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A Comprehensive Study of Arsenic Removal From Aqueous Solution Using Low-Cost Adsorbents

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Abstract

Arsenic poisoning in water is a global concern for many years due to its high carcinogenic and toxic effect on the human body. Adsorption is one of the promising technology to treat arsenic-contaminant water. Recently, natural adsorbent modified with metal oxide/hydroxide is being studied widely, because of its great removal efficiency, inexpensive and eco-friendly properties.

In the present study, two low-cost adsorbents namely Aerocrete and Vermiculite (modified with iron oxy-hydroxide) were assessed for arsenic (both As(III) and As(V)) removal. The maximum removal of As(V) was ~99% at pH 6 for both adsorbents (3g/L). Optimum removal of As(III) was observed at a pH range of 6 to 8. Both Langmuir and Freundlich isotherms described the adsorption equilibrium data. A pseudo-second-order kinetic model fitted well with the experimentally obtained kinetic data. No significant effect on the adsorption of As(III) was observed in the presence of ions (i.e., Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}, SO_4^{2-}, or Cl^{-}). Results showed that the proposed adsorbents (Aerocrete and Vermiculite) are promising in removing As(III) from the water.

Keywords

Adsorption, Arsenic, Central composite design, Response surface method

Co-Authorship Statement

This thesis work is a collaborative effort by the present author and Dr. Pankaj Chowdhury, Dr. Kyriakos Manoli, Dr. Binay K Dutta and Dr. Ajay K Ray. Chapter 3 will be submitted for publication in the near future with the present author as primary author and Dr. Chowdhury as second author, Dr. Ray as a third author and Dr. Dutta as the fourth author. For this paper, the first author designed and did all the experiments and wrote the manuscript. Dr. Chowdhury helped in the literature review and provided valuable feedback on the manuscript, Dr. Ray supervised the author, provided direction for this research, and gave his valuable comments where Dr. Dutta helped the first author how to conduct experiments.

Chapter 4 will be submitted for publication in the near future with the present author as primary author and Dr. Manoli as second author, Dr. Ray as a third author For this work, the first author designed and did all the experiments and wrote the manuscript. Dr. Manoli helped in results analysis, editing and provided his valuable comments. Dr. Ray provided direction for this research and gave his valuable feedback. Dr. Dutta provided his feedback in experimental design. Also, Dr. Dutta helped in designing the fixed bed column filter (discussed in section 4.3).

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Chapter 1

1 Introduction

The present research describes the performances of two modified adsorbents (Aerocrete and Vermiculite) in terms of Arsenic (As) removal. The research results show that both of these materials are very effective in As (As(III) and As(V)) removal from aqueous solution and low cost to produce. Response surface methodology (RSM) is used in this study for experimental design and process optimization. Especially RSM is used to measure the effect of the independent variables and their interaction with the response function. Also, a fixed bed column is developed to study the practical applicability of the adsorbents (Aerocrete and Vermiculite) in continuous flow mode.

This particular section discusses motivation and scope of the present research followed by objectives of the present research and its contribution towards the state of the art of As removal using adsorbents are presented. A general outline of the larger thesis is given at the end of this section.

1.1 Background and Motivation

Arsenic in drinking water is a serious health concern in many countries around the world. Approximately 226 million people from 105 countries and territories are exposed to As contamination [1]. Continuous exposure to As contaminated water can cause various health problems including cancer and birth complications. Long-term exposure to As causes lung, skin, kidney and bladder cancer, as well as skin pigmentation changes, skin thickening, neurological disorders (hyperkeratosis), nausea and loss of appetite [2,3] wherein short-term exposure, people, could suffer abdominal pain, vomiting, and diarrhea [2]. There is no effective treatment for diseases due to As contamination, and it is always recommended "prevention is better than cure" policy in As poising. The best solution to get rid of arsenic poisoning related problems is to provide arsenic free safe drinking water. However finding an arsenic free water source in As-contaminated areas is very difficult because it has been observed that arsenic safe groundwater sources get arsenic contamination after a few years (Michael and Voss, 2008). Therefore, the supply of centrally treated arsenic-free drinking water is always preferable but due to high installation cost, lack of infrastructure and maintenance, on-site treatment technologies are popular. Many physicochemical techniques have been developed to remove As from water and wastewater. Conventional As removal technologies are oxidation[3,4], coagulation and flocculation [5,6], adsorption[7–9], ion-exchange[10,11], membrane filtration[12,13] etc. However, these methods have several disadvantages including slow or insufficient As removal, complex system, use of chemicals, pH adjustment, disposal of the residual As sludge and high operational and capital cost.

WHO and US-EPA follow 10 ppb (0.01 mg/L) standard for As in drinking water, however many countries (e.g., China, Bangladesh, Mexico, Nepal) around the world still retained in the previous WHO guideline (0.05 mg/L)[9]. Most of the conventional As removal methods are highly effective with higher initial As concentration (> 100 mg/L) in water, but residual As concentration less than 0.05 mg/L is water quality standard for many counties. Therefore, a simple treatment method is required to remove As efficiently with low operational and capital cost. In addition, an effective As removal method should produce minimum sludge and simple design with low environmental impacts.

1.2 Scope of Research

In groundwater, As concentrations have uncertain horizontal spatial distribution but provide a certain consistent vertical pattern, i.e. high As concertation (>50 ppb) rarely found near at deeper groundwater (>150 m below earth surface) [14,15]. Initially deep wells produce low As contaminated groundwater[16] but in long-term As leached/transported through soil with percolated water which eventually increases the As concentration in the deeper water sources [17,18]. Also, there is no effective treatment of As contamination except consumption of As free water, advancement of As removal technologies are necessary. The best solution to arsenic contamination problem is the use of treated surface water. Developing and maintain arsenic free surface water treatment system is expensive, time-consuming and investment intensive. Hence a sustainable, cost-effective and less maintenance required method is essential for As removal from surface water.

Among all conventional As removal techniques, adsorption is an effective and popular water treatment process due to its high removal capacity, low cost, simple in design and no chemical sludge [8,9,19]. Activated carbon[20], metal oxide/hydroxides (e.g., ferric-oxide-hydroxide, aluminum oxides, titanium oxides, magnesium oxides, silicon oxides) [21] and ion exchange resins are mostly used adsorbents in water and wastewater treatment. Nowadays studies are more focused on developing low-cost adsorbents with high effectiveness (i.e., modified activated carbon, clay minerals, other synthetic and natural oxides, sand, agriculture, industrial waste and concrete materials) for As removal to establish a cost-effective treatment process, especially in developing countries [22]. The cement-based low-cost adsorbent obtained from concrete wastes have been noticed as an effective adsorbent to remove arsenate, phosphate and borate anions lately [23]. Recently, the two newly developed concrete based adsorbent Aerocrete and Vermiculite have been showed effective removal of cadmium, copper and lead [24]. In this study, the effectiveness of two low-cost adsorbents (Aerocrate and Vermiculite modified with iron oxyhydroxide) in terms of As(V) and As (III) removal are examied. The primary objectives of the present work are presented in the following subsection.

1.3 Research Objectives

The main objective of this work is to develop a simple and effective treatment process to remove arsenic from aqueous solution using the low-cost adsorbent Vermiculite and Aerocrete. The following objectives are investigated:

I. Optimize the response and experimental conditions in adsorption of As(V) using the central composite design (CCD) under response surface methodology.
II. Analyze adsorption behavior of As(V) using two isotherm models: Langmuir and Freundlich adsorption isotherm.
III. Investigate the removal efficiency of Arsenic As(III) varying pH, initial concentration of As(III), amount of adsorbent, contact time using two adsorbents: Aerocrate and Vermiculite.
IV. Determine the adsorption isotherm parameters and kinetic parameters for As(III) adsorption.
V. Develop a fixed bed filter column to assess the practical applicability of adsorbents regarding As removal.

1.4 Outline of the Thesis

Chapter 2 provides a review of the literature related to As removal techniques with their advantages and disadvantages. As contamination and toxicity were also discussed in this chapter. The efficiency of two adsorbents namely Aerocrete and Vermiculite (modified with iron oxyhydroxide) in terms of As(V) removal from aqueous solution is discussed in chapter 3. Also the advantage of response surface method (RSM) and its applicability in adsorption study are shown in chapter 3. Removal of As(III) from aqueous solution using concrete-based adsorbents, i.e. Aerocrete and Vermiculite are discussed in chapter 4. Design details of a packed bed adsorption column also discussed in chapter 4. Conclusions and future works are given in chapter 5.

Chapter 2

2 Literature Review

As contamination and As removal technologies developed in the past are reviewed in this present chapter. The following section describes As contamination, and its toxic nature. Literature regarding As removal using adsorption technologies is reviewed subsequently.

2.1 Arsenic Contamination and Its Toxicity

Arsenic contamination in natural water is a worldwide concern due to its toxic and carcinogenic effect on human health. Many countries around the world namely USA, China, Chile, Bangladesh, Taiwan, Mexico, India are affected by arsenic poising [25]. Long-term exposure of arsenic contaminated water may cause skin lesions, cancer of the skin, liver lungs and kidney. The US-EPA (the United States Environmental Protection Agency) guideline for As in drinking water is 10 ppb from January 2001[9]. However, many developing countries follow the previous limit 50 ppb set by US-EPA because of unavailability of testing facilities for lower concentrations.

Arsenic is the 20th most abundant element in earth crust reaches into the environment through natural process (weathering reactions, volcanic emission) and also by the anthropogenic activities (e.g., mining, combustion of fossil fuels, wood preservatives)[26]. Normally inorganic forms of As species are more toxic than organic forms to a living organism. The LD_{50} (oral) for inorganic As ranges from 15–293 mg (As) kg^{-1} bodyweight in rat[27]. Inorganic trivalent arsenite As(III) and pentavalent arsenate As(V), are the predominant forms of arsenic, mostly found in water [28].

As(V) predominates in oxygen-rich surface water where As(III) is present in reducing environments such as groundwater [7]. As(V) species are AsO^{3-}_4, $HAsO^{2-}_4$, $H_2AsO^-_4$ while H_3AsO_3, $H_2AsO^-_3$, $HAsO^{2-}_3$, and AsO_3^{3-} are the As(III) species [9]. pH and redox potential are the important factors to determine the state of arsenic in water. In the pH range 4 to 10, As(V) is negatively charged where As(III) is neutral [29]. AsO^{3-}_4, $HAsO^{2-}_4$, $H_2AsO^-_4$. Some commonly found As compounds are given in Figure 2.1. Toxicity of Arsenite (trivalent oxidation state of As) is the highest among all arsenic compound. The quantity of As absorbed by a human body depends upon the form of As and exposure pathway.

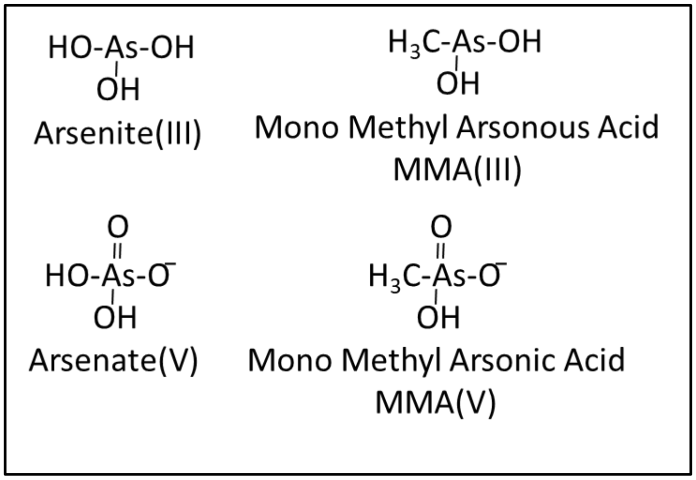


Figure 2.1 Few commonly found As compounds structure

The gastrointestinal tract can absorb inorganic As if it is in food or water. However, absorption is easier if As is already dissolved. Therefore, As contamination in water is more detrimental than contamination in food [30]. Presence of Fe (III) with As has less toxic effects compared to Fe(II) with As [31]. The following section discusses the chemical properties of arsenic. Arsenic distribution around the world is discussed the following subsection.

2.2 Arsenic Distribution

Arsenic is a ubiquitous metalloid, ranks 14th in seawater, 20th in natural abundance and 12th in the human body[27]. As was isolated in 1250 A.D., it has been using in different fields, i.e. metal enrichment, medical, agriculture, and electronics, etc. As concertation in seawater is less than 2 μg L^{-1} where As level varies in between 1-10 μg L^{-1} in contaminated surface and groundwater[27]. Also As concentration varies from 0.15- 0.45 μg L^{-1} in freshwater and the maximum concentration found in thermal water are 8.5 mg L^{-1} in Japan[27]. Table 2.1 summarized information regarding countries affected by As contamination around the world and maximum acceptable limits respectively. In 1993, the World Health Organization (WHO) revised guidelines for As in drinking water from 50 μg L^{-1} to 10 μg L^{-1}. As a result, most of the developed countries (i.e., Germany, Australia, France, USA, etc.) lowered As permissible limits, however, developed countries like Bangladesh and China have retained the previous WHO guideline of 50 μg L^{-1}. The following section discussed the chemical properties of arsenic.

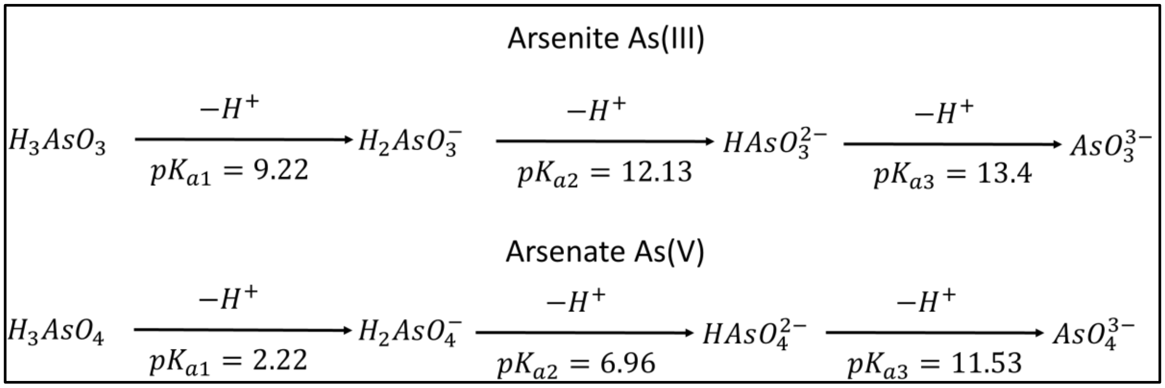
Table 2.1 Spatial distribution of Arsenic in different parts of the world and maximum permissible limits*

Continent	Location	Arsenic Source	Concentration ($\mu g\ L^{-1}$)	Maximum Permissible Limits ($\mu g\ L^{-1}$)
America	Pampa, Cordoba, Argentina	Groundwater	100-3810	50
	Chile	Groundwater	470-770	50
	Lagunera, Mexico	Well waters	8-624	50
	Peru	Drinking water	500	50
	Northeastern Ohio, USA	Natural Origin	<1-100	10
	Western USA	Drinking Water	1-48,000	10
Europe	Hungary	Deep groundwater	1-174	10
	Romania	Drinking water bores	1-176	10
	South-West Finland	Well water; Natural Origins	17-980	10
Asia	Bangladesh	Well Waters	<10-1000>	50
	West Bengal, India	Groundwater; soil sediments	3-3700	10
	Nepal	Drinking water	8-2660	50
	Hanoi, Vietnam	Groundwater, soil sediments	1-3050	10
	Xinjiang, PR China	Well Water	0.05-850	50
	Inner Mongolia, China	Drinking water; bores	1-2400	50
	Ronpibool, Thailand	Water contaminated by tin mining waste	1-5000	10
	Fukuoka, Japan	Natural origin	0.001-0.293	10
	Mekong river floodplain, Cambodia	Groundwater	1-1340	10

* Most of the information of this table obtained from V. Sharma and M. Sohn (2012)[32]

2.3 Chemistry of Arsenic

Arsenic is a metalloid, commonly found as a compound with an atomic mass of 74.9 g/mol. In inorganic form, As exists in four oxidation states, i.e., arsenate (+V), arsenite (+III), arsenic (0) and arsine (-III). As(III) and As(V) are the dominant forms of arsenic present in groundwater which is most commonly used for drinking purpose in developed countries[33]. pH and Redox potential (Eh) are significant factors control speciation of As(III) and As(V). The dissociation reactions and corresponding equilibrium constants of As(III) and As(V) at various pH are shown in Figure 2.2. The dissociation constants of As(III) are pK_{a1}= 9.22; pK_{a2}=12.13; pK_{a3}= 13.40 which means at pH 9.22 As(III) will be 50% dissociated. Figure 2.3 describes the distribution of As(III) and As(V) as a function of pH[34]. Mostly As(III) exists as a neutral molecule at neutral and slightly acidic conditions where at pH>8 significant amount of anionic species can be found (Figure 2.3). In contrary As(V) is almost completely dissociated at a pH 6.96 and present in the form of 50% monovalent and 50% divalent anion (Figure 2.3).



