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REMOVAL OF ARSENIC USING SYNTHETIC IRON OXYHYDROXIDE

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled “Removal of Arsenic Using Synthetic Iron Oxyhydroxide”. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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LIST OF SYMBOLS AND ABBREVIATIONS

α -FeOOH	- Goethite
As	- Arsenic
AMD	- Acid Mine Drainage
CCME	- Canadian Environmental Quality Guidelines
FeOOH	- Iron Oxyhydroxide/Ferrihydrite
g	- gram
JCPDS	- Joint Committee on Powder Diffraction Standards
ICP-OES	- Inductively Coupled Plasma Optical Emission Spectrometry
MCL	- Maximum Contaminant Level
SEM	- Scanning Electron Microscopy
UPM	- Universiti Putra Malaysia
XRD	- X-ray Diffraction

PENYINGKIRAN ARSENIK MENGGUNAKAN FERUM OKSIHIDROKSIDA

SINTETIK

ABSTRAK

Penyingkiran arsenik daripada air sisa lombong menggunakan ferum-oksida sebagai bahan penjerap semakin banyak digunakan kerana ia mudah dan murah. Dalam kerja penyelidikan ini, beberapa serbuk sampel ferum oksihidroksida sintetik yang terpilih telah diperolehi. Selepas menjalankan pencirian, serbuk sampel ini digunakan sebagai bahan penjerap dalam eksperimen penyingkiran arsenik. Serbuk-serbuk sampel ini diletakkan dalam 250 mL flask konikal berasingan yang mengandungi 100 mL larutan piawai As (V) pada pelbagai kepekatan (5, 7, dan 9 ppm). Eksperimen berlangsung selama 8 jam dengan mengambil 20 mL isipadu sampel alikuat pada interval masa 1, 3, 5, and 8 jam. Kepekatan As dalam setiap sampel alikuat selepas eksperimen penyingkiran telah dianalisa menggunakan ICP-OES. Paten XRD bagi sampel serbuk yang telah diperolehi menunjukkan ciri-ciri puncak utama bagi goetit dan hematit. Morfologi permukaan sampel serbuk mempamerkan ciri-ciri denritik dan bersifat sangat porous. Ciri-ciri ini didapati meningkatkan perolehan As daripada larutan piawai yang disediakan. Peratusan penyingkiran As pada pelbagai kepekatan larutan adalah dalam julat 28.9% to 99.2%. Pencirian sisa pepejal selepas eksperimen penyingkiran As juga telah dijalankan. Dari analisis fasa XRD, kehadiran arsenik oksida (As_2O_3) telah dikenalpasti. Dari fotomikrograf SEM, permukaan sisa pepejal didapati lebih licin dan kurang bersifat dendritik. Oleh itu, spesies arsenik boleh diandaikan telah dijerap masuk ke dalam liang-liang di atas permukaan serbuk sampel sintetik ferum oksihidroksida selepas eksperimen penyingkiran arsenik.

REMOVAL OF ARSENIC USING SYNTHETIC IRON OXYHYDROXIDE

ABSTRACT

Removal of arsenic from mine waste water using iron-oxide-based absorbents are getting prevalent as using the absorbents are simpler and of low cost. In this research work, selected samples of synthetic iron oxyhydroxide powder were obtained. After characterization, these sample powders were used as an absorbent in the arsenic removal experiment. The powdered samples were placed in separate 250 mL conical flask containing 100 mL of As (V) standard solution of varying concentrations (5, 7, and 9 ppm). The experiment was conducted for 8 hours with 20 mL volume of aliquot samples taken at 1, 3, 5, and 8 hours interval hour. The concentration of the As after the removal experiment in each aliquot sample was analysed using ICP-OES. The XRD pattern of the powdered samples obtained showed major characteristic peaks of goethite and hematite. Surface morphology of the powdered samples displayed dendritic features and were highly porous. These features were found to enhance the recovery of As from the standard solution prepared. The percentage of As removed at varying concentration of As was found to be in the range of 28.9% to 99.2%. The solid residues after the arsenic removal experiment were also characterised. From XRD phase analysis, the presence of arsenic oxide (As_2O_3) was detected. The surfaces of the solid residues were observed to be smoother and less dendritic from the SEM photomicrograph. It can be assumed that arsenic species were adsorbed into the pores on the surface of the synthetic iron oxyhydroxide powder samples after the arsenic removal experiment.

