escape in the effluent. The point on the S-shaped curve at which the solute concentration reaches its maximum allowable value is referred to as breakthrough. The point where the effluent solute concentration reaches 90% of its influent value is usually called the “point of column exhaustion” [7-9].

The concentration of arsenic from the effluent for 5hr MCS column and 24hr MCS column of ash is shown in Figures 3. The plot of C/C_0 vs. time (for a constant flow rate) is shown in Fig. 4, where C is the concentration remained after adsorption and C_0 is the initial concentration of arsenic. The curve looks like characteristic ‘S’ shaped but position of breakpoint is different for 5hr and 24hr MCS columns.

As seen in Fig.3 and Fig.4, the breakthrough curves of arsenic from two different column systems occurred after 1439 min for 5hr MCS column and 1050 min for 24hr MCS column. Compared to the 24hr MCS column system, the breakthrough of arsenic in 5hr MCS was found

to be significantly delayed showing the superior performance of 5hr MCS sorbent versus the 24hr MCS sorbent in removing . The point of column exhaustion occurred after 2603 min and 3737 min for 24hr MCS and 5hr MCS, respectively. The corresponding volumes of the synthetic solution treated until breakthrough were 14.39 L for 5hr MCS column and 10.5 L for 24hr MCS column while 37.37 L and 26.03 L of the synthetic solution were treated until the point of the sorbent exhaustion for 5hr MCS column and 24hr MCS column, respectively.



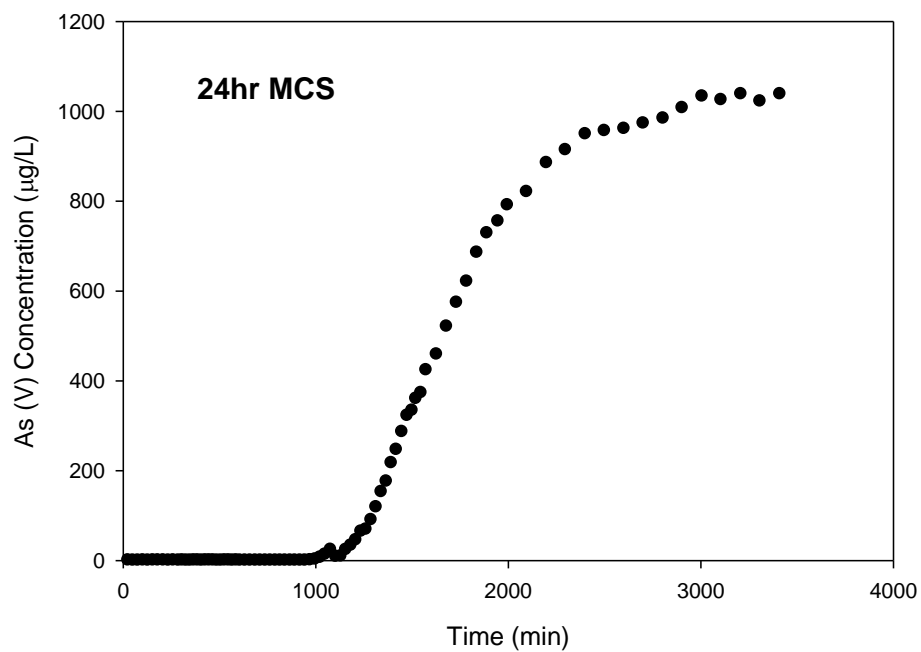
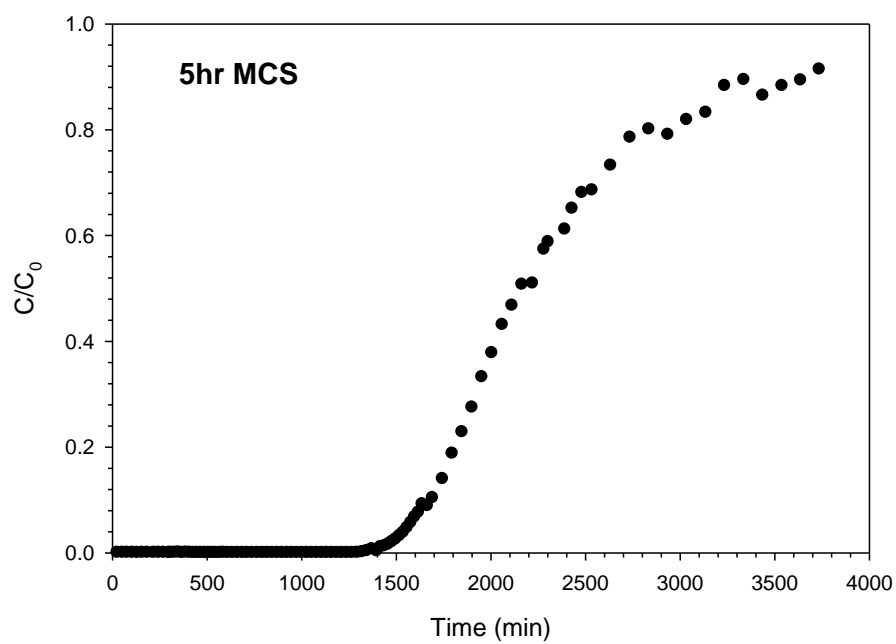


Fig.3. Breakthrough curve (arsenic concentration) for arsenate adsorption by column operation technique for 5hr and 24hr MCS: initial conc. of arsenate=1 mg/L.



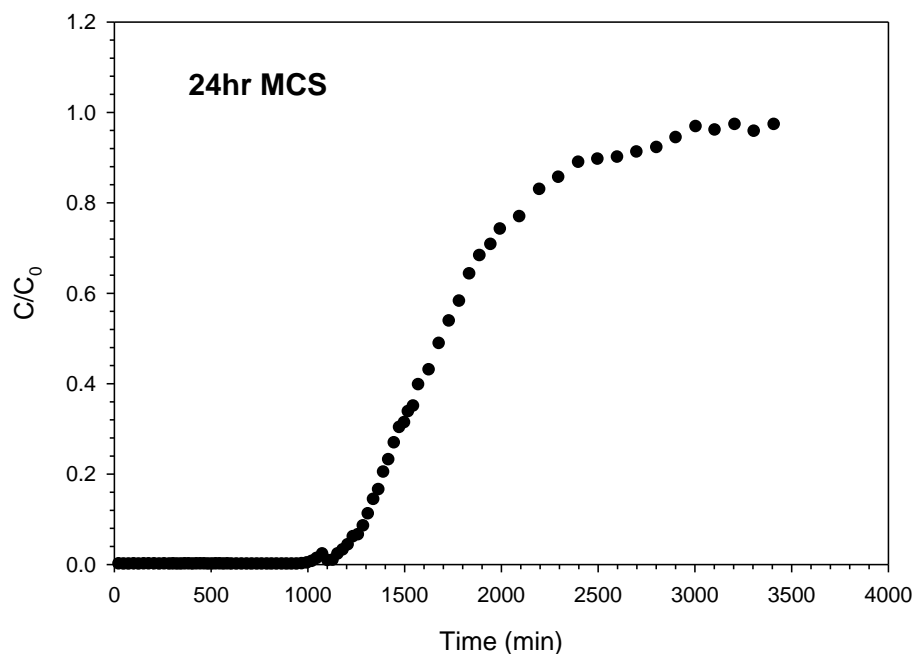


Fig.4. Breakthrough curve(C/C_0) for arsenate adsorption by column operation technique for 5hr and 24hr MCS: initial conc. of arsenate=1 mg/L.

The As(V) uptake (mg/kg) of both 5hr and 24hr column versus time is presented in Fig.5. As shown in Fig.5, a higher As(V) adsorption was obtained for 5hr MCS column versus the 24hr MCS column after breakthrough.

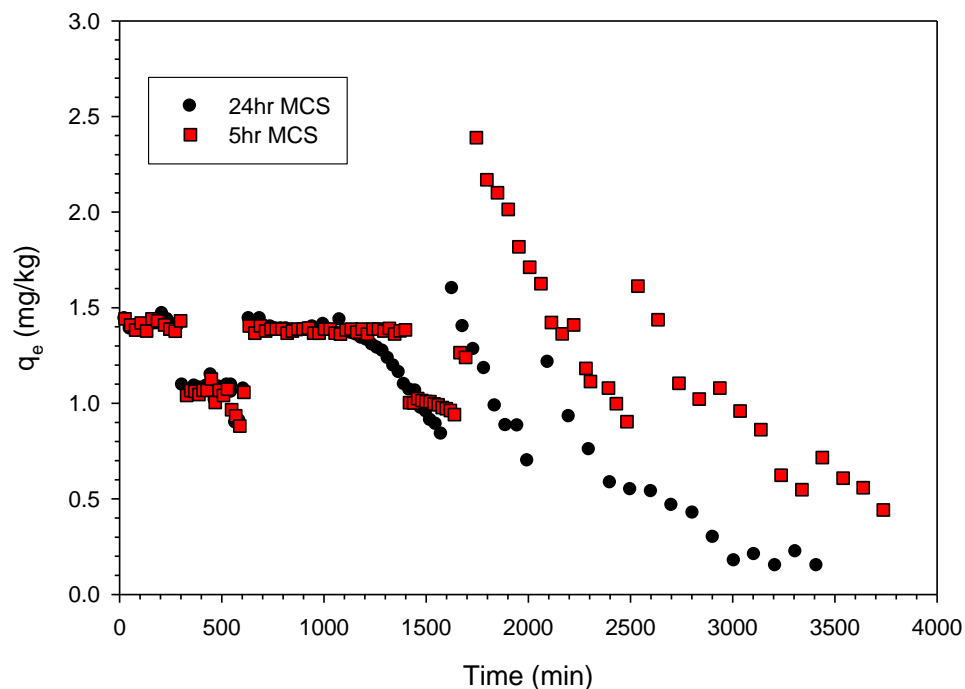


Fig.5. As(V) uptake for 5hr and 24hr MCS through column operation technique for initial conc. of arsenate=1 mg/L.

The pH of the effluents were plotted as a function of time for both 5hr and 24hr MCS column in Figure 6. The pH for the effluents for 5hr MCS column and 24hr MCS column were almost the same and they were within the range of 8 to 8.5. The pH of the effluent increased gradually from the pH of 8 up to pH of 8.4 within the first 1000 min of the column study for both 5hr and 24hr MCS column. The stable pH of 8.45 were observed for the effluents of both 5hr and 24hr MCS columns after breakthrough.

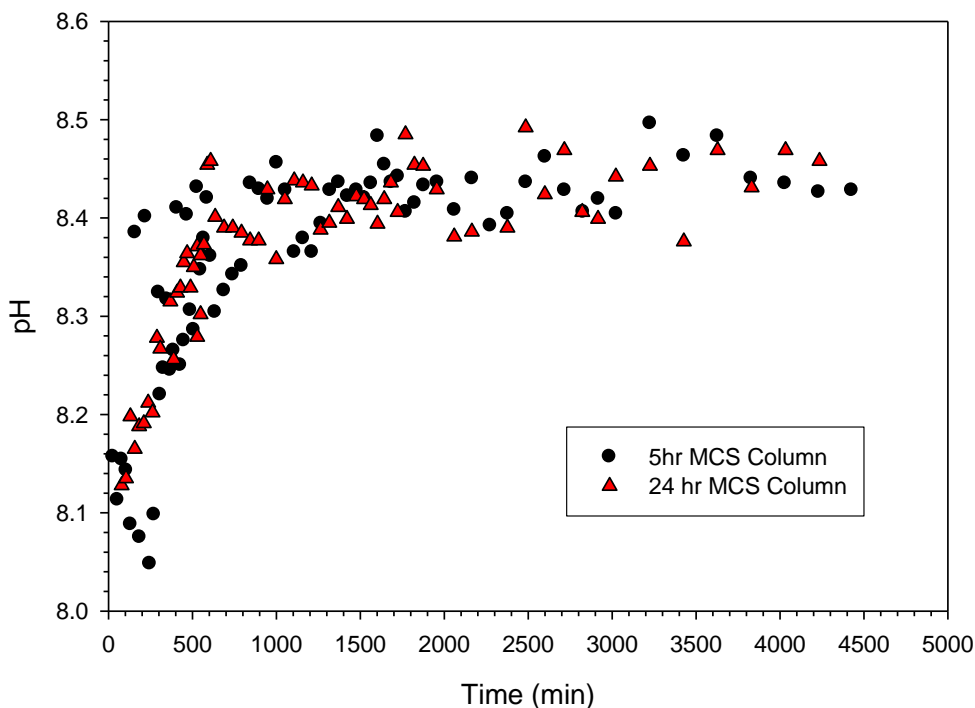


Fig.6. pH of the effluents for 5hr and 24hr MCS through column operation technique for initial conc. of arsenate=1 mg/L.

3.3. Evaluation of basic adsorption column design parameters

The total adsorbed As(V) quantity q_{total} (mg) in the column for a given flow rate (Q) and feed concentration (C_0) can be found by calculating the area under the breakthrough curve (A), which is obtained by integrating the adsorbed As(V) concentration (C_{ads} , $\mu\text{g/L}$) = inlet As(V) concentration (C_0) – effluent As(V) concentration (C) versus time t (min) plot by the following equation:

$$q_{\text{total}} = \frac{QA}{10^6} = \frac{Q}{10^6} \int_{t=0}^{t=\text{tot}} C_{\text{ads}} dt \quad (1)$$

The equilibrium arsenic uptake per unit mass of adsorbent, q_e (mg/kg), is calculated according to the following equation:

$$q_e = \frac{q_{\text{total}}}{M} \quad (2)$$

where M (kg) is the amount of adsorbent.

The total adsorption capacity of the sorbents using 150 g of the MCS in the columns were calculated as 165.9 mg/kg for 5hr MCS column and 127.3 mg/kg for 24hr MCS column, respectively.

The flow rate represents the empty bed contact time (EBCT) in the column, as described in the following equation [10]:

$$\text{EBCT (min)} = \text{bed volume (mL)} / \text{flow rate (mL/min)}$$

The EBCT between the adsorbent and adsorbate for the studied column was calculated as 9.8 min.

As the feed arsenic solution passes through the column, the adsorption zone, where the bulk of adsorption occurs, moves out of the column and the concentration of effluent increases with increasing time. The formation and movement of the adsorption zone can be evaluated

mathematically [11,12]. The time required for the adsorption zone to move the length of its own height down the column once it has become established can be calculated as:

$$t_z = \frac{V_s}{Q_w} \quad (3)$$

where Q_w is influent flow rate (mL/min) and V_s is the total volume of the solution treated between breakthrough and exhaustion (mL) .

The time required for the adsorption zone to become established and move completely out of the bed can be written as:

$$t_E = \frac{V_E}{Q_w} \quad (4)$$

where V_E is the total volume of the solution treated to the point of exhaustion (mL).

The rate at which the adsorption zone is moving up or down through the bed is

$$U_z = \frac{h_z}{t_z} = \frac{h}{t_E - t_f} \quad (5)$$

where h_z is the height of adsorption zone (cm), h is the total bed depth (cm) and t_f is time required for the adsorption zone to initially form (min).

The value of t_f can be calculated as follow:

$$t_f = (1 - F)t_z \quad (6)$$

The fraction (F) of MCS present in the adsorption zone at breakthrough which still possessing the ability to remove As(V) is represented as:

$$F = \frac{S_z}{S_{\max}} = \frac{\int_{V_B}^{V_E} (C_0 - C) dV}{C_0(V_E - V_B)} \quad (7)$$

where S_z is amount of arsenic that has been removed by the adsorption zone from breakthrough to exhaustion, S_{\max} is the amount of arsenic removed by the adsorption zone if completely exhausted, C_0 is the initial arsenic concentration ($\mu\text{g/L}$), C is the arsenic concentration at a given instant of time t and V_B is the total volume of solution treated to the point of breakthrough (mL).