Arsenite As(III)

$$H_3AsO_3 \xrightarrow[pK_{a1} = 9.22]{-H^+} H_2AsO_3^- \xrightarrow[pK_{a2} = 12.13]{-H^+} HAsO_3^{2-} \xrightarrow[pK_{a3} = 13.4]{-H^+} AsO_3^{3-}$$

Arsenate As(V)

$$H_3AsO_4 \xrightarrow[pK_{a1} = 2.22]{-H^+} H_2AsO_4^- \xrightarrow[pK_{a2} = 6.96]{-H^+} HAsO_4^{2-} \xrightarrow[pK_{a3} = 11.53]{-H^+} AsO_4^{3-}$$

Figure 2.2 Dissociation of As(III) and As(V)

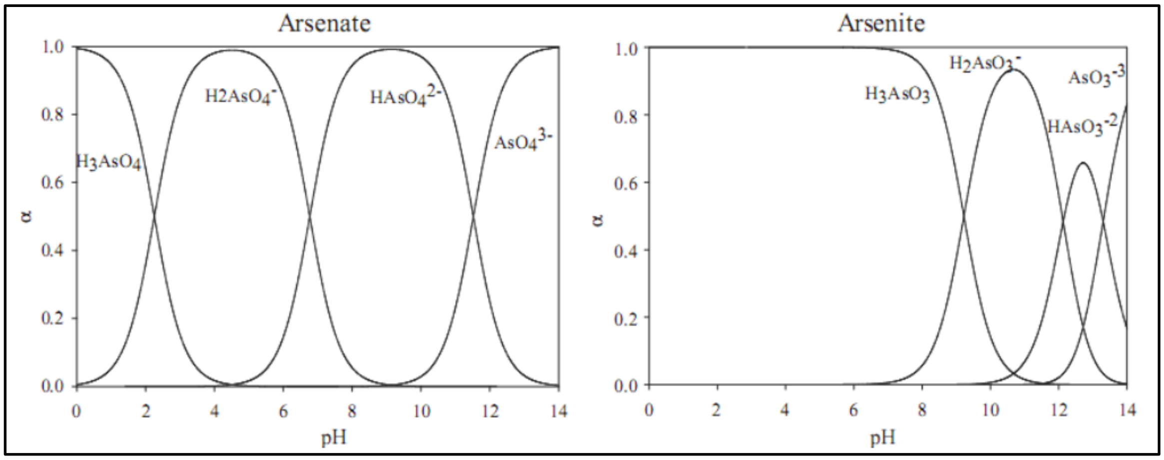


Figure 2.3 Distribution of arsenate (As (V)) and arsenite (As(III)) as a function of pH where α is a fraction of total concentration

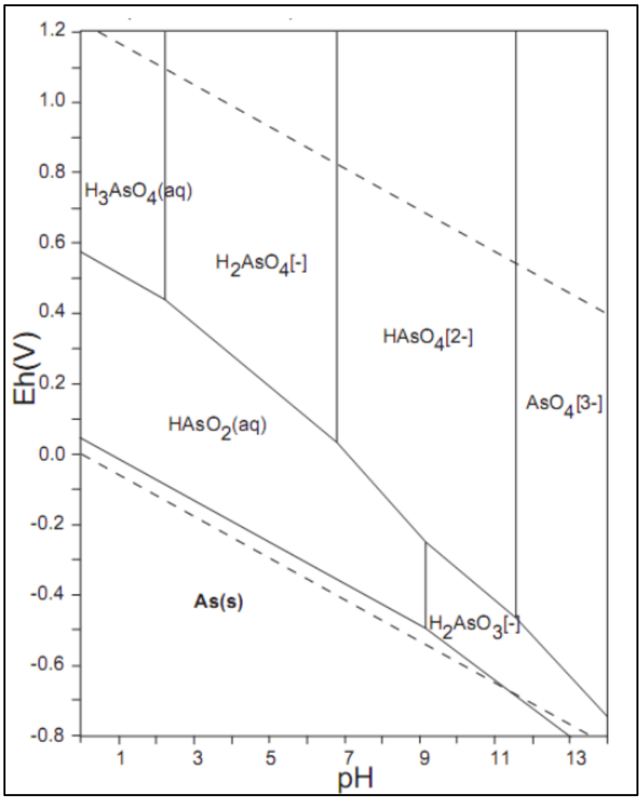


Figure 2.4 Eh-pH diagram of aqueous Arsenic speciation

The combined effects of Redox potential (Eh) and pH on aqueous arsenic speciation and oxidation state shown in Figure 2.4. The amount of protonation is a significant factor in governing the mobility of these chemical species of both As(V) and As(III). Generally, pH range of groundwater within 6 – 8 and Eh -0.05V to + 0.05 V. Under these conditions, As(III) is uncharged and in more reducing environments where As(V) under oxidizing conditions and negatively charged. The movement of As(V) is slow by electrostatic attraction to positively charged particles, such as iron hydroxides[35]. As a result, As(III) is more mobile than As(V) in groundwater. The difference in charge has significant effects on the removal of both the arsenic species (As(III) & As(V)) from aqueous solution, because neutral, uncharged molecules cannot be or are less effectively removed by most treatment methods[36]. As(III) can be oxidized to As(V) at low Eh-potential of 0.1-0.2 mV by using dissolved oxygen as an oxidant, but the oxidation of As(III) by oxygen is a very slow process and may convert only a small fraction. Hence, groundwater with high oxygen concentration may also contain some As(III) [36], and it is often found in stable association with the dissolved iron and manganese[37]. Presently available As removal technologies are discussed in the following section.

2.4 Arsenic Removal Technologies

There are many methods viz. adsorption, oxidation with precipitation, coagulation, ion-exchange and membrane separation conventionally used for As removal from water. Advantages and disadvantages of the technologies developed for arsenic removal are discussed in Table 2.2.

2.4.1 Coagulation and Flocculation

One of the highly documented arsenic removal technique involved coagulation and flocculation using lime softening or metal salt. Coagulation is a separation process for

Table 2.2 Comparisons of Arsenic removal technologies [9]

Process	Advantages	Disadvantages
Oxidation and precipitation		
Air oxidation	Relatively simple, slow process but cost-effective; In-situ As removal is possible; Oxidized other organic and inorganic components present in the water	Mostly effective for As(V) removal and stimulate the oxidation process
Chemical oxidation	Relatively faster and simple; produce less residual Kills microbes and oxidized other impurities	pH needs to be controlled efficiently, and an oxidation step is needed
Coagulation/electrocoagulation/co-precipitation		
Alum coagulation	Relatively simple in operation and low capital cost Durable chemicals are available and effective for a wide range of pH	Produces toxic residuals and As removal efficiency is relatively low Pre-oxidation is required some cases
Iron coagulation	Chemicals are available and efficient than alum coagulation	Sedimentation and filtration are required Average As(III) removal efficiency
Adsorption and ion-exchange methodology		
Activated carbon	Relatively simple in operation with less operation and maintenance cost Commercially available and in-situ operation is possible Effectively remove As	Replacement required after four or five regenerations
Iron coated sand	Cost effective; efficiently remove As(III) and As(V); regeneration does not require	Produce toxic solid waste
Ion-exchange resin	Well defined medium and capacity; pH-independent and exclusively ion specific resin to remove As	High-tech operation and maintenance and high-cost medium Reaeration creates toxic sludge; less removal of As(III)
Membrane technologies		
Nanofiltration	Removal efficiency is high	High capital and maintaining cost, pre-conditioning; a larger amount of water rejection
Reverse osmosis	No toxic solid	Very high operation and maintenance cost

removal of colloids by neutralizing the forces that keep them apart. Rapid mixing is required in this process. Flocculation is a physical process which promotes contact between destabilized particles and bind the particles into larger clumps. An anionic flocculant will react with a positively charged suspension, adsorbing on the particles and destabilized either by charge neutralization or bridging. Arsenic removal efficiency using this method significantly depends upon coagulant dosage, pH, initial As concentration and the valence of the arsenic species. Ferric salts are generally used as a coagulant. Karcher et al., (1999)[38] used ferric chloride and lime-poly ferric sulphate as the coagulants where Han et al., (2002)[39] applied ferric chloride and ferric sulphate as flocculants for removal of arsenic. Results showed that these coagulants were effective in As removal in the presence of ferric complexes. However, this method is not effective to reduce the As concertation below the acceptable limits. Also, safe separation, filtration, and disposal of As-contaminated sludge are some drawbacks of this method.

2.4.2 Membrane Filtration

The principle of membrane filtration is to remove macromolecules in the size range 500-500,000 nm using a pressure gradient across a selectively permeable membrane. Membrane filtration process can be divided into four categories: microfiltration(MF), ultrafiltration(UF), nanofiltration(NF) and reserves osmosis(RO). Among these four, RO and NF were mostly used for arsenic removal[40]. RO and NF can remove As(V) with rejection percentage over 95%, but they were not equally effective in removing As(III)[40]. However, it has been found that RO or NF method was equally effective regarding As(III) and As(V) removal if aromatic polyamide thin composite membranes are used and its solution pH independent[41]. But membrane separation process has a few drawbacks, i.e.

due to small pores of the membranes which make them more likely to foul. Also, it has higher operational cost and needs experienced personnel to conduct the overall process.

2.4.3 Ion Exchange

In the ion exchange process, electrostatically held ions on the surface of solid are exchanged with similar charged ionic species in an aqueous solution. This is a reversible non-destructive process where the structure of the solid does not change permanently. This method generally used for potable water treatment, i.e., softening, iron, nitrate, and fluoride removal as well as ammonia, phosphate, nitrate and heavy metals removal from municipal waste water[42]. For arsenic removal, ion exchange resins were used with either chloride or hydroxide ions at exchange sites, is placed in one or more packed columns. The arsenic-contaminated water is passed through the column and the arsenic "exchanges" for hydroxide or chloride ions. After some time the resin becomes saturated which means exchange sites that were loaded with chloride or hydroxide ions replaced by As. This event requires regeneration of ion exchange material which increases the operation and maintenance cost of the treatment facility.

The efficiency of ion exchange process depends upon multiple factors, i.e., solution pH, total dissolved solids (TDS), the concentration of competing ions, redox potential, sulfate and nitrate concentration in the solution, and influent arsenic concentration[43]. Ion exchange for arsenic removal is only applicable for low sulfate (<120 mg/l) and low TDS source water[9]. Disposal of As rich brine (mixed of ion exchange resin and regenerate) is a major issue of this method.

2.4.4 Adsorption

In arsenic removal, adsorption is used as a “front line of defense.” In this process, ions or molecules are removed by accumulating at the liquid or solid phase due to the participation of residual or unbalanced force. Adsorption can be categorized into two types: physical and chemical. Physical adsorption is driven by Vander Waal forces of attraction and electrostatic forces between adsorbate and adsorbent where chemical adsorption is caused by chemical attraction or chemical bond[42]. As adsorption is an exothermic process, therefore adsorption capacity depends upon temperature, pH, surface area of adsorbent and chemical properties of adsorbate[42]. The relationship between adsorption capacity of an adsorbent and amount of adsorbate adsorbed is studied by adsorption isotherms. Details about adsorption isotherms are discussed in the following sub-section.

2.4.4.1 Adsorption Isotherms

The adsorption process generally expressed in a mathematical relationship between the amount of solute adsorbed onto the adsorbent and the equilibrium concentration of the adsorbate in a solution at a given temperature. Several mathematical models have been used for adsorption isotherms. However, the following four models were most commonly used in the past.

2.4.4.1.1 Linear Isotherm Model

Liner isotherm model is a single parameter model, conceptually represents a simple partitioning or adsorption process. The model is expressed as follows:

$$q_e = KC_e \tag{2.1}$$

where q_e is the amount of adsorbate adsorbed per unit weight of solid at equilibrium; K is the distribution coefficient, and C_e is equilibrium concentration of adsorbate remaining in the solution at equilibrium. This model is not effective over large adsorbate concentration range.

2.4.4.1.2 Langmuir Model

Langmuir is a two-parameter model. This model assumes there is no interaction between adsorbing solutes and adsorption energy is constant for all surface sites, independent of surface coverage. Also, it assumes that each adsorb site can hold one molecule of adsorbate (monolayer coverage). The mathematical representation of the Langmuir model is given below:

$$q_e = \frac{bc_e q_m}{1 + bc_e} \qquad \textbf{(2.2)}$$

where q_e is amount of adsorbate adsorbed per unit weight of solid at equilibrium; c_e is equilibrium concentration of adsorbate remaining in the solution at equilibrium, and q_m is the maximum adsorption capacity per unit mass of adsorbent and b is the affinity of the active site

2.4.4.1.3 Freundlich Isotherm

This is an empirical and two-parameter model, widely used in isotherm study. This model allows for heterogeneous surface energies, i.e. different adsorption energy for different adsorption sites. Also, it assumes the frequency of sites associated with the higher free energy of adsorption decreases exponentially with an increase in the free energy. Freundlich isotherm can be expressed as follows:

$$q_e = k_f c_e^{\frac{1}{n}} \quad \textbf{(2.3)}$$

where q_e is amount of adsorbate adsorbed per unit weight of solid; k_f is a constant and indicator of adsorption capacity; c_e is equilibrium concentration of adsorbate remaining in the solution at equilibrium and 1/n is a measure of the intensity of adsorption. Lower n value is more favorable for adsorption.

2.4.4.1.4 Brunauer, Emmet, and Teller (BET) Isotherm

BET isotherm model is similar like Langmuir model but more generalized multi-layer model. This model assumes that essentially condensation occurs in all layers except the first layer and these layers have equal energies. It also assumes that there is no transmigration in between layers and layers of different thickness can coexist. The BET model can be expressed as follows:

$$q_e = \frac{q_m B c_e}{\left(c_s - c_e\right)\left[1 + (B-1)\frac{c_e}{c_s}\right]} \quad \textbf{(2.4)}$$

where q_e is amount of adsorbate adsorbed per unit weight of solid; c_e is equilibrium concentration of adsorbate remaining in the solution at equilibrium; q_m is the maximum adsorption capacity of a layer; B is dimensionless constant, relates to difference in free energy between adsorbate on first and successive layers and c_s is saturation concentration of adsorbate in solution. When $c_e << c_s$ and $B>>1$ BET isotherms approaches Langmuir isotherm. Graphical representations of linear, Langmuir, BET and Freundlich are given in Figure 2.5.

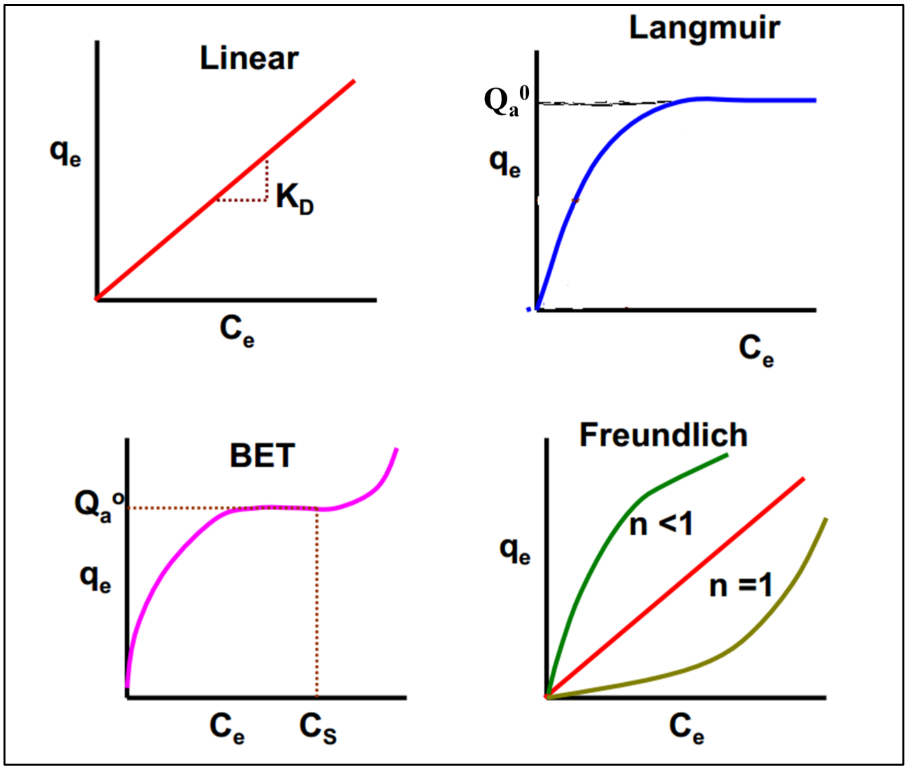


Figure 2.5 Commonly used adsorption isotherms

2.5 Arsenic Removal Using Adsorption

Adsorption of dissolved arsenic by adsorbents have been actively studied. Larger surface area, improved porosity, high adsorption capacity, and least waste generation make adsorption is an important remediation tool for arsenic removal. The appropriateness of adsorption based treatment for low skilled communities and developing countries arises due to its sludge free operation, cost-effectiveness and technical simplicity[44]. Generally, metal oxides/hydroxide, activated carbon, polymer resins or biological materials have been used as adsorbents. Iron has a high affinity for arsenic. Therefore arsenic removal using iron oxides is very popular[9]. Iron can remove As from aqueous solution either acting as a co-precipitant, adsorbent, contaminant-immobilizing agent or behaving as a reductant[26]. Iron-based oxide, hydroxides, and oxyhydroxides including amorphous hydrous ferric oxide (FeO-OH), goethite (α-FeO-OH) and hematite (α-Fe2O3), are prominent adsorbents for removing both As(V) and As(III) from aqueous solution[9]. As adsorption depends upon system concertation, pH and surface area of adsorbents. Amorphous hydrous ferric oxide (FeO-OH) has the highest adsorption capacity because it has maximum surface area[9]. On the other side at low pH, As(V) can easily remove whereas for As(III), maximum adsorption can be obtained between pH 4 and 9[45]. However, iron-based treatment methods are more effective in removing arsenate, rather than the more toxic arsenite, and so it requires oxidation as a pre-treatment[4]. Raven et al. (1998) [46] studied the adsorption behavior of As(III) and As(V) using ferrihydrite [$(Fe^{3+}O_3 \cdot 0.5(H_2O)$]. As relatively high As concertation, As(III) reacted quickly compare to As(V) and adsorption was almost accomplished in few hours. The high As(III) adsorption happened because of ferrihydrite was transformed to a ferric arsenite phase and not easily adsorbed at the surface. Roberts et al. [47] conducted a study for As removal by oxidizing naturally present Fe(II) to Fe(III) using aeration. Application of Fe(II) has an advantages over Fe(III) because it can partially be oxidized As(III). Also Fe(III) generated in this way have more adsorption capacity.