CHAPTER 1

INTRODUCTION

1.1 Research Background

Arsenic (As), a metalloid element, known as poisonous substances, formed either naturally or because of mining activities which contribute to the environmental pollution and health emergencies in several places. It is the 20th most abundant elements which comprising about (0.00005%) of the earth's crust (Mandal & Suzuki, 2002).

Today, many people are suffering from upstretched doses of arsenic exposure from air, food, water and soil. Exposure to heavy metals such as lead, cadmium, mercury, and arsenic could be the major threats for human health. Arsenic pollution spread mainly via intake of food and drinking water. (Mandal, 2017). Arsenic has been an inexplicable and fearsome element in the human history. Prolonged exposure to arsenic may cause some health manifestations such as cancers as As is referred as carcinogens. Moreover, arsenic pollution has become a main concern due to its increasing amount of arsenic contaminated water, air and soil. Most arsenic compounds are soluble in the water, giving the main reason why it can easily access water bodies such as rivers, lakes, and ponds and therefore may affect human and animals through ingestion of water (Flora, 2014).

Arsenic removal method has been improvised and various technologies are available depending on required conditions. Methods are including oxidation/precipitation technologies, coagulation/coprecipitation technologies, sorption and ion-exchange technologies, membrane technologies and others which will be discussed further in Chapter

2. Arsenic removal using absorbents such as activated carbon and iron-based hydroxides are getting more attention as previously this method are paid less attention. Some of the low-cost absorbents such as rice husks from agriculture by-product, char, coal, lignite, peat chars, red mud, blast furnace slags, Fe(III)/Cr(III) hydroxide waste, clay minerals, zeolites and fly ash (Mohan and Pittman, 2007) are also effective in the removal of arsenic contamination.

The iron oxide minerals usually used as adsorbents of arsenic in water are goethite, hematite, siderite, limonite, ferrihydrite, and magnetite. Goethite (α -FeOOH) is an iron oxide mineral containing 62.9% Fe, 27% O, and 10.1% H₂O. It consists of double bands of FeO(OH) octahedral, which share edges and corners to form a 2 × 1 octahedral tunnel partially bonded by H-bonds. It exhibits needle-shaped crystals with grooves and edges.

Hematite (Fe₂O₃) consists of 70% Fe and 30% O. Hematite is widely distributed in rocks of all ages and forms the most abundant and important iron ore. Siderite (FeCO₃) is frequently found as clay ironstone, impure by the mixture with clay materials, in concretions with concentric layers. Limonite (FeOOH · nH₂O) is a natural hydrous iron oxide mineral of uncertain identity.

The exact composition of ferrihydrite is uncertain, being variously given as FeO(OH), Fe₅O₆(OH)₃ · 3H₂O, 5Fe₂O₃ · 9H₂O, or Fe₂O₃ · 2FeO(OH) · 6H₂O. Ferrihydrite, a primary precipitate of iron-fixing bacteria or of the natural hydrolysis of iron salts in solution, is probably a precursor of goethite (limonite), feroxhyte, and many other iron minerals. Magnetite (Fe₃O₄) is one of the most abundant and widespread of iron oxide minerals. It is often pseudomorphs altered to hematite or goethite. Magnetite frequently occurs as octahedral crystals, with 22.4% Fe and 27.6% O (Gallegos-Garcia et al, 2012)

In this research work, the focus of arsenic removal is by using ferric oxyhydroxide, also known as hydrous ferric oxide and amorphous ferric hydroxide, a solid formed due to a

rapid hydrolysis of iron solutions at 20 to 30°C. The solid phase of ferric oxyhydroxide is usually completely amorphous as determined by X-ray diffraction, although a few broad reflections are sometimes observed indicating some crystalline character. Natural iron oxide material exhibiting similar diffraction patterns is often called ferrihydrite (Dzombak and Morel, 1990).