The percentage of the total column saturated at breakthrough is:

$$\% \text{ saturation} = \frac{h + (F - 1)h_z}{h} \times 100 \quad (8)$$

The values of the design parameters for the studied column were calculated and the results are tabulated in Table 3.

Table 3. Specification of MCS column and operating parameters

| MCS column | t_z (h) | t_E (h) | h_z (cm) | U_z (cm/h) | Bed saturation (%) |
|---------------|--------------|--------------|---------------|-----------------|-----------------------|
| 5hr MCS | 38.6 | 62.3 | 19.99 | 0.01 | 38.8 |
| 24hr MCS | 26.3 | 43.4 | 18.2 | 0.01 | 49.9 |

3.4. Analysis and modeling of column data

The shape of the breakthrough curve and the time or bed volume for breakthrough appearance are important characteristics for determining the dynamic response and operation of an adsorption column. Also, in order to design an adsorption column successfully, the prediction of the concentration–time profile from the breakthrough curve for the column effluents is needed. [13,14]. The adsorption process in the column study does not operate at steady state due to changing the of arsenic concentration as the feed solution moves through the bed at different times. The fundamental transport equations for the column adsorption process in this study are those of material balance between MCS and the synthetic solution. These equations can be written as follow:

$$\frac{\partial C_t}{\partial t} + U_0 \left(\frac{\partial C_t}{\partial Z} \right) + \frac{(1 - \varepsilon)}{\varepsilon} \rho \left(\frac{\partial q}{\partial t} \right) = E \left(\frac{\partial^2 C_t}{\partial Z^2} \right) \quad (9)$$

where ε is the void fraction in the bed, C_t is the phenol concentration in solution ($\mu\text{g/L}$), U_0 is linear velocity (cm/min) and can be calculated by dividing the flow rate (cm^3/min) to the column section area (cm^2), Z is the column depth (cm), q is the arsenic adsorption capacity at t (mg/kg) and E is a dispersion coefficient (cm^2/min).

The second equation is $(1 - \varepsilon) \left(\frac{\partial q}{\partial t} \right) = r$ where r is actually the adsorption rate r (mg/L.min)

which depends on the adsorption mechanism. This mechanism may be controlled by diffusion and reaction within the adsorbent particles or by mass transfer from the bulk solution to the surface of the adsorbent. So the mathematical description of adsorption rate must be added to these transport equations given for the fixed bed. The adsorption isotherm equation is the fourth and final key equation for the mathematical modeling of a column adsorption process [15].

All these equations derived to model the system with theoretical rigor are differential in nature and usually require complex numerical methods to solve. Such a numerical solution is not usually difficult, but often does not fit experimental results especially well. Hence, several simple mathematical models have been developed for describing and analyzing the lab-scale column studies for the purpose of industrial applications [16-18]. So in this study two well-known models, Adams–Bohart and Thomas models, were applied for the prediction of breakthrough curves.

3.4.1. Adam–Bohart model

The Adam–Bohart model is frequently selected for the determination of fixed-bed column breakthrough for the initial state of the operation. The main assumption in this model is that the concentration of the adsorbate and also equilibrium does not take place instantaneous and the adsorption rate is proportional to the residual capacity of the adsorbent. [7, 19]. The mass transfer rates obey the following equations:

$$\left(\frac{\partial q}{\partial t}\right) = -K_{AB} q C_t \quad (10)$$

$$\left(\frac{\partial C_t}{\partial Z}\right) = -\frac{K_{AB}}{U_0} q C_t \quad (11)$$

where k_{AB} is the kinetic constant ($L/\mu g \text{ min}$). In order to solve these differential equation systems some assumptions were made including: (i) the concentration field is considered to be low and (ii) for $t \rightarrow \infty$, $q \rightarrow N_0$, where N_0 is the saturation concentration ($\mu g/L$). The solution of above equations can be written as [20] :

$$\ln\left(\frac{C_t}{C_0}\right) = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U_0} \quad (12)$$

where C_0 ($\mu g/L$) and C ($\mu g/L$) are the inlet and effluent concentration of arsenic, respectively. The values of k_{AB} and N_0 can be obtained from a plot of $\ln(C_t/C_0)$ versus t . For finding the Adams–Bohart parameters a linear relationship between $\ln(C_t/C_0)$ and time was applied for the relative concentration up to $C_t/C_0 = 0.5$ for all breakthrough curves and then the values of

saturation concentration (N_0) and kinetics constant (k_{AB}) were calculated through the intercept and slope of the plots. The values of these parameters are given in Table 4. As shown in Fig.7 for 5hr and 24hr MCS column breakthrough curves, this model has a good agreement with the experimental data just for the initial part of breakthrough curves, suggesting that Adams–Bohart model may be valid for the adsorption processes where relative concentration region was up to almost 0.4 at the operating conditions where as large discrepancies were found between the experimental and predicted curves above this level for the arsenic adsorption in 5hr and 24hr MCS column. Based on Fig.7 and Table.4, less deviation was found between the experimental and predicted data for 24hr MCS column versus the 5hr MCS column within the C/C_0 range of 0 to 0.4.

Table 4. Parameters predicted by the Adam–Bohart model

| | Z(cm) | $C_0(\mu\text{g/L})$ | Q (mL/min) | $U_0(\text{cm/min})$ | $k_{AB}(\text{L}/\mu\text{g min})$ | $N_0 (\mu\text{g/L})$ | R^2 |
|----------|-------|----------------------|------------|----------------------|------------------------------------|-----------------------|-------|
| 5hr MCS | 20 | 1067 | 10 | 2.04 | 4.0×10^{-6} | 253026.4 | 0.919 |
| 24hr MCS | 20 | 1067 | 10 | 2.04 | 6.2×10^{-6} | 187986 | 0.930 |

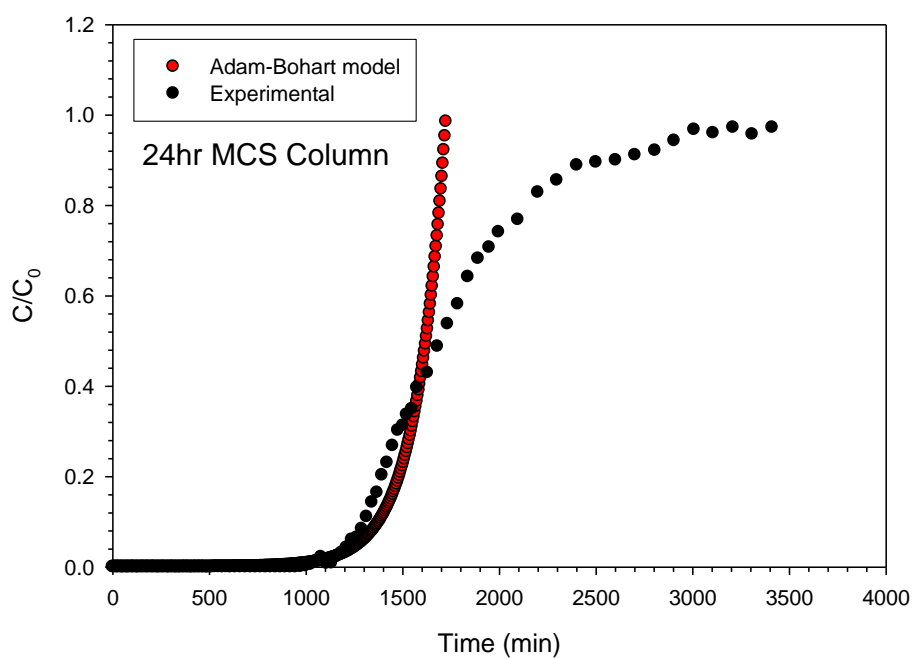
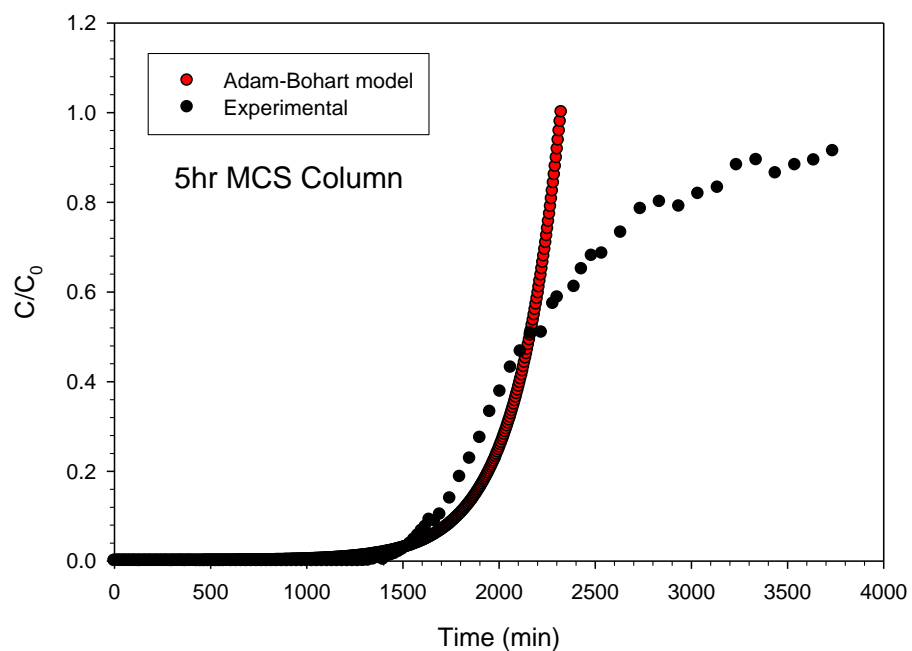


Fig.7. Comparison between experimental and predicted breakthrough curves by Adams–Bohart model at flow rates: 10 mL/min, inlet As(V) concentration = 1067 $\mu\text{g/L}$ and bed height = 20 cm.

3.4.2. Thomas model:

The maximum adsorption capacity of an adsorbent is also needed in design of a column adsorption process. Traditionally, the Thomas model is used to fulfil the purpose. Thomas equation is one of the most general models that is often used to interpret column data. This model supposes that adsorption process follows Langmuir isotherm for equilibrium and also obeys second-order reversible reaction kinetics. Especially in the absence of internal and external diffusion limitation, this model can be used well [21]. The Thomas model can be represented as the following form:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{K_{Th}}{Q} q_0 X - K_{Th} C_0 t\right)} \quad (13)$$

where K_{Th} is the Thomas rate constant (L/min.µg) , Q is the flow rate of solution (mL/min), q_0 is the maximum solid-phase concentration of the solute (mg/kg) and X is the mass of adsorbent (kg). The linearized form of Thomas model is given by:

$$\ln\left(\frac{C_0}{C_t} - 1\right) = \frac{K_{Th} q_0 X}{Q} - K_{Th} C_0 t \quad (14)$$

The kinetic coefficient K_{Th} and the adsorption capacity of the bed q_0 can be determined from a plot of $\ln [(C_0/C)-1]$ versus t at a given flow rate. The primary weakness of the Thomas solution is that its derivation is based on second order reaction kinetics. Adsorption is usually not limited by chemical reaction kinetics but is often controlled by interphase mass transfer. This discrepancy can lead some error when this method is used to model adsorption process.

The Thomas model was applied to the data at C/C_0 ratios higher than 0.01 with respect to flow rate and inlet arsenic concentrations for the determination of the kinetic coefficients in the studied column system (Fig.8). A linear regression was then performed on each set of transformed data to determine the coefficients from slope and intercept. The correlation coefficient (R^2) as well as the model parameters (K_{Th} and q_0) for both 5hr MCS and 24hr MCS experimental breakthrough curves obtained from the curve fitting is presented in Table 5. As can be concluded from the Table 5, there is very good consistency between the experimental and predicted data by Thomas model for 5hr and 24hr MCS columns. The experimental values of bed capacity for both 5hr and 24hr MCS column was very close to predicted values from Thomas equation where there was 25.8% and 24.7% error was obtained for the calculated maximum solid-phase concentration of the arsenic versus the experimental value for the 5hr MCS and 24 hr MCS column, respectively.

Table 5. Parameters predicted by the Thomas model

| | $C_0(\mu\text{g/L})$ | $Q \text{ (mL/min)}$ | K_{Th} ($\text{L}/\mu\text{g}\cdot\text{min}$) | $q_{0,\text{cal}}$ (mg/kg) | $q_{0,\text{exp}}$ (mg/kg) | R^2 | % Error |
|----------|----------------------|----------------------|---|--|--|-------|---------|
| 5hr MCS | 1067 | 10 | 2.24×10^{-6} | 123.05 | 165.87 | 0.915 | 25.8 |
| 24hr MCS | 1067 | 10 | 2.62×10^{-6} | 95.9 | 127.3 | 0.949 | 24.7 |

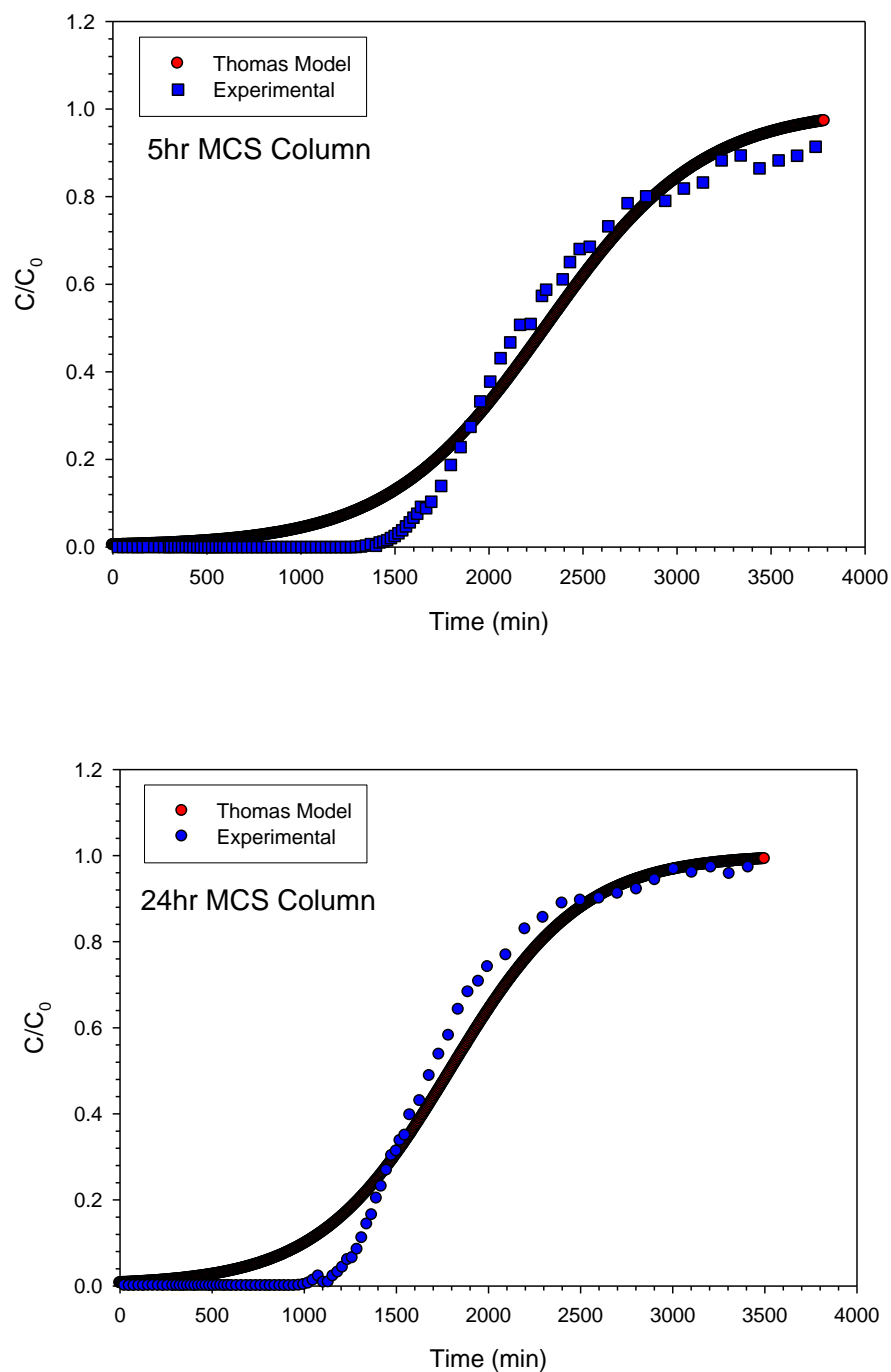


Fig.8. Comparison between experimental and predicted breakthrough curves by Thomas model at flow rates: 10 mL/min, inlet As(V) concentration = 1067 $\mu\text{g/L}$ and bed height = 20 cm.

