การขจัดสารหนูปนเปื้อนในน้ำบนเม็ดอะลูมินาเอิบชุ่มด้วยเหล็กออกไซด์

นางสาวอรุณลักษณ์ จิรธนภิญโญ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Arsenic Removal from Contaminated Water over Iron Oxide Impregnated Activated Alumina

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อรุณลักษณ์ จิรธนภิญโญ : การขจัดสารหนูปนเปื้อนในน้ำบนเม็ดอะลูมินาเอิบชุ่มด้วยเหล็กออกไซด์. (ARSENIC REMOVAL FROM CONTAMINATED WATER OVER IRON OXIDE IMPREGNATED ON ACTIVATED ALUMINA) อ.ที่ปรึกษาวิทยานิพนธ์หลัก : รศ. ดร. นุรักษ์ กฤษดานุรักษ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม : ดร. กิติโรจน์ หวันตาหลา, 62 หน้า.

การศึกษาการดูดซับสารหนู (อาร์เซนิก, As) ในน้ำเสียสังเคราะห์โดยเม็ดอะลูมินาและเม็ดอะลูมินาปรับปรุงด้วยเหล็กซึ่งถูกเตรียมโดยวิธีเอิบชุ่มและการแคลไซน์ ฟังก์ชั่นบอกซ์เบห์นเกนดีไซน์ในโปรแกรมมินิแท็บถูกใช้ค้นหาสภาวะเหมาะสมที่เอื้อให้สามารถกำจัดสารมลพิษดังกล่าวออกจากน้ำได้ดีที่สุด การทดลองเบื้องต้นชี้ให้เห็นว่า เม็ดอะลูมินาเอิบชุ่มด้วยเหล็กมีประสิทธิภาพในการกำจัดสารหนูทั้งอาร์เซไนต์ As (III) และอาร์เซเนต As (V) สูงกว่าเม็ดอะลูมินา เม็ดอะลูมินาเอิบชุ่มด้วยเหล็กจึงถูกศึกษาต่อภายใต้สภาวะต่างๆ ซึ่งออกแบบโดยฟังก์ชั่นบอกซ์เบห์นเกนดีไซน์ การทดลองทั้งหมด 30 ชุดถูกทดลองแบบแบช ภายใต้ 3 ตัวแปรอิสระคือ พีเอช (3, 6 และ 9), ปริมาณเหล็กในหน่วยร้อยละต่อน้ำหนักเม็ดอะลูมินา (2, 4 และ 6%), และความเข้มข้นเริ่มต้นของอาร์เซเนต (100, 300 และ 500 μg/L) ส่วนตัวแปรตามคือ ร้อยละของการกำจัดอาร์เซเนต การคำนวณผลการทดลองด้วยโปรแกรมมินิแทบพบว่าในนาทีที่ 15 ของการทดลองดูดซับ สภาวะที่เอื้อต่อการกำจัดอาร์เซเนตสูงสุดคือ พีเอช 3, ปริมาณเหล็กร้อยละ 2.57 ต่อน้ำหนักเม็ดอะลูมินา และ ความเข้มข้นเริ่มต้นของอาร์เซเนตเท่ากับ 100 μg/L โดยสามารถกำจัดอาร์เซเนตได้ร้อยละ 77.64. สภาวะที่เอื้อต่อการกำจัดอาร์เซเนตสูงสุด ณ พีเอชเป็นกลางซึ่งเป็นพีเอชของน้ำใต้ดินพบว่าคือ พีเอช 7, ปริมาณเหล็กร้อยละ 4.53 ต่อน้ำหนักเม็ดอะลูมินา และ ความเข้มข้นเริ่มต้นของอาร์เซเนตเท่ากับ 100 μg/L โดยสามารถกำจัดอาร์เซเนตได้ร้อยละ 62.50 ในนาทีที่ 15

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต……………….……………...........
ปีการศึกษา 2554 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก…………....
ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์ร่วม………......

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KEYWORDS : BOX-BEHNKEN DESIGN/ARSENIC/IRON OXIDE/ACTIVATED ALUMINA

AROONLAK JIRA-THANA-PINYO: ARSENIC REMOVAL FROM CONTAMINATED WATER OVER IRON OXIDE IMPREGNATED ACTIVATED ALUMINA. ADVISOR: ASSOC. PROF. NURAK GRISDANURAK, Ph.D., CO-ADVISOR: KITIROTE WANTALA, Ph.D., 62 pp.

Activated alumina (AA) and Iron oxide impregnated on activated alumina (FeAA) by wet impregnation method were investigated in arsenate (As (V)) removal from synthetic water. Box-Behnken Design was utilized to reveal the optimization of FeAA performance to adsorb the toxic pollutant. The result from the pre-test indicated that FeAA provided better percent removal than AA for both arsenite (As (III)) and arsenate (As (V)). Therefore, merely FeAA was further experimented under various conditions obtained from Box-Benhken design. There were 30 analytical sets of FeAA in total conducted in batch tests based on three independent variable that are pH (3, 6 and 9), % Fe loading per alumina (2, 4 and 6%), and initial As (V) concentration (100, 300 and 500 μg/L). The dependent variable was percentage of As (V) removal. The calculation result from Box-Benhken design at 15th minute revealed that the optimal condition was pH of 3, %Fe loading per alumina weight of 2.57 and As (V) initial concentration of 100 μg/L provided the highest percentage removal of 77.64. At neutral pH which is the pH of groundwater, %Fe loading per alumina weight of 4.53 and As (V) initial concentration of 100 μg/L provided the optimal condition with a percentage removal of 62.50, at 15th minute.

Field of Study: Environmental Management Student's Signature…………..…………
Academic Year: 2011 Advisor's Signature……………………......
Co-advisor's Signature…………..……...

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LIST OF ABBREVIATIONS

AA	Activated alumina
AAS	Atomic Adsorption Spectrophotometer
As	Arsenic
As (III)	Arsenite, As^{3+}
As (V)	Arsenate, As^{5+}
BBD	Box-Behnken Design
BET	Brunauer-Emmett-Teller
C_0	Initial concentration
C_t	A concentration at a time
Eq.	Equation
FeAA	Iron oxide coated activated alumina
g	gram
h	hour
Kg	kilogram
m^2g^{-1}	Meter square per gram
mg/L	Milligram per liter
min	minute(s)
pHpzc	Point of zero charge
ppb	Parts per billion or μg/L
ppm	Parts per million or mg/L
RSM	Response Surface Methodology
SEM	Scanning Electron Microscope
XRD	X-Ray Diffraction

CHAPTER I

INTRODUCTION

1.1 Background

Arsenic (As) has been a main concern in sources for drinking water of many countries around the world including several parts of the United States, Thailand, Taiwan, China, Vietnam, Bangladesh, and Nepal. Those regions are encountered As in groundwater in higher concentration than WHO's guideline of 10 μg per liter, causing various types of cancer, neurological effects, cardiovascular disease, and diabetes (Smedley et al., 2002). The major source of high As concentration in drinking water naturally occurs from water that has filtered through As-rich rocks and As with higher concentrations tends to rather be encountered more in groundwater than in surface water which is sources of drinking water. Anthropogenic As contamination can also cause an important effect, including industrial or mining activities (Charlet, et al., 2001), fossil fuel combustion, the utilization of arsenical herbicides, pesticides and the making use of As as an additive in order for livestock feed, especially for poultry. Even though the utility of arsenical products, for example herbicides and pesticides, has significantly declined in the last few decades, it is still commonly used for wood preservation (Smedley and Kinniburgh, 2002). The main issue of As in water contamination is to reveal the level of As contamination which is not easy due to As has no taste, no odor, and no color even in the high As contamination.

The largest population suffered from As natural poisoning in history points to Bangladesh (Rahman et al., 2000). Arsenic concentration in groundwater in the country encountered over the range of <1-2,300 ppb and the pH value is neutral. The As concentration greater than Bangladesh standard for drinking water of 50 ppb is found in 61 districts, which is 150,000 km^2, out of total 64 districts in the country. Thirty-five million Bangladeshis is thought to have been consuming groundwater having As at concentration > 50 ppb and about 57 millions drinking water containing > 10 ppb. One of the main reasons of the huge scale of the problems is that the main drinking water source in Bangladeshis is groundwater (Smedley et al., 2002).

In Thailand, the health problems from drinking water documented as the worst identified case is caused by mining activity in Ron Phibun District, Nakhon Si Thammarat Province. The contamination area covers 100 km^2. This case of As poisoning resulting in health problems was first recognized in the area (year 1987), which some 15,000 people are thought to have been consuming water with > 50 ppb and over 1,000 people have been examined with As-related skin disorders (especially in Ron Phibun town and the areas nearby). The average and range concentrations are found as 218 ppb and 4.8–583 ppb, respectively, and pH range of aquifer is 6.05 to 7.12 (Smedley, 2002). Other than drinking the As-bearing water, other activities such as clean their bodies including face and hair in shallow-well water can lead people to unintentionally uptake As into their bodies. This is due to after bathing, people in the hot climate of Ron Phibun dry off their bodies by evaporation rather than by toweling. Therefore, As is likely left on the skin surface. Although the people normally use spoon for eating main rice meals, As residues could enter into ingestion system from handling food (Oshikawa et al., 2007).

1.2 Objectives:

1.2.1 To integrally investigate effects of initial As concentration, pH, and iron oxide coating on activated alumina (FeAA) for As removal.

1.2.2 To evaluate the liability of FeAA on Fe leaching.

1.3 Hypotheses:

1.3.1 Iron oxide can enhance the adsorption performance of activated alumina (AA) on As [As (III) and As (V)] removal from arsenic-bearing water.

1.3.2 Initial As concentration, pH and iron oxide coating on AA are affected on the efficiency of As removal.

1.4 Scope of the Study:

The experiment of this study is composed of four parts.

1.4.1 The preparation of iron oxide coating on activated alumina (FeAA) using impregnation method.

- 2%, 4% and 6% FeAA are prepared from 0.5, 1.0 and 1.5 M $Fe(NO_3)_3 \cdot 9H_2O$ per 10 g of AA.

- Calcination temperature is 550^{o} C with heating rate at 2.5^{o}C/min.

1.4.2 The comparison of As (III) and As (V) removal on AA and FeAA

- The condition is pH 3, and initial As (III) and As (V) concentration of 300 ppb.

- The adsorbents are AA and 6%FeAA.

1.4.3 The experiment based on Box-Behnken Design (BBD)

- Thirty sets of batch test designed by BBD function in Minitab 15.

- The conditions are relied on pH 3, 6 and 9, iron coating on AA of 2, 4 and 6%, and initial As (V) concentrations of 100, 300 and 500 ppb.

1.4.4 The Fe leaching test

- The optimum condition obtained from BBD is tested for Fe leaching at different times up to 24 hours.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Arsenic speciation

The main As species encountered in clinical and environmental samples are As (III), As (V), arsenious acids (H_3AsO_3, $H_2AsO_3^{-}$, $HAsO_3^{2-}$), As acids (H_3AsO_4, $H_2AsO_4^{-}$, $HAsO_4^{2-}$), dimethylarsinate (DMA), monomethylarsonate (MMA), arsenobetaine (AB) and arsenocholine (AC) (Kumaresan and Riyazuddin, 2001). These forms present in several oxidation states, namely -3, 0, +3 and +5, and create a complexity of its chemistry in the environment. However, As in inorganic form as oxyanion of As (III) or As (V) are mostly found in natural waters, while As metal rarely befalls, and the oxidation state of -3 of As is discovered only in very reducing environments (Smedley et. al., 2002).

In aqueous systems, As expresses anionic behavior. Both As (III) and As (V) form protonated oxyanions in the solutions. Redox potential (Eh) and pH are the most crucial determinants restricting As speciation, which the degree of protonation rely on pH (Figure 2.1 and Table 2.1).

On one hand, As (V) is stable in oxidizing conditions, for example aerobic water. The predominate As (V) species in solution are $H_2AsO_4^{2-}$ between pH 2.2 and 6.9, and $HAsO_4^{2-}$ between pH 6.9 and 11.5 whereas $H_3AsO_4^{0}$ and AsO_4^{3-} may be presented in ultomately acidic and alkaline conditions, respectively. On the other hand, As (III) is stable in moderately reducing conditions such as anaerobic water. H_3AsO_3 predominates at low pH up to pH 9.2, and $H_2AsO_3^{-}$ from pH 9.2-12 (Smedley and Kenneth, 2002). $HAsO_3^{2-}$ appears only when the pH exceeds 12 (Kumaresan and Riyazuddin, 2001).

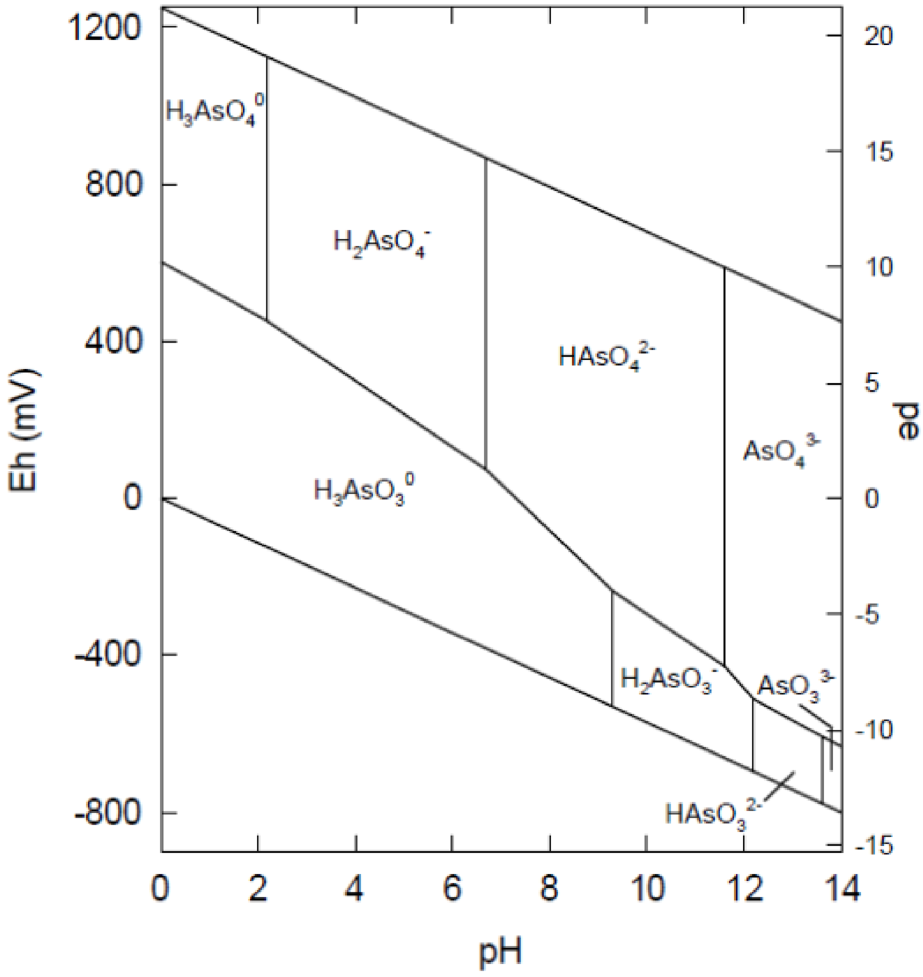

Figure 2.1 Eh-pH diagram of aqueous As species at 25ºC and 1 bar total pressure (Smedley and Kinniburgh, 2002).