All ferric iron minerals are naturally occurring oxyhydroxides. The FeOOH composition includes four polymorphs based on the spatial arrangement of octahedra. The most common are goethite (α -FeOOH), lepidocrocite (γ -FeOOH), akageneite (β -FeOOH) and feroxyhyte (δ' -FeOOH). Ferrihydrite and schwertmannite are both poorly crystalline hydrated oxyhydroxides. Ferrihydrite occur exclusively as nanoparticles in either a somewhat more crystallized “six lines” form, so-called because it displays six lines in X-ray diffraction or a more poorly crystalline “two-line” form which exhibits only two broad X-ray diffraction lines. Schwertmannite has the same structure as akageneite but bears a sulfate complex in the tunnel structure instead of chloride ion for akageneite.

1.2 Arsenic Contamination Issues in Malaysia

Pollution of arsenic are not only abundance in mining effluents, but also can contaminated groundwater, streams and lakes. In Malaysia, the most concern of arsenic pollution might be generated from bauxite mining in Pahang as reported by News Strait Times in 2015. Bauxite mining in Pahang not only cause a serious environmental pollution, which turned the whole city of Kuantan into red land in Mars but also produced high amount of arsenic with other carcinogens release into the water sources. An independent laboratory tests were conducted in Pantai Pengorak and Sungai Pengorak by obtaining five live fish samples to determine the metal concentration in the fish. The Food Regulation 1985 states that the acceptable level for arsenic in fish and fishery product is 1mg/kg. Unfortunately, the mean reading for arsenic in the fish samples that were submitted for the test was 101.5mg/kg, very much higher than the acceptable level. The lab results also showed high traces of other heavy metals, including iron, zinc, copper, nickel and lead (Shah, 2015).



Figure 1.1: Bauxite Contamination Area in Pahang

(source: cleanmalaysia.com)

Apart from the arsenic pollution at the mining area in Malaysia, a recent study was conducted to investigate the level of arsenic (As) in Peninsular Malaysia. Soil samples and accumulation of As in *Centella asiatica* (Pegaga botanical name) was collected from 12 sampling sites in Peninsular Malaysia. Four sites were selected which were at UPM (clean site), Balakong (semi-polluted site), Seri Kembangan (semi-polluted site) and Juru (polluted site). All sampling sites had high arsenic levels exceeding the Canadian Environmental Quality Guidelines (CCME) guideline (12 $\mu\text{g/g dw}$) except for Kelantan, P.Pauh, and Senawang. Klang was reported having the highest arsenic content in soil (57.05 $\mu\text{g/g dw}$). The findings of this study indicated that the leaves, stems and roots of *Centella asiatica* are an ideal bio monitors of arsenic pollution (Ong et al 2012).

Metalloid element arsenic is categorized as harmful for the environment and human beings. Arsenic are usually associated with the metallic sulfide ore bodies. Sulfide oxidation under meteoric conditions leads to acidification of waters and release of high concentrations of sulfates and metal(oid)s such as Fe, As, Cd, Cu, Zn, and Pb. The oxidative leaching of sulfide-rich mining wastes is known as acid mine drainage (AMD). Under these conditions a poorly-crystalline oxyhydroxysulfate, schwertmannite, spontaneously precipitates on AMD-affected riverbeds (Cruz-Hernández et al, 2017).

1.3 Significant of Research

Arsenic contaminations not only can be found in surface water but also in groundwater. Arsenic pollution has proved to bring causes of many health effects in the world. It is important to treat the arsenic immediately.