4. CONCLUSION

The results of the column adsorption process in the packed column showed that the 5hr and 24hr manganese coated sand (MCS) can be employed for removal of arsenic successfully. The maximum capacity of column was found to be about 165.7 mg/kg for 5hr MCS sorbent and 127.3 mg/kg for 24hr MCS sorbent for flow rate of 10 mL/min, initial concentration of 1067.81 µg/L and 20 cm bed height. The breakthrough curves of arsenic from two different column systems occurred after 1439 min for 5hr MCS column and 1050 min for 24hr MCS column. The point of column exhaustion occurred after 2603 min and 3737 min for 24hr MCS and 5hr MCS, respectively. The corresponding volumes of the synthetic solution treated until breakthrough were 14.39 L for 5hr MCS column and 10.5 L for 24hr MCS column while 37.37 L and 26.03 L of the synthetic solution were treated until the point of the sorbent exhaustion for 5hr MCS column and 24hr MCS column, respectively. Two well-known models, Adams–Bohart and Thomas models, were applied for the prediction of breakthrough curves. The Thomas model was found to be in good agreement with experimental data and could be used for prediction of experimental results as well. Also Adams–Bohart model showed a good correlation especially with the initial part of breakthrough curves.

5. REFERENCES

- [1] WHO, 2004. Guidelines for Drinking Water Quality, third ed. Volume 1. Recommendations.
- [2] Chang, Y.Y., Kim, K.S., Jung, J.H., Yang, J.K. and Lee, S.M.: Application of iron-coated sand and manganese-coated sand on the treatment of both As(III) and As(V). *Water Science & Technology*, 55(1–2) :69–75, 2007.

- [3] Kumpiene, J., Lagerkvist, A. and Maurice, C.: Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments –A review. *Waste Management*, 28 :215–225, 2008.
- [4] Zhanga, G., Qu, J., Liu, H., Liu, R. and Wu, R.: Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. *Water Research*, 41(9):1921– 1928, 2007.
- [5] Chang, Y.Y., Song, K.H. and Yang, J.K.: Removal of As(III) in a column reactor packed with iron-coated sand and manganese-coated sand. *J Hazard Mater.* 150 (3):565–72, 2008.
- [6] Lee, S.M., Kim, W.G., Yang, J.K. and Tiwari, D.: Sorption behaviour of manganese-coated calcined-starfish and manganese-coated sand for Mn(II). *Environ. Technol.*, 31:445–453, 2010.
- [7] Lim, A.P. and Aris, A.Z.: Continuous fixed-bed column study and adsorption modeling: Removal of cadmium (II) and lead (II) ions in aqueous solution by dead calcareous skeletons. *Biochemical Engineering Journal*, 87:50–61, 2014.
- [8] Maji, S.K., Pal, A. and Pal, T.: Arsenic removal from real-life groundwater by adsorption on laterite soil. *Journal of Hazardous Materials*, 151:811–820, 2008.
- [9] Kundu, S., Kavalakatt, S.S., Pal, A., Ghosh, S.K., Mandal, M. and Pal, T.: Removal of arsenic using hardened paste of Portland cement: batch adsorption and column study. *Water Research*, 38:3780–3790, 2004.
- [10] Netpradit, S., Thiravetyan, P. and Towprayoon, S.: Evaluation of metal hydroxide sludge for reactive dye adsorption in a fixed-bed column system. *Water Res.* 38:71–78, 2004.
- [11] Kundu, S. and Gupta, A.K.: Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC). *Journal of Colloid and Interface Science.*, 290:52–60, 2005.
- [12] Benefield, L.D., Judkins, J.F. and Weand, B.L.: *Process Chemistry for Water and Wastewater Treatment* Prentice Hall, Englewood Cliffs, NJ (1982).
- [13] Meng, M., Feng, Y., Zhang, M., Liu, Y., Ji, Y., Wang, J., Wu, Y. and Yan, Y.: Highly efficient adsorption of salicylic acid from aqueous solution by wollastonite-based imprinted adsorbent: A fixed-bed column study. *Chem. Eng. J.* 225:331–339, 2013.
- [14] Sun, X., Imai, T., Sekine, M., Higuchi, T., Yamamoto, K., Kanno, A. and Nakazono, S.: Adsorption of phosphate using calcined Mg₃–Fe layered double hydroxides in a fixed-bed column study. *Journal of Industrial and Engineering Chemistry* (2013).
<http://dx.doi.org/10.1016/j.jiec.2013.12.057>.
- [15] Aksu, Z. and Gönen, F.: Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochemistry*, 39:599–613, 2004.
- [16] Kumar, P.A. and Chakraborty, S.: Fixed-bed column study for hexavalent chromium removal and recovery by short-chain polyaniline synthesized on jute fiber. *J. Hazard. Mater.*, 162, 1086–1098, 2009.

- [17] Han, R.P., Zou, L.N., Zhao, X., Xu, Y.F., Xu, F., Li, Y.L. and Wang, Y.: Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column. *Chem. Eng. J.*,149:123–131.2009.
- [18] Vinodhini, V. and Das, N.: Packed bed column studies on Cr (VI) removal from tannery wastewater by neem sawdust. *Desalination*, 264:9–14,2010.
- [19] Goel,J., Kadirvelu,K., Rajagopal,C. and Garg,V.K.: Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies. *J. Hazard. Mater*,B125: 211–220, 2005.
- [20] Ahmad, A. and Hameed, B.: Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. *J. Hazard. Mater*, 175:298–303, 2010.
- [21] Thomas, HC.: Heterogeneous ion exchange in a flowing system. *J Am Chem Soc.*,66:1664–6, 1944.

Chapter IX

IX. CONCLUSIONS AND RECOMMENDATIONS

1. CONCLUSIONS

The removal of arsenic from water using different manganese oxides were investigated in this study. First, the ability of four different pure manganese oxides (MnO , Mn_3O_4 , Mn_2O_3 and MnO_2) with different oxidation states was investigated for As(V) removal from solutions with different ionic backgrounds including DI water, 2.5 mM HCO_3^- and 5.5 mM HCO_3^- solutions. The Mn_2O_3 and Mn_3O_4 sorbents showed promising performance in removing the As(V) from all three solutions while MnO_2 and MnO worked well at higher sorbent dosages. A 10 g/L of Mn_2O_3 and Mn_3O_4 was found to be needed in order to meet the EPA standard level for arsenic in drinking water while this dosage was 10 times higher for MnO and MnO_2 adsorbents. The effect of contact time on the As(V) removal efficiency onto manganese oxides showed that the equilibrium can be achieved at less than 10 hr for all manganese oxides. Also, the As(V) removal by Mn_2O_3 was found to be faster than Mn_3O_4 . The results of adsorption isotherm study showed that: the general arsenate adsorption capacity of the manganese oxides was in the order of $\text{Mn}_3\text{O}_4 > \text{Mn}_2\text{O}_3 > \text{MnO}_2 > \text{MnO}$, the As(V) adsorption potential for Mn_3O_4 and Mn_2O_3 was higher than MnO_2 and MnO , the favorable adsorption system on Mn_3O_4 and Mn_2O_3 was achieved, the As(V) adsorption onto the sorbents in DI water, 2.5mM HCO_3^- solution and 5.5mM HCO_3^- solution was found to be an exothermic process and the As(V) adsorption process

onto the surface of Mn_3O_4 and Mn_2O_3 was found to be chemisorption while the nature of arsenate by adsorption process by MnO_2 and MnO was physisorption.

The As(V) adsorption capacity of all manganese oxides at the arsenic standard level ($10 \mu\text{g/L}$) was compared in three different solutions with different ionic background: DI, 2.5mM HCO_3^- and 5.5mM HCO_3^- solutions. The results confirmed the higher arsenic removal efficiency of Mn_3O_4 and Mn_2O_3 versus MnO_2 and MnO . The adsorption capacity of the sorbents decreased in 2.5mM HCO_3^- and 5.5mM HCO_3^- solutions due to the higher pH of the solutions and the competing effect of other ions specially bicarbonate on the limited active sites on the surface of the sorbents. In general the results showed that the arsenic removal efficiency of manganese oxides with the oxidation states of 3 (Mn^{3+}) or the combination of oxidation number of 2 and 3 (Mn^{2+} , Mn^{3+}) were able to remove higher amount of arsenic versus the other manganese oxides with the oxidation number of $2+$ (Mn^{2+}) or $4+$ (Mn^{4+}).

Kinetics, equilibrium and the effect of pH and ionic strength on the adsorption and removal of As(V) using crystalline manganese (II,III) oxide was investigated. The results showed the effectiveness of crystalline manganese oxide (II,III) powder (Mn_3O_4) for removal of As(V) from water. The adsorption of arsenic onto the surface of Mn_3O_4 was confirmed by the surface charge analysis and zeta potential measurements. The Mn_3O_4 sorbent was able to remove greater than 99% of arsenic under the condition of adsorbent dosage 20 g/L , pH of 6.6-8.3, temperature of 25°C and contact time of 24 hr. The maximum adsorption capacity of the sorbent in DI water and synthetic solution was found to be 345 mg/kg and 256 mg/kg , respectively. The adsorption

process could be explained by the pseudo-second order kinetics model. The removal of arsenic decreased with increasing pH. The adsorption of As(V) with the presence of other ions decreased in order of: phosphate > bicarbonate > calcium ~ sulfate. The arsenic removal ability of the Mn_3O_4 was tested in two different real groundwaters as well. An arsenic removal efficiency of >99% resulted by applying the crystalline Mn_3O_4 sorbent to the groundwaters indicating the Mn_3O_4 ability to be used as a practical efficient sorbent for arsenic removal.

The adsorption of As(V) and As(III) onto crystalline manganese (III) oxide (Mn_2O_3) in batch systems was also investigated. The adsorption of As(III) and As(V) was fast and occurred within 60 min of contact time. Based on the kinetics data modeling, the pseudo-second order kinetic model was found to best correlate to the experimental data for adsorption of both As(III) and As(V) onto Mn_2O_3 . The arsenic removal efficiency of 99.9% in both DI water and synthetic solution was achieved at the sorbent dosage of 20 g/L. Favorable adsorption of As(III) and As(V) onto Mn_2O_3 occurred where the binding of As(V) onto Mn_2O_3 was found to be stronger than that of As(III) while a higher removal of As(III) than As(V) was obtained. The presence of phosphate and bicarbonate reduced arsenic removal efficiency while the presence of calcium and sulfate did not show any noticeable effect on the adsorption of arsenic. The adsorption of As(V) showed dependence on pH with the highest uptake at pH 2. On the other hand, adsorption of As(III) was relatively independent of solution pH. The surface charge analysis of the sorbent indicated that H_3AsO_3 was likely oxidized to the arsenate species on the surface of Mn_2O_3 , with As(V) species forming inner-sphere complexes on the surface of Mn_2O_3 . According to the acid dissociation constants of As(III) and As(V) species, zeta potential measurements and the effect

of pH on adsorption, a likely mechanism responsible for the oxidation of As(III) to As(V) on the surface of Mn_2O_3 was proposed. The arsenic removal ability of Mn_2O_3 was tested in two different arsenic spiked real groundwater samples collected from northern and central Illinois. The results showed that an optimum dosage of 20 g/L of the crystalline Mn_2O_3 sorbent was able to remove a greater than 99.5% of As(III) and As(V) from contaminated groundwaters and meet the standard level. Based on effective adsorption and sorbent re-use capacity, crystalline Mn_2O_3 was a potentially sustainable sorbent for removal of both As(III) and As(V) from water. Manganese (III) oxide sorbent was also tested for the removal of arsenic from the different coal fly ash leachates (PZ8-3, PZ8-4 and PZ8-5) and the results were compared with arsenic adsorption from a synthetic solution. The analysis showed that the generated ash leachates contained only As (V).

The physical properties of the ash samples showed that all three ash samples were alkaline in nature with pH of more than 7. The XRD results confirmed the presence of crystalline iron (III) oxide and silica in the ash. The surface analysis of ash particles by TEM, SEM and XEDS showed that the ash samples were heterogeneous. A 10 g/L of Mn_2O_3 sorbent was able to remove greater than 98% of arsenic from ash leachates. The Mn_2O_3 sorbent reduced the arsenic concentration from ash leachates below the EPA standard limit in 60 min of contact time. The kinetics experiment showed that adsorption of arsenic was rapid and followed pseudo-second-order kinetics. The Temkin, Langmuir, Freundlich and D-R adsorption models were applied to equilibrium adsorption isotherm data. The adsorption isotherm data were best fitted to the Langmuir isotherm indicating monolayer adsorption process. The results of D-R isotherm model

for the As(V) adsorption onto Mn_2O_3 in PZ8-3, PZ8-4 leachates and synthetic solution indicated that chemical adsorption governed the adsorption of arsenic onto the surface of Mn_2O_3 while in PZ8-5 leachate, the combination of chemisorption and physisorption with the dominant former one governed the arsenic adsorption. In general Mn_2O_3 was found to be a promising adsorbent for uptake and removal of arsenic from ash leachates containing arsenic.

After the preliminary study of different manganese oxides, the development of a manganese oxide coated sand (MCS) as an alternative and potentially sustainable sorbent was investigated and its ability to remove As(V) and As(III) from aqueous solution was studied. For the development process, the source of manganese, the mixing time, combination percentage of aluminum manganese coated sand, pH adjustment versus no pH adjustment coating process and the sorbent calcination time in furnace was optimized with MnCl_2 and AlCl_3 as sources of manganese and aluminum. The 24 hr mixing time was achieved as the optimum mixing time. The synthesis of MCS using 50% MnCl_2 and 50% AlCl_3 was found to be the most effective combination of manganese-aluminum coating solution. A comparable results with no pH adjustment process were obtained for As(V) adsorption, however adjusting the pH of the coating solution improved the As(III) adsorption onto the MCS in general. Although, a higher arsenic removal was obtained by MCS with the calcination time of 5 hr in general, the pH adjusted MCS with maximum calcination time, 24 hr furnace exposure, was also considered as promising sorbent due to comparable arsenic removal efficiency with the 5hr furnace exposed MCS in the more practical solution, solution with the ionic background. Therefore, the 5hr and 24hr furnace exposed MCS obtained from pH adjusted coated solution with MnCl_2 and AlCl_3 as their sources

of manganese and aluminum, respectively was developed as the most efficient sorbents for the As(III) and As(V) removal from aqueous solution. The optimized MCSs were characterized by SEM/EDX and XPS. The SEM images of the 5hr and 24hr furnace exposed MCS indicated the coated sands as a rough coated surface where no uniform coating was visible. Also, the formation of aluminum and manganese oxides was observed in clusters on the surfaces. The Mn, Al, C, O, Si, Na and Cl was achieved as the main constituents of MCS according to the EDAX results. A higher manganese content was observed on 5hr furnace exposed MCS versus the 24hr furnace exposed MCS. The XPS analysis of Al 2p core spectra of the 5hr and 24hr furnace exposed MCS showed the presence of aluminum as Al_2O_3 on both MCSs while the analysis of Mn 2p resulted that the manganese exhibited oxidation between Mn^{3+} and Mn^{4+} with the predominant Mn^{3+} .