Pena et al. (2005) [48] studied removal of As(III) and As(V) using nanocrystalline titanium dioxide (TiO_2). TiO_2 was very effective in terms of As(V) removal at pH<8 and highest amount of As(III) removal done at pH~7.5. The capacity of nanocrystalline TiO_2 was higher for As(III) and As(V) removal compared to fumed TiO_2 and granular ferric oxide. The main challenge was the presence of competing anion e.g. phosphate, silicate and carbonate in water. Removal of As(III) and As(V) was investigated using commercially available TiO_2 varying pH and initial adsorbate concentration[7]. The adsorption capacity of As(V) was higher compared to As(III) onto TiO_2 at pH 4 while the adsorption capacity of As(III) increased at pH 9. The Langmuir and Freundlich isotherm equations interpreted the adsorption of arsenic using TiO_2 suspensions. Apart from iron and TiO_2, activated carbon is a good As adsorbent. Using activated carbon, adsorption capacity depends on adsorbate chemical properties, activated carbon properties, pH, temperature, ionic strength, etc. Eguez and Cho (1987) [49] examined adsorption of As(V) and As(III) using activated charcoal as an adsorbent. The capacity of As(III) adsorption on activated carbon was constant at pH 0.16–3.5. However, for As(V), maximum adsorption was established at pH 2.35 over the pH range of 0.86–6.33.

Chapter 3

3 As(V) Removal using Aerocrete and Vermiculite

Based on: Mrinmoyee Mondal, Pankaj Chowdhury, Ajay K Ray, Binay K. Dutta "Removal of As(V) using two different low-cost adsorbents Aerocrete and Vermiculite modified with iron oxy-hydroxide: a central composite design approach" (manuscript under preparation).

This chapter discusses the effectiveness of two low-cost adsorbents (Aerocrate and Vermiculite modified with iron oxyhydroxide) in terms of As(V) removal. These adsorbents were provided by the National Research Tomsk Polytechnic University, Tomsk, Russia. Aerocrete and Vermiculite have the high removal capacity of copper, lead, and cadmium with the advantages such as lower cost, producing no sludge and disposable in a landfill [24]. Therefore, we would like to investigate the performance of these two adsorbents in As(V) removal. Central composite design under response surface methodology is applied to optimize the experimental parameters (i.e., pH, adsorbent dose, initial As(V) concentration). The details of these adsorbents are given in the materials and methods section.

Response surface methodology (RSM) is a convenient statistical tool broadly used for experimental design and process optimization to build an empirical model[50]. The influence of operating conditions on response function can be determined by RSM. The first step of RSM is to select an experimental design which will determine the required experiments, need to be performed in a certain experimental region. Generally, factorial design is used when the data set represents linear response function, and three-level factorial, central composite design or Box-Behnken are applied for quadratic response function in the presence of curvature. Central composite design (CCD) under RSM is the most common approach which fits the quadratic model to define the relationship between the response and factors and optimize the response using a minimum number of experiments [50,51]. It is a useful method to determine the individual and interactive effect of the variables on the response function.

In this study, the face-centered central composite design has been used to build a regression model of As(V) adsorption by varying three independent variables, i.e. adsorbent dosage (g/L), initial pH, the initial concentration of metal ion (mg/L) in a certain range. The following section provides details about materials and methods followed in this study followed by result and discussions.

3.1 Materials and Methods:

3.1.1 Chemicals and Solutions:

As(V) stock solution of 1000 mg/L concentration was prepared by dissolving 4.16 g of Sodium salt of arsenic acid, Sodium arsenate dibasic heptahydrate (98% purity, Sigma Aldrich, Canada) in 1L of ultra-pure water (18.2 $M\Omega$) obtained with a Milli-Q water purification system (Thermo Scientific, BarnsteadTM EasypureTM RODi). Working standard solutions were prepared from stock solution by further dilution. Analytical grade reagents were used without further purification. Nitric acid (HNO_3; 68%) were obtained from VWR International (Mississauga, Ontario, Canada).

3.1.2 Preparation of Adsorbent

The adsorbent, Aerocrete and Vermiculite (>99% purity) were provided by the National Research Tomsk Polytechnic University, Tomsk, Russia. The molecular composition is given by Table 3.1 [24]. Cellular concrete materials were crushed in an agate mortar and screened at sieves with 1.5 - and 2.5 mm openings. The fraction from 1.5 to 2.5 mm was used in the supported adsorbent preparation by soaking in the ferric chloride (RusKhlor Association, Russia) aqueous solution with the subsequent addition of the 0.5-M aqueous solution of sodium hydroxide (JSC KhimProm, Russia) at 50 °C. The adsorbents were rinsed with distilled water until pH 6.5 to 7.2 and dried at 140 °C.

Table 3.1 Chemical properties of Aerocrete and Vermiculite

Aerocrete		Vermiculite	
Component	Weight percentage (%)	Component	Weight percentage (%)
$3CaO\cdot Al_2O_3$	3-6	K_2O	5-8
$3CaO\cdot SiO_2$	22-30	Fe_2O_3	5-9
$2CaO\cdot SiO_2$	8-2	Al_2O_3	12-18
Al_3O_3	2-3	MgO	20-24
SiO_2	60-65	SiO_2	38-49
		TiO_2	1-2
Al, TiO_2, MgO, K_2O, NaOH, CO_2 and H_2O	-----	CaO	0.7-1.5
		MnO, FeO, Na_2O, Cr_2O_3, CO_2 and H_2O	-----

The adsorbents are farther crashed with a mortar pestle, and the average particle size are 31 nm for Aerocrete and 36 nm for Vermiculite.

3.2 Batch Adsorption Experiments

The batch experiments were carried out with a series of 50 ml Erlenmeyer flasks containing

As(V) solution and a required amount of adsorbent and were agitated at 220 rpm with a mechanical shaker at room temperature 24 ±1° C for 4 hours. At the end of the equilibrium period, 10 ml of the samples were filtered through 0.45 µm filter, and concentration of As(V) was measured by inductively coupled plasma-optical emission spectrometer (Varian Vista Pro ICP-OES, Model- AXIAL, ID-14531). The Initial pH was adjusted to the desired value by adding 0.1M of HNO_3 and/or 0.1 M NaOH solutions.

The amount of As(V) adsorbed (q_e in mg/g), and the percentage removal (%) were calculated by the expression:

$$q_e = \frac{(c_0 - c_e)V}{m} \tag{3.1}$$

$$\text{Removal (\%)} = (1 - \frac{c_e}{c_0}) \times 100 \tag{3.2}$$

where c_0 and c_e are the initial and equilibrium concentrations of As(V) in solution (mg/L), V is the volume of solution (L), and m is mass of the adsorbent (g).

3.3 Experimental design and statistical analysis

A 2^3 central composite face-centered design was employed to determine the effect of major operating factors on arsenic removal and to find the combined effect of factors in maximum arsenic removal efficiency. Usually, adsorption of As(V) is dependent on various factors such as metal the initial As (V) concentration, pH of the solution, amount of adsorbent, temperature and time, etc [52]. In this study adsorbent dosage (x_1), initial pH (x_2) and initial concentration of arsenic (x_3) are selected to find the optimum condition for maximum removal of arsenic. The adsorption equilibrium time (4 hours) is fixed by some initial experiments and temperature (24 ±1º C) is used as room temperature. The three independent factors were studied at three different levels, coded -1, 0, +1 for low, middle and high respectively as presented in Table 3.2. Since different variables are expressed in different units and different range, so the independent variables need to be coded to compare the significance of their effect on response.

Table 3.2 Independent factors and their coded levels for the experimental design

Coded	X_1	X_2	X_3
level	Adsorbent dosage (g/L) (x_1)	pH (x_2)	Initial As concentration (mg/L) (x_3)
−1	0.5	6	12
0	2	7	22
+1	3.5	8	32

The experiment for center point was carried out six times to estimate the errors. The relation between real values x_i and coded values X_i is given by the equation:

$$X_i = \frac{x_i - x_0}{\Delta x_i} \tag{3.3}$$

where x_i is the real value of the ith independent variable, x_0 is the real value of the same independent variable at the center point and Δx_i is the step change. The mathematical relationship between the response Y (percentage removal of As(V)) and the variables X_1, X_2 and X_3 can be explained by the empirical second order polynomial equation:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad \textbf{(3.4)}$$

where, b_0 is the model constant coefficient, the linear effects of the factor, b_{ii} is the quadratic effects and b_{ij} is the two-way interaction effects for i=1,2,3. The software Minitab 17 was used to determine the coefficients for fitting the mathematical model. The optimum values of the factors were obtained by solving the regression equations and analyzing the response plot. The validity of the model was analyzed by student's t-test, p-value, F-value, correlation coefficient (R^2).

3.4 Results and Discussion

3.4.1 Textural Properties

Surface area and pore size of adsorbent are important information to understand the adsorption mechanism. The Brunauer-Emmett-Teller (BET) method of nitrogen thermal adsorption-desorption was used to determine the value of adsorbent surface properties using Tristar II 3020, Micromeritics Instrument Corporation (V1.03). The physicochemical properties including BET surface area, pore volume, pore size is given by Table 3.3 for Aerocrete and Vermiculite modified by iron oxyhydroxide. Type IV isotherm and a type-H_2 hysteresis loop were observed from the N_2 adsorption-desorption isotherm of the sample Aerocrete (Figure 3.1). BET surface area and pore volumes are 193 m^2/g and 0.3 cm^3/g for Aerocrete and 16 m^2/g ,0.3 cm^3/g for Vermiculite respectively.

Table 3.3 Textural properties of Aerocrete and Vermiculite

Adsorbent	BET surface area (m^2/g)	BJH pore volume (cm^3/g)	BJH Pore size (nm)	Average Particle Size (nm)
Aerocrete	193	0.28	4.9	31.1
Vermiculite	168	0.28	5.5	35.7

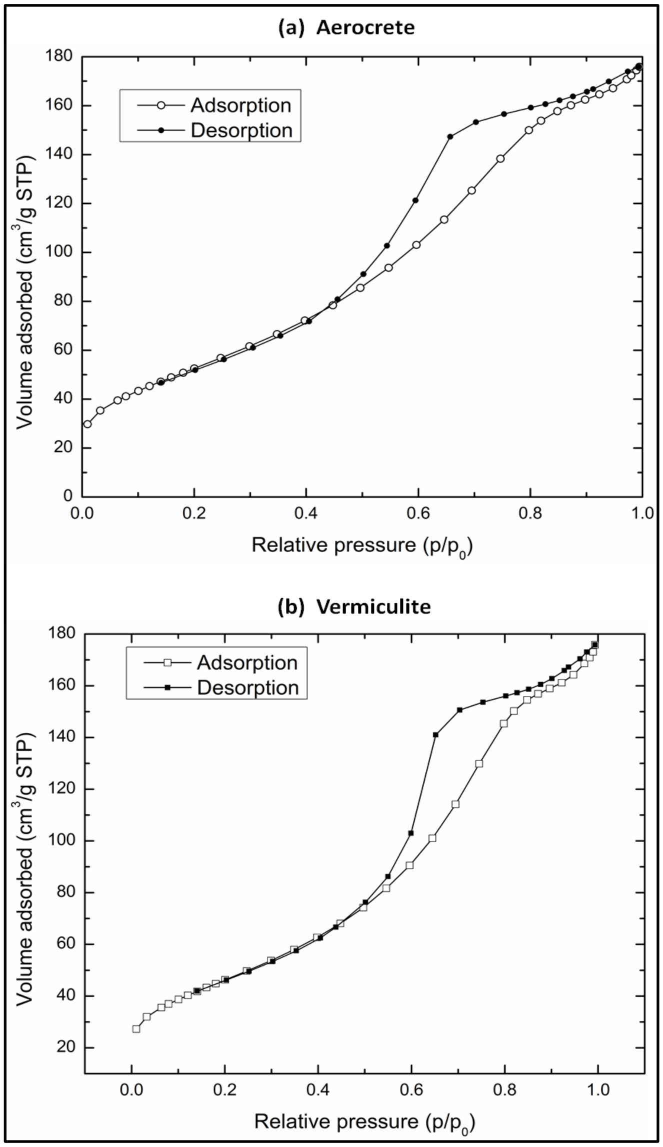


Figure 3.1 N_2 adsorption-desorption isotherm for (a) Aerocrete and (b) Vermiculite

3.4.2 Regression Model and Statistical Analysis

A quadratic model was used, to determine the relationship between the response variable and the independent factors. Using the experimental data, the final model of As(V) adsorption over Aerocrete and Vermiculite modified with iron-hydroxide was described by:

$$Y_{Aerocrete} = 79.23 + 30.46X_1 - 2.40X_2 - 9.77X_3 - 17.32X_1^2 + 0.88X_2^2 + 1.94X_3^2 + 0.53X_1X_2 + 4.23X_1X_3 - 1.01X_2X_3$$

(3.5)

and

$$Y_{Vermiculite} = 75.86 + 37.26X_1 - 2.38X_2 - 12.18X_3 - 19.68X_1^2 + 0.37X_2^2 + 1.70X_3^2 + 0.48X_1X_2 + 3.66X_1X_3 - 0.13X_2X_3$$

(3.6)

where Y is the response (percentage removal of As(V)), X_1, X_2, and X_3 are coded values of adsorbent dosage, pH, initial As(V) concentration respectively. The significance of the quadratic model and each coefficient in the model were tested by the value of F, p and R2, and Table 3.4 (for Aerocrete) and Table 3.5 (for Vermiculite) showed the ANOVA for the model equation. The model F-value (99.18 for Aerocrete, 80.35 for Vermiculite) and very low p-value ($0.000<0.05$) indicate that the model is statistically significant at 95% confidence level. In both cases, the lack of fit is insignificant, which implied that the quadratic model is valid. The coefficient of determinations (R^2) are 0.9890 and 0.9864 indicates the model is reliable on the removal of As(V) onto the two adsorbent. All the p-values of X_1, X_3, X_1X_3, X_1^2 are less than 0.05, which indicates that these variables are statistically significant. Hence, neglecting the higher order statistically insignificant term the model for Aerocrete and Vermiculite can be described as

$$Y_{Aerocrete} = 79.23 + 30.46X_1 - 2.40X_2 - 9.77X_3 - 17.32X_1^2 + 4.23X_1X_3 \quad (5a)$$

$$Y_{Vermiculite} = 75.86 + 37.26X_1 - 2.38X_2 - 12.18X_3 - 19.68X_1^2 + 3.66X_1X_3 \quad (6a)$$

Table 3.6 showed that experimental and model predicted values of As(V) removal were is reasonable agreement. The correlation coefficients (R^2) between the experimental and model predicted values were obtained as 0.989 and 0.986 as shown in Figure 3.2.

It is clear from the model coefficient that adsorbent dosage has highest first order as well as second-order effect on the removal of As(V) for both the adsorbent. The first order main effects of initial concentration are highly significant as compared to its quadratic effect (Table 3.4 & Table 3.5).

Table 3.4 Analysis of variance (ANOVA) of As(V) removal efficiency (%) using Aerocrete

Source	Sum of squares	Degrees of freedom	Mean square	F-value	p-value
Model	11690.5	9	1298.95	99.18	0.000
X_1	9277.1	1	9277.1	708.38	0.000
X_2	57.4	1	57.4	4.38	0.063
X_3	953.7	1	953.7	72.82	0.000
X_1X_2	2.3	1	2.3	0.17	0.687
X_1X_3	143.2	1	143.2	10.93	0.008
X_2X_3	8.2	1	8.2	0.63	0.447
X_1^2	827.6	1	827.6	63.2	0.000
X_2^2	2	1	2	0.15	0.705
X_3^2	10.1	1	10.1	0.77	0.401
Residual	131.0	10	13.10		
Lack of fit	103.8	5	20.76	3.82	0.084
Pure error	27.2	5	5.44		
Total	11821.5	19			
R^2= 0.98		Adjusted R^2= 0.97		Predicted R^2= 0.97	

Table 3.5 Analysis of variance (ANOVA) of As(V) removal efficiency (%) using vermiculite

Source	Sum of squares	Degrees of freedom	Mean square	F-value	p-value
Model	17730.8	9	1970.1	80.35	0.000
X_1	13882.4	1	13882.4	566.20	0.000
X_2	56.4	1	56.4	2.30	0.160
X_3	1483.3	1	1483.3	60.50	0.000
X_1X_2	1.9	1	1.9	0.08	0.788
X_1X_3	106.9	1	106.9	4.36	0.049
X_2X_3	0.1	1	0.1	0.01	0.940
X_1^2	1065.3	1	1065.3	43.45	0.000
X_2^2	0.4	1	0.4	0.02	0.905
X_3^2	8	1	8	0.32	0.582
Residual	245.2	10	24		
Lack of fit	179.9	5	36	2.76	0.145
Pure error	65.3	5	13.1		
Total	17976	19			
R^2= 0.98		Adjusted R^2= 0.97		Predicted R^2= 0.90	

Table 3.6 Design matrix for the central composite design: experimental conditions in terms of coded units and responses.