Table 2.1 As (III) and As (V) species in different pHs

pH	**As (III)**
< 9.2	H_3AsO_3
9.2 – 12.2	$H_2AsO_3^-$
12.2 – 13.6	$HAsO_3^{2-}$
> 13.6	AsO_3^{3-}

pH	**As (V)**
< 2.2	H_3AsO_4
2.2 – 6.9	$H_2AsO_4^-$
6.9 – 11.5	$HAsO_4^{2-}$
> 11.5	AsO_4^{3-}

As (III) has been considered as more toxic oxidation state than As (V) (about ten times). This is due to As (III) has ability to react with sulfhydryl groups of protein by increasing the residence time (Nagarnaik et al., 2002) and weakening the function of many proteins (Jiang et al., 2009). The sulfhydryl groups of lipoic acid is illustrated in Figure 2.2.

$$CH_2(\mathbf{SH})\text{-}CH_2,\text{-}CH(\mathbf{SH})\text{-}(CH_2)_4\text{-}COOH$$

Figure 2.2 Chemical molecule of a lipoic acid

As (III) is more mobile and more stable than As (V) in aqueous solution especially at pH greater than 7. Hence, it is difficult to remove by simple adsorption and precipitation process due to higher stability and solubility in natural waters (Nagarnaik et al., 2002).

When pH increases, the solubility of most metal cations found in groundwater is strictly limited by precipitation or co-precipitation. The metal cations, for instance Pb^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, and Zn^{2+} are not only able to precipitate or co-precipitate with an oxide, hydroxide, phosphate mineral, carbonate, but also able to strongly be adsorbed to hydrous metal oxides, organic matter or clay. Most oxyanions including As (V), on the contrary, tend to become less strongly adsorb as the pH increases (Dzombak, 1990).

2.2 Arsenic elimination using various adsorbents

Adsorption is one of varietal technologies that have been improved for As removal from water. The technique is widely studied by a number of researchers since it is considered to be easy in term of operation and less expensive in term of cost. It is also utilized in point-of-use (POU) water treatment equipment for household use, such as in the states. Moreover, it is a probable process for As removal (Lin and Wu, 2001), especially in Bangladesh. Many researchers have been studying on activated alumina (AA) and iron oxide coated on different kinds of support material as adsorbents for arsenic removal from water (Lin and Wu, 2001; Singh and Pant, 2004; Kundu and Gupta, 2005; Hsu et al., 2008).

2.2.1 Activated alumina

Activated alumina (AA) is alumina oxide (Al_2O_3) with its surface expressing a net positive charge bringing about an attraction for arsenic until pH> zero point charge (pH_{zpc}). In EPA's list, AA is stated as one of the best available technologies (BATs) for As removal apart from lime softening, ion exchange, reverse osmosis, electro-dialysis reversal, coagulation/filtration and nanofiltration (EPA, 2000). Nevertheless, ion exchange requires a high amount of salt and area for associated brine disposal. Reverse osmosis is not appropriate for small utilities as it is not only too costly and complicated, but also dumps too much water. Coagulation/filtration is also a complicated treatment process which is neither affordable nor operable for small utilities (Thomson, 2003). Among of these methods, On the contrary, AA adsorption has been considered in term of operation and cost. Furthermore, commercial availability, capability to regenerate and lack of requirement for chemicals, the high capacity, and selectivity for As removal are also advantages (Murcott, 1999).

In addition to the selectivity for As, AA has a particular tendency for adsorption of As without any interfered by ions competition. However, the addition of organics has a much stronger effect. Eq. 2.1 shows the general selectivity order for As selectivity of AA. Activated alumina more prefers to adsorb As (V) such as $H_2AsO_4^-$ than As (III) such as H_3AsO_3 (EPA, 2000).

$$OH^- > H_2AsO_4- > Si(OH)_3O^- > F^- > HSeO_3^- > TOC > SO_4^{2-} > H_3AsO_3 \quad \text{Eq. 2.1}$$

2.2.2 Iron oxide

Octahedral with a central Fe ion surrounded by O or OH ions is the basic structure of all iron oxides. Ferric oxides [Fe_2O_3, Fe^{3+}] including hematite (α-Fe_2O_3, bright red), and maghaemite (γ-Fe_2O_3, reddish brown) are considered as good adsorbent for water treatment (Streat et al., 2008). Therefore, hematite is the most stable iron oxide under ambient conditions (Han et al., 2011). The function of iron oxide as adsorbent is based on the surface functional group similar to AA.

Iron oxides are well known that they have a strong affinity to As in water as a result of their partial positive charges and large surface areas (Lin and Wu, 2001). Nonetheless, most occurrences of iron oxides is in a form of fine powder, which is the main limitation for their utility due to after the adsorption process, the iron oxides cannot be readily separated from water (Lai et al. 2000) and also cannot be regenerated. Therefore, iron oxides are used to coat or impregnate on solid materials in order to conquer the problem and increase efficiency of the solid materials. Iron oxide-coated cement (IOCC) was discovered as an effective adsorbent in removing As (V) from an aqueous environment. It could be regenerated about 97 ± 0.5% of the IOCC fixed bed with 10% NaOH (Kundu and Gupta, 2005). Hsu et al., (2008) found that the removal efficiencies of iron oxide coated sands under the same condition of pH and adsorbent quantity indicated in the order as the following: As(V) > As(V) + As(III) > As(III). A study of iron-oxide-coated natural rock to remove As from water collected from a real site in Taiwan (the initial As concentration in total was 40 ppb) revealed that 15 g/L of the adsorbent could remove around 75% of As within 6 hours at room temperature (Maji et al., 2011). Unlike AA, however, those supporting media from nature do not have the property of As selectivity. An adsorption study of As (III) over iron coated AA by impregnation compared to regular activated alumina showed that the As (III) uptake enhanced from 0.158 to 0.286 mg/g due to the impregnated iron oxide (Kuriakose et al., 2004). Another study of iron oxide impregnated on the activated alumina (IOIAA) was found that impregnation and calcination of iron oxide on AA can significantly increases the removal performance for both As (III) and As (V). At equilibrium of the adsorption process, the highest As (III) removals by AA and IOIAA are 94.2% and 96.8%, respectively, whereas the maximum As (V) removals by AA and IOIAA are 96.1% and 98.4%, respectively.

With regard to the impact of iron oxide, a study the effect of iron oxide dose coated on support media is rarely found, whereas the observation on adsorbent dose is more available. Pan et al, (2010) studied on iron oxide dose on diatomite and encountered that, at pH 7.5, a particle size of 0.11 mm diatomite coated with iron oxide once, twice and thrice gave results of As (V) adsorptive capacities as the order of: twice > once > thrice. Another study of Pan et al, 2010 at the same pH but the particle size of diatomite was changed to 0.43 mm. The iron oxide coating levels were one to five times. The order changed to: three times > two times > one time > four times > five times. Hsu et al., 2008 observed the outcome of using iron-oxide coated sands as adsorbent with various loadings of 4-24 g/L to remove As (V), the initial concentrations of As was fixed at 200 ppb and the initial pH of solution was 5, the percent removal was discovered to raise from 52.5 to 99.9%. Maji et al., 2011 verified the performance of a series of adsorbent dose, which is iron oxide coated natural rock, from 5 to 15 g/L on As removal from real arsenic-bearing groundwater when temperature, an agitation speed, pH, initial volume of ground water samples, contact time, and initial concentration of As were kept constant at 25±2 °C, 180 rpm, 7.5 and 50 ml, and 40 ppb, respectively. The result indicated that the loading of 15 g/L offered highest percent removal around 75%. Hence, these three parameters, which are pH, initial concentration of As and iron oxide coated on AA, are become into the area of interest of this study.

Other than the As adsorption capability, the release of iron oxides during As treatment process is another factor that cannot be ignored. Although iron oxide is not as dangerous as As at the same concentration in term of health and acute impact, water with the presence of iron ion beyond a certain level can cause unpleasant appearance such as odor, turbidity, metallic taste. The WHO guideline value for iron ion in drinking water is 0.3 ppm (Bordoloi et al., 2011). Leaching test from iron oxides coated on media were not carried out in Kundu and Gupta, (2005), Maji et al., (2011), while Pan et al, 2010 claimed that iron concentration in the solutions from all pH were below the detection limit after all As elimination tests, Hsu et al., 2008 reported that the maximum total iron ion released from surface of iron oxide coated sand was found to be 2.6 ppm at pH 5 with a leaching ratio of 0.011% after 8 hours. These notifications are signs that iron leachate should be investigated in further.

2.3 Adsorption mechanisms of As (III) and As (V) on oxide surfaces

Metal ions on the oxide surface fulfill their coordination shells with OH groups as soon as they expose to water. These OH groups can attach or release H^+ depending upon pH and this creates the surface charge. The presence of these OH groups, namely OH_2^+, OH and O^- creates the adsorption properties of oxides. The As adsorption on metal oxides is occurred by ligand exchange with OH and OH_2^+ surface groups on the metal oxides (Smedley et al., 2002). The adsorption mechanism of As (III) and As (V) on a mineral surface, such as (hydr)oxides of iron and aluminum, can be divided into outer-sphere surface complexation and inner sphere surface complexation (Cheng et al., 2009).

Outer-sphere surface complexation (Non-specific adsorption) The electrostatic attraction between a charged surface of an adsorbent and an oppositely charged ion in aqueous is involved in the adsorption process. The weakly adsorbed anion locates at a certain distance from the mineral surface as illustrated in Figure 2.3. The formation of this complex is sensitive to ionic strength.

Inner-sphere complexation (Specific adsorption) The inner-sphere complexation has different formations of a coordinative complex with the mineral surface as shown in Figure 2.3 (b) – (d). This complexation is stronger than outer-sphere complexation due to the bonds of inner-sphere complex are more difficult to destroy than outer-sphere bonds. The electrostatic forces close to the mineral surface rely on the changes in ionic strength. However, anions that correlate directly with the oxide surface are relatively independent of ionic strength.

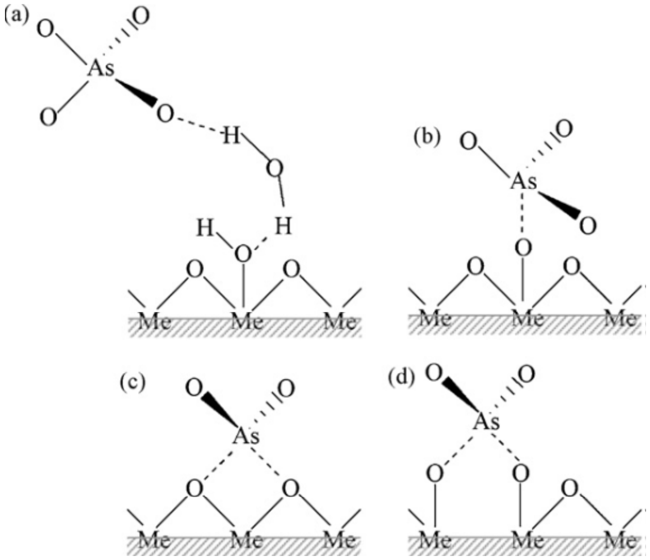

Figure 2.3 As (V) molecules adsorbed on metal (hydr)oxide surfaces: (a) outer-sphere surface complexation; (b) mononuclear monodentate inner-sphere complexation; (c) mononuclear bidentate inner-sphere complexation; and (d) binuclear bidendate inner-sphere complexation. (Cheng et al., 2009)

The surface adsorption is impacted by 3 major effects including (Singh and Pant, 2006)

(1) The net charge of the ion pairs on the surface.
(2) The interactions between species, thus localizing in the interphase of solid and solution.
(3) Steric hindrance from the size of adsorbate at the hydroxyl surface sites.

2.3.1 Oxide surface of activated alumina

AA is hydrophilic. The acid-base surface hydroxyl groups are the dominant influence to arise the ion adsorption behavior of AA. The oxide surface for developing an electrical charge promoting adsorption is controlled by the protonation and de-protonation of those surface hydroxyl groups. An example of a mechanism of As removal in acid solution can be explained by Eq. 2.2 (Singh and Pant, 2006).

$$AlOH + H^+ + H_2AsO_3^- \rightarrow AlH_2AsO_3^- + H_2O \qquad \text{Eq. 2.2}$$

2.3.2 Oxide surface of iron oxide

The oxidation of As (III) to As (V) can very effectively occur by Fe (III) as shown in Eq. 2.3 (Sivaraman, 2004). This characteristic of iron oxide can enhance the efficiency of As (III) removal.

$$2Fe^{3+} + HAsO_2 + 2H_2O \rightarrow 2Fe^{2+} + H_3AsO_4 + 2H^+ \qquad \text{Eq. 2.3}$$

As for the adsorption on iron oxide, once As contact with the iron oxides, the soluble As (III) and As (V) form surface complexes with the solid hydroxide surface sites and result in ferric arsenite or ferric arsenate. The responsible mechanism for As removal on precipitated iron oxides is explained by the reaction in the simplified equations displayed in Eq. 2.4 and Eq. 2.5 (Katsoyiannis and Zouboulis, 2002).

$$\text{[Metal support]-FeOH} + H_3AsO_3 \xrightarrow[\text{As (III) sorption}]{\text{Sorption process}} \text{[Metal support]-Fe-}H_2AsO_3 + H_2O \qquad \text{Eq. 2.4}$$

$$\text{[Metal support]-FeOH} + H_3AsO_4 \xrightarrow[\text{As (V) sorption}]{\text{Sorption process}} \text{[Metal support]-Fe-}H_2AsO_4 + H_2O \qquad \text{Eq. 2.5}$$

The ions of As (V) are adhered directly with the functional group of iron oxide surface. Iron oxides mainly adsorb As through specific adsorption, namely chemisorptions. Eq. 2.6 - 2.8 describe more mechanisms in detail for As (V) sorption on the surface of iron oxides (Katsoyiannis and Zouboulis et al., 2002).

$$FeOH^{1/2-} + H^{+}(aq) + AsO_4^{3-}\,(aq) \overset{k_1 \text{ (monodentate)}}{\Longleftrightarrow} FeOAsO_3 + H_2O \qquad \text{Eq. 2.6}$$

$$2FeOH^{1/2-} + 2H^{+}(aq) + AsO_4^{3-}\,(aq) \overset{k_2 \text{ (bidentate)}}{\Longleftrightarrow} Fe_2O_2AsO_2 + 2H_2O \qquad \text{Eq. 2.7}$$

$$2FeOH^{1/2-} + 3H^{+}(aq) + AsO_4^{3-}(aq) \overset{k_3 \text{ (protonated bidentate)}}{\Longleftrightarrow} Fe_2O_2AsOOH + 2H_2O \qquad \text{Eq. 2.8}$$

2.4 Adsorption Theory

2.4.1 Adsorption principle and types

Adsorption is a process of an adsorbate (gas or liquid) adhering onto the surface of an adsorbent, which is solid phase by accumulating on the surface. The adsorption is generally categorized as exhibiting physisorption or chemisorptions.

Physisorption or physical adsorption; the adsorbate is held on the surface of adsorbent by a weak intermolecular force through Van der Waals interactions.