There are many enhanced treatment processes have been developed to deeply eliminate arsenic from water. Precipitation/coprecipitation process causes dissolved arsenic to form low-solubility solid minerals. Adsorption process for arsenic removal is realized through arsenic species on special solid adsorbents, such as activated carbon. Ion exchange process uses synthetic resins to remove dissolved ions from water. Membrane separation process, including microfiltration, reverse osmosis, electrodialysis, ultrafiltration, and nanofiltration, has also proved to be effective for arsenic removal from water

Amongst the many techniques of arsenic removal used in the industry, the removal using iron-based adsorbents such as iron oxyhydroxides may be the most favourable technology as it is an economical process and cost saving. Removal of arsenic using synthetic iron oxyhydroxides are getting more attention in recent years due to its high affinity to arsenic element. Furthermore, the process of the removal is very simple and does not need many equipment and materials.

With the occurring of arsenic contamination produced from the bauxite mining in Pahang, there is urgent need to research about the effective methods to solve this kind of the problem. This research work is initiated as after several research has been done regarding arsenic removal using iron oxyhydroxides.

1.4 Objectives

The objectives of this research work are:

- 1) To conduct characterization study on the synthetic iron oxyhydroxide samples obtained.
- 2) To study the effectiveness of the synthetic iron oxyhydroxide samples in the removal of arsenic at varying concentration of the arsenic solution.

1.5 Scope of Research Work

In this research, selected samples of synthetic iron oxyhydroxide samples were obtained from the previous researcher (Ikhwan, 2016) and used as an absorbent in the removal of arsenic experiment. All synthetic iron oxyhydroxide samples were analysed by SEM and XRD before the arsenic removal experiment for characterization study.

In the arsenic removal experiment, synthetic iron oxyhydroxide samples were studied to determine the effectiveness in the removal of arsenic. Three different concentration of arsenic standard solution (5, 7 and 9 ppm) were prepared and experiments were conducted for 8 hours. The filtrate solution was analysed by ICP-OES analysis and the solid residues were oven-dried and sent for XRD analysis.

Detailed experimental procedures were discussed in Chapter 3. All results from SEM, XRD and ICP-OES analysis were discussed in Chapter 4.

1.6 Thesis Outline

This thesis is divided into the following chapters: Introduction, Literature Review, Methodology, Results and Discussions, Conclusions and Recommendations.

Chapter 1 introduces the project and provides background information relevant to this research. Chapter 2 provides the summary of scholarly paper related to the research and Chapter 3 outlined the method used for this research. Next, Chapter 4 discussed the outcome of the research and Chapter 5 summarizes the conclusions of this work and identifies new recommendations for future studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Arsenic, a toxic element present in the minerals, is a global environmental challenge both in mining and water industry. The aftermath effect of acid mine drainage that occurred raised attention from the society as it is harmful if not treated properly. It is either mobilized through hydrometallurgical and pyrometallurgical processes or occurred naturally in natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other activities. Arsenic is not very harmful in low quantities but when the activities such as mining, combustion of fossil fuels and the use of pesticides are not controlled, it will create a bigger impact and thus, the arsenic are classified as the dangerous contaminants (Mohan and Pittman, 2007).

Arsenic may be found naturally in the arsenic-containing minerals such as arsenopyrite, realgar, orpiment and enargite. Arsenic that results from mining activities is mostly from pyrometallurgical of copper and lead. Arsenic is a member of nitrogen family, group 15 element in the periodic table along with nitrogen, phosphorus, arsenic, antimony, bismuth, and ununpentium. It has 33 protons but the most stable isotopes that occurs naturally is arsenic-75 (^{75}As). Other general properties of arsenic including melting and boiling point are summarized in the Table 2.1.