No. of Experiment	Run	Adsorbent dosage (g/L)	pH	Initial As concentration (mg/L)	Removal of As (V) (%)			
					Aerocrete		Vermiculite	
					Observed	Predicted	Observed	Predicted
1	2	-1	-1	-1	50.62	50.18	34.65	34.45
2	7	1	-1	-1	99.00	101.5	98.25	102.6
3	12	-1	1	-1	45.10	46.35	30.11	30.93
4	17	1	1	-1	98.43	99.86	97.94	97.17
5	8	-1	-1	1	25.99	24.21	2.97	3.04
6	3	1	-1	1	93.58	92.53	87.35	85.84
7	9	-1	1	1	19.26	16.33	4.06	-1.01
8	5	1	1	1	86.68	86.77	80.34	79.86
9	16	-1	0	0	27.06	31.50	14.55	18.92
10	10	1	0	0	95.48	92.42	95.05	93.44
11	18	0	-1	0	81.86	82.56	80.61	77.87
12	15	0	1	0	77.08	77.77	67.62	73.12
13	1	0	0	-1	95.26	90.99	90.56	86.34
14	11	0	0	1	65.80	71.46	55.00	61.98
15	14	0	0	0	76.26	79.31	75.75	75.86
16	6	0	0	0	79.36	79.31	84.09	75.86
17	13	0	0	0	78.26	79.31	74.93	75.86
18	4	0	0	0	79.80	79.31	74.56	75.86
19	19	0	0	0	82.69	79.31	75.62	75.86
20	20	0	0	0	81.62	79.31	75.75	75.86

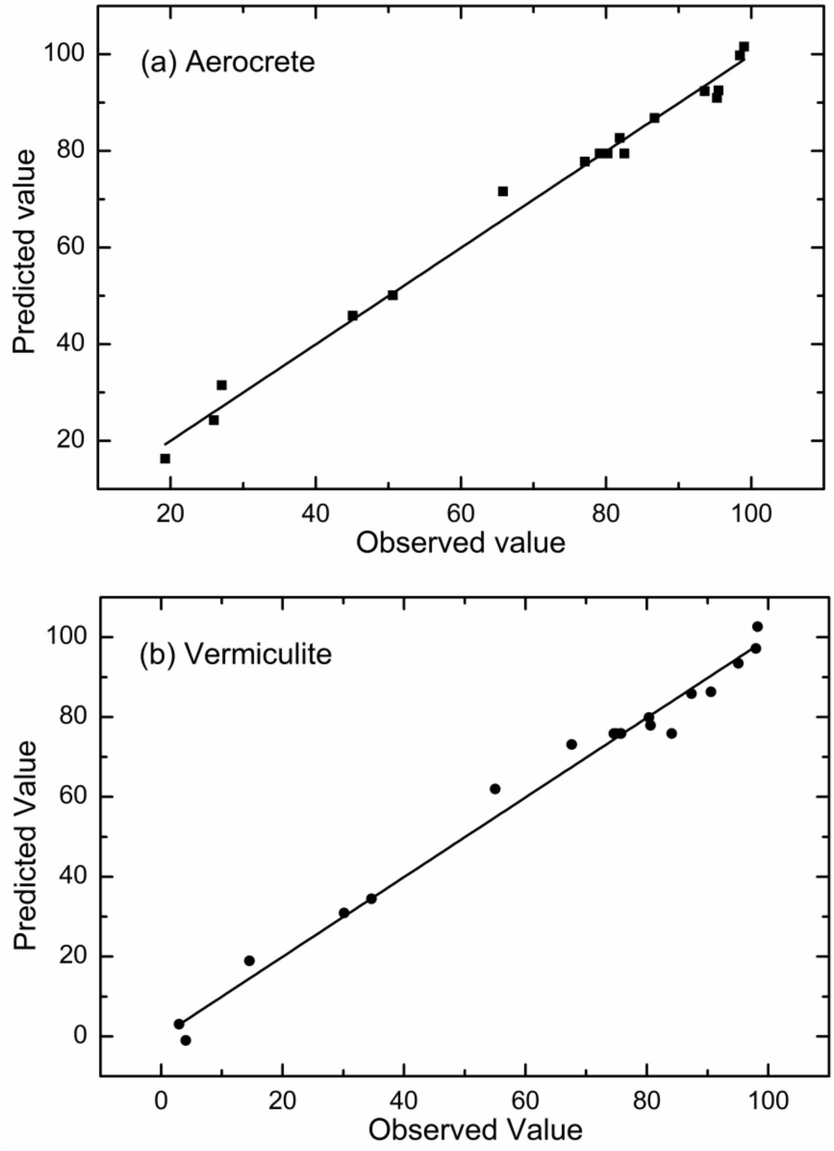


Figure 3.2 Predicted values vs. experimentally observed values of As(V) removal using (a) Aerocrete and (b) Vermiculite

3.4.3 Verification of Optimum Prediction by the Model

Triplicate experiment was performed under the optimal conditions, predicted by the model to verify the response surface prediction. The maximum percent removals of As(V) from the experiment were found to be 99.96% (Aerocrete)and 98.95% (Vermiculite) for two different adsorbents which were comparable with the values obtained by the model (Table

3.7). 3.1g/L of Aerocrete and 3.3 g/L of Vermiculite, the initial concentration of 12 mg/L at solution pH 6 were found as optimum conditions to get the maximum removal of As(V). Four experiments within the range but different from the face-centered response design point were carried out to test the reliability of the response model. Table 3.8 shows a good agreement between the response function prediction and experimental results.

Table 3.7 Verification of the model predicted optimum conditions

Optimum pH	Initial As(V) concentration (mg/L)	Adsorbent	Adsorbent dosage (g/L)	Removal of As(V) (%)	
				Model predicted value	Experimental value
6	12	Aerocrete	3.1	102.7	99.96
		Vermiculite	3.3	102.9	98.95

Table 3.8 Comparison of model predicted values and experimental values of As (V) removal in different experimental conditions

Adsorbent	Initial As(V) concentration (mg/L)	pH	Adsorbent dosage (g/L)	Removal of As(V) (%)	
				Model predicted value	Experimental value
Aerocrete	17	7	0.5	38.91	35.25
	12	6	3	102.91	99.85
Vermiculite	17	7	0.5	26.41	29.35
	12	6	3	102.12	98.65

3.4.4 Effect of Independent Factors on As(v) Removal (%)

The contour plots (Figure 3.3) describe the combined effect of independent variables on As(V) removal onto two different adsorbents. The figure are reprasented as a function of two factors holding the other factor at the center level.

3.4.4.1 Effect of Adsorbent Dosage

In this study, the effect of adsorbent dosage is found to be highest on the removal of As(V) as shown in ANOVA results (Table 3.4 and Table 3.5). It shows the linear and quadratic effect on the removal of As(V) which are highly significant ($p<0.0001$). The removal of As(V) increased from 40% to 80% when the adsorbent dosage increased from 0.5 to 2g/L (Aerocrete) and 0.5 to 2.75g/L (Vermiculite) for all initial concentration of As(V) and pH within the range. The maximum As(V) removal (99% and 95%) are obtained at adsorbent dosage 3.5g/L when the initial As(V) concentration and pH are at a low level for both adsorbent Aerocrete and Vermiculite (Figure 3.3 a, b, d and e). The combined effects of adsorbent dosage and initial concentration were highly significant ($p<0.0001$). Availability of higher surface area at the higher mass of adsorbent might be the reason for the increase of percentage removal of the metal ion with an increase in adsorbent dosage.

3.4.4.2 Effect of Initial pH

From the ANOVA table, the main effects of pH and the combined effects of pH with two other factors are not statistically significant for two adsorbents. It might be due to the small range of pH (6 to 8). From the Figure 3.3(b) and Figure 3.3(e), the As(V) removal at any pH using Aerocrete and Vermiculite, almost same for all fixed adsorbent dosage when initial As(V) concentration is 22 mg/L, although the lower pH shows better removal (95%) of As(V). Figure 3.3c and Figure 3.3f shows that the removal of As(V) decreased with increasing pH. It can be concluded that the natural pH range does not influence the removal of As(V) significantly when adsorbent dosage and metal ion concentration are fixed for both the adsorbent. In the pH range 6 to 8, $H_2AsO^-_4$ and $HAsO^{2-}_4$ are the predominant species of As(V), the electrostatic forces between negatively charged As(V) species and the usually positively charged adsorbent surface might be the reason for better removal of As(V) in natural pH range.

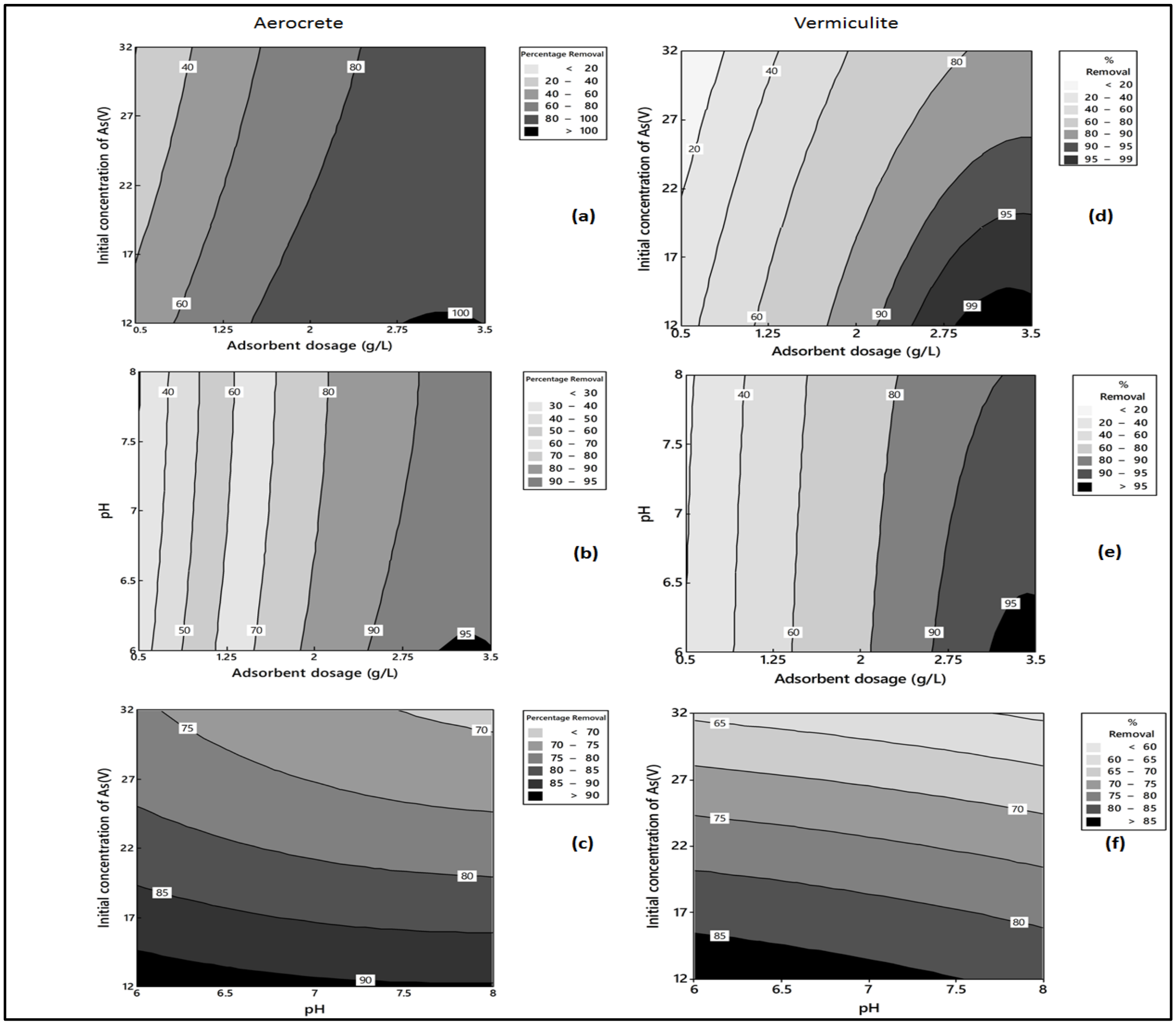


Figure 3.3 (a-c): Contour plot for combine effect Adsorbent dosage and initial As(V) concentration (b) pH and adsorbent dosage (c) initial As(V) concentration and pH for As(V) removal on Aerocrete. (d-f): Same for Vermiculite

3.4.4.3 Effect of Initial As(V) Concentration

The main effect of initial As(V) concentration and combined effect with adsorbent dosage were highly significant on As(V) removal for both the adsorbent according to the ANOVA table (Table 3.4 and Table 3.5). It is obvious that the percentage removal of As(V) decreases gradually with the increase in initial As(V) concentration (Figure 3.3 a, d, c, f). The maximum removal was obtained at the minimum initial As(V) concentration. As(V) removal decreases for a fixed adsorbent dosage at high initial metal ion concentration due to the decreased number of available active sites on the adsorbent surface[50].

3.4.5 Adsorption Isotherm

Adsorption isotherm is an equilibrium relation between the amount of adsorbed per unit mass of adsorbent and the concentration of adsorbate at a constant temperature (Fig 3.4). In this study, the Langmuir and Freundlich isotherm model is used to describe the adsorption mechanism. The As(V) concentration is 12 mg/L, and the adsorbent dosage varies from 0.5-3.5 g/L at pH 6 when the temperature (24 ±1° C) and contact time remained constant.

The Langmuir isotherm based on the assumptions of monolayer adsorption with the uniform active site on the surface can be expressed by the linearized form as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m}\left(\frac{1}{c_e}\right) \qquad \textbf{(3.7)}$$

And the Freundlich isotherm involves heterogeneous adsorbent surface with multilayer distribution of adsorbate were described as:

$$\ln q_e = \ln k_f + \frac{1}{n}\left(\ln c_e\right) \qquad \textbf{(3.8)}$$

where q_e is the amount of As(V) adsorbed per unit mass of adsorbent (mg/g), c_e is the equilibrium concentration of As(V) (mg/L), q_m is the maximum adsorption capacity and b is the affinity of the active site (L/mg) for Langmuir adsorption whereas k_f (mg/g) and

n is the Freundlich constant represented as the adsorption capacity and adsorption intensity. Plot $\frac{1}{q_e}$ vs. $\frac{1}{c_0}$ for Langmuir and $\ln q_e$ vs. $\ln c_e$ for Freundlich are drawn to evaluate the isotherm parameters and regression coefficient (R^2) respectively (Figure 3.5 and Figure 3.6).