Chemisorption; an adsorbate adheres to the surface of an adsorbent by the formation of a chemical bond.

2.4.2 Factors affecting adsorption

1. Adsorbent properties

Generally, surface area is directly proportional to the adsorption efficiency. However, in the case that the surface area is not accessible to the targeted adsorbate, the high surface area may not lead to high adsorption capacity. Therefore, surface chemistry of the adsorbent including solubility, chain length, molecular weight, and polarity can affect to the adsorption capacity.

2. Adsorbate properties

Typically, adsorption efficiency is inversely proportional to adsorbate solubility. Non-polar adsorbate tends to produce more adsorption capacity than polar adsorbate as the non-polar adsorbate is easily transferred in water. Furthermore, chain length, molecular weight, polarity, and degree of ionization are also important factors to be considered.

3. pH

The pH value is identified as a primary dominance governing adsorption efficiency for ionized species. Both the charge on the adsorbent surface and the ionization of the adsorbent are affected by pH of solution.

4. Effect of electrolyte

The charge, specific species and concentration of background electrolyte are impacted the adsorption as the background-electrolyte ions which can compete with the targeted adsorbate for available adsorption sites or can suppress charges that present on the surface of adsorbent (Cooper, 2010)

2.4.3 Adsorption isotherm

The interactions between the adsorbate and the adsorbent can be determined by adsorption isotherm. In the adsorption process, the adsorbate that adheres on the surface of the adsorbent can possibly desorb and be suspended into the solution. The adsorption process is continuing until it reaches the equilibrium which the adsorption and desorption rates are equal. The adsorbate concentration in the solution and on the surface of the adsorbent is no longer changing. Many isotherm equations for gas-phase adsorption can also be extended to describe liquid-phase adsorption. These equations are the Langmuir, Freundlich, Toth, Dubinin-Radushkevich and Sips equations. Nevertheless, the Langmuir and Freudlich equations are the most frequently applied to correlate liquid phase adsorption (Taylor & Francis Group, 2007).

1. The Langmuir Isotherm

The Langmiur isotherm model assumes that

- The surface pattern of the adsorbent is homogenous.
- There is no interaction or movement of the adsorbate on the surface of the adsorbent.
- The adsorbate is accumulated on each site of the adsorbent as monolayer.
- The adsorption mechanical is exactly the same throughout the adsorption process.

The equation of Langmuir isotherm is represented in Eq. 2.9.

$$\frac{1}{qe} = \frac{1}{qmax} + \left(\frac{1}{qmax \cdot KL}\right)\frac{1}{Ce} \qquad \text{Eq. 2.9}$$

Where

qe is the equilibrium adsorbate concentration on the adsorbent (mol/g)

Ce is the equilibrium adsorbate concentration in the solution (mol/L)

Qmax is the monolayer adsorption capacity of the adsorbent (mol/g)

K_L is the Langmuir adsorption constant (L/mol) related to the free energy of adsorption.

2. The Freundlich Isotherm

Generally, the Freundlich isotherm is used to explain adsorption onto heterogeneous systems. A linear form the Freundlich isotherm is shown in Eq. 2.10 (O¨zcan et al, 2005).

$$\text{In } qe = \text{In } K\text{F} + \frac{1}{n}\text{In } Ce \qquad \text{Eq. 2.10}$$

Where

K_F is the constant of Freundlich equilibrium (L/g).

n is the adsorption intensity.

The adsorption isotherm and kinetics of AA and FeAA have been studied in some research as listed in Table 2.2. However, studying the isotherm and kinetics were considered to use high initial concentration of As to approach equilibrium. There is a limited number of the As research studying on initial As concentrations at low level, even though As can be harm at low degree of concentration.

Table 2.2 Adsorption isotherm and kinetics of AA and FeAA

Adsorbent	As species	Initial concentration (ppb)	Kinetic model	Adsorption isotherm	q_e mg/g	References
AA	As (III)	Between 790 and 4,900	Pore diffusion model	Freundlich and Langmuir ($R^2 > 0.93$)	0.77 at pH 3.3	Lin and Wu, 2001
AA	As (III)	500 and 1,500	first-order kinetics	-	-	Singh et al., 2006
FeAA	As (III)	1,400 - 2,300	first-order kinetics and pseudo second order	Freundlich and Langmuir ($R^2 > 0.98$)	0.03 - 0.378	Kuriakose et al., 2004
FeAA	As (III)	1,600, 2,100 and 2,300	first-order kinetics and pseudo second order	-	0.378	Singh et al., 2006
AA	As (V)	Between 2,850 and 11,500	Pore diffusion model	Freundlich and Langmuir ($R^2 > 0.93$)	12.34 at pH 2.6	Lin and Wu, 2001
AA	As (V)	500 and 1,500	first-order kinetics	-	-	Singh et al., 2006
FeAA	As (V)	1,600, 2,100 and 2,300	first-order kinetics	Langmuir	-	Singh et al., 2006

2.5 Design of Experiment (DOE)

In traditional multifactor experiments, one-factor-at-a-time method is employed to obtain optimization that is so-called univariate optimization. A single factor is varied while all the other factors are remained constant at a specific set of conditions. The disadvantages of this kind of approach are time-consuming and not cost effective. Moreover, feasible interaction impacts between factors are completely neglected and misleading summaries may be deduced as the effects of one factor can be subject to the level of the other factors relevant in the optimization, especially, when the interaction effects is large. Hence, design of experiment (DOE) is involved as alternative multivariate optimization designs for which the levels of the other variables are changed and observed concurrently. DOE also offers other benefits that are saving time and money because of the reduction of the number of experiment and maximizing significance (Ferreira et al., 2007).

Accomplishment of screening the factors to be studied is the first step of multivariate optimization by DOE so as to acquire the significant effects of a certain analytical system. After the significant factors are determined, the optimal operation conditions are obtained by using Response Surface methodology (RSM). RSM is a type of statistical and mathematical for designing experiments, creating models, estimating involved significance of various independent variables and identifying optimal conditions for beneficial responses. RSM is not utilized to understand the mechanism of a system but to determine the optimal operating conditions at a specific operating condition in order to optimize and comprehend the performance of complicated systems (Zhang and Zheng, 2009).

RSM based upon Box-Behnken designs (BBD) has been broadly employed to determine interactive effects as well as the optimal conditions for multivariable systems including sorption process. BBDs are second-order designs relied on three level incomplete factorial designs. There are two kinds of variables that are the responses (Y) and factors

(X_1, X_2, …, X_k). The responses are dependent variables and their values rely on the levels of the factors. The factor levels are coded as -1, 0 and +1 that represent low, central point or middle and high, respectively (Tripathi et al., 2009). BBDs do not consist of combinations that all factors are concurrently at their highest or lowest levels. Therefore, these designs are helpful in avoiding experiments conducted under extreme conditions, which undesirable results may happen. The amounts of experiments (N) can be obtained from $N = 2k(k-1)+C_0$; where k is the number of factors and C_0 is the number of central points (Ferreira et al., 2007). Albeit BBDs are optimum or near-optimum, they are sometimes too large for a practical use. Meaning is they consists more runs than needed to fit a second-order model when the number of factors is five or more than that. Hence, BBD with five or more factors is rarely found to be used in practice.

BBD is a spherical composed of a central point and the middle points of the edges of the cube encircled on the sphere. It contains three interlocking 2^2 factorial design and all points are laying on the surface of the sphere surrounding the central point as demonstrated Figure 2.4.

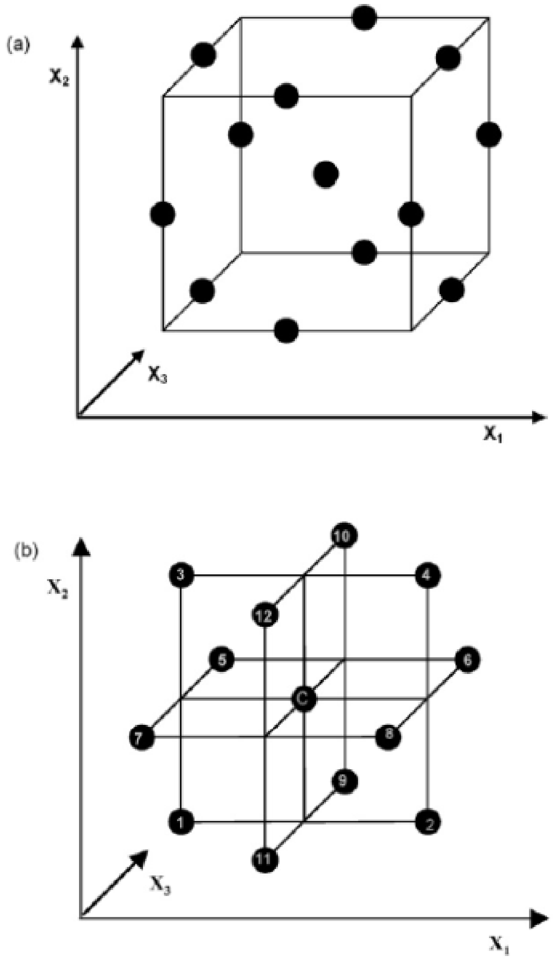

Figure 2.4 (a) A cube for BBD with three interlocking 2^2 factorial designs, (b) Three interlocking 2^2 factorial designs with a central point. (Ferreira et al., 2007).

BBD is considering linear terms including square terms and linear by linear interaction terms. A quadratic response model can be explained as a general regression equation in Eq. 2.11.

$$Y = \beta_0 + \Sigma\beta_i x_i + \Sigma\beta_{ii} x^2_{ii} + \Sigma\beta_{ij} x_i x_j + \varepsilon \qquad \text{Eq. 2.11}$$

where, βo is the offset term (intercept), βi is the slope or linear impact of the input factor x_i, β_{ii} is the quadratic impact of input factor x_i and β_{ij} is the linear by linear interaction impact between the input factor x_i and x_j. All β values are constant values. (Tripathi et al., 2009)

Some of the main effects as well as low order interactions can affect a system with many variables. It might be supposed that the higher order interactions are not large relative to the low order interaction. There, two-way interactions are considered. Analysis of Variance (ANOVA) is a statistical method that subdivides the total variation in a group of data into constituent parts related with the specific cause of variation to test hypotheses on the parameters of the model. ANOVA is used to test the statistical significance of the ratio of mean square variation due to the regression and mean square residual error. The result of ANOVA can indicate whether the equation is able to sufficiently represent the actual relationship between the response (Y) and the significant factors (X). There are two values playing important roles in ANOVA that are Fisher F value and p value. Fisher F value is used to signify that all of the variation in the response can be described by the regression equation or not. If the F value is larger than F-critical value, it can be concluded that the regression equation can explain the variation in the response. As for p value, its function is to estimate whether F value is great enough to signify statistical significance. A model is statistically significant when p value is lower than 0.05 that is confidence level is 95% (Tripathi et al., 2009).

CHAPTER III

METHODOLOGY

3.1 Material and Instrument

3.1.1 Material

(a) Activated alumina

3.1.2 Chemical

(a) $Fe(NO_3)_3 \cdot 9H_2O$ (s)
(b) As (III) standard solution 1000 ppm (l)
(c) As (V) standard solution 1000 ppm (l)
(d) HNO_3 (l)
(e) 0.1 M NaOH (l)
(f) 0.1 M HNO_3 (l)

3.1.3 Instrument

(a) Horizontal electric shaker
(b) Oven
(c) Atomic Adsorption Spectroscopy
(d) X-ray Diffraction (XRD)
(e) Scanning Electron Microscopy (SEM)
(f) N_2 adsorption-desorption isotherm apparatus
(g) Zeta sizer
(h) Furnace oven

3.2 Experimental procedures

3.2.1 Adsorbent preparation (AA and FeAA)

Activated alumina (AA) is soaked in deionized water for 24 hours. After that, it is rinsed with deionized water several times and then dried in an oven at 110°C for 2 hours.

Iron oxide coated activated alumina (FeAA) is prepared by impregnation method and calcination. The solutions of 0.5, 1, and 1.5 M $Fe(NO_3)_3 \cdot 9H_2O$ are used to prepare 2, 4, and 6% of FeAA, respectively. Seven milliliters of a certain concentration of $Fe(NO_3)_3 \cdot 9H_2O$ is added to 10 g of the cleaned AA drop by drop. The soaked AA is left for 60 min, dried in an oven at 110^oC for 2 hours and calcined at 550^oC for 3 hours with the heating rate of 2.5^oC/min. After cooling to room temperature and rinsing with de-ionized water until the supernatant was clear, the iron oxide impregnated activated alumina is obtained and stored in a bottle.

3.2.2 The comparison of As (III) and As (V) adsorption on AA and FeAA removal efficiency

Batch tests, using 100 ml of As (III) synthesis water with initial concentration of 300 ppb under pH 3 and AA 1.0 g, are conducted in 250 ml erlenmayer flasks to examine the adsorption. The flasks with synthesis water are placed in a horizontal shaker at 120 rpm. The supernatants are collected for 1 ml at 0, 15, 30, 60, and 120 min, filtered through 0.45 µm syringe filters and diluted with 2% HNO_3 to 10 ml. The collected supernatants are measured for As by Graphite-Furnace Atomic Absorption Spectroscopy.

Batch tests of As (V) are separately conducted with the same experiment. As for FeAA batch tests, only AA is changed to 6% FeAA and the same process with AA are followed.

3.2.3 Response surface methodology based on Box-Behnken design (BBD).

The adsorbent and the As ion species that give the best percent removal from the previous experiment is further studied on adsorption experiment. There are 30 runs in total including two replicates and six replicates of center point designed by response surface methodology based upon Box-Behnken Design (BBD) in Minitab 15 Statistical Software program. The program designation is relied on three factors (three independent variables) influencing removal efficiency (dependent variable or response) that are pH (X_1), iron concentrations (X_2) and initial As concentrations (X_3). Each parameter has three amounts of factor levels that are pH (3, 6, 9), iron coated on AA (2%, 4% and 6% FeAA) and initial As (V) concentrations (100, 300, 500 ppb). Therefore, the DOE is three-level-and-three-factor Box-Behnken design (BBD) with six replicated center points.

The steps of experiment in this part are also the same as AA's in 3.2.2, apart from dilution step of 100 ppb As synthesis water is omitted.

3.2.4 Interpretation the results obtained from 4.3 by using DOE function in Minitab 15 Statistical Software program.

The laboratory results from 4.3 are statistically calculated by using DOE function in Minitab 15 to attain

(i) Interactions of pH, Fe dose on AA and initial As concentration on As removal.
(ii) Optimal condition.

3.2.5 The optimal condition is tested on Fe release from FeAA into water

In the last part, the Fe dose and As type in the optimal condition revealed by BBD in 3.2.4 is employed to further study about Fe release overtime under the optimal condition.

Batch tests, using 200 ml of synthesis water using AA 2.0 g under the pH of optimal condition, are conducted in 250 ml erlenmayer flasks to examine the Fe release. The flasks with the synthesis water are placed in a horizontal shaker at 120 rpm. The supernatants are collected for 3 ml at 0, 3, 6, 12, and 24 hours, filtered through 0.45μm syringe filters and measured for the concentration of Fe by AAS.

3.3. Measurement and characterization

3.3.1 Graphite-Furnace Atomic Absorption Spectroscopy (GF-AAS)

Arsenic analysis is done by a GFAAS using 100 ppb As (V) standard as a stock of standard, 100 ppb Ni as makeup solution, 2% HNO_3 as a blank and 0.2% HNO_3 as a cleaning solution.