The surface of this metalloid is shiny but when the pressure exerted, it will crumble into powder like a non-metal. That is why it also can be a conductor or semiconductor. Arsenic can lose the electron, which can easily exhibit +3 and +5 oxidation states. Naturally,

it will mostly combine with oxygen and sulphur though it may combine with many elements to form a covalent compound. In its pure form, it is brittle and grey metal but naturally, it is found along with copper, nickel, iron and silver as oxides and sulphides. (Flora, 2014)

Table 2.1: General Properties of Arsenic

(<http://www.rsc.org/periodic-table/element/33/arsenic>)

Property	Value
Symbol	As
Group	15
Period	4
Block	P
Atomic number	33
Melting Point	Sublimes at 616°C, 1141°F, 889 K
Boiling Point	Sublimes at 616°C, 1141°F, 889 K
Density (g/cm-3)	5.75
Relative Atomic Mass	74.922
Key Isotopes	⁷⁵ As
Electron Configuration	[Ar] 3d10 4s2 4p3

Arsenic that dissolved naturally in water coexist as +3 and +5. As³⁺ and As⁵⁺ usually bond with oxygen to form arsenite, As(III) and arsenate, As(V) (Henke, 2009). Arsenic mainly occurred as inorganic form in natural water as oxyanions of trivalent (+3) arsenite or as pentavalent (+5) arsenate and their ratio in natural water is 1:4. Example of inorganic compound of arsenic are As₂O₃, As₂O₅, and arsenic sulphides such as As₂S₃, HAsS₂, and HAsS₃³⁻. This inorganic arsenic is stable in oxygenated waters. Arsenates are steady under aerobic or oxidizing conditions while arsenic are steady under anaerobic or slightly reducing conditions. In reducing waters, arsenite, As(III) is founded in the form of arsenious acid that ionizes according to the following equation:



The acid-base dissociation reactions of arsenic can be described as:



pKa is the pH at which the dissociation of the reactant is 50% complete. The dominant organic forms found in water are methyl and dimethyl arsenic compound such as monomethyl arsenous acid (MMA (III)), monomethyl arsenic acid (MMA(V)), dimethyl arsenous acid (DMA(III)) and dimethyl arsenic acid (DMA(V)). (Pal, 2015). Arsenic (V) and arsenic (III) are said to be significant in groundwater. Arsenic (V) was chosen because it is effective to be removed by iron-oxide-based absorbents (Clifford and Ghurye, 2011).

Prolonged exposure to arsenic is dangerous; thus, it must be treated immediately using specific water treatment process to meet the water quality standard. In India, many people that drinking arsenic contaminated water are suffering skin lesions and those who suffered from non-cirrhotic portal fibrosis contained high arsenic in their liver. Some other cases might cause hyperpigmentation and hyperkeratosis which the result of chronic arsenicosis diagnose. The pigmentation commonly appears as finely freckled and “raindrop” pattern. Other features of chronic arsenicosis are the weakness, anaemia, peripheral neuropathy, hepatomegaly, chronic lung disease and peripheral vascular disease. These manifestations are variable occurred depending on different populations and conditions (Willard et al 2003).

Serious mitigation measures must be taken to reduce the probability of increasing arsenic exposure due to the rapid industrialization today. Efficient and economic methods of treatment must be established or adapted from another type of technologies. Treatment of arsenic has proved to be a difficult task to accomplish since it changes valence states and reacts differently depending on varying toxicity and mobility. The Maximum Contaminant Level (MCL) that provides the measurement for arsenic in drinking water was recently reduced by the United States Environmental Protection Agency (EPA) from 50 ppm to 10 ppm to protect the consumers from prolonged effect of chronic arsenic exposure.

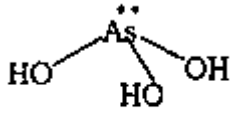
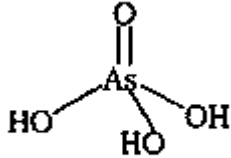
Arsenic shows variations from <0.5 to 5000 mg/l under natural conditions. Oxidising (under conditions of high pH) and reducing aquifers and areas affected by geothermal, mining and industrial activity provide a nurturing environment for high concentrations of arsenic. In many of the cases, natural sources have been found to contribute towards high level concentration of Arsenic. Meanwhile, mining activities result to high occurrence of arsenic locally. Furthermore, arsenic pollution increases at local levels due to industrial and agricultural activities. (Panagiotaras et al 2012).