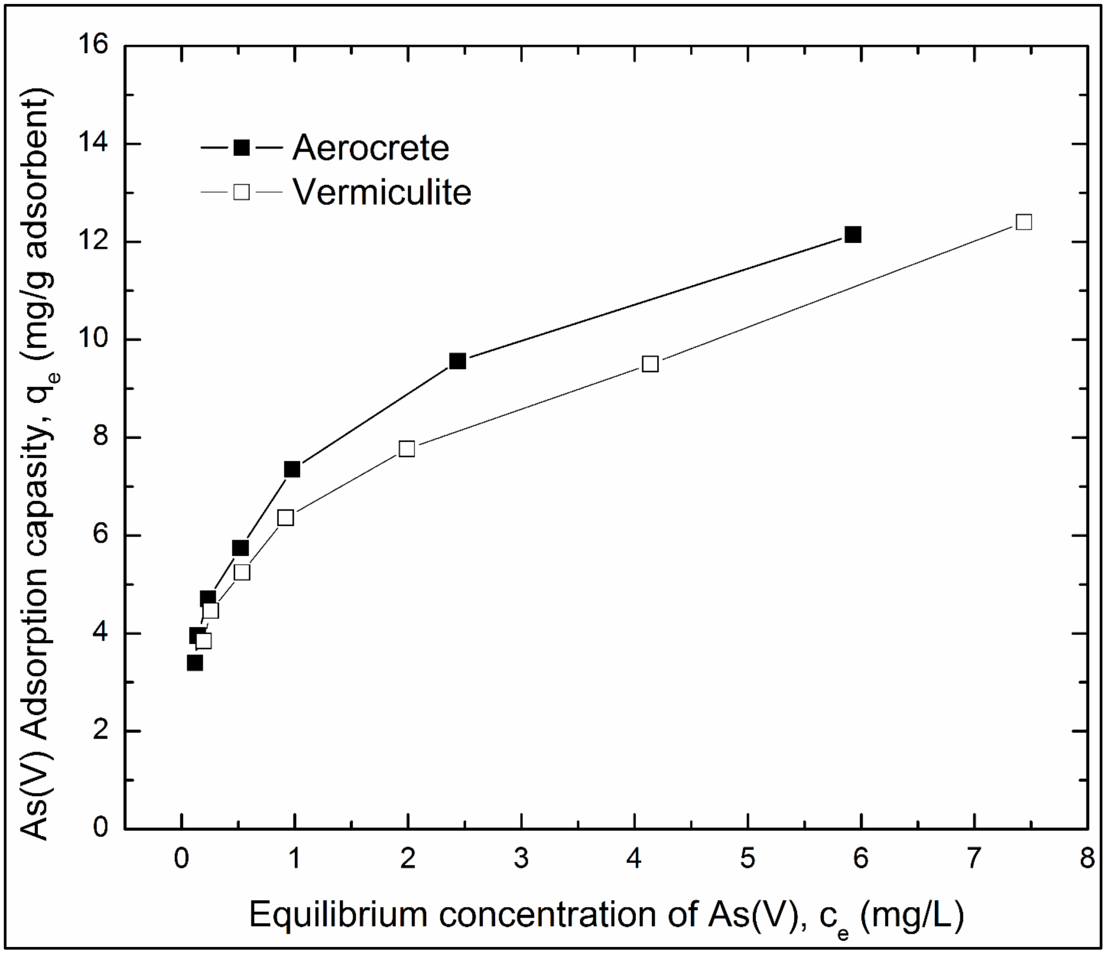


Figure 3.4 Adsorption Isotherm of As(V) on Aerocrete and Vermiculite

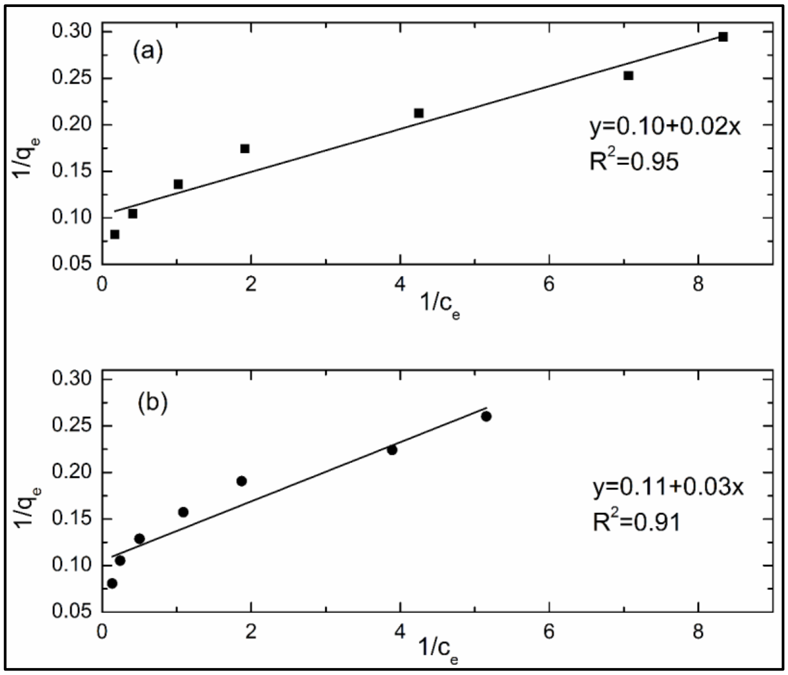


Figure 3.5 Langmuir adsorption isotherm for two different adsorbents **(**a) Aerocrete (b) Vermiculite

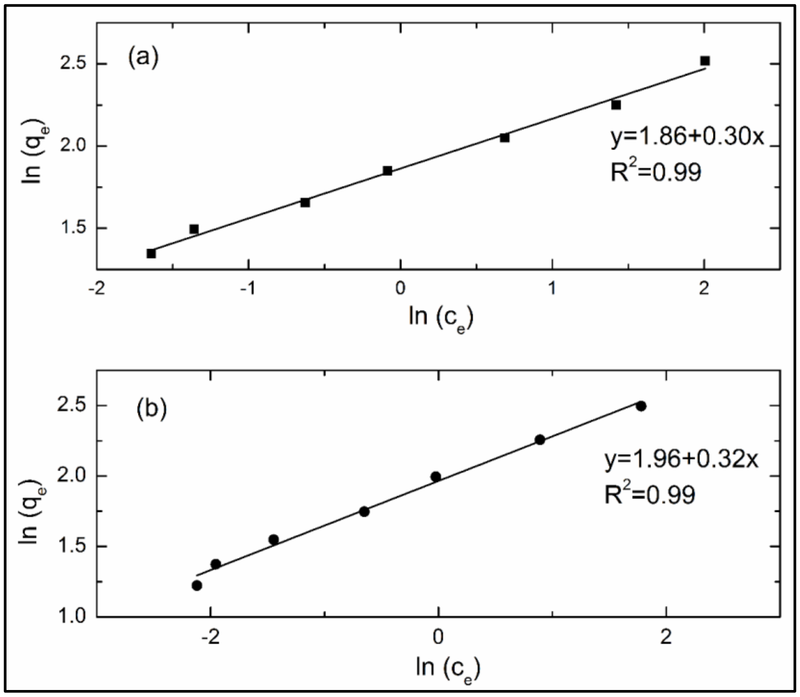


Figure 3.6 Freundlich adsorption isotherm for two different adsorbents **(**a) Aerocrete (b) Vermiculite

Results from the Table 3.9 indicates the adsorption data fitted the Langmuir model reasonably well (R^2 =0.95 and R^2 =0.91), but Freundlich isotherm model shows better adsorption for both the adsorbent Aerocrete (R^2 =0.99) and Vermiculite (R^2 =0.99). The higher value of n for both adsorbents suggests Freundlich adsorption is favorable. Furthermore, the maximum adsorption capacity of As(V) was 10 mg/g and 9.1 mg/g by Aerocrete and Vermiculite respectively. The dimensionless equilibrium parameter R_L is determined to explain whether the Langmuir adsorption is favored or not. The expression for is given by:

$$R_L = \frac{1}{\left(1 + bc_0\right)} \tag{3.9}$$

Where c_0 is the initial arsenic concentration (mg/L), and b is the Langmuir constant (Table 3.8). Adsorption is favorable when $R_L > 1$, unfavorable when $R_L > 1$, liner for $R_L = 1$ and irreversible if $R_L = 0$ [53].

In this study for initial As(V) concentration 12 mg/L the value of R_L was 0.01 and 0.02 indicating that adsorption is favorable but the values were close to zero implies adsorption was irreversible.

Table 3.9 Isotherm parameters of As(V) adsorption using Aerocrete and Vermiculite at pH 6

Adsorbent	**Langmuir**			**Freundlich**		
	q_m	b	R^2	k_f	n	R^2
Aerocrete	10	5	0.95	6.42	3.3	0.99
Vermiculite	9.1	3.7	0.91	7.1	3.1	0.99

3.5 Conclusions

As(V) adsorption on modified Aerocrete and Vermiculite is measured successfully. Both the adsorbent have higher adsorption capacity. The main effects of adsorbent dosage and initial As(V) are highly significant where pH effect is not statistically significant within their range (at 95% confidence level) for both adsorbents. Maximum removal 99.96% (Aerocrete) and 98.95% (Vermiculite) and the optimum conditions are presented below: adsorbent dosage 3.1g/L (Aerocrete) and 3.3 g/L (Vermiculite), pH 6, initial As(V) concentration 12 mg/L. Langmuir and Freundlich isotherm model is fitted well with the adsorption data for both adsorbents which states the existence of different active site of the adsorbents.

Chapter 4

4 Removal of As(III) Using Concrete-Based Adsorbents

Based on: Mrinmoyee Mondal, Kyriakos Manoli, Ajay K Ray, Binay K. Dutta "Removal of arsenic(III) from aqueous solution by concrete-based adsorbents" (manuscript submitted).

This chapter discusses the adsorption efficiency of As(III) onto two concrete-based low-cost materials, i.e., Aerocrete and Vermiculite impregnated by ferric oxyhydroxide. The presence of heavy metals, which are the main group of inorganic pollutants, in the aquatic environment, is a global environmental concern due to their toxicity and abundance [54]. Arsenic is a ubiquitous heavy metal (e.g., more than 245 minerals contain As) that occurs naturally in Earth's crust [27]. Arsenic pollution in natural waters has become a serious global concern due to the toxic and carcinogenic effect on the human body. Long-term exposure to arsenic-contaminated water causes keratosis, hyperpigmentation, anemia, liver fibrosis, lung cancer, skin cancer, and neurological disorder [55,56]. Millions of people around the world in both developed and developing countries are at risk of arsenic poisoning [9]. Not only natural but also anthropogenic activities are responsible for introducing arsenic to the environment. For example, soil erosion, volcanic activity, and mineral leaching are some of the natural processes introduce arsenic to water [57]. Mining, fossil fuel combustion, industrial activities, agriculture applications, smelting and landfilling are some examples of anthropogenic activities which release arsenic to the environment [58]. Arsenic concentrations in groundwater, surface waters, and thermal water vary from µg/L to mg/L [25,27].

Several oxidation states (-3, 0, +3, and +5) of arsenic can be found in nature. Two inorganic forms of arsenic, i.e., arsenite (As(III)) and arsenate (As(V)), are more common in natural waters [59]. Both As(III) and As(V) are hazardous, but As(III) is 60 times more toxic than As(V) [60]. Due to its high toxicity, the United States Environmental Protection Agency (USEPA) and European Union reduced the standard for arsenic concentration in drinking water from 50 µg/L to 10 µg/L [35,61]. As(III) is found as H_3AsO_3, $H_2AsO^-_3$, $HAsO^{2-}_3$, and AsO_3^{3-} in the groundwater. Uncharged H_3AsO_3 is the predominant species under reducing condition at pH less than 9.2 [35]. Therefore, removal of As(III) is difficult compared to As(V) at natural pH range. As(III) is more toxic, mobile and soluble in water [62], thus it is necessary and important to develop a technology to remove As(III) from water. This study deals with the removal of As(III) from water by adsorption.

Various technologies such as coagulation, precipitation, ion exchange, oxidation, adsorption, and membrane separation have been applied to remove arsenic from water and wastewater [21,32,56,58]. Among those, adsorption is one of the most popular water-treatment processes due to its simple design, high removal capacity, low operational cost and low environmental impacts [63]. Various adsorbents such as activated alumina [64], activated carbon [65], metal oxides/hydroxides including ferric oxide-hydroxide, aluminum oxides, titanium oxides, magnesium oxides, and silicon oxides have been studied for the removal of arsenic from water [66]. Some of these materials have unsatisfactory removal capacity for As(III) or high cost for unising in developing countries. Hence, the development and use of low-cost natural adsorbents with high effectiveness are getting more attention. Many materials have been tested as a low-cost adsorbent such as agriculture products [67], industrial wastes, concrete wastes [23], red mud [57], clay minerals [68], fly ash [69], and Portland cement [70]. Ferric oxides and hydroxides exhibit high affinity towards both As(III) and As(V) species [71]. Several studies showed that ferric impregnated materials like activated carbon, sand, alumina, polymeric materials, and concrete could effectively remove arsenic from aqueous solution [58,71]. Most of the studies above focused on the development of the adsorbent and the adsorption isotherms and kinetics, and limited work has been done so far on the effect of ions usually present in drinking water, surface waters, groundwater and wastewater on the removal of heavy metals by adsorption.

The present study investigates the adsorption of As(III) in the water on two ferric infused materials, i.e. Aerocrete and Vermiculite. Aerocrete is an aerated autoclaved light concrete belongs to the group of cellular concrete, which is widely used in construction work. Cellular concrete contains a porous structure with a large surface area. [72]. Vermiculite is another cheap and readily available concrete-based adsorbent found in North America, Russia, India, and South Africa [73]. This material exhibited satisfactory adsorption properties in the removal of heavy metals such as Ba, Cd, Co, Cr, Mn, Ni, Pb, Zn and As [74]. Recently, two iron-based adsorbents were synthesized, i.e. aerated autoclaved light concrete modified with ferric oxyhydroxide, and Vermiculite concrete modified with ferric oxyhydroxide [24]. These materials showed effective adsorption capacity for Cd, Cu, Pb and As(V) [24].

In this study, the removal of As(III) in aqueous solution by adsorption on aerated autoclaved light concrete modified with ferric oxyhydroxide (Aerocrete hereafter), and Vermiculite concrete modified with ferric oxyhydroxide (Vermiculite hereafter) was investigated, and compared with common adsorbents such as titanium dioxide (TiO_2) and silicon dioxide (SiO_2). The objectives of the present work are to: (i) assess the effect of pH on the adsorption of As(III), (ii) determine adsorption isotherm parameters, (iii) evaluate the effect of initial concentration of As(III) and contact time, (iv) determine adsorption kinetic parameters, and (v) investigate the effect of anions (Cl^-, SO_4^{2-} and HCO_3^-), monovalent cation (Na^+), and divalent cations (Ca^{2+} and Mg^{2+}) on the removal of As(III) by adsorption on Aerocrete and Vermiculite.

4.1 Materials and Methods

4.1.1 Chemicals

ReagentPlus grade arsenite salt sodium arsenite (≥98.0% purity), sodium chloride (≥99.5% purity), magnesium chloride hexahydrate (≥99.0% purity) and TiO_2 (Aeroxide P25) were purchased from Sigma Aldrich, Canada. Reagent grade sodium sulfate, calcium chloride, sodium bicarbonate were bought from Caledon Laboratory Chemicals (Georgetown, Ontario Canada). 12 ml (16×100 mm) polypropylene test tube and 0.45 µm polypropylene filters and 68% concentrated pure nitric acid obtained from VWR International (Mississauga, Ontario, Canada). As(III) solutions were prepared by dissolving Sodium arsenite in doubly distilled water passed through 18.2 MΩ water purification system (Thermo Scientific, BarnsteadTM EasypureTM RODi) (Milli-Q water). $Cacl_3$, $Mgcl_2$, Na_2SO_4, $NaHCO_3$, and NaCl were used to prepare aqueous solutions of Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO^{3-}, Na^+, and Cl^- in Milli-Q water, respectively. Analytical grade reagents were used without further purification.

The adsorbents, Aerocrete and Vermiculite (≥99.0% purity) were provided by the National Research Tomsk Polytechnic University, Tomsk, Russia. The adsorbents were further crashed with a mortar pestle. The characteristics (i.e. surface area and particle size) of the adsorbents (i.e. Aerocrete, Vermiculite, TiO_2 and SiO_2) used in the study are presented in Table 4.1.

Table 4.1 Characteristics of Adsorbents

Adsorbent	**Surface area (m^2/g)**	**Particle size (nm)**	**Pore volume (cm^3/g)**
Aerocrete	193	31	0.28
Vermiculite	168	36	0.28
TiO_2	35-65	21	-
SiO_2	480	250000-500000	0.75

4.1.2 Batch Adsorption Experiments

The batch experiments were performed in Erlenmeyer flasks containing 50 ml As(III) solution and a desired amount of adsorbent (in Milli-Q water), agitated at 220 rpm using a mechanical shaker (MaxQ 4000, the Barnstead|Lab-line) at room temperature (i.e. 24 ± 1^{o} C). Samples (10 ml) taken at different contact times were filtered through 0.45 µm to remove the adsorbent and then analyzed for As(III). The initial pH of the solution was adjusted to the desired value by adding 0.1 M of HNO_3 and/or 0.1 M NaOH solutions. To assess the impact of ions (i.e. Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-}, and HCO_3^{-}) on the adsorption of As(III) by Aerocrete and Vermiculite, the ions were individually added to the As(III) solution prior to the addition of the adsorbent.

The amount of As(III) adsorbed (q_e in mg/g), and percentage of removal (%) of As(III) were calculated by Eq. 4.1 and Eq. 4.2 respectively:

$$q_e = \frac{(c_0 - c_e)V}{m} \tag{4.1}$$

$$\text{Removal}(\%) = (1 - \frac{c_e}{c_0}) \cdot 100 \tag{4.2}$$

where c_0 and c_e (mg/L) are the initial and equilibrium concentrations of As(III) in solution respectively, V (L) is the volume of solution, and m (g) is the mass of the adsorbent.

4.1.3 Adsorption Isotherm and Kinetic Models

4.1.3.1 Isotherm Models

The Langmuir and Freundlich isotherm model were used to determine the isotherm parameters. The Langmuir isotherm based on the assumption of monolayer adsorption on homogeneous active site with no interaction among the adsorbed molecules defined by Eq. 4.3 [75]

$$q_e = \frac{bc_e q_m}{1 + bc_e} \tag{4.3}$$

The linear form of the Langmuir isotherm model is given by:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{bq_m}\left(\frac{1}{c_e}\right) \tag{4.4}$$

where q_e (mg/g) is the amount of As(III) adsorbed per unit mass of adsorbent, c_e (mg/L) is the equilibrium concentration of As(III), q_m (mg/g) is the maximum adsorption capacity and b (L/mg) is the affinity of the active site.