3.3.2 X-ray Diffraction (XRD)

The crystalline phases of synthesized iron oxide are investigated by XRD using CuKα radiation at a generator voltage and current of 40kV and 40 mA, respectively. The XRD patterns are in the range of 2Θ from 20^o to 90^o with the scanning speed of 5.0°/min.

3.3.3 Scanning Electron Microscope (SEM)

The surface morphology is studied by SEM.

3.3.4 The Brunauer-Emmett-Teller (BET) Analysis

The BET specific surface areas of AA and FeAA are calculated from N_2-sorption isotherm apparatus at liquid nitrogen temperature (77 K) with gas adsorption surface area analyzer (Quantachrome, USA).

3.3.5 Zero potential

Zero point charge value of the adsorbents is studied by Zeta sizer.

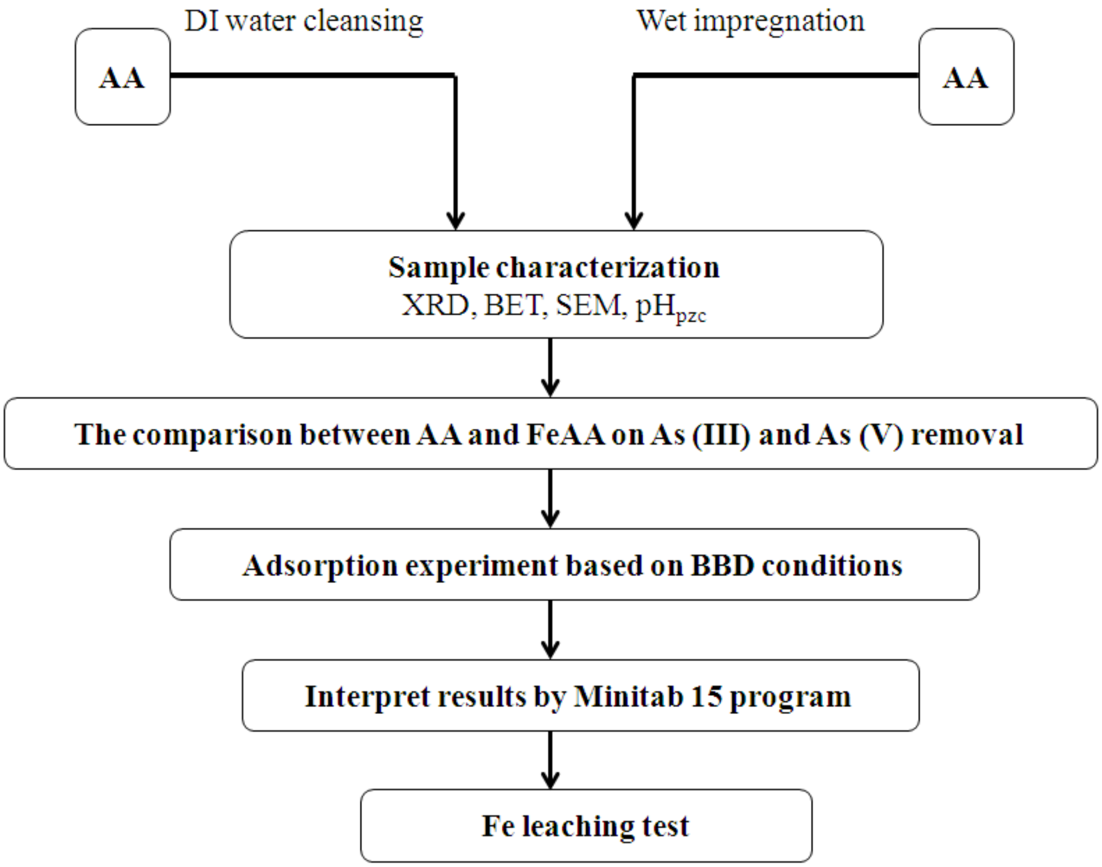

Figure 3.1 Diagram of experimental scheme

CHAPTER IV

RESULTS AND DISCUSSION

This chapter presents the physical properties of AA and FeAA that relate to their adsorption capability. The characterizations are exposed by X-ray diffraction (XRD), Brunauer-Emmett-Teller technique (BET) analysis, zero pointcharge (pH_{pzc}) and Scanning electron microscopy (SEM). The adsorption capacity, the response surface model and the optimization condition obtained from BBD including iron oxide leaching test are also discussed.

4.1 Adsorbent characterization

4.1.1 Scanning Electron Microscope (SEM)

AA and FeAA prepared from three different concentrations of $Fe(NO_3)_3 \cdot 9H_2O$ were observed their surface morphologies by SEM with magnification of 3,500X and 10,000X. From the result in Figure 4.1(c) and Figure 4.1(g), AA had a rough surface. Figure 4.1(h) and Figure 4.1(d) illustrate the adhesion of iron oxide layer on AA (2%FeAA) as well as the cracks between sheets of the layer showing some parts of AA as the original inner surface. On the contrary, 4%FeAA in Figure 4.1(e) and 4.1(i), and 6%FeAA in Figure 4.1(f) and 4.1(j) appear as uniformly coated surface, some cracks were visible. The number of cracks on 4%FeAA was more than on 6%FeAA as the iron oxide particles less clogged the surface of 4%FeAA.

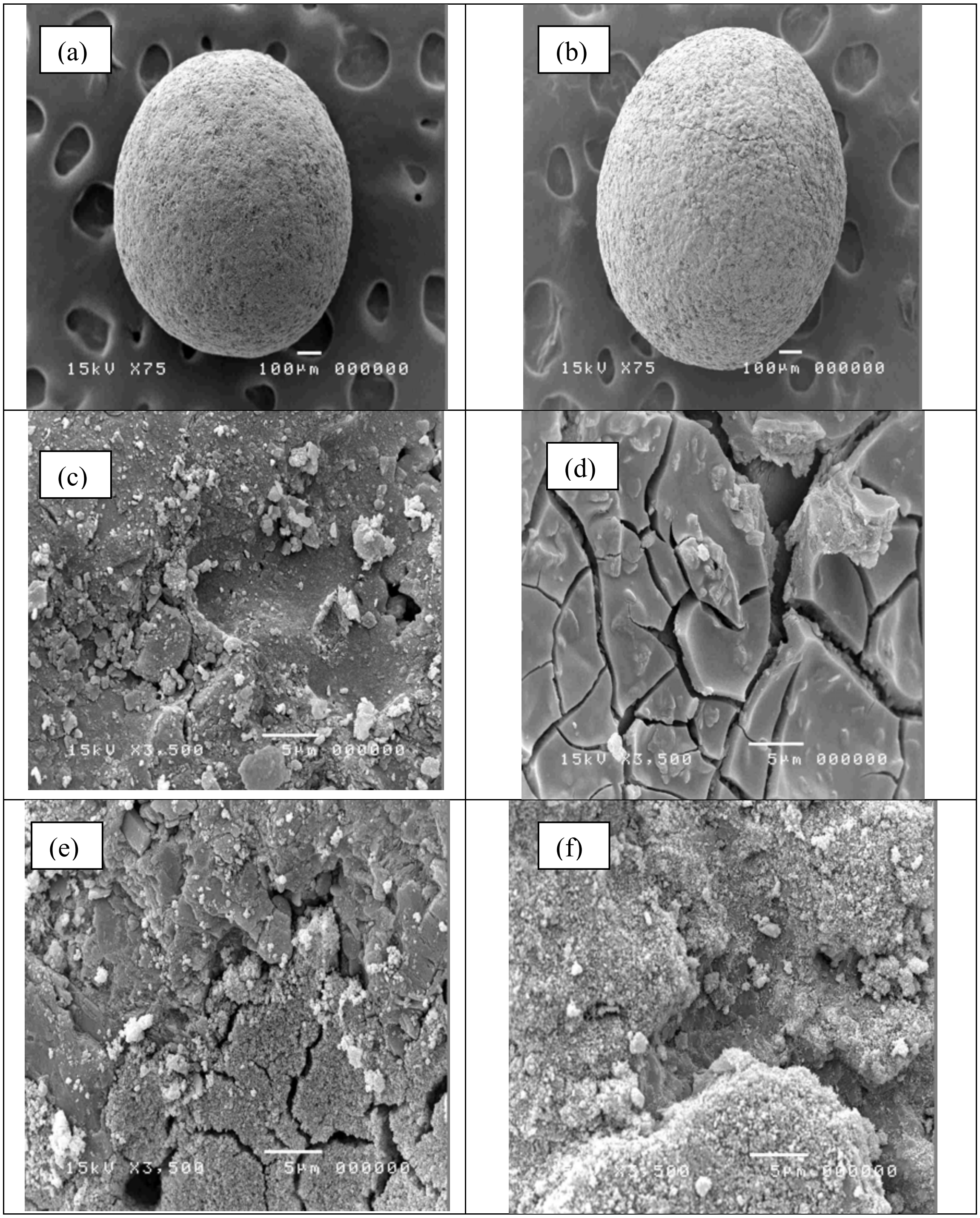

Figure 4.1 Scanning Electron Microscopy (SEM) photographs taken at 75X magnification of (a) and (b), at 3,500X magnification of (c) AA, (d) 2%FeAA, (e) 3%FeAA and (f) 4%FeAA.

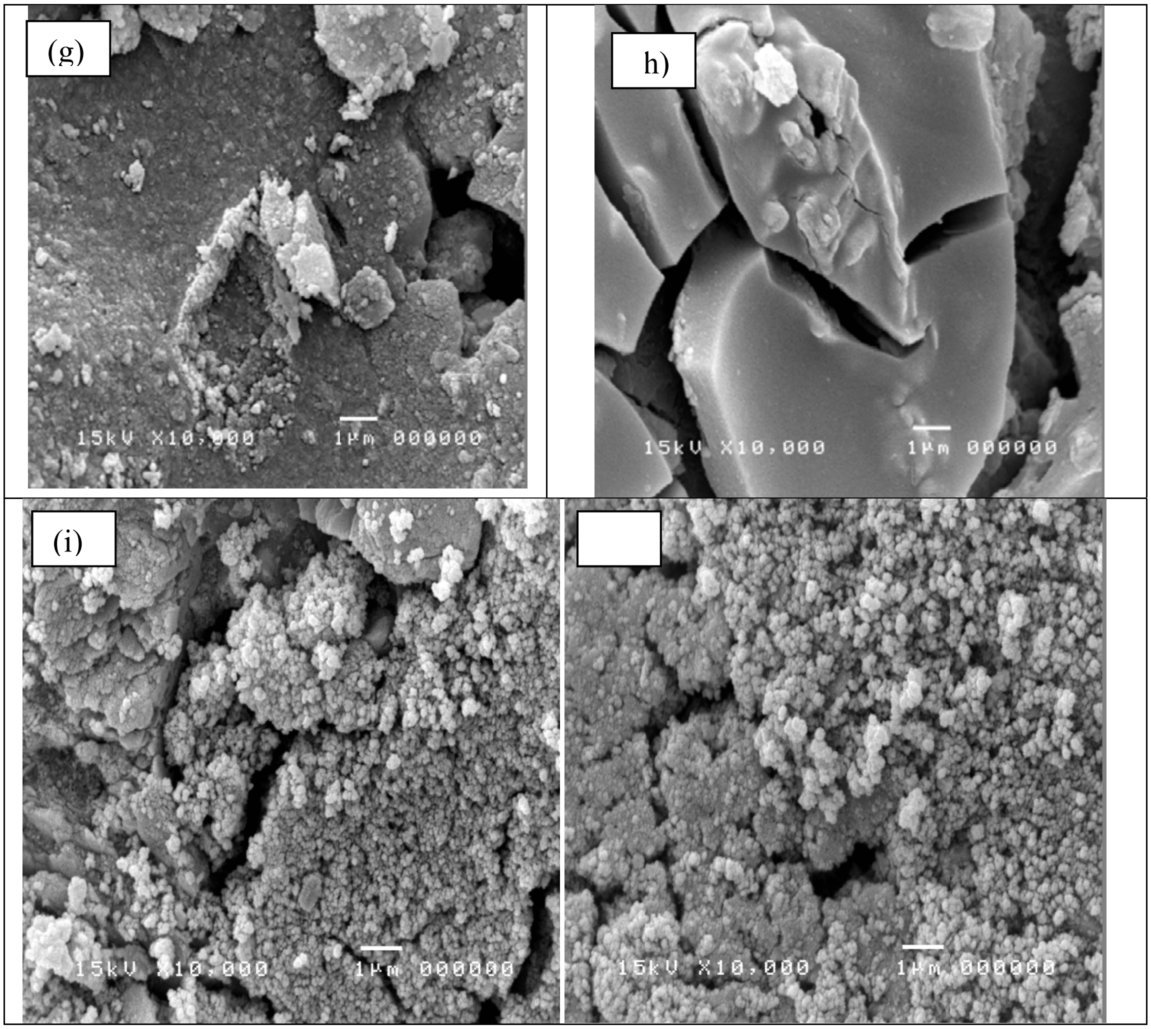

Figure 4.1 (continued) Scanning Electron Microscopy (SEM) photographs taken at 10,000X magnification of (g) AA, (h) 2%FeAA, (i) 3%FeAA and (j) 4%FeAA

4.1.2 X-ray Diffraction (XRD)

The scrap of the coated iron oxide from 6%FeAA was measured by XRD and illustrated in Figure 4.2. The XRD spectrum exhibited a mixture of the characteristic of alpha-ferric oxide (α-Fe_2O_3) or called hematite and goethite (α-FeOOH). Hematite was found that the main peaks locating at 2Θ 24.33^{o}, 33.25^{o}, 35.73^{o}, 41.07^{o}, 54.16 and 62.74. Whereas, goethite was found that the main peaks locating at 2Θ = 21,4° , 26,6° , 33,4° , 36,9° and

53,6°. The results were confirmed by the database in XRD reported by Gülen et al, 2011 and Ferreira, 2011, respectively.