2.2 Arsenic Contamination in Wastewater

Arsenic contamination in wastewater can be treated using various kind of method that is suitable depending on the situation or preferences from the actual industry. The example of main arsenic removal technologies is oxidation/precipitation, coagulation, sorption and ion exchange techniques, and membrane technologies. Each of the technology has its own advantages and disadvantages. Specifically, this project focused more on the sorption and ion exchange technology using iron-oxide-based absorbents. Similarly, arsenic removal using activated carbon through adsorption process were reported by Mohan and Pittman (2007).

Arsenic is possibly unique among the heavy metalloids and oxyanion-forming elements (e.g., As, Se, Sb, Mo, V, Cr, U, Re) in its sensitivity to mobilization at the pH values typically found in ground waters (pH 6.5–8.5) and under both oxidizing and reducing conditions (Gallegos-Garcia et al, 2012). Arsenic in the environment can occur in several oxidation states (-3, 0, +3, +5) and as both organic and inorganic As. However, in natural waters, inorganic arsenic is predominant and is found as oxyanions of trivalent arsenite ($\text{H}_3\text{As(III)O}_3$) or pentavalent arsenate (e.g. $\text{H}_2\text{As(V)O}_4$). In surface waters, organic arsenic compounds may be produced by biological activity but are rarely important quantitatively. Both arsenite and arsenate are very different including their structure and behaviour. Table 2.2 compares the characteristic differences between arsenite, As(III) and arsenate, As(V).

Table 2.2: Characteristic Differences between Arsenite, As(III) and Arsenate, As(V)

	Arsenite, As(III)	Arsenate, As(V)
Occurrence	Low-oxygen groundwaters, hydrothermal waters	Oxidizing groundwaters, surface water
Behaviour (Mohan & Pittman, 2007)	Hard acid, forming complexes with oxides and nitrogen	Soft acid, forming complexes with sulfides
Structure (Henke, K. 2009)	 <p style="text-align: center;">Arsenite (As(III))</p>	 <p style="text-align: center;">Arsenate (As(V))</p>

Arsenic is a metalloid listed in group 15 of the periodic table. It exists in nature in the oxidation states +V (arsenate), +III (arsenite), 0 (arsenic) and -III (arsine). Arsenic speciation is controlled by a variety of factors, the most important of which are pH and redox potential. In aqueous systems, arsenic exhibits anionic behaviour. In case of oxygenated waters, arsenic acid predominates only at extremely low pH (< 2). In the pH range of 2 to 11, it is in the form of H_2AsO_4^- and HAsO_4^{2-} . In mildly reduced conditions and low pH values, arsenious acid converted to H_2AsO_3^- as the pH increases. When the pH exceeds 12, HAsO_3^{2-} does appear (Figure 2.1). Figure 2.1 shows the Eh-pH diagram of arsenic at 25°C and 1 bar total pressure (Panagiotaras et al, 2012).

In the presence of sulphide and in low pH conditions, HAS2 can form, arsine derivatives and arsenic metal can occur under extreme reducing conditions. In different environmental conditions arsenic readily changes its valence state and chemical form. Some conditions that may affect arsenic valence and speciation are presented: pH – in the pH range of 4 to 10, As(V) species are negatively charged in water, and the predominant As(III) species is neutral in charge; redox potential; the presence of complexing ions, such as ions of sulfur, iron, and calcium; microbial activity. Adsorption-desorption reactions can also affect the mobility of arsenic in the environment. Geomaterials such as clays, carbonaceous materials, and oxides of iron, aluminum, and manganese are sediment components that may participate in adsorptive reactions with arsenic.