Freundlich isotherm model describes multilayer adsorbent on the heterogeneous adsorbent surface with the nonhomogeneous active site. The Freundlich model is described by Eq. 4.5 [76]:

$$q_e = k_f c_e^{\frac{1}{n}} \tag{4.5}$$

The linear form of Freundlich isotherm equation is followed by,

$$\ln q_e = \ln k_f + \frac{1}{n}\left(\ln c_e\right) \tag{4.6}$$

where, q_e (mg/g) is the amount of adsorbate adsorbed per unit mass of adsorbent, c_e (mg/L) is the equilibrium concentration of adsorbate, k_f ((mg/g).(L/mg)$^{1/n}$) and n are the Freundlich constants represented as the adsorption capacity and adsorption intensity respectively.

4.1.3.2 Kinetic Models

Two kinetic models, i.e. pseudo-first order and pseudo-second order, based on solid capacity were used to determine the kinetic parameters. The pseudo-first order model is described by Eq. 4.7:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{4.7}$$

The linearized form after integration can be expressed by Eq. 4.8:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4.8}$$

The pseudo-second order model based on the adsorption equilibrium capacity is expressed by Eq. 4.9:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad \textbf{(4.9)}$$

Its linearized form after integration is given by Eq.4.10:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad \textbf{(4.10)}$$

where q_t (mg/g) is the amount of As(III) adsorbed at time t (min), q_e (mg/g) is the amount of adsorbed As(III) at equilibrium time, k_1 (min^{-1}) is the rate constant of the pseudo-first order kinetic model, and k_2 (g/mg min) is the rate constant of the pseudo-second order kinetic model.

4.1.4 Analytical Methods

The total concentration of arsenic in solution was measured by an inductively coupled plasma-optical emission spectrometer (Varian Vista Pro ICP-OES, Model-AXIAL). ICP standards of 0.01 mg/L, 0.1 mg/l, 1 mg/L, 10 mg/L of As(III) were used for the calibration curve. A solution of 0.1 mg/L of As(III) was used as a quality assurance standard. The samples with a concentration greater than 10 mg/L were diluted using 2% nitric acid solution. The wavelengths used for sample analysis were 188.980 nm, 193.696 nm, and 197.198 nm.

4.2 Results and Discussion

Figure 4.1 shows the As(III) removal efficiencies by Aeroctere and Vermiculite at different pH values, at a constant amount of adsorbent (1 g/L) and initial concentration of As(III) (11.5 mg/L).

4.2.1 Effect of pH

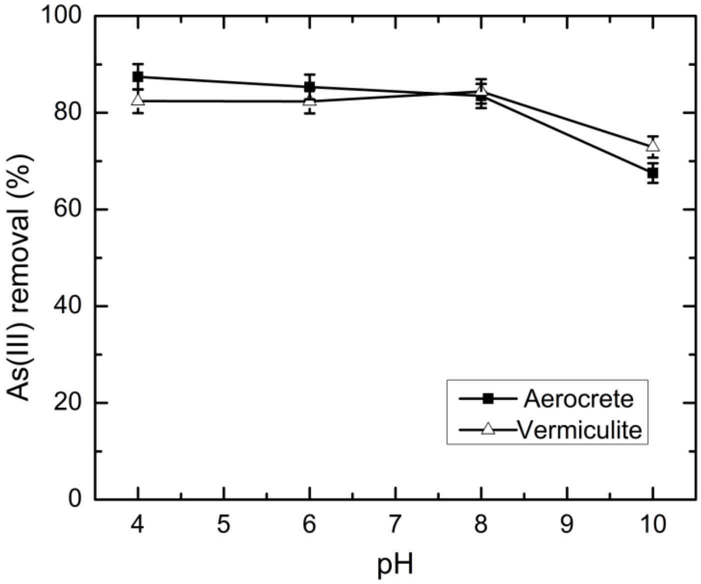


Figure 4.1 Effect of initial pH on the adsorption of As(III) by Aerocrete and Vermiculite. (Experimental conditions: [As(III)]=11.5 mg/L; [Adsorbent]=1 g/L; Time=4 h; T=24±1 ℃).

The percentage of removal of As(III) was constant (~85%) at the pH range of 4-8 for both adsorbents used. In both cases, i.e. Aeroctere and Vermiculite, the removal of As(III) decreased from ~85% to ~70% at pH 10 (Figure 4.1). As(III) removal using Aerocrete and Vermiculite did not show a significant dependence on initial pH at the pH range of 4-8. Particularly, the high removal efficiency of As(III) at initial pH range of 6-8 is important for water-treatment applications because it is consistent with regulatory criteria (e.g. standards for secondary effluent wastewater discharged to surface waters), hence no pH adjustment is required. Thus, further experiments were performed at pH 7.

The pH has a great influence on the speciation of As(III) in water. Uncharged H_3AsO_3 is the predominating species at pH less than 9.2, $H_2AsO^-_3$ at pH 9-12, $HAsO_3^{2-}$ at pH from 12-13, and AsO_3^{3-} for a pH higher than 13 [27]. The pH also affects the surface charge of adsorbent, i.e. positively charged bellow point of zero charge, and negatively charged above the point of zero charge. As(III) is negatively charged at a pH higher than 9.2. The electrostatic attraction between neutral As(III) species and the positively charged iron-based adsorbent surface is probably the adsorption mechanism for a pH up to 8. The low removal at higher pH can be explained by the electrostatic repulsion force between negative As(III) species and negative adsorbent surface sites [77].

4.2.2 Adsorption Isotherms

The equilibrium adsorption of As(III) was measured at different amounts of adsorbent (i.e. 0.5 g/L, 1 g/L, 1.5 g/L, 2 g/L, 2.5 g/L and 3 g/L) for Aerocrete, Vermiculite, SiO_2, and TiO_2, at 10 mg/L initial As(III) concentration, 24 ±1° C and pH 7. Interestingly, no adsorption of As(III) in water by SiO_2 was observed at the studied experimental conditions hence the isotherm parameters could not be determined for SiO_2. The experimental data were fitted using the linearized equation of Langmuir and Freundlich, i.e. Eq. 4.4 and Eq. 4.6 respectively isotherm model.

Figure 4.2 and Figure 4.3 show the Langmuir and Freundlich isotherms respectively. The isotherm parameters are presented in Table 4.2. Both Langmuir and Freundlich isotherm models fit well the experimental data for As(III) adsorption onto Aerocrete and Vermiculite ($R^2 \geq 0.94$) (Figures. 4.2 a-b, 4.3a-b and Table 4.2). The maximum adsorption capacity (q_m) was determined as 15.15 mg/g and 13.51 mg/g for Aerocrete and Vermiculite respectively.

Table 4.2 Langmuir and Freundlich isotherm parameters for As(III) adsorption on Aerocrete, Vermiculite, and TiO_2 at pH 7 and 24±1℃.

Adsorbent	Langmuir			Freundlich		
	q_m (mg/g)	b (L/mg)	R^2	k_f ((mg/g).(L/mg)$^{1/n}$)	n	R^2
Aerocrete	15.15	1.46	0.94	8.42	1.96	0.95
Vermiculite	13.51	1.17	0.97	6.61	2.08	0.99
TiO_2	3.52	0.69	0.85	1.82	4.13	0.88

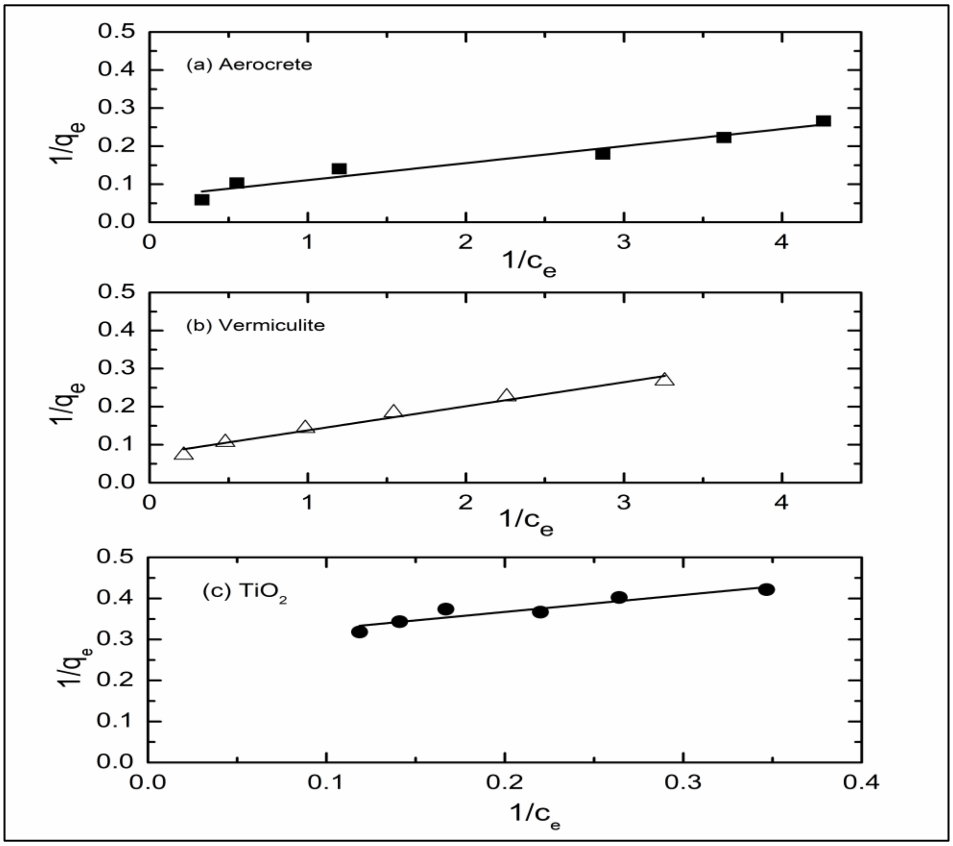


Figure 4.2 Langmuir adsorption isotherm for (a) Aerocrete, (b) Vermiculite, and (c) TiO_2, at pH 7 and 24±1℃.

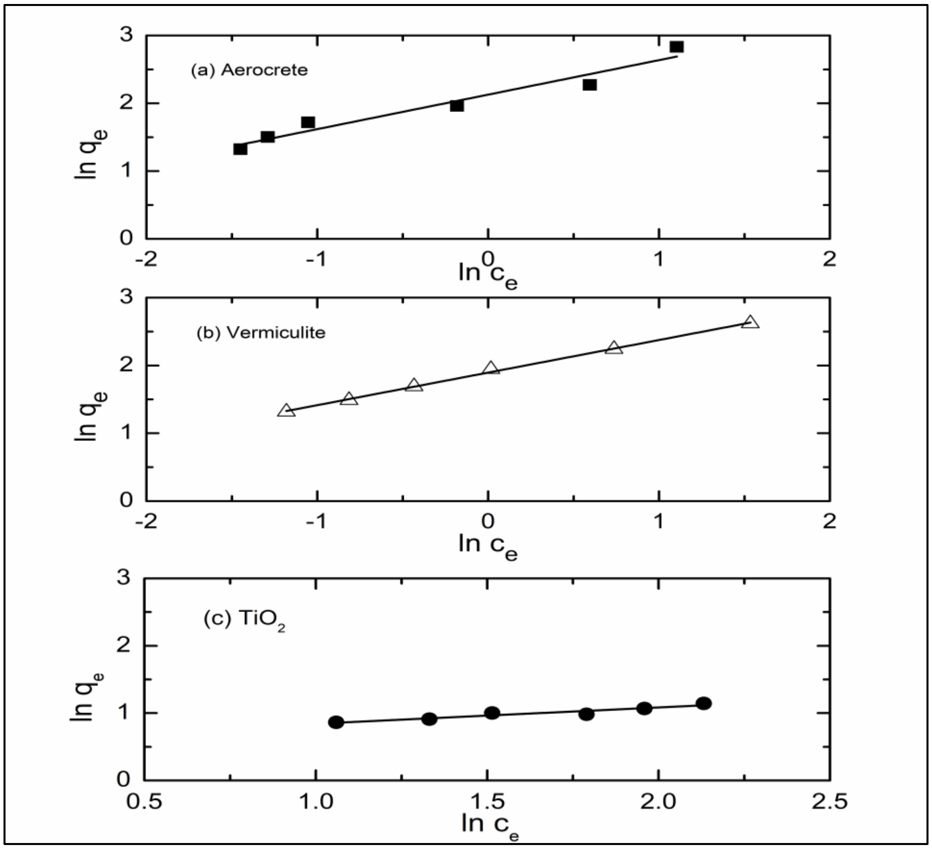


Figure 4.3 Freundlich adsorption isotherm for adsorbent (a) Aerocrete (b) Vermiculite and (c)TiO_2, at pH 7 and 24±1℃.

The dimensionless Langmuir parameter R_L (separation factor) represents the ratio of the unused adsorption capacity to maximum adsorption capacity (Eq. 4.11) [78]:

$$R_L = \frac{1}{(1+bc_0)} \tag{4.11}$$

where c_0 is the initial As(III) concentration (mg/L), and b is the Langmuir constant (Table 4.2). Langmuir adsorption is favorable for $0 < R_L < 1$, unfavorable for $R_L > 1$, linear for $R_L = 1$, and irreversible for $R_L = 0$ [64]. For an initial As(III) concentration of 11.5 mg/L, the value of R_L is 0.06 and 0.07 for Aerocrete and Vermiculite respectively indicating that adsorption is favorable. The fact that the determined Freundlich parameter n is higher than 1 (Table 4.2) suggests nonhomogeneous multilayer adsorption of As(III) on the studied adsorbents[79]. The higher value of Freundlich parameter n (i.e. 1.96 for Aerocrete and 2.08 for Vermiculite) indicates high intensity and favorable adsorption of As(III) implying that As(III) is easily adsorbed by Aerocrete and Vermiculite. As(III) adsorption onto Aerocrete and Vermiculite follows both Langmuir and Freundlich isotherm models which demonstrate that adsorption of As(III) is not restricted to a monolayer coverage only (ions are also adsorbed onto the heterogeneous surface of the iron-based adsorbent with various kind of active site).

The isotherm study with TiO_2 was conducted to compare the adsorption efficiency of As(III) by TiO_2 with Aerocrete and Vermiculite at the same experimental conditions. The correlation coefficient (R^2) is 0.85 for Langmuir and 0.88 for Freundlich isotherm. The maximum adsorption of As(III) on TiO_2 was determined as 3.52 mg/g which is lower than ones determined for Aerocrete and Vermiculite (Table 4.2). A similar result of As(III) adsorption on TiO_2 at pH 9 was reported [7]. The results show clearly that Aerocrete and Vermiculite are more efficient in removing As(III) from water at pH 7. For this reason, the kinetics of As(III) adsorption were investigated for Aerocrete and Vermiculite only. The surface area is 35 to 65 m^2/g for TiO_2, 193 m^2/g for Aerocrete and 168 m^2/g for Vermiculite. High surface area and great affinity towards iron-based adsorbent might be the reason for high removal of As(III) onto Aerocrete and Vermiculite compared to TiO_2.

4.2.3 Effect of Initial Concentration of As(III) and Contact Time

The effect of different initial As(III) concentration is presented in Figure 4.4. It is clearly shown that an increase of the initial concentration of As(III) increases the adsorption capacity of Aerocrete and Vermiculite (Figure 4.4). The increased driving force due to higher initial As(III) concentration allows overcoming mass transfer resistance between the adsorbent and its medium, resulting in higher adsorption capacity[80]. The equilibrium time increased with increasing As(III) concentration (Figure 4.4). Importantly, the adsorption reaches equilibrium within 60 min regardless of the As(III) concentration used (i.e. 1 mg/L, 5.5 mg/L or 11.5 mg/L). The adsorption behavior remains unchanged at higher contact times. As(III) at an initial concentration of 1 mg/L could be removed almost completely by both adsorbents (1 g/L) within 10 min of contact time (Figure 4.4). Initially, the adsorption of As(III) was fast, indicating the availability of unused active sites on the adsorbent surface, then site saturation occurs gradually with increasing time and plateau is reached (Figure 4.4).

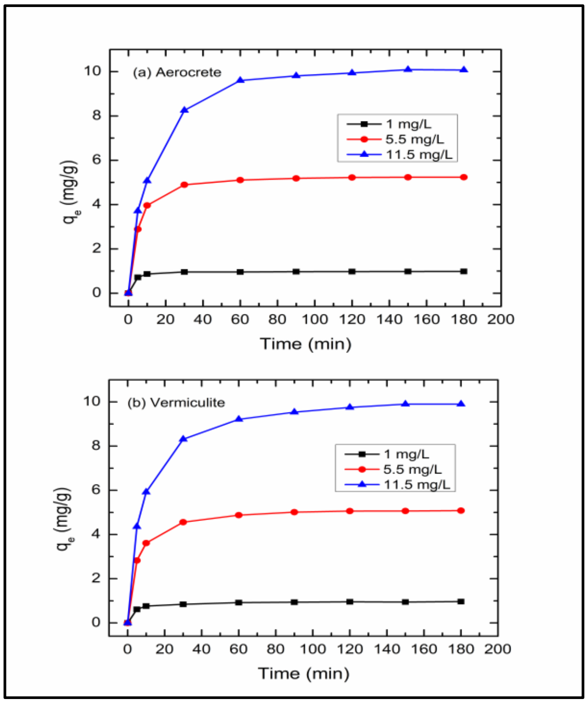


Figure 4.4 Effect of initial concentration of A(III) adsorption onto (a) Aeroctere, and (b) Vermiculite. (Experimental conditions: [Adsorbent]=1 g/L; pH=7; T=24±1℃).