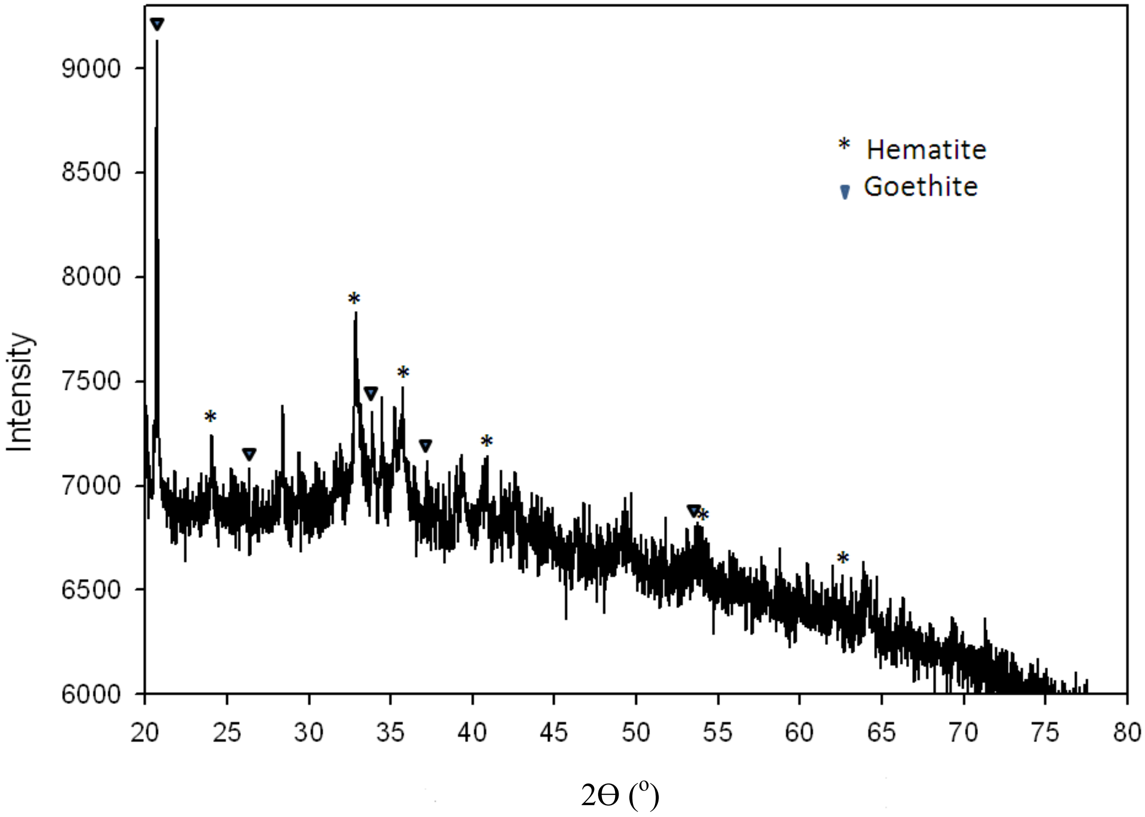

Figure 4.2 XRD pattern of the scraped from 6%FeAA

4.1.3 Specific surface area analysis

Specific surface area of AA and the synthesized FeAAs were calculated by Brunauer-Emmett-Teller (BET) equation from N_2 sorption isotherm and the results of BET surface area are summarized in Table 4.1. The adsorbents arranged in order of the BET surface area from high to low are 2%FeAA, 4%FeAA, AA and 6%FeAA. The highest surface area apparently belongs with 2%FeAA that is higher than the surface of AA for 137.38 m^2/g. This may be the result that displays in the SEM photograph exhibiting iron oxide layer on AA and visible cracks that can highly increase the surface area.

Table 4.1 The surface of AA and the synthesized FeAAs obtained from Brunauer-Emmett-Teller analysis

Adsorbents	Surface (m^2/g)
AA	182.9
2% FeAA	320.28
4% FeAA	183.4
6% FeAA	172.5

4.1.4 Point of zero charge

Figure 4.3 displays the surface charge as a function of solution pH. The curves show that the surface charge abates as the pH is increased. The intersection of two curves with x-axis offers the point of zero charge (pHpzc) which is 7.6 for AA and 8.9 for 6%FeAA, respectively. At the pHpzc, the total charge from anions and cations at the surface of the adsorbents is equal to zero. The surface charge expresses negative when the results indicate that iron oxide can improve the pHpzc of AA.

4.2 Arsenic adsorption on AA and FeAA

The initial concentration of the As species was 300 ppb, pH of solution was 3.

4.2.1 Arsenic adsorption on AA

Arsenic adsorption on AA in a low concentration for both As (III) and As (V) are shown in Figure 4.4. The result of the first 120 min revealed that, AA could remove As (V) better than As (III).

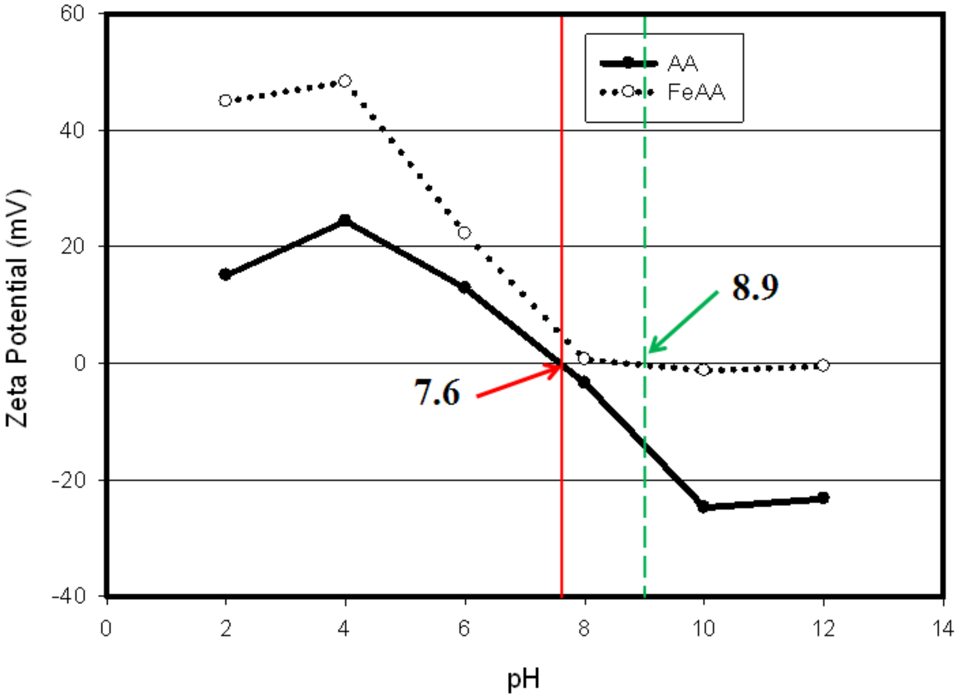

Figure 4.3 Zeta potential of AA and the synthesized 6%FeAA

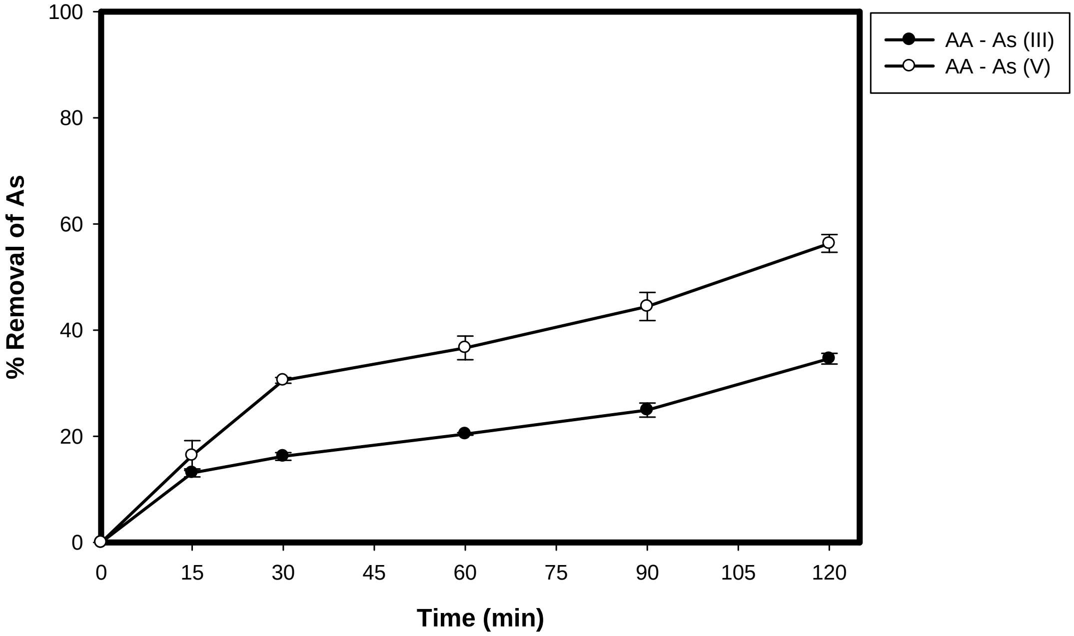

Figure 4.4 As (III) and As (V) adsorption on AA

At 15th min, the percent removals were 13.09% and 16.35% for As (III) and As (V), respectively. The difference at this point was not much different. After the process was kept going until 60th min and 120th min, the difference appeared more obviously as the percent removals were and 20.43% and 34.62% for As (III), and 36.65% and 56.31% for As (V), respectively. The more time duration of adsorption, the more As pollutants were eliminated. However, the removal of As was not complete within 120 min.

4.2.2 Arsenic adsorption on 6%FeAA

Figure 4.5 illustrates the As adsorption performance of 6%FeAA for As removal of both species. At the adsorption time of 15th, the percent removal for As (III) and As (V) were 33.86% and 55.35%, respectively. At 60th, the percent removal for As (III) and As (V) were 59.34%, and 99.04%, respectively.

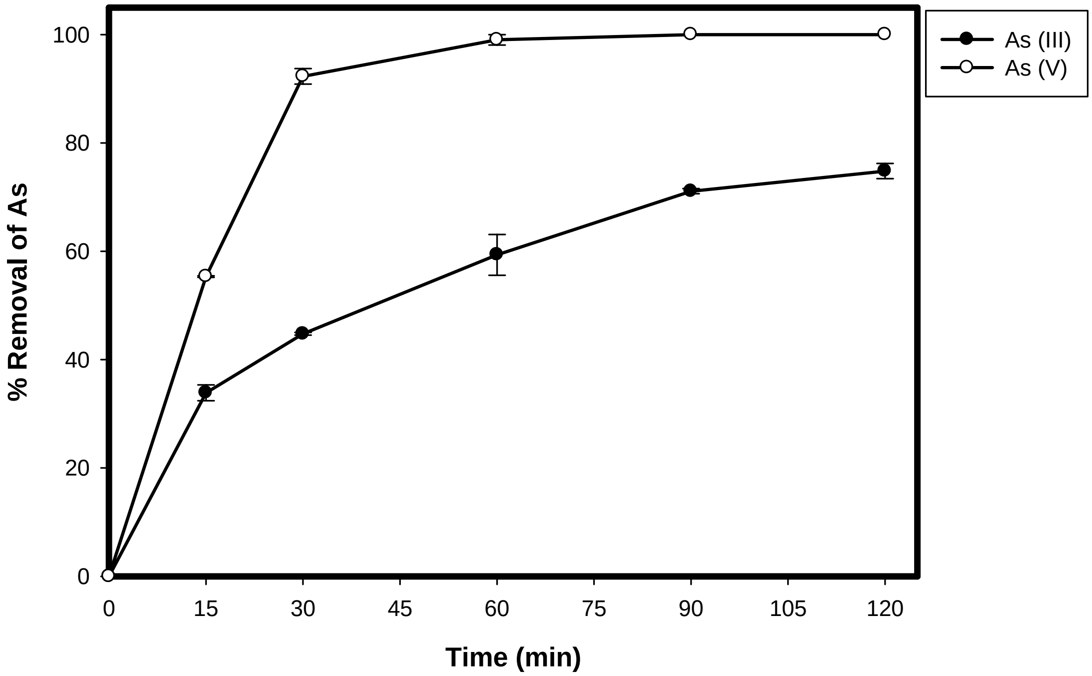

Figure 4.5 As (III) and As (V) adsorption on 6%FeAA

The adsorption was kept processing and a result about 60th min showed that As (V) was completely eliminated. The prepared 6%FeAA was unable to utterly remove As (III) at 120th min. The best As (III) removal efficiency of 6%FeAA was 74.80%.

4.2.3 The comparison of As (III) and As (V) adsorption on AA and 6%FeAA

The adsorption capacities of the given adsorbents are illustrated in Figure 4.6. At pH 3, As (III) was in non-ionic H_3AsO_3 form whilst As (V) was in $H_2AsO_4^-$ form. The outcome indicates that 6%FeAA offered the higher adsorption capability to remove both As (III) and As (V) than AA. Furthermore, 6%FeAA itself was capable to remove As (V) better than As (III).

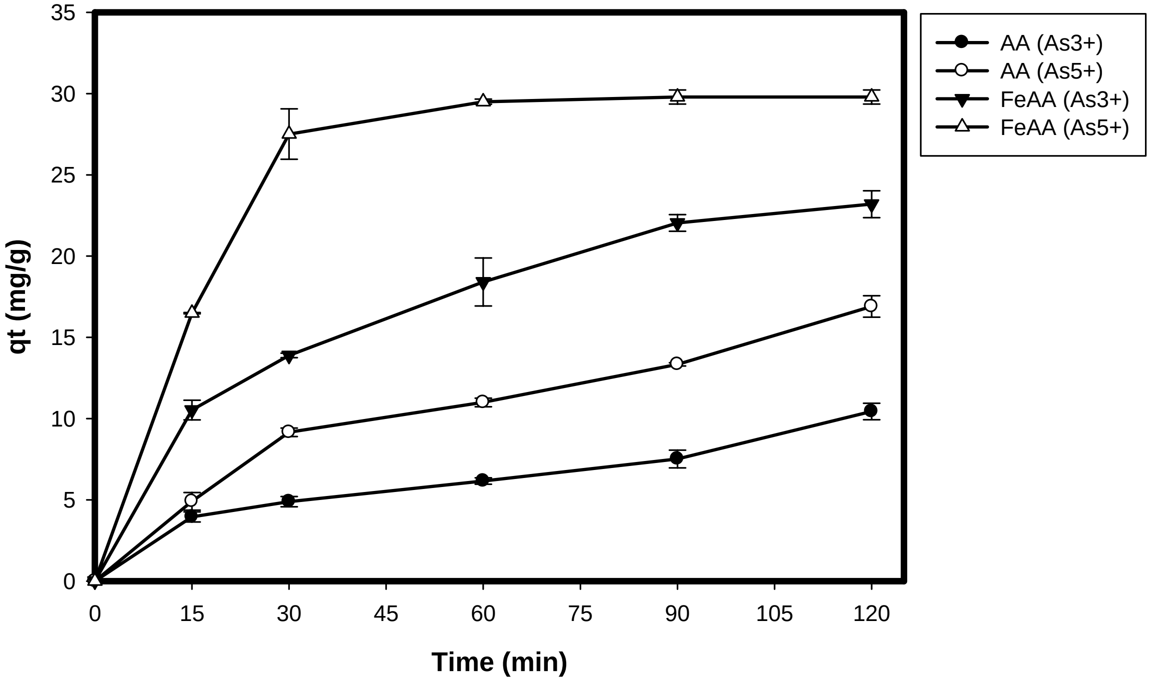

Figure 4.6 The adsorption capacity of AA and 6%FeAA

The adsorption capacity was calculated from Eq. 4.1.

$$\mathrm{qt} = \frac{(\mathrm{Co}-\mathrm{Ct})\mathrm{V}}{1000\mathrm{W}} \qquad \text{(Eq. 4.1)}$$

Where qt is the adsorption capacity in mg/L, C_0 is an initial concentration of As (V) in ppb, C_t is a concentration of As at time t in ppb, V is the volume of the solution in mL and W is the weight of the dry absorbents in g.

6%FeAA can remove As better than AA due to First, FeAA has redox capability to oxidize As (III) to As (V). Second, according to zeta potential result, FeAA has more positively charge sites than AA.