The ability of the developed MCSs, 5 hr and 24 hr furnace exposed MCS, in removing As(III) and As(V) from aqueous solution and the effects of adsorbent dosage, contact time, initial solution pH, and co-existing ions on the arsenic removal efficiency by MCSs was investigated in batch system. The zeta potential measurements proved the adsorption of arsenic onto the surface of MCSs and formation of inner-sphere complexes at the surface of MCSs. The results of the co-existing ion effect study showed that phosphate anions exerted the highest negative effect while calcium, bicarbonate and sulfate did not inhibit both As(III) and As(V) adsorption process even though they coexisted at very high concentration. The kinetics experiment showed that for the adsorption of arsenic onto MCS, a two-step mechanism occurs. First a rapid adsorption occurs during the first 60 min after which equilibrium is slowly achieved. The isotherm modeling study

showed that the affinity of As(V) and As(III) to bind with the 5hr furnace exposed MCS in both DI and synthetic solution was higher than the 24hr furnace exposed MCS. The applied sorbents showed comparable affinity to adsorb As(III) versus As(V). The nature of arsenic adsorption process onto 24hr furnace exposed MCS in DI and synthetic solution and 5hr furnace exposed MCS in DI solution was found to be physisorption. The combination of physisorption and chemisorption and with the dominant former one governed the As(III) and As(V) adsorption onto 5hr furnace exposed MCS in DI solution. The maximum adsorption of arsenic was obtained in the pH range from 3.0 to 10.0 suggesting that the MCS can be successfully utilized in drinking water processes and the pH does not need adjustment. In general, the developed 5hr and 24hr furnace exposed MCS was observed as an effective sorbents for rapid removal of arsenite and arsenate from natural waters in the pH range of 3-10 in batch systems. The adsorption capacities of the MCS sorbents are shown in Table 1.

Table 1. Arsenic adsorption capacity of MCS sorbents

| Solution | 5hr MCS | 24hr MCS | Mn₂O₃ | Mn₃O₄ |
|------------------------------|----------------|-----------------|------------------------------------|------------------------------------|
| As(III) + Synthetic Solution | 222 mg/kg | 208 mg/kg | 370 mg/kg | - |
| As(V) + Synthetic Solution | 345 mg/kg | 313 mg/kg | 257 mg/kg | 256 mg/kg |

The ability of developed 5hr and 24hr manganese coated sand (MCS) for removal of arsenic were also tested in a packed column. The breakthrough curves of arsenic from two different column systems occurred after 1050 min for 24hr MCS column and 1439 min for 5hr MCS

column. The corresponding volumes of the synthetic solution treated until breakthrough were 14.4 L for 5hr MCS column and 10.5 L for 24hr MCS column. The point of column exhaustion occurred after 2603 min and 3737 min for 24hr MCS and 5hr MCS, respectively. The 37.4 L and 26.0 L of the synthetic solution were treated until the point of the sorbent exhaustion for 5hr MCS column and 24hr MCS column, respectively. In order to predict the breakthrough curves, two well-known models (Adams–Bohart and Thomas models) were applied. Based on the modeling results, Adam–Bohart model showed a good correlation with experimental data especially with the initial part of breakthrough curves. On the other hand, the results of Thomas model were in a good agreement with experimental data showing its ability for prediction of experimental results in a column study.

2. RECOMMENDATIONS

In order to enhance the adsorption ability of the developed sorbent, different manganese and aluminum sources with different concentration can also be considered. Optimizing the pH of coating solution is also needed to synthesize a more effective sorbent. Adjusting the pH of the coating solution at lower pH will likely improve the arsenic removal efficiency in decreasing the cost of a post-buffering process. The clean sand used as the matrix for the coated sand sorbent may be replaced with the local soil or local clay for applications in water treatment or in the liner system of chemical landfills and coal fly ash disposal facilities, respectively. The ability of the developed MCS sorbent to adsorb other contaminants besides arsenic at the same time from aqueous solutions can also be studied.

CITED LITERATURE

- [1] Abedin,M., Cotter-Howells,J., and Meharg,A.A.: Arsenic uptake and accumulation in rice (*Oryza sativa* L.) irrigated with contaminated water. *Plant and Soil*, 240(2):311-319, 2002.
- [2] Ahmad, A. and Hameed, B.: Fixed-bed adsorption of reactive azo dye onto granular activated carbon prepared from waste. *J. Hazard. Mater*, 175:298–303, 2010.
- [3] AkhtarAhmad,S.,Ullah Sayed,M.H.S.,Shampa,B.,Haque Khan,M.,Faruquee,M.H., Abdul,J., bdul Hadi,S. and Kabir Talukder,H.: Arsenic in drinking water and pregnancy outcomes. *Environmental Health Perspectives*, 109(6):629-631, 2001.
- [4] Aksu,Z. and Gönen,F.: Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves. *Process Biochemistry*, 39:599–613, 2004.
- [5] Alkane, M., Demirbas, O., Celikcapa, S., Dogan, M.: Sorption of acid red 57 from aqueous solution onto sepiolite, *J. Hazard. Mater.* B116: 135– 145, 2004.
- [6] Altundogan,H.S.,Altundogan,S.,Tumen,F. and Bildik,M.: Arsenic removal from aqueous solutions by adsorption on red mud, *Waste Manage.* 20 (8):761–767, 2000.
- [7] Altundogan,H.S.,Altundogan,S.,Tumen,F.,Bildik,M.: Arsenic adsorption from aqueous solutions by activated red mud. *Waste Manage*,22 :357–363,2002.
- [8] American Coal Ash Association, Coal Combustion Product (CCP) Production & Use Survey Results, American Coal Ash Association, 2011, p. 1 - <http://www.acaa-usa.org>.
- [9] An, B., Fu, Z., Xiong, Z., Zhao, D. and SenGupta, A.K.: Synthesis and characterization of a new class of polymeric ligand exchangers for selective removal of arsenate from drinking water. *React. Funct. Polym*, 70:497–507, 2010.
- [10] Ansell, R.O., Dickinson, T. and Povey, A.F.: An X-ray photo-electron spectroscopic study of the films on coloured stainless steel and coloured ‘Nilomag’ alloy 771. *Corros. Sci*,18, 245-256, (1978).
- [11] Aposhian, HV: Biochemical toxicology of arsenic. 1989. Rev Biochem Toxicol. New York, NY: Elsevier/North Holland. 10:265–299, 1989
- [12] Arias, M., Astray,G., Fernández-Calviño,D., García-Río, L., Mejuto, J.C., Nóvoa-Muñoz, J.C. and Pérez-Novo, C.: Sorption behavior of arsenic by iron and aluminum oxides coated quartz particles.*Fresenius Environmental Bulletin*. 17(12a), 2008.
- [13] Arsenic in drinking water (1999). National Research Council. p:193-222. National Academy Press, Washington D.C.

- [14] ATSDR, Agency for Toxic Substances and Disease Registry. 2007. Toxicological profile for arsenic. Draft for Public Comment. Atlanta GA [updated 2007 August, accessed 2008 January 14]. Available from: <http://www.atsdr.cdc.gov/toxprofiles/tp2.html>.
- [15] Aydin, H. and Baysal, G.: Adsorption of acid dyes in aqueous solutions by shells of bittim (*Pistacia khinjuk* stocks). *Desalination*, 196:248–259,2006.
- [16] Badruddoza,A.Z.M.,Shawon,Z.B.Z., Rahman,M.T.,Hao,K.W.,Hidajat,K. and Uddin,M.S.: Ionically modified magnetic nanomaterials for arsenic and chromium removal from water .*Chem. Eng. J.* 225:607–615, 2013.
- [17] Badruzzaman,M.,Westerhoff,P.,Knappe,D.R.U.: Intraparticle diffusion and adsorption of arsenate onto granular ferric hydroxide (GFH). *Water Res*,38 (18):4002–4012,2004.
- [18] Bajpai, S. V., and Chaudhuri, M.: Removal of arsenic from ground water by manganese dioxide-coated sand. *J. Environ. Eng.*, 125(8):782–784, 1999.
- [19] Bang, S.,Patel,M.,Lippincott,L.,Meng,X.: Removal of arsenic from groundwater by granular titanium dioxide adsorbent. *Chemosphere* ,60 (3):389–397, 2005.
- [20] Basu,T. and Ghosh,U.C.: Nano-structured iron(III)–cerium(IV) mixed oxide: Synthesis, characterization and arsenic sorption kinetics in the presence of co-existing ions aiming to apply for high arsenic groundwater treatment. *Applied Surface Science.*, 283 : 471–481, 2013.
- [21] Basu,T., Gupta,K., Ghosh,U.C.: Performances of As(V) adsorption of calcined (250 °C) synthetic iron(III)–aluminum(III) mixed oxide in the presence of some groundwater occurring ions. *Chem. Eng. J.*,183(15):303–314,2012.
- [22] Bekci, Z., Ozveri,C., Seki,Y., Yurdakoc,K.: Sorption of malachite green on chitosan bead. *J. Hazard. Mater*, 154:254–261, 2008.
- [23] Benefield, L.D., Judkins, J.F. and Weand, B.L.: Process Chemistry for Water and Wastewater Treatment Prentice Hall. *Englewood Cliffs*, NJ (1982).
- [24] Benjamin, M.M., Sletten, R.S., Bailey, R.P. and Bennett, T.: Sorption and filtration of metals using iron oxide-coated sand. *Water Res*, 30 (11): 2609–2620, 1996.
- [25] Berg,M.,Tran,H.C.,Nguyen,T.C.,Pham,H.V.,Schertenleib,R.and Giger,W.:Arsenic contamination of groundwater and drinking water in Vietnam: a human health threat. *Environ. Sci. Technol.* 35 (13):2621– 2626, 2001.
- [26] Bissen, M. and Frimmel, F.H.: Arsenic- a review. Part II: Oxidation of arsenic and its removal in water treatment. *Acta Hydrochimica Hydrobiology*, 31(2): 97-107, 2003.
- [27] Blanchard, G. and Maunaye, M., Martin, G.: Removal of heavy metals from waters by means of natural zeolites. *Water Res*,18:1501- 1507, 1984.

- [28] Boddu, VM., Abburi, K., Talbott, J.L., Smith, E.D. and Haasch, R.: Removal of arsenic(III) and arsenic(V) from aqueous medium using chitosan-coated biosorbent. *Water Res.*, 42:633-642, 2008.
- [29] Howell, R.J.: Sorption of arsenic by iron oxides and oxyhydroxides in soils. *Appl. Geochem.*, 9 (3):279–286, 1994.
- [30] Brandhuber, P. and Amy, G.: Alternative methods for membrane filtration of arsenic from drinking water. *Desalination*, 140: 1-14, 2001.
- [31] Bundschuh, J., Farias, B., Martin, R., Storniolo, A., Bhattacharya, P., Cortes, J., Bonorino, G. and Albouy, R.: Groundwater arsenic in the ChacoPampean Plain, Argentina: case study from Robles county, Santiago del Estero Province. *Appl. Geochem.* 19 (2):231–243, 2004.
- [32] Caceres, D.D., Pino, P., Montesinos, N., Atalah, E., Amigo, H. and Loomis, D.: Exposure to inorganic arsenic in drinking water and total urinary arsenic concentration in a Chilean population. *Environ. Res.*, 98 (2):151–159, 2005.
- [33] Cebrian, M.E., Albores, A., Aguilar, M. and Blakely, E.: Chronic arsenic poisoning in the North of Mexico. *Hum. Toxicol*, 2 :121–133, 1983.
- [34] Chakraborti, D., Sengupta, M.K., Rahman, M.M., Ahamed, S., Chowdhury, U.K. and Hossain, M.A.: Groundwater arsenic contamination and its health effects in the Ganga–Meghna–Brahmaputra plain. *J. Environ. Monit*, 6 (6) : 74–83, 2004.
- [35] Chakraborty, S., Dureja, V., Bhattacharya, G., Maity, S. and Bhattacharjee, S.: Removal of arsenic from ground water using low cost ferruginous manganese ore. *Water. Res.*, 36(3): 625-632, 2002.
- [36] Chammui, Y., Sooksamiti, P., Naksataa, W., Thiansema, S. and Arqueropanyo, O.: Removal of arsenic from aqueous solution by adsorption on Leonardite. *Chem. Eng. J.*, 240:202–210, 2014.
- [37] Chandra, V., Park, J., Chun, Y., Lee, J.W., Hwang, I.C., Kim, K.S.: Water-dispersible magnetite-reduced graphene oxide composites for arsenic removal. *ACS Nano*, 4(7):3979–3986, 2010.
- [38] Chang, Y.Y., Kim, K.S., Jung, J.H., Yang, J.K. and Lee, S.M.: Application of iron-coated sand and manganese-coated sand on the treatment of both As(III) and As(V). *Water Science & Technology*, 55(1–2):69–75, 2007.
- [39] Chang, Y.Y., Song, K.H. and Yang, J.K.: Removal of As(III) in a column reactor packed with iron-coated sand and manganese-coated sand. *J. Hazard. Mater.* 150(3): 565–572, 2008.
- [40] Chatterjee, A., Das, D., Mandal, B.K., Chowdhury, T.R., Samanta, G. and Chakraborty, D.: Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 1. Arsenic species in drinking water and urine of the affected people. *Analyst*, 120:643–656, 1995.