4.2.4 Adsorption Kinetics

Three different initial concentrations (1 mg/L, 5.5 mg/L, 11.5 mg/L) are used to study the adsorption kinetics. The linearized form of pseudo-first and pseudo-second order kinetic models were applied to fit the kinetic data (Figure 4.5 and Figure 4.6). The adsorption rate constants are presented in Table 4.3. Based on R^2 values, the pseudo-second order model fits experimental data better than the pseudo-first order model for both adsorbents (Figure 4.5, Figure 4.6, and Table 4.3) which indicates that chemisorption most probably controls the adsorption of As(III) on Aeroctere and Vermiculite[81][79]. Previous studies also reported that adsorption of As(III) follows pseudo-second kinetics for iron oxide coated cement [59], water treatment residuals containing iron and manganese [82], and hydrous iron oxide impregnated alginate beads [71]. The second-order rate constant (k_2), decreased with increased As(III) initial concentration, indicates the slower adsorption by Aerocrete and Vermiculite at a high solute concentration (Table 4.3). The q_e values obtained from pseudo-second order model are in good agreement with the q_e values obtained experimentally.

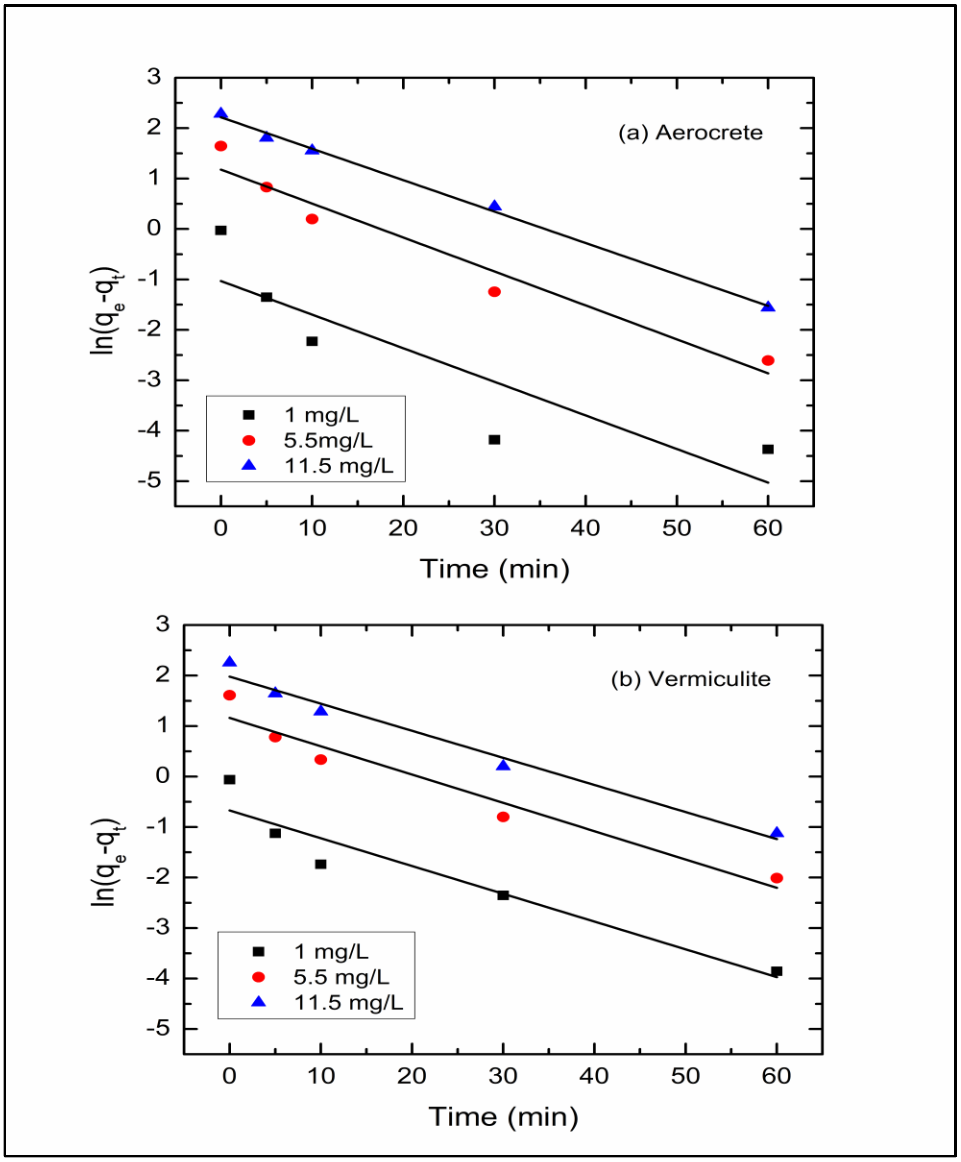


Figure 4.5 Pseudo first-order kinetic model for A(III) adsorption onto (a) Aeroctere and (b) Vermiculite, at pH 7 and 24±1℃.

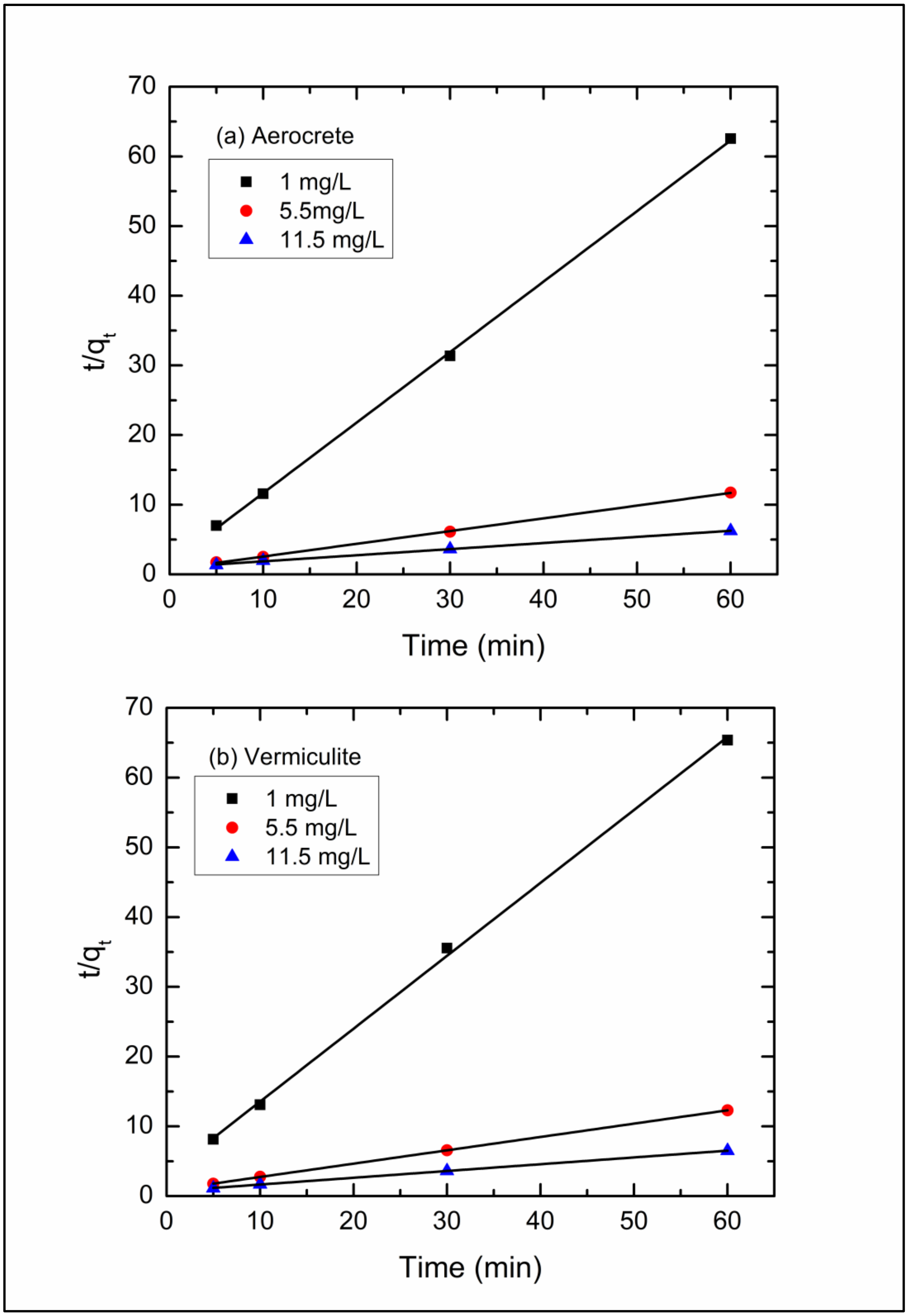


Figure 4.6 Pseudo second-order kinetic model for As(III) adsorption onto (a) Aeroctere and (b) Vermiculite, at pH 7 and 24±1℃.

Table 4.3 Pseudo-first and pseudo-second order kinetic model parameters for As(III) adsorption onto Aerocrete and Vermiculite at pH 7 and 24±1℃.

			Pseudo-first order				**Pseudo-second order**			
Adsorbent	**Initial As(III) concentration mg/L**	**$q_{e,exp}$**	**Equation**	**R^2**	**k_1 (min^{-1})**	**$q_{e1,cal}$**	**Equation**	**R^2**	**k_2 (g/mg·min)**	**$q_{e2,cal}$**
Aerocrete	1.0	0.97	$\ln(q_e-q_t)=-1.03-(-0.07)t$	0.71	0.07	0.36	$t/q_t=1.55+1.01t$	0.99	0.660	0.99
	5.5	5.18	$\ln(q_e-q_t)=1.178-(-0.07)t$	0.93	0.07	3.25	$t/q_t=0.73+0.18t$	0.99	0.044	5.55
	11.5	9.81	$\ln(q_e-q_t)=2.21-(-0.06)t$	0.99	0.06	9.12	$t/q_t=0.99+0.09t$	0.99	0.008	11.11
Vermiculite	1.0	0.94	$\ln(q_e-q_t)=-0.67-(-0.06)t$	0.89	0.06	0.51	$t/q_t=3.1+1.04t$	0.99	0.350	0.96
	5.5	5.08	$\ln(q_e-q_t)=1.16-(-0.06)t$	0.93	0.06	3.19	$t/q_t=0.83+0.19t$	0.99	0.043	5.26
	11.5	9.54	$\ln(q_e-q_t)=1.98-(-0.05)t$	0.97	0.05	7.24	$t/q_t=0.69+0.1t$	0.99	0.014	10.00

4.2.5 Effect of Ions on the Adsorption of As(III)

Drinking water, groundwater, surface waters, and wastewater contain ions which may have a positive or negative effect on adsorption of As(III). The impact of common ions(Ca^{2+}, Mg^{2+}, Na^{+}, SO_4^{2-}, HCO_3^{-} and Cl^{-}) on the efficiency of As(III) adsorption onto Aerocrete and Vermiculite was investigated. The concentrations of the individually added ions were selected to be consistent with their concentrations usually found in wastewater[83][84]. No significant effect of Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}, or Cl^{-} on As(III) adsorption onto Aerocrete and Vermiculite was observed (Figure 4.7). This can be explained by the As(III) strong binding ability to the iron oxyhydroxide surface compared to other ions. Sulfate had no effect when Aerocrete was used. In the case of Vermiculite, the As(III) removal slightly decreased from 59% to 49% in the presence of sulfate (Figure 4.7). It has been reported that sulfate has weak affinity towards iron oxyhydroxide surface due to the similar chemical structure to arsenic, so that it may hinder As(III) adsorption onto the adsorbent [85]. Overall, the effect of ions on the removal of As(III) in water by adsorption on Aerocrete and Vermiculite was minimal justifying the applicability of the studied adsorbents to remove As(III) in more realistic conditions.

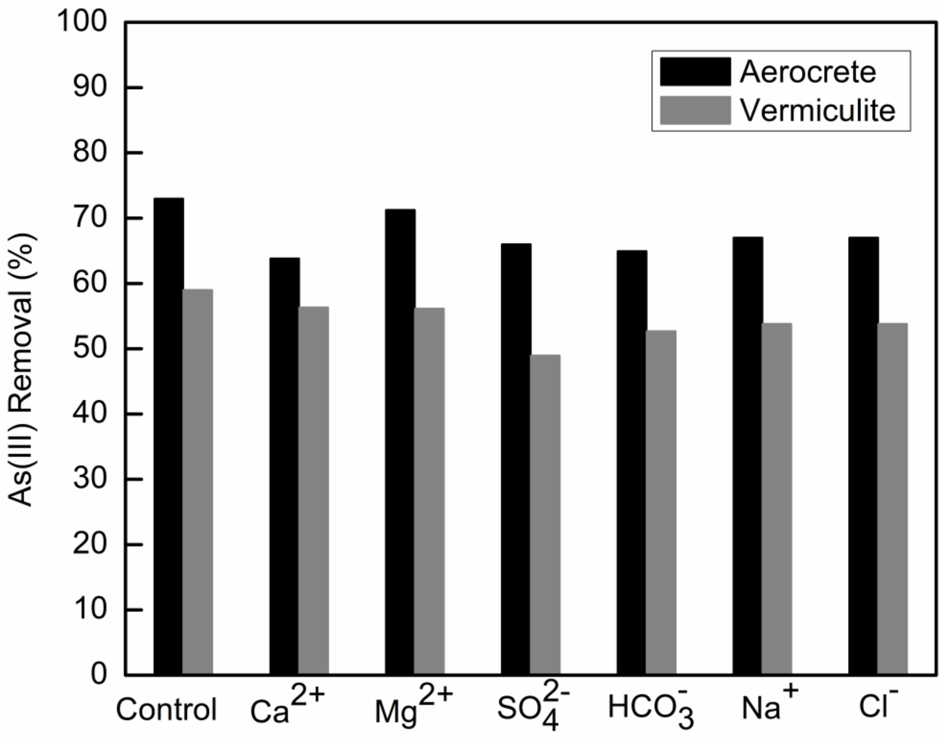


Figure 4.7 Effect of calcium (Ca^{2+}; $CaCl_2$), magnesium (Mg^{2+}; $MgCl_2.6H_2O$), sulfate (SO_4^{2-}; Na_2SO_4), bicarbonate (HCO_3^-; $NaHCO_3$), sodium (Na^+, NaCl), chloride (Cl^-, NaCl) on removal of As(III) by Aerocrete and Vermiculite.(Experimental conditions: [As(III)]=11.5 mg/L; [Adsorbent]=0.5 g/L; pH=7; T=24±1 ℃, [Mg^{2+}]=[HCO_3^-]=1 mM, [SO_4^{2-}]=[Ca^{2+}]=2 mM, [Na^+]=[Cl^-]=4 mM).

4.3 Column Design and Results

Batch adsorption process may not be suitable for large-scale water treatment, so a fixed bed column is often used in large-scale treatment process to remove the contaminant from waste/drinking water. The objective of the column test is to quantify the parameters which are required to design industrial scale fixed bed adsorption columns. Various low-cost adsorbents have been studied for their applicability in the treatment of different types of effluents. In this study, the potential of two concrete-based low-cost materials, i.e.

Aerocrete and Vermiculite impregnated by ferric oxyhydroxide were studied for the removal of As(III) in a fixed column.

4.3.1 Fixed Bed Column

Fixed-bed column experiments were conducted in a stainless-steel column (1 cm in diameter and 12 cm in length) packed with 1.5 g of the adsorbent with bed height 2 cm. Design details of the fixed bed column are given in Figure 4.8a, and the schematic diagram of continuous column experiment using packed bed column filter is given in Figure 4.8b. As(III) solution of 1mg/L, 5 mg/L and 10 mg/L concentration were fed in the up-flow mode, and the flow rate was 9 ml/min, controlled by a peristaltic pump (Masterflex L/S Digital Economy Drive, model 7518-60). The effluent was collected after a certain time interval from the same beaker. A magnetic stirrer was used to mix the influent and effluent properly. Laboratory experimental setup is shown in Figure 4.9. The results of preliminary experiment are given in Appendix-A.