At 120th min, the adsorption capacity 6%FeAA for As (III) and As (V) were 23.19 and 29.79 μg/g, respectively, where as AA were 10.43 and 16.89 μg/g, respectively. This result indicates that the iron oxide was able to improve and modify the adsorption ability of AA due to AA had no redox capability to oxidize As (III) to As (V) but the Fe (III) on the iron oxide had. The Fe (III) was not only capable to adsorb As (III) from the solution and formed ferric arsenite ($Fe\text{-}H_2AsO_3$), but Fe (III) was also able to partly oxidize As (III) in the solution to As (V), which was more suitable specie for the adsorption. The As (V) formed a complex with Fe (III) on the iron oxide surface and became ferric arsenate ($Fe\text{-}H_2AsO_4$). The final pHs of all batch studies were exhibited in Table 4.2.

Also, the zero point charge of 6%FeAA was more than AA indicating that 6%FeAA had more positively charged sites on the surface than AA.

Table 4.2 Final pHs of As (III) and As (V) removal over AA and 6%FeAA

Adsorbent	As species	Initial pH	Final pH
AA	As (III)	3	6.1
	As (V)	3	7.1
6%FeAA	As (III)	3	7.6
	As (V)	3	8.3

From the mentioned result above, As (V) adsorption on 6%FeAA indicated the best removal efficiency. Thus, As (V) adsorption on FeAA was selected for further studying in the second part based on BBD to reveal the main and interactive effects of the three crucial independent variables.

4.3 The response surface methodology (RSM) based on Box-Behnken design (BBD)

In a system of an adsorption, there are several parameters that can individually or interactively affect the activities of the process. In this study, three factors or independent variables were interesting to be studied about their impacts to As (V) removal efficiency, which was the response or dependent variable. The research was also including analysis of variance for the response, optimization condition and response surface analysis of the adsorption, and verification of model and experimental confirmation.

4.3.1 Design of Experiment

A three factor level of BBD with three central points of factors was employed to investigate the simple and interactive impacts between the variables to the removal as well as the statistical significance. The details of the three factors are elaborated in Table 4.3. The factors were designed as X_1, X_2 and X_3 that are Initial pH, %Fe and Initial concentration of As (V), respectively. Each factor has three levels that are low, medium and high represented by -1, 0 and 1, respectively.

Table 4.3 The level and range of independent variables (X_i) chosen for As (V) adsorption

Independent variables	**Factor (X_i)**	**Range and level**		
		-1	**0**	**+1**
Initial pH	X_1	3	6	9
%Fe	X_2	2	4	6
Initial concentration of As (V) in ppb	X_3	100	300	500

The experiment was conducted according to 30 runs of the experimental conditions designed by BBD for non-systematic bias of the response. The actual design of the experiments and their responses are shown in Table 4.4.

4.3.2 Fitting model and analysis of variance (ANOVA)

The experimental response in Table 4.4 is related to the independent variable, which is the response or the independent variable by a quadratic model shown in Eq. 4.2.

$$\text{As (V) removal (\%)} = 61.81-15.86X_1+0.17X_2-3.55X_3+8.31X_1X_2 +0.38X_1X_3-0.07X_2X_3-10.10X_1^2-5.66X_2^2+3.27X_3^2 \quad \text{(Eq. 4.2)}$$

Where As (V) removal (%) is at 15th min in %, X_1, X_2 and X_3 are the coded factors mentioned in Table 4.4.

Table 4.4 The actual design of experiments and the response of As (V) removal by adsorption

Run orders	**Factors (independent variables)**			**Experimental Response (%)**	**Predicted value (%)**	Final pH
	Initial pH	%Fe	Initial concentration of As (V) (ppb)	Percent removal at 15th minute		
1	9	2	300	21.27	21.72	9.50
2	6	2	500	59.69	55.77	9.13
3	3	6	300	55.93	53.76	7.78
4	6	4	300	60.13	61.81	9.45
5	6	4	300	71.66	61.81	9.74
6	9	4	100	38.26	42.29	9.39
7	9	6	300	37.04	38.67	10.06
8	9	6	300	37.44	38.67	10.11
9	3	4	100	78.22	74.77	5.03
10	3	4	500	66.01	66.90	9.14
11	6	6	100	62.97	63.21	7.49
12	9	2	300	20.63	21.72	9.56
13	6	4	300	55.78	61.81	9.04
14	6	4	300	55.73	61.81	9.12
15	9	4	500	45.16	35.95	10.86
16	6	6	500	53.98	55.96	8.42
17	6	4	300	66.96	61.81	9.66
18	6	2	100	58.37	62.73	7.04
19	3	4	100	70.62	74.77	4.89
20	6	2	100	64.93	62.73	7.21
21	6	2	500	52.70	55.77	9.09
22	3	6	300	53.13	53.76	7.74
23	6	4	300	60.62	61.81	9.37
24	3	4	500	64.10	66.90	9.11
25	6	6	500	60.10	55.96	8.66
26	6	6	100	62.61	63.21	7.46
27	9	4	500	27.42	35.95	10.07
28	3	2	300	72.02	70.05	6.77
29	9	4	100	50.03	42.29	9.47
30	3	2	300	70.95	70.05	6.81

The significant factors in the regression model were estimated by employing Analysis of Variance (ANOVA). The quadratic model's ANOVA results are present in Table 4.5 indicating that the model equation can acceptably be used to explain the As (V) adsorption on FeAA under a wide range of operating condition. The P value and F value in the ANOVA analysis assists to determine which effects (factors and interactions) are statistically significant. F value that is greater than F critical and P value is smaller than 0.05 at 95% confidence indicate the significance of the effects.

F value of the regression model is 23.31 (F critical $_{(0.05,\,9,\,20)}$ is 2.39) and P value is 0.00. F values of linear, square and interaction regression are 50.48, 12.84 and 6.61 (F critical $_{(0.05,\,3,\,20)}$ is 3.10), respectively, and P values are 0, 0, and 0.003, respectively. This infers that the model is significant for As (V) removal. As for lack of fit, the F value is 0.32 which is lower than F critical $_{(0.05,\,3,\,17)}$ of 3.20 implying that the lack of fit is not significant to the pure error.

Table 4.5 Analysis of Variance for percent removal (Y) of As (V)

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Regression	9	5854.49	5854.49	650.50	23.31	0.000
Linear	3	4225.93	4225.93	1408.64	50.48	0.000
Square	3	1074.84	1074.84	358.28	12.84	0.000
Interaction	3	553.73	553.73	184.58	6.61	0.003
Residual Error	20	558.09	558.09	27.90		
Lack-of-Fit	3	30.06	30.06	10.02	0.32	0.809
Pure Error	17	528.03	528.03	31.06		
Total	29	6412.58				

Where DF is degree of freedom

Seq SS is the sequential sums of squares.

Adj SS is the adjusted (partial) sums of squares.

Adj MS is the adjusted means squares.

F is F-value calculated by dividing the factor MS by the error MS.

P is P-values range from 0 to 1. Determines the appropriateness of rejecting the null hypothesis in a hypothesis test.

The P value was used to analyze the significance of regression coefficients listed in Table 4.6.

Table 4.6 Coefficient of estimated regression of the quadratic model for As (V) removal

Term	**Coef**	**SE Coef**	**T**	**P**	**Note**
Constant	61.8140	2.157	28.663	0.000	Significant
pH	-15.8578	1.321	-12.008	0.000	Significant
%FeAA	0.1649	1.321	0.125	0.902	Non- significant
As (V) conc.	-3.5530	1.321	-2.690	0.014	Significant
pH*pH	-10.1022	1.944	-5.197	0.000	Significant
%FeAA*%FeAA	-5.6613	1.944	-2.912	0.009	Significant
As (V) conc.*As (V) conc.	3.2654	1.944	1.680	0.109	Non- significant
pH*%FeAA	8.3107	1.868	4.450	0.000	Significant
pH*As (V) conc.	0.3785	1.868	0.203	0.031	Significant
%FeAA*As (V) conc.	-0.0734	1.868	-0.039	0.969	Non-significant

R^2 = 91.30%, R^2 (pred) = 81.24%, R^2 (adj) = 87.38%

It is noticed from the data at 95% confidence ($P_{value} < 0.05$) that pH of the solution and the initial As (V) concentration show significant effects on the adsorption (P values of 0.000 and 0.014, respectively) whereas %FeAA shows no significance. The coefficient with a positive value indicates an effect that supports the optimization, whereas a negative value represents an opposite relationship between the factor and the response. Coefficients indicate quadratic relationships or interaction terms. It also expresses that the relation between responses and factors is not merely linear. In other words, when more than one factor are changed simultaneously, a factor is able to produce different degree of response.

The pH (Coef = -15.86) indicates the higher effect on As (V) removal than initial As (V) concentration (Coef = -3.55). The increase of pH gives negative effect stronger than the increase of As (V) concentration. The pH of the solution is therefore needed to be importantly controlled. Since the surface charge of FeAA relies on pH of the solution. The site of positive charge that is attractive to As (V) abated when pH increased. Therefore, the more increase of pH creates more inhibiting condition for the surface to form a complex with As (V). The interaction effects on the As (V) removal, P value of 0.000 indicates the statistical significance between pH of the solution and %FeAA whereas P value of 0.031 indicates the statistical significance between pH and initial As (V) concentration. Both interactions supported the As (V) removal.

The fit of the quadratic model were measured by using the coefficient of determination (R^2) ranging from 0 to 1. The closer the R^2 value is to 1 the higher the predictive power of the model. The determination coefficient of the predicted model or R^2 is 91.30%. However, the interactions of some parameters do not exist. Therefore, the model is adjusted to the equation as shown in Eq.4.3 and the new determination coefficient was called adjusted R^2, which is 87.38%. The difference between R^2 and adjusted R^2 is not large. This indicates the low effects from other factors that were not included in the three independent variables.

$$\text{As (V) removal} = 61.81-15.86X_1+0.17X_2-3.55X_3+8.31X_1X_2-10.10X_1^2-5.66X_2^2 \quad \text{(Eq. 4.3)}$$

This implies that the regression model rather fits to the experimental values and it is able to offer a great explanation of the relationship between the factors and the response.

4.3.3 Adequacy check of the model

The model adequacy is done in order to investigate the fitted model to ensure that it gives an adequate approximation to the actual system and to verify that all of the lease squares regression assumptions are not violated. The normal probability plot of this study is shown in Figure 4.7. From the figure, it is summarized that the residuals are distributed normally.

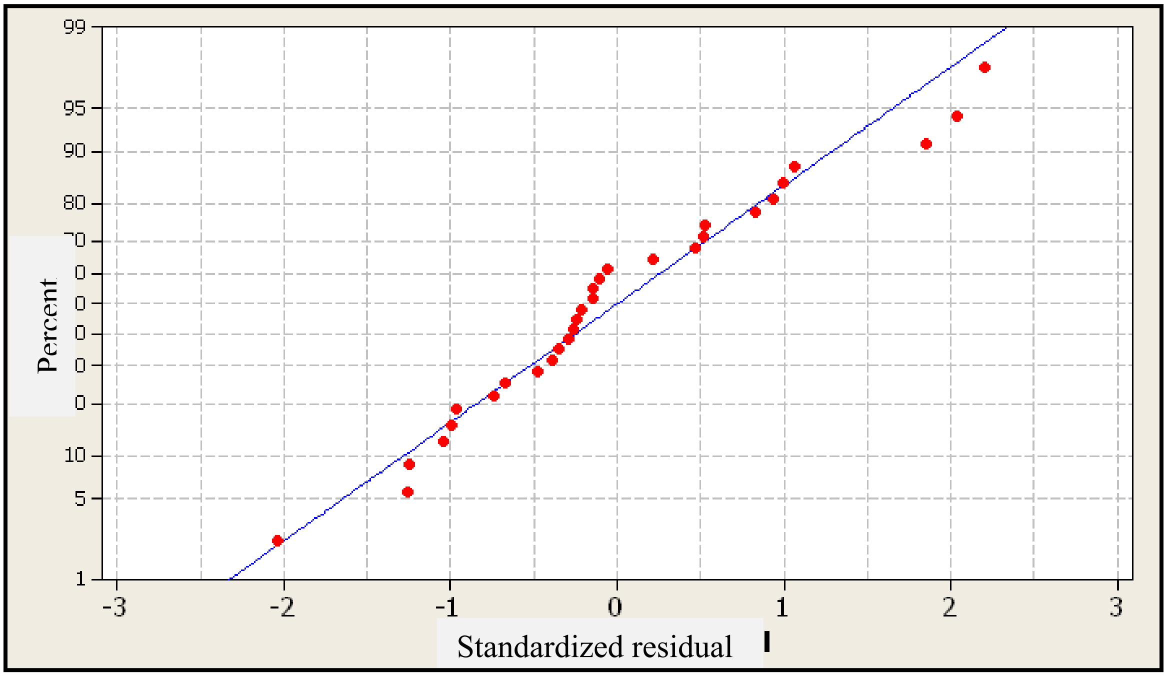

Figure 4.7 A normal probability plot of standardized residual for As (V) removal (Response is percent removal)

The residual values, which are the outcome of the predicted results subtracted from the experimental results, were between -8.52 and 9.85. Thus, the standardized values were between -2.04 and 2.21. The standardized values can be calculated from Eq. 4.4.

$$\text{Standardized residual} = \frac{\text{Residual}}{\text{Standard Deviation of Residual}} \qquad \text{(Eq. 4.4)}$$

Figure 4.8 is the plot between standardized residuals and predicted data. The standardized residuals are in the interval range of ± 2.5. The plot illustrates a random scatter in which the variance of studied data is constant in regard to all of the responses.

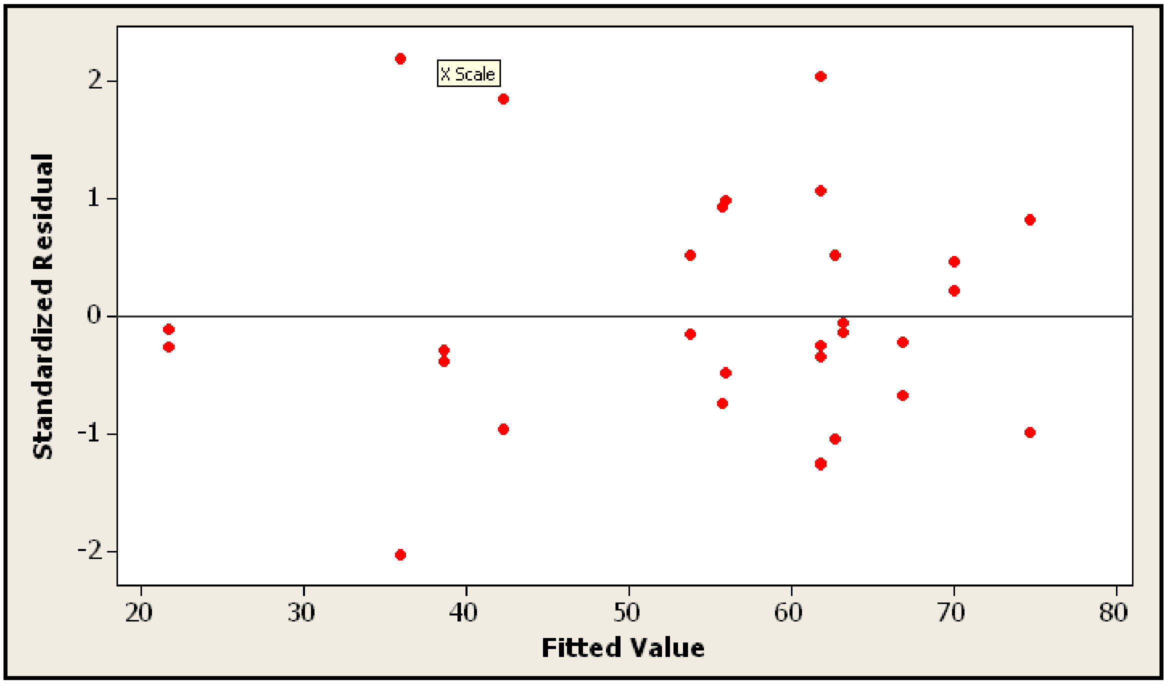

Figure 4.8 Versus Fit for As (V) removal (Response is percent removal)

4.3.4 Main effect and interaction effect

The crucial factors are displayed in Main effect plot that is Figure 4.9. The main effect refers to the effect created by one of the factors. This type of representation describes the contribution of changing one of the three factors to the removal efficiency for adsorption process. The graph shows that the removal efficiency of As (V) decreased when pH increased from 3 to 6 and the efficiency greatly decreased from pH 6 to 9. When pH increased and the positively charged sites of FeAA are decreased.