- [41] Cheng, R.C.; Liang, S.; Wang, H. and Beuhler, M.D.: Enhanced coagulation for arsenic removal. *J. Am. Water Works Ass*, 86(9):79-90, 1994.
- [42] Cheunga,W.H., Szetob, Y.S., McKay, G.: Intraparticle diffusion processes during acid dye adsorption onto chitosan. *Bioresource Technology*, 98(15):2897–2904, 2007.
- [43] Choong, T.S.Y., Chuah, T., Robiah, Y., Gregory Koay, F. and Azni, I.: Arsenic toxicity, health hazards and removal techniques from water: an overview. *Desalination*, 217:139–166, 2007.
- [44] Chuang,C.L.,Fan, M.,Xu, M.,Brown,R.C.,Sung,S.,Saha,B. and Huang, C.P.: Adsorption of arsenic(V) by activated carbon prepared from oat hulls.*Chemosphere*, 61 (4):478–483,2005.
- [45] Clifford, D. and Lin, CC.: Arsenic (III) and arsenic (V) removal from drinking water in San Ysidro, New Mexico, EPAy 600yS2-91y011, US EPA, Cincinnati 199.
- [46] Clifford, D.A. and C.C. Lin.: Ion Exchange, Activated Alumina, and Membrane Processes for Arsenic Removal from Groundwater, Proceedings of the 45th Annual Environmental Engineering Conference, University of Kansas, February 199. 1995.
- [47] Criscuoli, A., Majumdar, S., Figoli, A., Sahoo, G.C., Bafaro, P., Bandyopadhyay, S. and Drioli, E.: As(III) oxidation by MnO₂ coated PEEK-WC nanostructured capsules. *J. Hazard. Mater.* 211–212:281–287, 2012.
- [48] Cullen,W.R. and Reimer,K.J.: Arsenic speciation in the environment. Chemical review, 89:713-764,1989.
- [49] Dambies, L.,Vincent, T. and Guibal, E.:Treatment of arsenic-containing solutions using chitosan derivatives: uptake mechanism and sorption performance. *Water Res*, 36 :3699–3710, 2002.
- [50] D'Arcy, M., Weiss,D.,Bluck,M. and Vilar,R.: Adsorption kinetics, capacity and mechanism of arsenate and phosphate on a bifunctional TiO₂–Fe₂O₃ bi-composite. *J. Colloid Interf. Sci*, 364:205–212, 2011.
- [51] Das,D.,Chatterjee,A.,Mandal,B.K.,Samanta,G.,Chakroborty,D. and Chanda,B.: Arsenic in groundwater in six districts of West Bengal, India: the biggest arsenic calamity in the world. Part 2. Arsenic concentration in drinking water, hair, nails, urine, skin-scales and liver tissues (biopsy) of the affected people. *Analyst* ,120 :917–924,1995.
- [52] Davies, S.H.R. and Morgan, J.J.: Manganese (II) oxidation kinetics on metal oxide surfaces. *J. Colloid Interf. Sci.* 29:63–77, 1989.
- [53] Deschamps,E.,Ciminelli,V.S.T.,Weidler,P.G.,Ramos,A.Y.: Arsenic sorption onto soils enriched with manganese and iron mineral. *Clays clay Miner*, 51: 197-204, 2003.

- [54] Dias, A., Sa, R.G., Spitale, M.C., Athayde, M. and Ciminelli, V.S.T.: Microwave-hydrothermal synthesis of nanostructured Na-birnessites and phase transformation by arsenic(III) oxidation. *Materials Research Bulletin*. 43:1528-1538, 2008.
- [55] Dodd, M.C., Vu, N.D., Ammann, A., Le, V.C., Kissner, R., Pham, H.V., Cao, T.H., Berg, M. and von Gunten, U., Kinetics and mechanistic aspects of As(III) oxidation by aqueous chlorine, chloramines, and ozone: relevance to drinking water treatment. *Environ. Sci. Technol*, 40:3285–3292, 2006.
- [56] Donia, A.M., Atia, A.A. and Mabrouk, D.A.: Fast kinetic and efficient removal of As(V) from aqueous solution using anion exchange resins. *J. Hazard. Mater*, 191:1–7, 2011.
- [57] Doua, X., Zhang, Y., Zhao, B., Wu, X., Wu, Z. and Yang, M.: Arsenate adsorption on an Fe–Ce bimetal oxide adsorbent: EXAFS study and surface complexation modeling. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 379:109–115, 2011.
- [58] Dousov, B., Grygar, T., Martaus, A., Fuitov, L., Koloušek, D. and Machovi, V.: Sorption of As(V) on aluminosilicates treated with Fe(II) nanoparticles. *J. Colloid Interf. Sci.*, 302 (2): 424–431, 2006.
- [59] Driehaus, W., Seith, R., and Jekel, M.: Oxidation of arsenite(III) with manganese oxides in water treatment. *Water Res.*, 29(1):297–305, 1995.
- [60] Dubinin, M.M. and Radushkevich, L.V.: Equation of the characteristic curve of activated charcoal. *Chem. Zentr.* 1:875, 1947.
- [61] Dutta, P.K., Ray, A.K., Sharma, V.K. and Millero, F.J.: Adsorption of arsenate and arsenite on titanium dioxide suspensions. *J. Colloid Interf. Sci.* 278:270–275, 2004.
- [62] Edwards, M.: Chemistry of arsenic removal during coagulation and Fe-Mn oxidation, *Water Works Assoc.* 86(9): 64-78, 1994.
- [63] Eguez, H.E., Cho, E.H.: Adsorption of arsenic on activated charcoal, *J. Metals*, 39:38–41, 1987.
- [64] Elizalde-Gonzalez, M.P., Mattusch, J. and Einicke, W.D., Wennrich, R.: Sorption on natural solids for arsenic removal. *Chem. Eng. J.* 81:187–195, 2001.
- [65] Elizalde-Gonzalez, M.P., Mattusch, J., and Wennrich, R.: Application of natural zeolites for preconcentration of arsenic species in water samples. *J. Environ. Monit.*, 3(1):22-26, 2001.
- [66] EPA. Implementation guidance for the arsenic rule. EPA report-816-D-02-005, Cincinnati, USA, 1998.
- [67] Ferguson, M.A., Hoffmann, M.R. and Hering, J.G.: TiO₂-Photocatalyzed As(III) Oxidation in Aqueous Suspensions: Reaction Kinetics and Effects of Adsorption. *Environ. Sci. Technol.* 39:1880–1886, 2005.

- [68] Ferguson, J.F. and Gavis, J.: A review of the arsenic cycle in natural waters. *Water Res.* (11):1259-1274, 1972.
- [69] Figoli, A., Cassano, A., Criscuoli, A., Mozumder, M.S.I., Uddin, M.T., Islam, M.A. and Drioli, E.: Influence of operating parameters on the arsenic removal by nanofiltration. *Water Res.* 44:97–104, 2010.
- [70] Finkelman, R.B., 1995. Modes of occurrence of environmentally-sensitive trace elements in coal. In: Swaine, D.J., Goodarzi, F. (Eds.), *Environmental Aspects of Trace Elements in Coal*. Springer.
- [71] Frau, F., Addari, D., Atzei, D., Biddau, R., Cidu, R. and Rossi, A.: Influence of Major Anions on As(V) Adsorption by Synthetic 2-line Ferrihydrite. Kinetic Investigation and XPS Study of the Competitive Effect of Bicarbonate. *Water Air Soil Pollut.* 205(2010) 25–41.
- [72] Freundlich, H.M.F.: Über die adsorption in losungen, *Z. Phys. Chem.* 57A :385-470, 1906.
- [73] Gallagher, P.A.; Schewegel, C.A.; Wei, X. and Creed, J.T.: Speciation and preservation of inorganic arsenic in drinking water sources using EDTA with IC separation and ICP-MS detection. *Journal of Environmental Monitoring*, 3: 371-376, 2001.
- [74] Gao, Y. and Mucci, A.: Individual and competitive adsorption of phosphate and arsenate on goethite in artificial seawater. *Chem. Geol.* 199:91–109, 2003.
- [75] Genç-Fuhrman, H., Bregnhøj, H. and McConchie, D.: Arsenate removal from water using sand–red mud columns. *Water Res.* 39(13):2944–2954, 2005.
- [76] Genç-Fuhrman, H., Tjell, J.C. and McConchie, D.: Adsorption of arsenic from water using activated neutralised red mud. *Environ. Sci. Technol.* 38:2428-2434, 2004.
- [77] Ghurye, G. and Clifford, D.: As(III) oxidation using chemical and solid-phase oxidants. *J. Am. Water Works Ass.* 96 (1):84–96, 2004.
- [78] Ghurye, G., Clifford, D. and Tripp, A.: Iron coagulation and direct microfiltration to remove arsenic from groundwater. *J. Am. Water Works Ass.* 96 (4):143–152, 2004.
- [79] Giles, D.E., Mohapatra, M., Issa, T.B., Ananda, S., Singh, P.: Iron and aluminium based adsorption strategies for removing arsenic from water. *Journal of Environmental Management.* 92(12):3011–3022, 2011.
- [80] Goel, J., Kadirvelu, K., Rajagopal, C. and Garg, V.K.: Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies. *J. Hazard. Mater.* B125: 211–220, 2005.
- [81] Gregor, J.: Arsenic removal during conventional aluminum-based drinking-water treatment. *Water Res.* 35(7):1659-1664, 2001.

- [82] Grossl, P.R., Eick, M., Sparks, D.L., Goldberg, S. and Anisworth, C.C.: Arsenate and chromate retention mechanism on goethite. 2. Kinetic evaluation using pressure-jump relaxation technique. *Environ. Sci. Technol.*, 31(2):321-326, 1997.
- [83] Gu, Z., Fang, J. and Deng, B.: Preparation and evaluation of GAC-based iron-containing adsorbents for arsenic removal. *Environ. Sci. Technol.*, 39 (10):3833-3843, 2005.
- [84] Guidelines for Drinking-Water Quality, vol. 1, third ed., World Health Organization, 2008, p. 491.
- [85] Gulens, J. and Champ, D.R.: Influence of redox environments on the mobility of arsenic in ground water. *Chemical modelling in aqueous systems*: 81-95, 1979.
- [86] Gupta, K., Maity, A. and Ghosh, U.C.: Manganese associated nanoparticles agglomerate of iron(III) oxide: Synthesis, characterization and arsenic(III) sorption behavior with mechanism. *J. Hazard. Mater.* 184:832-842, 2010.
- [87] Gupta, V.K., Saini, V.K. and Jain, N.: Adsorption of As(III) from aqueous solutions by iron oxide-coated sand. *J. Colloid Interf. Sci.*, 288(1):55-60, 2005.
- [88] Gupta, K., Bhattacharyya, S., Chattopadhyay, D., Mukhopadhyay, A., Biswas, H., Dutt, J., Ranjan Ray, D., N. and Ghosh, U.C.: Ceria associated manganese oxide nanoparticles: Synthesis, characterization and arsenic(V) sorption behavior. *Chem. Eng. J.*, 172 (1):219-229, 2011.
- [89] Han, R.P., Zou, L.N., Zhao, X., Xu, Y.F., Xu, F., Li, Y.L. and Wang, Y.: Characterization and properties of iron oxide-coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column. *Chem. Eng. J.*, 149:123-131, 2009.
- [90] Han, R., Zou, W., Zhang, Z., Shi, J. and Yang, J.: Removal of copper (II) and lead(II) from aqueous solution by manganese oxide coated sand: I. Characterization and kinetic study. *J. Hazard Mater.*, 137(1):384-395, 2006.
- [91] Harvey, C.F., Swartz, C.H., Badruzzaman, A.B.M., Keon-Blute, N., Yu, W., Ali, M.A., Jay, J., Beckie, R., Niedan, V., Brabander, D., Oates, P.M., Ashfaq, K.N., Islam, S., Hemond, H.F. and Ahmed, M.F.: Arsenic mobility and groundwater extraction in Bangladesh. *Science*, 298:1602-1606, 2002.
- [92] He, Y.T., Hering, J.G.: Enhancement of arsenic(III) sequestration by manganese oxides in the presence of iron(II). *Water Air Soil Pollut.* 203:359-368, 2009.
- [93] Hering, J.G.; Chen, P.Y.; Wilkie, J.A. and Elimelech, M.: Arsenic removal from drinking water during coagulation. *J. of Env. Eng.*, 123(8):800-807, 1997.
- [94] Hering, J.G.; Chen, P.Y.; Wilkie, J.A.; Elimelech, M. and Liang, S.: Arsenic removal by ferric chloride. *J. Am. Water Works Ass.*, 88(4):155-167, 1996.

- [95] Hering, J.G. and Dixit, S.: Contrasting Sorption Behavior of Arsenic(III) and Arsenic(V) in Suspensions of Iron and Aluminum Oxyhydroxides. *ACS Symp. Ser.*, 915:8–24, 2005.
- [96] Hlavay, J. and Polyak, K.: Determination of surface properties of iron hydroxide-coated alumina adsorbent prepared for removal of arsenic from drinking water. *J. Colloid Interf. Sci.*, 284 (1): 71–77, 2005.
- [97] Ho, Y.-S. and McKay, G.: Pseudo-second order model for sorption processes. *Process Biochem*, 34:451–465, 1999.
- [98] Ho, Y.S. and McKay, G.: The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat. *Can. J. Chem. Eng.*, 76:822–827, 1998.
- [99] Ho, Y.S., Porter, J.F. and McKay, G.: Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Water Air Soil Pollut.*, 141(1-4):1-33, 2002.
- [100] Ho, Y.S.: Removal of copper ions from aqueous solution by tree fern. *Water. Res.*, 37(10):2323–2330, 2003.
- [101] Ho, Y.S. and Mackay, G.: The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.* 34:735–742, 2000.
- [102] Ho, Y.S.: Review of second-order models for adsorption systems. *J. Hazard. Mater.*, B136:681–689, 2006.
- [103] Hodi, M., Polyak, K. and Hlavay, J.: Removal of pollutants for drinking water by combined ion-exchange and adsorption methods. *Environ. Int.* 21:325–331, 1995.
- [104] Holm, T.R.: Effects of CO₃²⁻/bicarbonate, Si, and PO₄³⁻ on arsenic sorption to HFO. *J. Am. Water Works Ass.*, 94(4):174–181, 2002.
- [105] Huang, C., Ke, Q., Costa, M. and Shi, X.: Molecular mechanisms of arsenic carcinogenesis. *Mol Cell Biochem*, 255(1-2): 57–66, 2004.
- [106] Huang, Y.-H., Shih, Y.-J. and Cheng, F.-J.: Novel KMnO₄- modified iron oxide for effective arsenite removal. *J. Hazard. Mater*, 198, (2011)1–6.
- [107] Huffman, G.P., Huggins F.E., Shah N. and Zhao, J.: Speciation of arsenic and chromium in coal and combustion ash by XAFS spectroscopy. *Fuel Processing Technology*. 39:47–62, 1994.
- [108] Huggins, F.E. and Huffman, G.P.: X-ray Absorption Fine Structure (XAFS) Spectroscopic Characterization of Emissions from Combustion of Fossil Fuels. *International Journal of the Society of Materials Engineering for Resources*, 10, 1–13. 2002.
- [109] Huggins, F.E., Shah, N., Huffman, G.P. and Robertson, J.D.: XAFS spectroscopic characterization of elements in combustion ash and fine particulate matter. *Fuel Processing Technology*, 65–66:203–218, 2000.