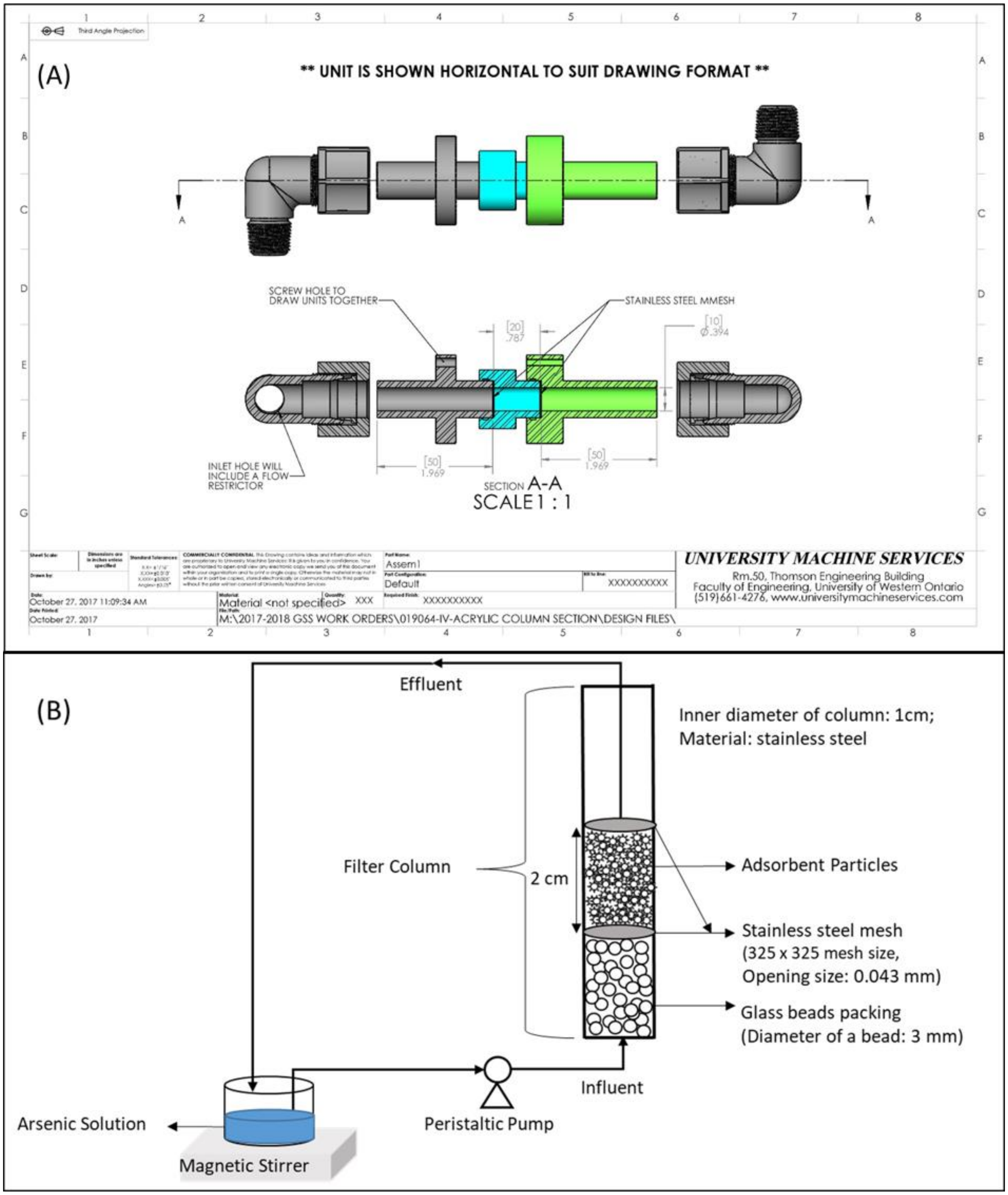


Figure 4.8 (a) Design details of packed bed adsorption column; (b) Schematic diagram of continuous column experiment using packed bed column filter

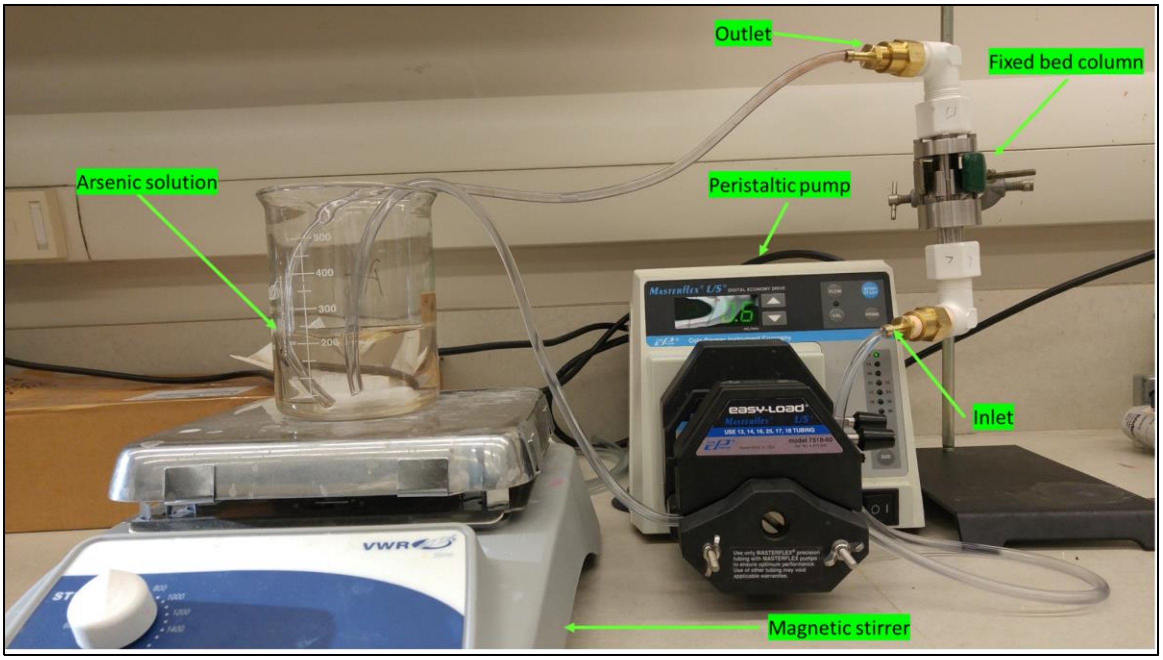


Figure 4.9 Laboratory experimental setup using packed bed column filter

4.4 Conclusions

In this study, the adsorption efficiency of As(III) in water using two new low-cost adsorbents (i.e. Aerocrete and Vermiculite impregnated by iron oxyhydroxide) was investigated, and the results were compared with two commercially available adsorbents, i.e. TiO_2, and SiO_2. Initially, the effect of the pH was studied resulting in the use of pH 7 as the optimum pH. Aerocrete and Vermiculite had high removal efficiency towards As(III) compare to TiO_2, where SiO_2 could not remove As(III) from water (Figure 4.10 and 4.11). The maximum adsorption capacities of As(III), derived from Langmuir model, were determined as 15.15 mg/g, 13.51 mg/g, and 3.52 mg/g, for Aerocrete, Vermiculite, and TiO_2 respectively.

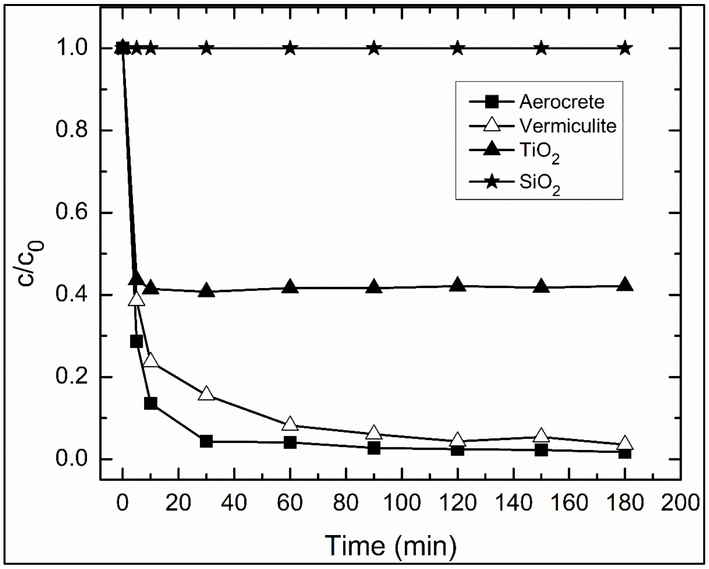


Figure 4.10 As(III) adsorption on different adsorbent (Aerocrete, Vermiculite, TiO_2, SiO_2) (Experimental conditions: [As(III)]=1 mg/L; pH=7; T=24±1 ℃)

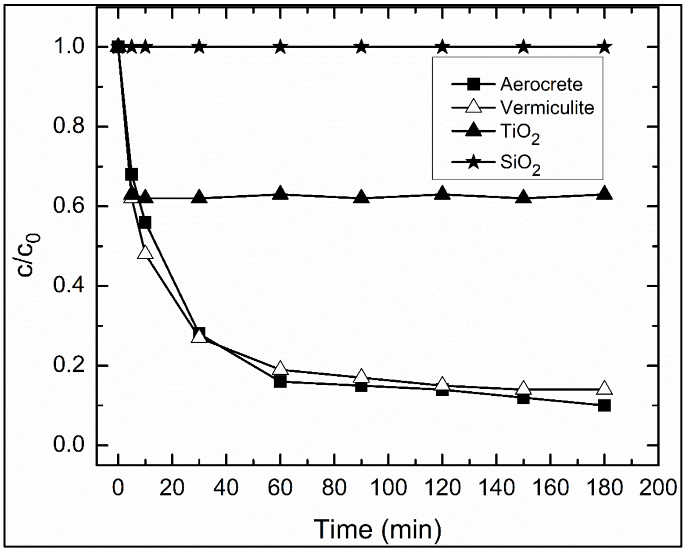


Figure 4.11 As(III) adsorption on different adsorbent (Aerocrete, Vermiculite, TiO_2, SiO_2) (Experimental conditions: [As(III)]=11.5 mg/L; pH=7; T=24±1 ℃)

The equilibrium adsorption data had a satisfactory agreement with both Langmuir and Freundlich isotherm models indicating the existence of different energy sites of the adsorbent surface.

As(III) adsorption follows pseudo-second order kinetics. This suggests that the adsorption process may be controlled by the chemical mechanism. Importantly, at a concentration of adsorbents of 1 g/L, As(III) could be removed almost completely within 10 mins, for both Aerocrete and Vermiculite, at As(III) initial concentration of 1 mg/L at pH 7 (Figure 4.11). A similar trend can be found for initial As concentration of 11.5 mg/L(Figure 4.12).

Significantly, the concentration of As(III) in the treated water was below the drinking water regulatory limit of 0.01 mg/L. The effect of the studied monovalent cation (Na^+), divalent cations (Mg^{2+} and Ca^{2+}), and anions (HCO_3^-, SO_4^{2-}, and Cl^-) on the adsorption of As(III) by Aerocrete and Vermiculite was not significant. This is important for the application of the proposed adsorbents to remove As(III) from water under more realistic conditions.

In column adsorption experiment of As(III), both adsorbents can remove almost 100 % of As(III) for all initial concentration (1 mg/L, 5.5 mg/L, 11.5 mg/L). However, adsorption time for maximum removal is 0.25 min at a lower initial concentration (1 mg/L) and 0.75 min for higher concentration (11.5 mg/L).

5 Summary and Future Work

In the present work discussed the performance of two adsorbents namely Aerocrete and Vermiculite for As(III) and As(V) removal. A face-centered central composite design of response surface methodology (RSM) was employed in this study to optimize effectiveness of three experimental variables i.e. adsorbent dosage (g/L), pH and initial As(V) concentration (mg/L) and also study the interactive effects of these variables on As(V) adsorption process. The analysis of variance (ANOVA) of the quadratic model shows that the predicted values are in good agreement with experimental data. Also, it shows that the main effect of adsorbent dosage and initial As(V) concentration, and interactive effect of adsorbent dosage and initial As(V) concentration on As(V) removal efficiency are highly significant. Maximum As(V) removal (≈ 99.96) is obtained at pH of 6, adsorbent dose of 3.1 g/L and initial As(V) concentration of 12 mg/L for Aerocrerte. At pH 6, adsorbent dose of 3.1 g/L and initial As(V) concentration 12mg/L are optimum conditions for maximum As(V) removal (≈ 98.95) for Vermiculite. The adsorption data are well fitted with the Langmuir and Freundlich isotherm model.

As(III), Adsorption experiments were performed to study the effect of initial pH, the initial concentration of As(III), contact time, and ions. Optimum removal of As(III) was observed at a pH range of 6-8. Both Langmuir and Freundlich isotherms described the adsorption equilibrium data. Langmuir isotherm showed that the maximum As(III) adsorption capacity of Aerocrete and Vermiculite is 15.15 mg/g and 13.51 mg/g respectively, which is much higher than the one observed using titanium dioxide (TiO_2), i.e. 3.52 mg/g. A pseudo-second order kinetic model fitted well with the experimentally obtained kinetic data. The pseudo-second order rate constants (k_2) were determined as 0.660 g/mg min, 0.044 g/mg min, 0.008 g/mg min and 0.35 g/mg min, 0.043 g/mg min, 0.014 g/mg min for Aerocrete and Vermiculite respectively. Importantly, As(III) could be removed almost completely by both adsorbents, at a contact time of 10 min, 1 g/L of adsorbent, 1 mg/L of initial As(III) concentration, pH 7, and 24±1℃. No significant effect on the adsorption of As(III) was observed in the presence of ions (i.e. Ca^{2+}, Mg^{2+}, Na^{+}, HCO_3^{-}, SO_4^{2-}, or Cl^{-}). Results showed that the proposed adsorbents (Aerocrete and Vermiculite) are promising in removing As(III) from the water. Also, we developed a fixed bed column for test the aplicability of these low cost adsorbents in industrial scale. Results show that Aerocrete and Vermiculite can remove As(III) satisfactorily in semi continuous batch mode. However the extensive test is required with different conditions e.g. varying pH, initial adsorbents concertation, with multiple ions etc.

5.1 The scope of Future Work

Aerocrete and Vermiculite are low-cost adsorbents with high removal capacities of As. But using in the small-scale, individual household or industrial scale both adsorbents need to satisfy many conditions which could be considered as future works of the present work.

- For example, effects of other ions existent were tested in batch experiments and with As(III), but for practical application, it needs to be tested under continuous flow with different conditions and with As(V).
- For the present study purpose, we used Milli-Q water for mixing As. However in actual field condition As contaminated water is mixed with other minerals and metals which could effect adsorbents removal capacity. Therefore testing of these adsorbents with actual As contaminated water could be another potential future work.
- The fixed bed column was tested under semi-continuous flow, but testing under continuous flow with different flow rate is required for the industrial application.
- The detail characterization of the adsorbents needs to be studied for a better understanding of the adsorption mechanisms.

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Appendix-A

Results of Column Experiment

Column adsorption experiment of As(III) was performed in semi-continuous batch mode with three different initial concentration: 1 mg/L, 5.5 mg/L, 11.5 mg/L using the adsorbents (1.5 g) Aerocrete and Vermiculite. Figure A.1 a and b describe that both adsorbents can remove almost 100 % of As(III) for all initial concentration. However, adsorption time for maximum removal is 0.25 min at a lower initial concentration (1 mg/L) and 0.75 min for higher concentration (11.5 mg/L). The rate of adsorption using Aerocrete is slightly higher than Vermiculite as shown in Table A.1.

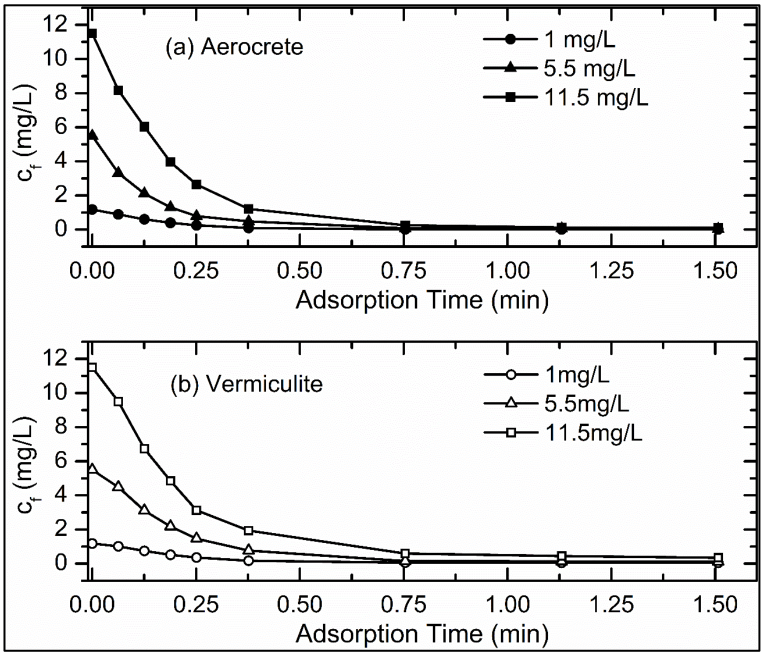

Figure A.1 Degradation of As(III) with respect to adsorption time in the column experiment

Table A.1 Average Rate of As(III) Adsorption obtained from batch and column experiment

Adsorbent	**Initial concentration of As(III) (mg/L)**	**Average Rate of As(III) Adsorption ($mg.g^{-1}.\min^{-1}$)**	
		Batch Experiment (Adsorbent dosage 1g/L)	**Column Experiment (Adsorbent dosage 6g/L)**
Aerocrete	1	0.016	0.257
	5.5	0.085	1.201
	11.5	0.16	2.487
Vermiculite	1	0.015	0.248
	5.5	0.081	1.185
	11.5	0.154	2.414

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Publications:

1. Mrinmoyee Mondal, Pankaj Chowdhury, Ajay K Ray, Binay K. Dutta “Removal of As(V) using two different low cost adsorbents Aerocrete and Vermiculite modified with iron oxy-hydroxide: a central composite design approach” (manuscript under preparation).

2. Mrinmoyee Mondal, Kyriakos Manoli, Ajay K Ray, Binay K. Dutta “Removal of arsenic(III) from aqueous solution by concrete-based adsorbents”, Separation and Purification Technology (under review).