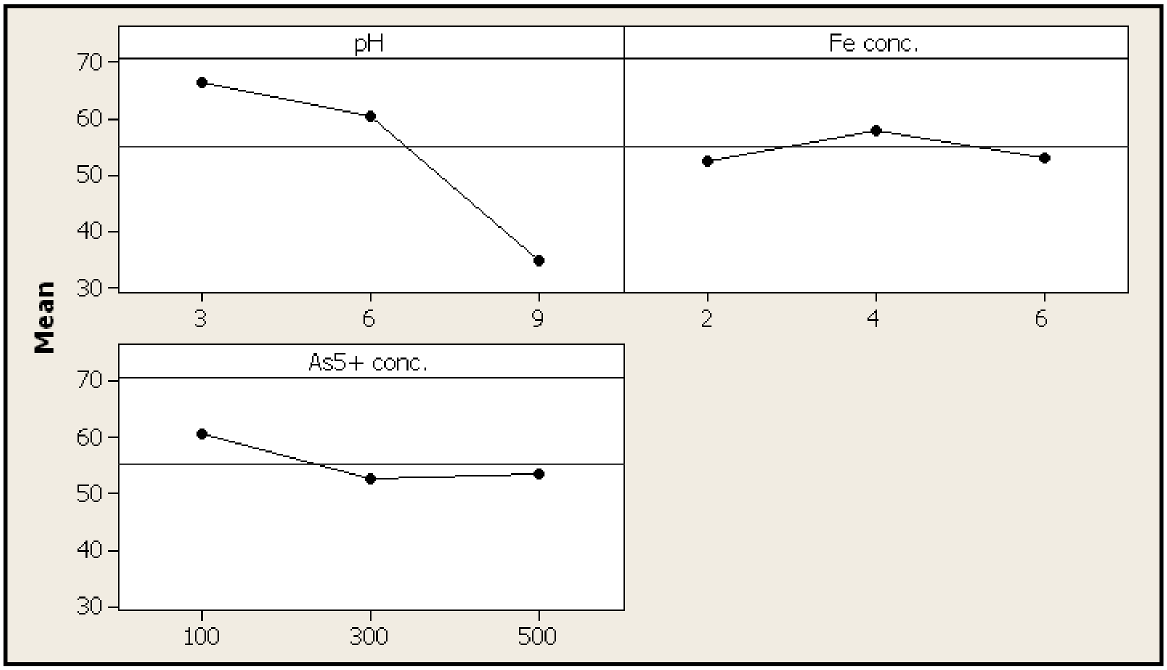

Figure 4.9 Main effect of plot for percent removal of As (V)

The concentration of Fe (%) for FeAA preparation shows the outcome that the removal efficiency is higher when the %Fe was changed from 2% to 4%. Then the efficiency reduced when the %Fe was increased from 4% to 6%. The cause of this phenomenon may be a result from the different surface areas and the adsorption sites of each prepared FeAA. The amount of iron oxide was increased resulting in higher As (V) removal as the more suitable sites for As (V) was increased. However, the more amount of iron oxide was able to clog the surface and cracks, resulting in the abatement of surface area. The percentage of As (V) removal was therefore decreased. The main effect of initial concentration of As (V) can also be observed. This result shows than the adsorption capacity is increased when the initial concentration is increased.

Furthermore, the three factors are plotted in order to observe the interaction effect in term of two-factor interaction effect as shown in Figure 4.10. The interaction plots are to elaborate the existence or not of interaction among the factors. The interaction effect is related to the case in which the impact of one factor is based on the value of another factor.

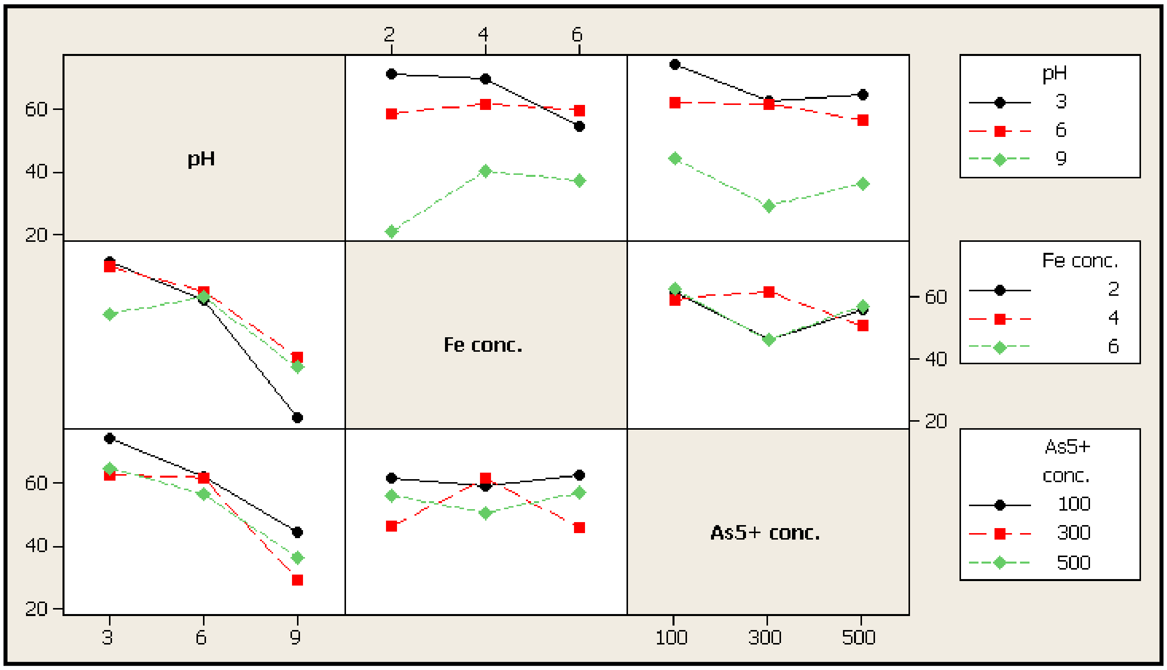

Figure 4.10 Interaction plot for percent removal of As (V) at 15th min (Data Means)

The results of all interactions show the existence of interaction between pH and %FeAA, and pH and initial As (V) concentration. This outcome was based on the results from ANOVA as given in Table 4.5, which has P-value smaller than 0.05 confirming significance at 95% confidence level.

The pH with the highest As (V) removal depended on amount of iron oxide on FeAA. Specifically, pH 3 was better when the FeAA was 2% and 4%FeAA, while pH 6 was slightly better than pH 3 when the FeAA is 6%FeAA. Besides, 2%FeAA was slightly better than 4%FeAA at pH 3, all %FeAA were almost equal at pH 6,and 4%FeAA was slightly better than 6%FeAA at pH 9. This interaction offered positive effect on As (V) removal due to the existence of FeAA was able to help increase As (V) removal under the unsuitable condition with high pH.

With regard to the interaction between pH and initial As (V) concentration, pH with the highest As (V) removal depended on the initial concentration of As (V). When the initial concentration were 100 and 500 ppb, the As (V) removal efficiency was better with pH 3, and pH 3 was slightly better than pH 6 when the initial concentration was 300 ppb. This interaction showed positive effect on As (V) removal as may be a result of As (V) expressed more negatively charge when pH increased. The more negatively charge of As (V), the more favor for As (V) removal on FeAA.

4.3.5 Optimization

After obtained the main and interaction effects, the optimization was carried out by Minitab software. The generated result from the program is illustrated in Figure 4.11. At 15th min, the best condition revealed a percent removal of 77.64% for pH 3, %FeAA of 2.57% and As (V) concentration of 100 ppb. In addition, the model was also calculated to find the optimal condition of natural groundwater at pH 7. The predicted condition from the program was pH 7, %FeAA of 4.53% and initial As (V) concentration of 100 ppb giving the removal efficiency of 62.50% as shown in Figure 4.12.

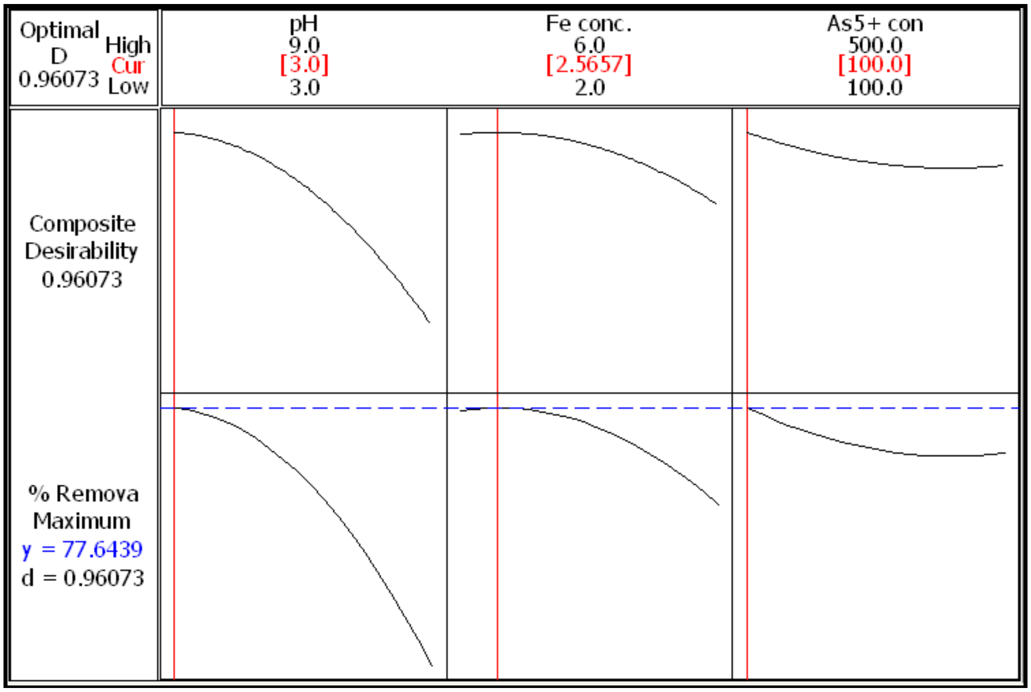

Figure 4.11 Optimization plot for the best As (V) percent removal by FeAA

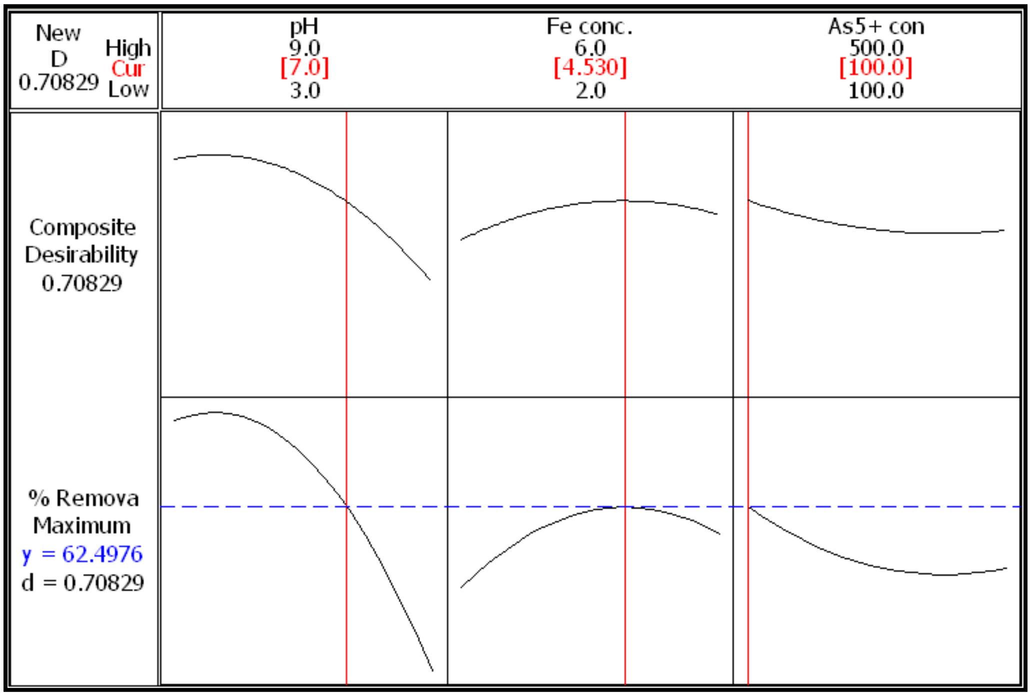

Figure 4.12 The optimization condition and percent removal by FeAA at pH 7

4.3.6 Verification of model

It is important to verify that the experimental response agrees with the predicted response in the same condition. The two selected conditions are used for adequacy and validation of the predicted response, namely percent removal. The results of six replications from the two experimental sets compared with the predicted response are shown in Table 4.7. The experimental response was 77.64±4.38% and 62.50±3.29%. The experimental outcomes reasonably agree with the predicted response.

Table 4.7 The verification of predicted and experimental responses at two different optimal conditions from RSM

Replication order	pH	%FeAA	Initial As (V) concentration (ppb)	Predicted response (%)	Experimental response (%)
1	3	2.57	100	77.64	73.47
2					77.24
3					78.89
4					79.60
5					73.26
6					75.89
1	7	4.53	100	62.50	60.74
2					59.21
3					64.24
4					63.60
5					63.17
6					61.58

4.4 The optimal condition is tested on Fe leaching from FeAA into water

The leaching test of iron ion is also tested in order to observe and ensure that the Fe leachate is not over the standard of WHO guideline (0.3 ppm) and even lower than The European Commission Directive (0.2 ppm). The concentrations of Fe in the solution of optimal conditions up to 24 hours are shown in Figure 4.13. It was found that the concentrations complied with the standards. However, iron oxide under acidic pH tends to release from FeAA into water.