- [110] Ishinishi, N., Tsuchiya, K., Vahter, M. and Fowler, B.A.: Arsenic. In: Friberg L, Nordberg GF, Vouk V, eds. Handbook on the toxicology of metals. Amsterdam, NL: Elsevier Science. 1986
- [111] Islam, M., Mishra, P.C. and Patel, R.: Fluoride adsorption from aqueous solution by a hybrid thorium phosphate composite. *Chem. Eng. J.* ,166(3):978-985, 2011.
- [112] Izquierdo, M. and Querol, X.: Leaching behaviour of elements from coal combustion fly ash: An overview. *International Journal of Coal Geology* .,94:54–66, 2012.
- [113] Jacukowicz-Sobala, I., Ociński, D. and Kociólek-Balawejder, E.: Synthesis and Evaluation of a Novel Hybrid Polymer Containing Manganese and Iron Oxides as a Sorbent for As(III) and As(V) Removal. *Ind. Eng. Chem. Res.* 52:6453–6461, 2013.
- [114] Jain, A., Raven, K.P. And Loeppert, R.H.: Arsenite and Arsenate adsorption on ferrihydrite: surface charge reduction and net OH⁻ release stoichiometry. *Environ. Sci. Technol.*, 33(8) :1179-1184. 1999.
- [115] Jain, C.K. and Ali, I.: Arsenic: occurrence, toxicity and speciation techniques, *Water Res.* 34 :4304–4312, 2000.
- [116] Jain, A. and Loeppert, R.H.: Effect of competing ions on the adsorption of arsenate and arsenite by ferrihydrite. *J. Environ. Qual.* 29:1422-1430, 2000.
- [117] Jang, M., Shin, E.W., Park, J.K., Choi, S.I.: Mechanisms of arsenate adsorption by highly-ordered nano-structured silicate media impregnated with metal oxides. *Environ. Sci. Technol.* 37 (21): 5062– 5070, 2003.
- [118] Jeong Y., Fan M. and Li N., 2005. The adsorption of arsenic (V) by iron and aluminum oxides [D]. Ph. D Dissertation, Iowa State University, USA.
- [119] Jimenez-Cedillo, M.J, Olguin, M.T., Fall, Ch. and Colin, A.: Adsorption capacity of iron- or iron-manganese-modified zeolite-rich tuffs for As(III) and As(V) water pollutants. *Appl Clay Sci.* 54:206-216, 2011.
- [120] Jones, D.R., 1995. The leaching of major and trace elements from coal ash. In Environmental Aspects of Trace Elements in Coal: Swaine, D.J., Goodarzi, F. (Eds.), Springer.
- [121] Jong, T. and Parry, D.L.: Removal of sulfate and heavy metals by sulfate reducing bacteria in short-term bench scale Upflow anaerobic bed reactor runs. *Water Res.* 37:3379- 3389, 2003.
- [122] Jubinka, L. and Rajakovic, V.: The sorption of arsenic onto activated carbon impregnated with metallic silver and copper. *Sep. Sci. Technol.* 27 (11) :1423–1433, 1992.
- [123] Kabata-Pendias, A., Pendias, H.: Trace elements in soils and plants, CRC Press, Boca Raton, FL, 2000.

- [124] Kanel, S.R., Manning, B., Cha, Q., Li, L., Choi, H.: Removal of arsenic(III) from groundwater by nanoscale zero-valent iron. *Environ. Sci. Technol.*, 39 (5):1291–1298., 2005.
- [125] Kang, Y., Liu, G., Chou, C-L, Wong, M.H., Zheng, L., Ding, R.: Arsenic in Chinese coals: Distribution, modes of occurrence, and environmental effects. *Sci. Total Environ.*, 412-413:1–13, 2011.
- [126] Kapaj, S., Peterson, H., Liber, K. and Bhattacharya, P.: Human Health Effects From Chronic Arsenic Poisoning—A Review. *J. Environ. Sci. Health Part A*, 41(10):2399-2428, 2006.
- [127] Karim, A.H., Jalil, A.A., Triwahyono, S., Sidik, S.M., Kamarudin, N.H.N., Jusoh, R., Jusoh, N.W.C. and Hameed, B.H: Amino modified mesostructured silica nanoparticles for efficient adsorption of methylene blue. *J. Colloid Interf. Sci.*, 386 (1):307-314, 2012.
- [128] Kartinen, E.O. and Martin, C.J.: An overview of arsenic removal processes. *Desalination*, 103:79–88, 1995.
- [129] Katsoyiannis, I.A. and Zouboulis, A.I.: Biological treatment of Mn(II) and Fe(II) containing groundwater: kinetic considerations and product characterization. *Water Res.* 38:1922–1932, 2004.
- [130] Khodadoust, A.P., Naithani, P., Theis, T. L., and Murarka, I.P.: Leaching Characteristics of Arsenic from Aged Alkaline Coal Fly Ash Using Column and Sequential Batch Leaching. *Ind. Eng. Chem. Res.*, 50:2204–2213, 2011.
- [131] Kim, M.J. and Nriagu, J.: Oxidation of arsenite in groundwater using ozone and oxygen. *Sci. Total Environ.* 247:71–79, 2000.
- [132] Kim, M.J.: Separation of inorganic arsenic species in groundwater using ion exchange method. *Bull. Environ. Contam. Toxicol.* 67:46–51, 2001.
- [133] Kipping, M.D., in: J. Lenihan, W.W. Fletcher (Eds.), Arsenic, the Chemical Environment, Environment and Man. *Glasgow*, 6:93–110, 1997.
- [134] Kocabas-Atakl, Z.Ö. and Yürüm, Y.: Synthesis and characterization of anatase nano-adsorbent and application in removal of lead, copper and arsenic from water. *Chem. Eng. J.* 225: 625–635, 2013.
- [135] Kumar, P.A. and Chakraborty, S.: Fixed-bed column study for hexavalent chromium removal and recovery by short-chain polyaniline synthesized on jute fiber. *J. Hazard. Mater.*, 162, 1086–1098, 2009.
- [136] Kumpiene, J., Lagerkvist, A. and Maurice, C.: Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments –A review. *Waste Management*, 28:215–225, 2008.

- [137] Kundu, S. and Gupta, A.K.: Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC). *J. Colloid Interf. Sci.*, 290:52–60, 2005.
- [138] Kundu, S. and Gupta, A.K.: Adsorptive removal of As(III) from aqueous solution using iron oxide coated cement (IOCC): evaluation of kinetic, equilibrium and thermodynamic models. *Sep. Purif. Technol.*, 52 (2):165–172, 2006.
- [139] Kundu, S., Kavalakatt, S.S., Pal, A., Ghosh, S.K., Mandal, M., Pal, T.: Removal of arsenic using hardened paste of Portland cement: batch adsorption and column study. *Water Res.* 38 (17):3780–3790, 2004.
- [140] Kunzru, S. and Chaudhuri, M.: Manganese amended activated alumina for adsorption/oxidation of arsenic. *J. Environ. Eng.* 131(9):1350–1353, 2005.
- [141] Kuriakose, S., Singh, T.S. and Pant, K.K.: Adsorption of As(III) from aqueous solution onto iron oxide impregnated activated alumina. *Water Qual. Res. J. Can.*, 39 (3):258–266, 2004.
- [142] Ladeira, A.C.Q., Ciminelli, V.S.T.: Adsorption and desorption of arsenic on an oxisol and its constituents. *Water Res.*, 38 (8): 2087–2094, 2004.
- [143] Lagergren, S.: Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska Vetenskapsakademiens. Handlingar*, Band 24:1-39, 1898.
- [144] Lakshmipathiraj, P., Narasimhan, B.R.V., Prabhakar, S. and BhaskarRaju, G.: Adsorption studies of arsenic on Mn-substituted iron oxyhydroxide. *J. Colloid Interf. Sci.*, 304(2):317–322, 2006.
- [145] Langmuir, I.: The constitution and fundamental properties of solids and liquids. *J. Amer. Chem. Soc.* 38:2221–2295, 1916.
- [146] Lee, S.M., Kim, W.G., Yang, J.K. and Tiwari, D.: Sorption behaviour of manganese-coated calcined-starfish and manganese-coated sand for Mn(II). *Environ. Technol.*, 31:445–453, 2010.
- [147] Lenoble, V., Bouras, O., Deluchat, V., Serpaud, B. and Bollinger J.-C.: Arsenic adsorption onto pillared clays and iron oxides. *J. Colloid Interf. Sci.* 255 (1):52–58, 2002.
- [148] Lenoble, V., Laclautre, C., Serpaud, B., Deluchat, V. and Bollinger, J.C.: As(V) retention and As(III) simultaneous oxidation and removal on a MnO₂-loaded polystyrene resin. *Sci Total Environ.*, 326(1-3):197–207, 2004.
- [149] Lenoble, V., Laclautre, C., Deluchat, V., Serpaud, B. and Bollinger, J.-C.: Arsenic removal by adsorption on iron(III) phosphate. *J. Hazard. Mater.*, 123 (1–3):262–268, 2005.
- [150] Leupin, O.X. and Hug, S.J.: Oxidation and removal of arsenic(III) from aerated groundwater by filtration through sand and zero-valent iron. *Water Res.* 39:1729–1740, 2005.

- [151] Li,R.,Li,Q.,Gao,S. and Shang,J.K.: Exceptional arsenic adsorption performance of hydrous cerium oxide nanoparticles: Part A. Adsorption capacity and mechanism. *Chem.Eng.J.*,185–186 :127-135,2012.
- [152] Li,X.,Qi,Y.,Li,Y.,Zhang,Y.,He,X., Wang,Y.: Novel magnetic beads based on sodium alginate gel crosslinked by zirconium(IV) and their effective removal for Pb²⁺ in aqueous solutions by using a batch and continuous systems .*Bioresource Technology* ,142:611–619, 2013.
- [153] Lim, A.P. and Aris, A.Z.: Continuous fixed-bed column study and adsorption modeling: Removal of cadmium (II) and lead (II) ions in aqueous solution by dead calcareous skeletons. *Biochemical Engineering Journal*,87:50–61,2014.
- [154] Lin,T.-F.,Wu,J.-K.: Adsorption of arsenite and arsenate within activated alumina grains: equilibrium and kinetics. *Water Res*, 35 (8):2049–2057, 2001.
- [155] Liu,J., Zheng,B., Aposhian,H.V., Zhou,Y., Chen,M.L., Zhang,A. and Waalkes,M.P.:Chronic Arsenic Poisoning from Burning High-Arsenic-Containing Coal in Guizhou, China. *Environmental Health Perspectives - New Series*, 110(2):119-122,2002.
- [156] Liu,J-S. and Hu,Y.: Characterization of Manganese Oxides/Au Nanocompsite Thin Films for Supercapacitor. *Int. J. Electrochem. Sci.*, 8:9231–9241, 2013.
- [157] Lodeiro, P., Kwan,S.M., Perez,J.T.,González,L.F.,Gérente,C.,Andrès,Y. and McKay,G.: Novel Fe loaded activated carbons with tailored properties for As(V) removal: Adsorption study correlated with carbon surface chemistry .*Chem. Eng. J.* ,215–216 :105–112,2013.
- [158] Lorenzen,L.,van Deventer,J.S.J. and Landi,W.M.: Factors affecting the mechanism of the adsorption of arsenic species on activated carbon. *Miner. Eng*, 8 (45):557–569, 1995.
- [159] Luo,X., Wang,X., Luo,S., Dong,R., Tu,X. and Zeng,G.: Adsorption of As (III) and As(V) from water using magnetite Fe₃O₄-reduced graphite oxide–MnO₂ nanocomposites. *Chem.Eng. J.*,187: 45–52,2012.
- [160] Maji,S.K, Pal,A. and Pal,T.: Arsenic removal from real-life groundwater by adsorption on laterite soil. *J. Hazard. Mater*, 151:811–820, 2008.
- [161] Maliyekkal,S.M., Philip,L. and Pradeep,T.: As(III) removal from drinking water using manganese oxide-coated-alumina: Performance evaluation and mechanistic details of surface binding. *Chem. Eng. J.* 153:101–107, 2009.
- [162] Maliyekkal,S.M., Sharma,A.K and Phili,L.: Manganese-oxide-coated alumina: A promising sorbent for defluoridation of water. *Water Res.*, 40:3497–3506, 2006.
- [163] Mandal, B.K. and Suzuki, K.T.: Arsenic round the world: a review, *Talanta*, 58:201–235, 2002.

- [164] Mane, V.S. and Babu, P.V.V.: Studies on the adsorption of Brilliant Green dye from aqueous solution onto low-cost NaOH treated saw dust. *Desalination*, 273:321–329, 2011.
- [165] Manna, B.R., Dey, S., Debnath, S. and Ghosh, U.C.: Removal of arsenic from groundwater using crystalline hydrous ferric oxide (CHFO). *Water Qual. Res. J. Canada*, 38:193–210, 2003.
- [166] Manning, B.A., Fendorf, S.E., Bostick, B. and Suarez, D.L.: Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.*, 36(5):976–981, 2002.
- [167] Manning, B.A., Goldberg, S.: Arsenic(III) and arsenic(V) adsorption on three California soils. *Soil Sci.*, 162 (12) :886–895, 1997.
- [168] Manning, B.A., Fendorf, S.E. and Goldberg, S.: Surface Structures and Stability of Arsenic(III) on Goethite: Spectroscopic Evidence for Inner-Sphere Complexes *Environ. Sci. Technol.* 32:2383–2388, 1998.
- [169] Martinson, C.A. and Reddy, K.J.: Adsorption of arsenic(III) and arsenic(V) by cupric oxide nanoparticles. *J Colloid Interface Sci.* 336 (2009) 406–411.
- [170] Masscheleyn, P.H., Delaune, R.D. and Patrick, W.H. Jr.: Effect of Redox Potential and pH on Arsenic Speciation and Solubility in a Contaminated Soil. *Environ. Sci. Technol.*, 25:1414–1419, 1991.
- [171] Matschullat, J.: Arsenic in the geosphere-a review. *Sci Total Environ.*, 249(1-3):297–312, 2000.
- [172] McNeill, L. S. and Edwards, M.: Soluble arsenic removal at water treatment plants. *J. Am. Water Works Ass.*, 87(4):105–113, 1995.
- [173] McNeill, L.S. and Edwards, M.: Arsenic removal during precipitate softening. *J. Am. Water Works Ass.*, 89(1):75–86, 1997.
- [174] Meng, X., Korfiatis, G.P., Bang, S. and Bang, K.W. Combined effects of anions on arsenic removal by iron hydroxides. *Toxicol Lett*, 133: 103 –111, 2002.
- [175] Meng, M., Feng, Y., Zhang, M., Liu, Y., Ji, Y., Wang, J., Wu, Y. and Yan, Y.: Highly efficient adsorption of salicylic acid from aqueous solution by wollastonite-based imprinted adsorbent: A fixed-bed column study. *Chem. Eng. J.* 225:331–339, 2013.
- [176] Min, S.Y., Kim, B.K., Park, S.J., Chang, Y.Y., and Yang, J.K., Removal Efficiency of Arsenic by Adsorbents having Different Type of Metal Oxides. *Environ. Eng. Res.*, 14(2):134–139, 2009.
- [177] Mohammad, S.: Arsenic chemistry in soils: an overview of thermodynamic predictions and field observations. *Water Air Soil Poll.* 93: 117–136, 1997.
- [178] Mohan, D., Pittman, C.: Arsenic removal from water/wastewater using adsorbent-A critical review. *J Hazard Mater.*, 142(1-2):1–53, 2007.

- [179] Mohan,D.,Pittman, C.U. Jr., Bricka, M., Smith, F.,Yancey, B., Mohammad,J.,Steele, P.H., Alexandre-Franco, M.F., Serrano,V.G. and Gong, H.: Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interf. Sci*,310: 57–73,2007.
- [180] Mok,W.M., and Wai,C.M.: Mobilization of arsenic in contaminated river waters. Arsenic in the environment. Part I: Cycling and characterization, J. O. Nriagu, ed., Wiley, New York, 99–117,1994.
- [181] Mondal, P.,Balomajumder,C. and Mohanty,B.: A laboratory study for the treatment of arsenic, iron, and manganese bearing ground water using Fe³⁺ impregnated activated carbon: effects of shaking time, pH and temperature. *J. Hazard. Mater*, (144):420–426, 2007.
- [182] Mondal,P., Majumder ,C. and Mohanty ,B.: Effects of adsorbent dose, its particle size and initial arsenic concentration on the removal of arsenic, iron and manganese from simulated ground water by Fe³⁺ impregnated activated carbon. *J. Hazard. Mater*, 150(3): 695–702. 2008.
- [183] Mondal,P.,Majumder,C.B. and Mohanty,B.: Laboratory based approaches for arsenic remediation from contaminated water: recent developments. *J. Hazard. Mater*, B137:464–479,2006.
- [184] Morales,K.H., Ryan,L., Tsung-Li,K., Meei-Maan,W. and Chien-Jen,C.: Risk of internal cancers from arsenic in drinking water. *Environmental Health Perspectives*,108(7):655-661. 2000.
- [185] Murugesan,G.S., Sathishkumar,M. and Swaminathan, K.: Arsenic removal from groundwater by pretreated waste tea fungal biomass.*Bioresour.Technol*,97 (3) :483–487, 2006.
- [186] Naidu, R., Smith, E., Owens, G., Bhattacharya, P., Nadebaum. 2006. Managing Arsenic in the Environment: From soil to human health. CSIRO.
- [187] Namasivayam,C. and Senthilkumar,S.: Removal of arsenic(V) from aqueous solution using industrial solid waste: adsorption rates and equilibrium studies. *Ind. Eng. Chem. Res*,37 (12) :4816–4822,1998.
- [188] National Research Council, 2000. Arsenic in Drinking Water. National Academy Press, Washington, DC.
- [189] Navarro,P. and Alguacil, F.J.: Adsorption of antimony and arsenic from a copper electrorefining solution onto activated carbon. *Hydrometallurgy*, 66 (1–3):101–105, 2002.
- [190] Nesbitt,H.W.,Canning,G.W. and Bancroft,G. M.: XPS study of reductive dissolution of 7 Angstrom-birnessite by H₃AsO₃, with constraints on reaction mechanism. *Cosmochim. Acta* ,62: 2097–2110,1998.
- [191] Netpradit, S.,Thiravetyan,P. and Towprayoon,S.: Evaluation of metal hydroxide sludge for reactive dye adsorption in a fixed-bed column system. *Water Res.* 38:71–78, 2004.

- [192] Neupane, G. and Donahoe, R.J.: Leachability of elements in alkaline and acidic coal fly ash samples during batch and column leaching tests. *Fuel*, 104:758–770, 2013.
- [193] Ng, K.S., Ujang, Z. and Le-Clech, P.: Arsenic Removal Technologies for Drinking Water Treatment. *Reviews in Environmental Science and Biotechnology*, 2(4):43-53, 2003.
- [194] Ntim, S.A. and Mitra, S.: Adsorption of arsenic on multiwall carbon nanotube–zirconia nanohybrid for potential drinking water purification. *J Colloid Interface Sci.* 375:154–159, 2012.
- [195] Oscarson, D. W., Huang, P. M., Defosse, C. and Herbillon, A.: Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments. *Nature*, 291:50 – 51, 1981.
- [196] Ouvreard, S., Simonnot, M.O. and Sardin, M.: Reactive behavior of natural manganese oxides toward the adsorption of phosphate and arsenate. *Ind. Eng. Chem. Res.* 41(11):2785-2791, 2002.
- [197] Pande, S.P.; Deshpande, L.S.; Patni, P.M. and Lutade, S.L.: Arsenic removal studies in some ground waters of West Bengal, India. *Journal of Environmental Science and Health*, A32:7:1981-1987, 1997.
- [198] Pandey, V.C. , Singh, J.S., Singh, R.P., Singh, N. and Yunus, M.: Arsenic hazards in coal fly ash and its fate in Indian scenario. *Resources, Conservation and Recycling.*, 55:819–835, 2011.
- [199] Pattanayak, J., Mondal, K., Mathew, S. and Lalvani, S.B.A.: Parametric evaluation of the removal of As(V) and As(III) by carbon based adsorbents. *Carbon.*, 38(4):589-596, 2000.
- [200] Pena, M.E., Korfiatis, G.P., Patel, M., Lippincott, L., Meng, X.: Adsorption of As(V) and As(III) by nanocrystalline titanium dioxide. *Water Res.* 11:2327–2337, 2005.
- [201] Peters, G.R., McCurdy, R.F. and Hindmarsh, T.J.: Environmental aspects of arsenic toxicity. *Critical Reviews in Environ. Sci. Technol*, 33(6):457-493, 1996.
- [202] Pettine, M., Campanella, L. and Millero, F.J.: Arsenite oxidation by H₂O₂ in aqueous solutions. *Geochim. Cosmochim. Acta*, 63: 2727–2735, 1999.
- [203] Pirilä, M., Martikainen, M., Ainassaari, K., Kuokkanen, T. and Keiski, R.L.: Removal of aqueous As(III) and As(V) by hydrous titanium dioxide. *J. Colloid Interf. Sci.*, 353:257–262, 2011.
- [204] Rahman, M.M., Mukherjee, D., Sengupta, M.K., Chowdhury, U.K, Lodh, D., Chanda, C.R., Roy, S., Selim, M.D., Quamruzzaman, Q., Milton, A.H., Shahidullah, S.M., Rahman, Md.T. and Chakraborti, D.: Effectiveness and reliability of arsenic field testing kits: are the million dollar screening projects effective or not? *Environ. Sci. Technol.* 36. 2002.

- [205] Rahman, M.M., Sengupta, M.K.,Ahamed, S.,Chowdhury,U.K., Hossain, M.A.,Das, B.,Lodh,D., Saha,K.C., Pati,S. and Kaies,I.: The magnitude of arsenic contamination in groundwater and its health effects to the inhabitants of the Jalangi—one of the 85 arsenic affected blocks in West Bengal. *India. Sci. Total Environ.* 338 (3):189–200, 2005.
- [206] Raji, C. and Anirudhan, T.S.: Batch Cr(VI) removal by polyacrylamide-grafted sawdust: Kinetics and thermodynamics. *Water. Res.*,32(12):3772-3780,1998.
- [207] Raven, K.P., Jain, A. and Loeppert, R.H.: Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelope. *Environ. Sci. Technol.*, 32(3):344-349. 1998.
- [208] Reed, B.E.,Vaughan, R. and Jiang,L.: As(III), As(V), Hg, and Pb removal by Fe-oxide impregnated activated carbon. *J. Environ. Eng.* 126:869–873, 2000.
- [209] Roberts,L.C.,Hug,S.J.,Ruettimann,T.,Khan,A.W. and Rahman,M.T.: Arsenic removal with iron(II) and iron(III) in waters with high silicate and phosphate concentrations. *Environ. Sci. Technol.*, 38 :307– 315,2004.
- [210] Robertson, F.N.: Arsenic in ground water under oxidizing conditions, south-west United States. *Environ. Geochem. Health* , 11:171–176, 1989.
- [211] Robinson,B.H., Brooks, R.R., Outred, H.A. and Kirkman, J.H.: The distribution and fate of arsenic in the Waikato River system, North Island, New Zealand. *Chem. Spec. Bioavailability*, 7 (3) :89–96,1995.
- [212] Rose, M., Lewis, J., Langford, N., Baxter, M., Origgi , S., Barber, M.: Arsenic in seaweed—forms, concentration and dietary exposure. *Food and Chemical Toxicology*, 45: 1263–1267, 2007.
- [213] Rossman,T.: Arsenic. In: Rom W and Markowitz S eds. Environmental and occupational medicine, 4th ed. Hagerstown, MD: Lippincott Williams & Wilkins.:1006–1017, 2007.
- [214] Rossman,T.G., Uddin,A.N., Burns,F.J. and Bosland,M.C.:Arsenite Is a Cocarcinogen with Solar Ultraviolet Radiation for Mouse Skin: An Animal Model for Arsenic Carcinogenesis. *Toxicology and Applied Pharmacology*, 176(1):64-71, 2001.
- [215] Rott, U. and Friedle, M.: Eco-friendly and cost-efficient removal of arsenic, iron and manganese by means of subterranean ground-water treatment. *Water Supply*: 18(1), 632-635. 2000.
- [216] Roy, M., Nilsson, L. and Pal, P.: Development of groundwater resources in a region with high population density: a study of environmental sustainability. *J. Environ. Sci.* 5: 251–267, 2008.
- [217] Saha,B.,Bains,R. and Greenwood,F.: Physicochemical characterization of granular ferric hydroxide (GFH) for arsenic(V) sorption from water. *Sep. Sci. Technol.* 40 (14):2909–2932. 2005.

- [218] Saha, K.C.: Diagnosis of arsenicosis. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 38(1):255-272, 2003.
- [219] Sancha, A.M.: Removal of arsenic from drinking water supplies: Chile experience. *Water Supply*, 18(1): 621-625, 2000.
- [220] Sancha, A.M., O’Ryan, R. and Perez, O.: The removal of arsenic from drinking water and associated costs: The Chilean case. Interdisciplinary perspectives on drinking water risk assessment and management Proceedings of the Santiago Symposium, September 1998, IAHS publ.260 2000, pp.17–25.
- [221] Sarkar, S., Blaney, L.M., Gupta, A., Ghosh, D. and SenGupta, A.K.: Use of ArsenXnp, a hybrid anion exchanger for arsenic removal in remote villages in the Indian subcontinent. *React. Funct. Polym.* 67:1599–1611, 2007.
- [222] Say, R., Yilmaz, N. and Denizli, A.: Biosorption of cadmium, lead, mercury, and arsenic ions by fungus *Penicillium Purpurogenum*. *Sep. Sci. Technol.* 38 (9):2039–2053, 2003.
- [223] Schoen, A., Beck, B., Sharma, R. and Dube, E.: Arsenic toxicity at low doses: epidemiological and mode of action considerations. *Toxicology and Applied Pharmacology*, 198(3):253-267, 2004.
- [224] Scott, K.N.; Green, J.F.; Do, H.D.; McLean, S.J.: *J. Am. Water Works Ass*, 87(4):114-126, 1995.
- [225] Scott, M. J., and Morgan, J. J.: Reactions at oxide surfaces. 1. Oxidation of As(III) by synthetic birnessite. *Environ. Sci. Technol.*, 29(8):1898–1905, 1995.
- [226] Seki, H., Suzuki, A., Maruyama, H.: Biosorption of chromium(VI) and arsenic(V) onto methylated yeast biomass. *J. Colloid Interf. Sci*, 281 (2):261–266, 2005.
- [227] Sen, T.K. and Sarzali, M.V.: Removal of cadmium metal ion (Cd^{2+}) from its aqueous solution by aluminum oxide (Al_2O_3): a kinetic and equilibrium study. *Chem. Eng. J.*, 142(3): 256-262, 2008.
- [228] Sharma, A.K., Tjell, J.C., Sloth, J.J. and Holm, P.E.: Review of arsenic contamination, exposure through water and food and low cost mitigation options for rural areas. *Applied Geochemistry*. 41:11–33, 2014.
- [229] Shih, M.C.: An overview of arsenic removal by pressure driven membrane processes. *Desalination*, 172:85–97. 2005
- [230] Shihabudheen M. Maliyekkal, Ligy Philip, T. Pradeep.: As(III) removal from drinking water using manganese oxide-coated-alumina: Performance evaluation and mechanistic details of surface binding. *Chem. Eng. J*, 153 (1-3):101-107, 2009.

- [231] Shrestha, R.R., Shrestha, M.P., Upadhyay, N.P., Pradhan, R., Khadka, R., Maskey, A., Maharjan, M., Tuladhar, S., Dahal B.M. and Shrestha, K.: Groundwater arsenic contamination, its health impact and mitigation program in Nepal, *J. Environ. Sci. Health Part A: Toxic/Hazard. Substances Environ. Eng.* 38 (1):185–200, 2003.
- [232] Sigrist, M.E., Brusa, L., Beldomenico, H.R., Dosso, L., Tsendra, O.M., Gonzalez, M.B., Picck, C.L. and Vera, C.R.: Influence of the iron content on the arsenic adsorption capacity of Fe/GAC adsorbents. *Env. Chem. Eng. J.*, 2:927–934, 2014.
- [233] Simeonidis, K., Gkinis, Th., Tresintsi, S., Martinez-Boubeta, C., Vourlias, G., Tsiaoussis, I., Stavropoulos, G., Mitrakas, M. and Angelakeris, M.: Magnetic separation of hematite-coated Fe₃O₄ particles used as arsenic adsorbents. *Chem. Eng. J.*, 168:1008-1015, 2011.
- [234] Singh, D.B., Prasad, G. and Rupainwar, D.C.: Adsorption technique for the treatment of As(V)-rich effluents. *Colloid Surf. A* ,111(1-2):49-56, 1996.
- [235] Singh, T.S. and Pant, K.K.: Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. *Sep. Purif. Technol*, 36:139–147, 2004.
- [236] Singh, T.S. and Pant, K.K.: Kinetics and mass transfer studies on the adsorption of arsenic onto activated alumina and iron oxide impregnated activated alumina, *Water Qual. Res. J. Can.* 41 (2) :147–156, 2006.
- [237] Singh, T.S. and Pant, K.K.: Experimental and modelling studies on fixed bed adsorption of As(III) ions from aqueous solution. *Sep. Purif. Technol*, 48 (3):288–296, 2006.
- [238] Smedley, P.L. and Kinniburgh, D.G.: Sources and behaviour of arsenic in natural water, Chapter 1 in United Nations Synthesis Report on Arsenic in Drinking Water, 2005.
- [239] Smedley, P.L., Nicolli, H.B., Macdonald, D.M.J., Barros, A.J. and Tullio, J.O.: Hydrogeochemistry of arsenic and other inorganic constituents in groundwaters from La Pampa, Argentina, *Appl. Geochem.* 17 (3): 259–284, 2002.
- [240] Smedley, P.L. and Kinniburgh, D.G.: A review of the source, behaviour and distribution of arsenic in natural waters. *Appl Geochem.*, 17(5):517-568, 2002.
- [241] Smith, E., Naidu, R. and Alston, A.M.: Arsenic in the soil environment: A review. *Adv Agronom*, 64: 149-195, 1998.
- [242] Sorg, T.J. and Logsdon, G.S.: Treatment technology to meet the interim primary drinking water regulations for inorganics. Part 2. *J. Am. Water Works Ass*, 71(8):379-387, 1978.
- [243] Steinmaus, C., Yuan, Y., Bates, M.N. and Smith, A.H.: Case-Control Study of Bladder Cancer and Drinking Water Arsenic in the Western United States. *American Journal of Epidemiology*, 158(12):1193-1201, 2003.
- [244] Stumm, W.: Chemistry of the Solid–Water Interface. New York: Wiley–Interscience, 1999.

- [245] Stumm, W. Chemistry of the solid-water interface; Wiley: New York, 1992.
- [246] Sun, G.: Arsenic contamination and arsenicosis in China. *Toxicol. Appl. Pharmacol.* 198 (3):268–271, 2004.
- [247] Sun,X., Imai,T., Sekine,M., Higuchi,T., Yamamoto,K., Kanno,A. and Nakazono,S.: Adsorption of phosphate using calcined Mg₃–Fe layered double hydroxides in a fixed-bed column study. *J. Ind. and Eng Chem.* (2013).<http://dx.doi.org/10.1016/j.jiec.2013.12.057>.
- [248] Sun,Z.,Yu,Y.,Pang,S. and Du,D.. Manganese-modified activated carbon fiber (Mn-ACF): Novel efficient adsorbent for Arsenic. *Applied Surface Science*, 284:100–106, 2013.
- [249] Suzuki,T.M.,Bomani,J.O.,Matsunaga,H. and Yokoyama,T.: Preparation of porous resin loaded with crystalline hydrous zirconium oxide and its application to the removal of arsenic. *React. Funct. Polym*, 43 (1–2):165–172, 2000.
- [250] Takamatsu,T., Kawashima, M. and Koyama, M.: The role of Mn²⁺ -rich hydrous manganese oxide in the accumulation of arsenic in lake sediments. *Wat. Res.*, 19(8):1029-1032, 1985.
- [251] Takanashi, H., Tanaka, A., Nakajima,T. and Ohki, A.: Arsenic removal from groundwater by a newly developed adsorbent. *Water Sci. Technol.*, 50 (8):23–32, 2004.
- [252] Tan, B.J., Klabunde, K.J. and Sherwood P.M.A.: XPS studies of solvated metal atom dispersed catalysts - evidence for cobalt-manganese particles on alumina and silica. *J. Am. Chem. Soc.* 113:855-861, 1991.
- [253] Tan, I.A.W, Ahmad, A.L., Hameed, B.H.: Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *J. Hazard. Mater.*, 164: 473-482, 2009.
- [254] Temkin, M.J. and Pyzhev, V.: Recent modifications to Langmuir isotherms. *Acta. Physiochim*, URSS 12:217–222, 1940.
- [255] Thirunavukkarasu, O.S., Viraghavan, T. and Suramanian, K.S.: Arsenic removal from drinking water using iron-oxide coated sand. *Water Air Soil Pollut*,142:95–111, 2003.
- [256] Thirunavukkarasu,O.S.,Viraraghavan,T.,Subramanian,K.S.,Chaalal,O and Islam,M.R.: Arsenic removal in drinking water—impacts and novel removal technologies. *Energy Sources*, 27:209–219, 2005.
- [257] Thomas, HC.: Heterogeneous ion exchange in a flowing system. *J Am Chem Soc.*, 66:1664–6, 1944.
- [258] Thornburg, K., Sahai, N.: Arsenic occurrence, mobility, and retardation in sandstone and dolomite formations of the Fox River Valley, Eastern Wisconsin. *Environ. Sci. Technol.* 38 (19):5087–5094, 2004.