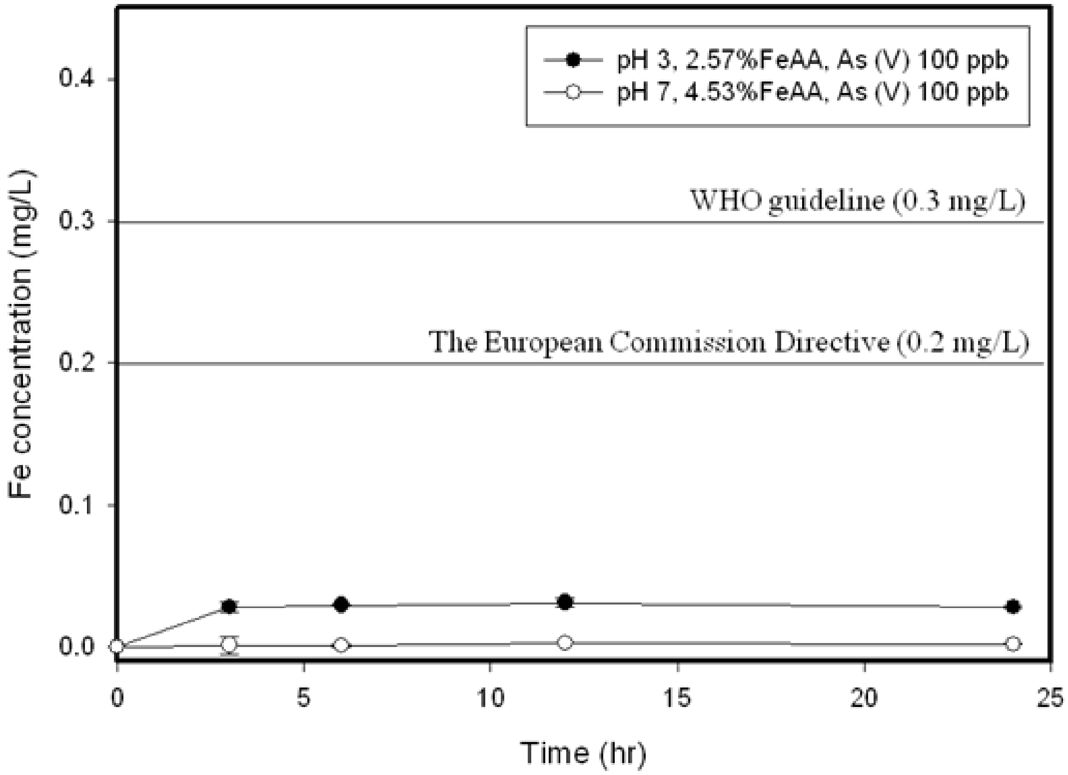

Figure 4.13 Fe leaching from FeAA under optimal conditions at different times

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

5.1.1 The obtained quadratic model can be effectively used to predict the actual result of As (V) removal.

5.1.2 The insignificant factors to As (V) removal were %FeAA, initial concentration of As (V)* initial concentration of As (V), and %FeAA* initial concentration of As (V).

5.1.3 The iron leachate from the synthesized FeAAs (2.57% and 4.53%FeAA) was discovered to comply with the standard of WHO guideline and the European Commission Direction.

5.2 Recommendations

5.2.1 The effects of competitive anions, such as As (III), phosphate, manganese, sulfate, should be further studied.

5.2.2 The prepared adsorbent (FeAA) that offers the optimal removal efficiency should be tested with natural groundwater in the real-world condition.

5.2.3 A column study with continuous flow should be further studied.

REFERENCES

Bordoloi S., Nath S. K., and Dutta R. K. Iron ion removal from groundwater using banana ash, carbonates and bicarbonates of Na and K, and their mixtures. Desalination (2011).

Charlet L., Ansari A.A., Lespagnol G., and Musso M. Risk of arsenic transfer to a semi-confined aquifer and the effect of water level fluctuation in North Mortagne, France at a former industrial site. The Science of the Total Environment 277 (2001) : 133- 147.

Cheng H., and others. Geochemical processes controlling fate and transport of arsenic in acid mine drainage (AMD) and natural systems. Journal of Hazardous Materials 165 (2009) : 13–26.

Cooper, A.M. Effect of Carbon Type on Arsenic and Trichloroethylene Removal Capacity of Iron (Hydr)oxide Nanoparticle Impregnated Granulated Activated Carbon. Master's Thesis, Environmental Technology, College of Technology and Innovation, Arizona State University, 2010.

Dzombak, D.A. Particles and Contaminant Behavior in Aquatic Systems, CIT Magazine (1990) : 19-23.

Ferreira, S.L.C., and others. Box-Behnken design: An alternative for the optimization of analytical methods, Analytica Chimica Acta 597 (2007) : 179–186.

Ferreira, T.P. Preparação e Caracterização de Materiais Híbridos de Magnetita/Polianilina por Polimerização in Situ. Mestrado tese, Universidade Estadual de Goiás, 2010.

Filho, N.L.D. and Carmo, D.R. Adsorption at Silica, Alumina, and Related Surfaces. Encyclopedia of Surface and Colloid Science 1 (2004).

Han, L.H., Liu H., and Wei Y. In situ synthesis of hematite nanoparticles using a low-temperature microemulsion method. Powder Technology 207 (2011) : 42–46.

Hsu, J.C., Lin C.J., Liao C.H., and Chen S.T. Removal of As(V) and As(III) by reclaimed iron-oxide coated sands. Journal of Hazardous Materials 153 (2008) : 817–826.

Jiang J., Bauer I., Paul A., and Kappler A. Arsenic redox changes by microbially and chemically formed semiquinone radicals and hydroquinones in a humic substance model quinine. Environ. Sci. Technol 43 (2009) : 3639–3645.

Katsoyiannis I.A. and Zouboulis I.A. Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. Water Research 36 (2002) : 5141–5155.

Kent, S.K. Adsorbent selection. [Online] Available from: www.adsorption.com/publications/AdsorbentSel1B.pdf

Kumaresan M. and Riyazuddin P. Overview of speciation chemistry of arsenic. Current Science 80 (April 2001).

Kundu S. and Gupta A.K. Analysis and modeling of fixed bed column operations on As(V) removal by adsorption onto iron oxide-coated cement (IOCC). Journal of Colloid and Interface Science 290 (2005) : 52–60.

Kuriakose S., Singh T.S., and Pant K.K. Adsorption of As(III) from Aqueous Solution onto Iron Oxide Impregnated Activated Alumina. Water Qual. Res. J. Canada 39 (2004) : 258–266.

Lai C.H., Lo S.L., and Chiang H.L. Adsorption/desorption properties of copper ions on the surface of iron-coated sand using BET and EDAX analyses. Chemosphere 41(2000) : 1249–1255.

Lin T.F. and Wu J.K. Adsorption of arsenite and arsenate within activated alumina grains: Equilibrium and kinetics. Wat. Res. 35 (2001) : 2049–2057.

Maji S.K., Kao Y.H., and Liu C.W. Arsenic removal from real arsenic-bearing groundwater by adsorption on iron-oxide-coated natural rock (IOCNR). Desalination (2011).

Malik A.H., Khan Z.M., Mahmood Q., Nasreen S., and Bhatti Z.A. Perspectives of low cost arsenic remediation of drinking water in Pakistan and other countries. Journal of Hazardous Materials 168 (2009) : 1–12.

Murcott S. Appropriate remediation technologies for arsenic-contaminated wells in Bangladesh, Arsenic in Bangladesh Ground Water at Wagner College Staten Island, New York, [Online]. 1999. Available from: http://www.physics.harvard.edu/~wilson/arsenic/remediation/arsenic_removal/murcott.html [1999, February]

Nagarnaik P.B. , Bhole A.G., and Natarajan G.S. Arseni removal of ground water – a state of art. Water Resources Journal (December 2002) : 51-66.

Oshikawa S., Geater A., Chongsuvivatwong V., and Chakraborti D. Arsenic contamination of Ronphibun residents associated with uses of arsenic-contaminated shallow-well water other than drinking. Journal of Environmental Science and Health Part A 42 (2007) : 1753–1761.

Pan Y.F., Chiou C. T., and Lin T.F. Adsorption of arsenic(V) by iron-oxide-coated diatomite (IOCD). Environ Sci Pollut Res 17 (2010) : 1401–1410.

Panthil S.R., Sharma S., and Mishral A.K. Recent status of arsenic contamination in groundwater of Nepal - a review. Kathmandu University Journal of Science, Engineering and Technology Vol. II, No.1 (December 2002) : 51-66.

Rahman M.H., Rahman M.M., Watanabe C., and Yamamoto K. Arsenic contamination of groundwater in Bangladesh and its remedial measures. Arsenic Contamination in Groundwater - Technical and Policy Dimensions : 9-22.

Singh T. S. and Pant K.K. Equilibrium, kinetics and thermodynamic studies for adsorption of As(III) on activated alumina. Separation and Purification Technology 36 (2004) : 139–147.

Singh T.S. and Pant K.K. Kinetics and mass transfer studies on the adsorption of arsenic onto activated alumina and iron oxide impregnated activated alumina. Water Qual. Res. J. Canada 41 (2006) : 147–156.

Smedley P.L., Kinniburgh D.G., Ryker S.J., and Stollenwerk K.G. Chapter 7, Chapter 1, Chapter 6, and Chapter 3, Alan H. Welch,Kenneth G. Stollenwerk, Arsenic in Ground Water Geochemistry and Occurrence, Massachusetts: Kluwer Academic publishers, 2002.

Streat M., Hellgardt K., and Newton N.L.R. Hydrous ferric oxide as an adsorbent in water treatment (Part 1 Preparation and physical characterization). Process Safety and Environmental Protection 8 (2008) : 1– 9.

Office of water. Technologies and costs for removal of arsenic from drinking water, targeting and analysis branch standards and risk management division office of ground water and drinking water United States Environmental Protection Agency Washington D.C. United States Environmental Protection Agency. [Online].2000. Available from : www.epa.gov/safewater [2000,Dec]

Thomson, B.M., Cotter T.J., and Chwirka, J.D. Design and operation of point-of-use treatment system for arsenic removal. Journal of Environmental Engineering, ASCE (June 2003) : 561-564.

Tripathi P., Srivastava V.C., and Kumar A. Optimization of an azo dye batch adsorption parameters using Box–Behnken design. Desalination 249 (2009) : 1273–1279.

United States Environmental Protection Agency (USEPA), Technologies and costs for removal of arsenic from drinking water. [Online]. 2000. Available from: www.epa.gov/ogwdw/arsenic/pdfs/treatments_and_costs.pdf [2000,December]

Zcan, A.O., Zcan, S.O., Tunali, S., Akar, T., Kiran, I. Determination of the equilibrium, kinetic and thermodynamic parameters of adsorption of copper(II) ions onto seeds of Capsicum Annuum. Journal of Hazardous Materials B124 2005 : 200–208.

Zhang Z. and Zheng H. Optimization for decolorization of azo dye acid green 20 by ultrasound and H_2O_2 using response surface methodology. Journal of Hazardous Materials 172 (2009): 1388–1393

APPENDIX

1. Calibration curve of As

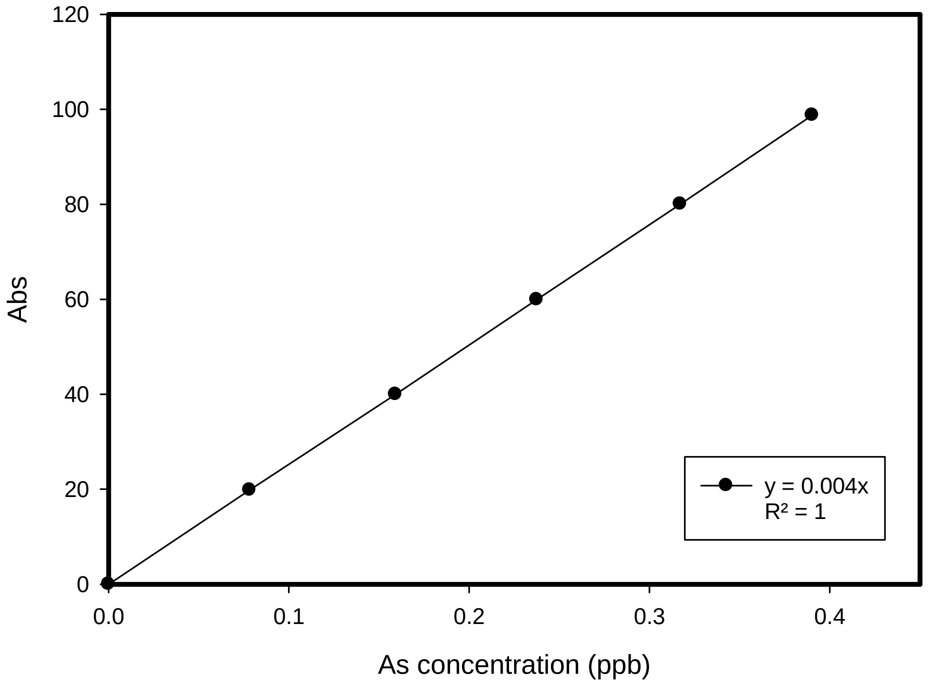

Figure A-1 Calibration curve of As

2. As (III) and As (V) adsorption efficiency of AA and 6%FeAA

Table A-1 The As (III) adsorption efficiency of AA for pH 3 and initial As (III) of 300 ppb.

AA (As III)			
Time (min)	**Ct/C0**	**qt**	**%Removal**
0	1.000	0.000	0.000
15	0.869	3.946	13.092
30	0.838	4.883	16.201
60	0.796	6.153	20.426
90	0.751	7.513	24.926
120	0.654	10.433	34.623

Table A-2 The As (V) adsorption efficiency of AA for pH 3 and initial As (V) of 300 ppb.

AA (As V)			
Time (min)	**Ct/C0**	**qt**	**%Removal**
0	1.000	0.000	0.000
15	0.837	4.907	16.349
30	0.695	9.153	30.521
60	0.634	10.994	36.649
90	0.556	13.333	44.445
120	0.437	16.894	56.309

Table A-3 The As (III) adsorption efficiency of 6%FeAA for pH 3 and initial As (III) of 300ppb.

6%FeAA (As III)			
Time (min)	**Ct/C0**	**qt**	**%Removal**
0	1.000	0.000	0.000
15	0.661	10.522	33.862
30	0.553	13.885	44.750
60	0.407	18.408	59.344
90	0.289	22.036	71.093
120	0.252	23.193	74.799

Table A-4 The As (V) adsorption efficiency of 6%FeAA for pH 3 and initial As (V) of 300 ppb.

6%FeAA (As V)			
Time (min)	**Ct/C0**	**qt**	**%Removal**
0	1.000	0.000	0.000
15	0.447	16.485	55.349
30	0.077	27.504	92.299
60	0.010	29.497	99.035
90	0.000	29.788	100.000
120	0.000	29.788	100.000

3. The optimal condition is tested on Fe leaching from FeAA into water

Table A-5 Fe leachate from FeAA under optimal conditions at different times

pH	%FeAA	Initial concentration of As (V) in ppb	Time (hr)	Fe concentration (ppm)
3	2.57	100	0	0.000
			3	0.028
			6	0.030
			12	0.031
			24	0.028
7	4.53	100	0	0.000
			3	0.002
			6	0.001
			12	0.003
			24	0.002

4. Point of zero charge

Table A-6 Zeta potential values at various pH values

pH	Zeta potential (mV)	
	AA	4.53%FeAA
2	15.07	44.90
4	24.40	48.23
6	12.87	22.22
8	-3.40	0.64
10	-24.77	-1.26
12	-23.23	-0.52

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