- [259] Tripathy, S.S. and Raichur, A.M.: Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water. *Chem. Eng. J.*, 138(1-3):179- 186, 2008.
- [260] Tseng, W.P., Chu, H.M., How, S.W., Fong, J.M., Lin, C.S. and Yeh, S.: Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan. *J. Natl. Cancer Inst.*, 40 (3): 453–463, 1968.
- [261] Umezawa, Y. and Reilley, C.N.: Effect of Argon Bombardment of Metal Complexes and Oxides Studied by X-Ray Photoelectron Spectroscopy. *Anal. Chem.* 50:1290-1295, 1978.
- [262] USEPA Fact Sheet: Drinking Water Standard for Arsenic (2001) http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations_factsheet.cfm.
- [263] USEPA, 2000. Technologies and costs for removal of arsenic from drinking water. US Environmental Protection Agency, EPA/815/R-00/028.
- [264] USEPA, 2001. Fact Sheet: Drinking Water Standard for Arsenic. <http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/regulations_factsheet.cfm>.
- [265] USEPA, Technologies and costs for removal of arsenic from drinking water. US Environmental Protection Agency, EPA report 815-R-00-028, 2000.
- [266] USEPA. (US. Environmental Protection Agency), 1997. IRIS (Integrated Risk Information System) On-line Database Maintained in Toxicology Data Network (TOXNET) by the National Library of Medicine. USEPA, Bethesda, MD.
- [267] Vahter, M., Concha, G., Nermell, B., Nilsson, R., Dulout, F. and Natarajan, A.T.: A unique metabolism of inorganic arsenic in native Andean women. *Environmental Toxicology and Pharmacology*, 293(4):455-462, 1995.
- [268] Vasudevan, S., Mohan, S., Sozhan, G., Raghavendran, N.S. and Murugan, C.V.: Studies on the oxidation of As(III) to As(V) by in-situ-generated hypochlorite. *Ind. Eng. Chem. Res.*, 45: 7729–7732, 2006.
- [269] Vaughan R.L. Jr. and Reed, B.E.: Modeling As(V) removal by a iron oxide impregnated activated carbon using the surface complexation approach. *Water Res.*, 39 (6):1005–1014, 2005.
- [270] Veličković, Z., Vuković, G.D., Marinković, A.D., Moldovan, M., Perić-Grujić, A.A., Uskoković, P.S. and Ristić, M.Đ.: Adsorption of arsenate on iron(III) oxide coated ethylenediamine functionalized multiwall carbon nanotubes. *Chem. Eng. J.* 181–182:174–181, 2012.
- [271] Velizarov, S., Crespo, J. and Reis, M.: Removal of inorganic anions from drinking water supplies by membrane bio/processes. *Rev. Environ. Sci. Biotechnol.*, 3:361–380, 2004.

- [272] Vinodhini, V. and Das, N.: Packed bed column studies on Cr (VI) removal from tannery wastewater by neem sawdust. *Desalination*, 264:9–14, 2010.
- [273] Viraghavan, T., Thirunavukkarasu, O.S. and Suramanian, K.S.: Removal of arsenic in drinking water by iron oxide-coated sand and ferrihydrite-batch studies. *Water Qual. Res. J. Can.* 36 (1): 55–70, 2001.
- [274] Viraraghavan, T., Subramanian, K.S. and Aruldoss, J.A.: Arsenic in drinking water—problems and solutions. *Water Sci. Technol.* 40 (2): 69–76, 1999.
- [275] Wadge, A., Hutton, M. and Peterson, P.J.: The concentrations and particle size relationships of selected trace elements in fly ashes from U.K. coal-fired power plants and a refuse incinerator. *Sci. Total Environ.*, 54:13–27, 1986.
- [276] Wagman, D.D., Evans, H.H., Parker, V.B., Schumm, R.H., Harlow, I., Bailey, S.M., Churney, K.L. and Butall, R.L.: The NBS tables of chemical thermodynamic properties. Selected values for inorganic and organic substances in SI units. *J. Phys. Chem.*, 2:392 Ref. Data II, 1982.
- [277] Wagner, C.D., Riggs, W.M., Davis, L.E., Moulder, J.F. and Muilenberg, G.E., Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer Corp., Eden Prairie, USA, 1979.
- [278] Wang, S. and Mulligan, C.N.: Occurrence of arsenic contamination in Canada: 3127 sources, behavior and distribution. *Sci. Total Environ.* 366:701–721, 2006.
- [279] Wang, Y. and Reardon, E.J.: A siderite/limestone reactor to remove arsenic and cadmium from wastewater. *Appl Geochem.*, 16:1241–1249, 2001.
- [280] Wang, J.P., Qi, L., Moore, M.R. and Ng, J.C.: A review of animal models for the study of arsenic carcinogenesis. *Toxicology Letters*, 133(1):17–31, 2002.
- [281] Wasay, S.A., Haron, M.J., Uchiumi, A. and Tokunaga, S.: Removal of arsenite and arsenate ions from aqueous solution by basic yttrium carbonate. *Water Res.* 30 (5) :1143–1148, 1996.
- [282] Watanabe, C., Kawata, A., Sudo, N., Sekiyama, M., Inaoka, T., Bae, M. and Ohtsuka, R.: Water intake in an Asian population living in arsenic-contaminated area. *Toxicology and Applied Pharmacology*, 198(3):272–282, 2004.
- [283] Weber, W.J. and Morris, J.C.: Kinetics of adsorption on carbon from solution. *Journal of Sanitary Engineering Division American Society of Civil Engineers*, 89 (1963) 31–59.
- [284] Wedepohl, K.H.: The composition of the continental crust. *Geochim Cosmochim Acta*, 59 :1217–1232, 1995.
- [285] Welch, K., Higgins, I., Oh, M. and Burchfiel, C.: Arsenic exposure, smoking and respiratory cancer in copper smelter workers. *Arch Environ Health*, 37:325–335, 1982.

- [286] WHO (World Health Organisation), Environmental Health Criteria, 18: Arsenic, World Health Organisation, Geneva, 1981.
- [287] WHO(World Health Organisation).Guidelines for drinking water quality. Geneva,1993,p-41.
- [288] WHO, 2004. Guidelines for Drinking Water Quality, third ed. Volume 1. Recommendations.
- [289] WHO,World Health Organization (WHO). Arsenic and arsenic compounds, 2nd edn. Environmental Health Criteria 224. Geneva CH [updated 2001; accessed 2008 April 2].Available from: <http://www.inchem.org/documents/ehc/ehc/ehc224.htm>
- [290] WHO. (2005). Diagnosis and treatment of chronic arsenic poisoning. http://www.who.int/water_sanitation_health/dwq/arsenicun4.pdf.
- [291] Wilkie, J.A. and Hering, J.G.: Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbate/adsorbent ratios and co-occurring solutes. *Colloids Surfaces A: Physicochemical and Engineering Aspects*, 107:97-110, 1996.
- [292] World Health Organization, 2008. Guidelines for Drinking-water Quality, third ed.
- [293] World Health Organization: Guidelines for Drinking-Water Quality,1: 491, 2008.
- [294] Wu,K., Liu,R., Liu,H., Zhao,X., and Qu,J.: Arsenic(III,V)Adsorption on Iron-Oxide-Coated Manganese Sand and Quartz Sand: Comparison of Different Carriers and Adsorption Capacities. *Environ. Sci. Technol*, 28(9): 643-651, 2011.
- [295] Wu,K., Liu,T.,Xue,W. and Wang,X.: Arsenic(III) oxidation/adsorption behaviors on a new bimetal adsorbent of Mn-oxide-doped Al oxide. *Chem. Eng. J.* 192(2012) 343–349.
- [296] WWCCPN, 2011. World-Wide Coal Combustion Products Network.See <http://www.wwccpn.org/2011>Last access: 2011.
- [297] Xu, Y.H., Nakajima,T. and Ohki,A.: Adsorption and removal of arsenic(V) from drinking water by aluminum-loaded shirasu-zeolite. *J. Hazard. Mater.* B92:275–287, 2002.
- [298] YaE,Y. and Ketris,M.P.: Arsenic in coal: a review. *International Journal of Coal Geology.*, 61:141–196, 2005.
- [299] Yan-Chu, H. Arsenic distribution in soils. Arsenic in the environment. Part I: Cycling and characterization, J. O. Nriagu, ed., Wiley, New York, 17–49, 1994.
- [300] Yoon, S.H. and Lee, J.H.: Oxidation mechanism of As(III) in the UV/TiO₂ system: evidence for a direct hole oxidation mechanism. *Environ. Sci. Technol.* 39:9695–9701, 2005.

- [301] Zeng,H., Fisher,B. and Giammar,D.E.: Individual and Competitive Adsorption of Arsenate and Phosphate To a High-Surface-Area Iron Oxide-Based Sorbent. *Environ. Sci. Technol.* 42 :147–152,2008.
- [302] Zeng,L.: Arsenic Adsorption from Aqueous Solutions on an Fe(III)-Si Binary. *Water Qual. Res. J. Canada.*,39:267-275,2004.
- [303] Zhang, F.S. and Itoh, H.: Iron oxide-loaded slag for arsenic removal from aqueous system. *Chemosphere*, 60 (3):319–325, 2005.
- [304] Zhang, G.S.,Qu, J.H.,Liu,H.J.,Liu,R.P. and Wu,R.C.: Preparation and evaluation of a novel Fe-Mn binary oxide adsorbent for effective arsenite removal. *Water Res*,41:1921–1928, 2007.
- [305] Zhang,G., Qu,J., Liu,H., Liu,R. and Wu,R.: Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. *Water Res*, 41:1921– 1928, 2007.
- [306] Zhang,H. and Selim,H.M.: Kinetics of arsenate adsorption–desorption in soils. *Environ. Sci. Technol*, 39 (16):6101–6108, 2005.
- [307] Zhang,S.,Niu,H.,Cai,Y.,Zhao,X. and Shia,Y.: Arsenite and arsenate adsorption on coprecipitated bimetal oxide nanomaterials:MnFe₂O₄ and CoFe₂O₄. *Chem.Eng. J*, 158(3):599-607,2010.
- [308] Zhang,T. and Sun,D.D.: Removal of arsenic from water using multifunctional micro-/nano-structured MnO₂ spheres and microfiltration. *Chem Eng J.*, 225:271–279,2013.
- [309] Zhanga,G., Qu,J., Liu,H., Liu,R. and Wu,R.: Preparation and evaluation of a novel Fe–Mn binary oxide adsorbent for effective arsenite removal. *Water Res*,41(9):1921– 1928,2007.
- [310] Zhao, F., Peng, P., Zheng, B., Tang, Y., Cong, Z. and Ren, D.: The Leaching Behavior of Cadmium, Arsenic, Zinc, and Chlorine in Coal and Its Ash from Coal-Fired Power Plant. *Environ. Eng. Sci.*, 23:68-76, 2006.
- [311] Zhao,X, Holl,W.H. and Yun,G.: Elimination of cadmium trace contamination from drinking water. *Water. Res.*,36(4):851-858,2002.
- [312] Zhao,Z., Jia,Y., Xu,L., Zhao,S : Adsorption and heterogeneous oxidation of As(III) on ferrihydrite. *Water Res*, 45 (19):6496–6504, 2011.

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For the Attention of:
Kamel Babeivelni
Department of Civil and Materials Engineering
University of Illinois at Chicago
Chicago, IL
kbabae2@uic.edu

August 12, 2014

Dear Kamel Babeivelni,

We are in receipt of your request to include the contents of the following article;

“Adsorption and removal of arsenic (V) using crystalline manganese (II,III) oxide: Kinetics, equilibrium, effect of pH and ionic strength”, *Journal of Environmental Science and Health, Part A, Toxic/Hazardous Substances and Environmental Engineering*, Volume 49, Issue 13.

to be incorporated in a PhD Thesis by Kamel Babeivelni for submission to the Faculty of the University of Illinois at Chicago.

As the author, you retain the right to include this article in a thesis or dissertation that is not to be published commercially, provided that acknowledgement to prior publication in the relevant Taylor & Francis journal is made explicit.

Sincerely,

A handwritten signature in cursive script that reads "Mary Ann Muller".

Mary Ann Muller
Permissions Coordinator
maryann.muller@taylorandfrancis.com

VITA

NAME: Kamel Babaeivelni

EDUCATION: Ph.D., Civil and Material Engineering, University of Illinois at Chicago, Chicago, Illinois, 2014

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Student Travel Award for EWRI World Congress, 2013 at Cincinnati, OH.

PUBLICATIONS AND PRESENTATIONS: Khodadoust, A.P., Theis, T.L., Murarka, I.P., Naithani, P. and Babaeivelni, K.: Uptake of arsenic by alkaline soils near alkaline coal fly ash disposal facilities, *Environ Monit Assess*, 185(12):10339-49, 2013.

Babaeiveli, K., Khodadoust, A.P.: Adsorption of fluoride onto crystalline titanium dioxide: Effect of pH, ionic strength and co-existing ions. *J. Colloid Interf. Sci*, 394:419–427, 2013.

Babaeiveli, K., Khodadoust, A.P., Bogdan, D.: Sorption Of Arsenic (V) Onto Commercial Mn_3O_4 : Effect Of pH, Ionic Strength, And Co-existing Ions. Accepted to Journal of Environmental Science and Health, Part A, Feb 2014.

Babaeiveli, K., Khodadoust, A.P.: Adsorption and Removal of Arsenic from Water using Crystalline Mn_2O_3 : Effect of pH and ionic strength on the adsorption behavior of arsenic (III) and arsenic (V). Submitted to Journal of colloid and interface science, March 2014.

Babaeiveli, K., Khodadoust, A.P.: Adsorption and Removal of Arsenic from Coal Fly Ash Leachate using Manganese Oxide Sorbent. Proceedings of Air & Waste Management Association's 106th Annual Conference & Exhibition, Chicago, Jun 2013.

Babaeiveli, K., Khodadoust, A.P.: Effect of pH and ionic strength on the removal of fluoride from water using titanium dioxide. Proceedings of 2013 World Environmental & Water Resources Congress, Cincinnati, May 2013.