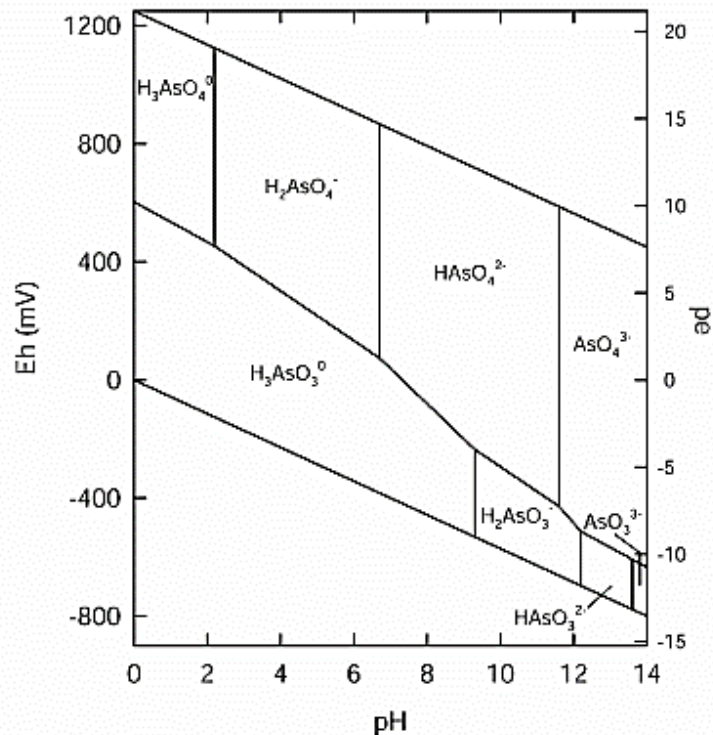


Figure 2.1: Eh-pH Diagram of Arsenic at 25°C and 1 Bar Total Pressure
(Panagiotaras et al, 2012)

Solution pH affects significantly the speciation of arsenic in solution. The affinity of each arsenic species to iron oxide mineral surfaces is different in strength. Therefore, the capacity of chemical adsorption of arsenic on iron oxide mineral surfaces varies with the arsenic species and thus with solution pH. It has been found that As(V) adsorption on iron oxide minerals decreased with increasing solution pH and reached the maximum value at a very low pH (Gallegos-Garcia, 2012).

Generally, the rate of oxidation of As(III) to As(V) is very low in natural waters, but can proceed measurably in several days in strongly alkaline or acid solutions. The speciation of As is important in controlling the mobility, bioavailability and toxicity. The mobility of As is mainly controlled by the presence of metal (hydr)oxides and since at the pH of natural water As(III) is present as a neutral species and As(V) is present in anionic form the sorption of As(V) is strongly favoured. Therefore As(III) is more mobile compared to As(V) in neutral to slightly acidic pH range. The presence of other competing ions also has an effect on the mobility of As.

Arsenic's toxicity and mobility has been proved to vary with its chemical form and state of valence. In sea water and surface water, arsenite and arsenate constitute the dominant species. In addition, it is in natural gas and shale oil that organic arsenic species can be found. Varying degrees of toxicity and solubility can be evidenced in chemical compounds that contain arsenic. The mobilization of arsenic in groundwater is controlled by several reactions i.e. dissolution/precipitation, adsorption/co-precipitation, and reduction/oxidation.

Furthermore, numerous processes have given a rise to the existing global account for high levels of arsenic in natural water: The weathering of sulfide minerals provides for the reductive dissolution of arsenic rich iron oxyhydroxide, Arsenic-rich pyrite or arsenopyrite oxidative dissolution. Arsenic – bearing minerals that interact with water. Iron oxyhydroxides constitute the most common cause for the widespread contamination from arsenic. This is due to the post effect that evidenced following the reaction of iron oxyhydroxides with organic carbon release arsenic into solution. The oxidation of sulphide minerals such as pyrite is a major source of arsenic. It has also been found to constitute the primary source in aquifers located in Wisconsin and Michigan (Panagiotaras et al, 2012).

2.3 Technologies Available in the Removal of Arsenic

Arsenic contaminated water must be treated immediately to protect the environment and human health by providing a better water quality. To achieve this goal, various kinds of methods and technologies has been researched and applied. Several major technologies of arsenic removal are listed below in the Table 2.3. Most technologies of arsenic removal discussed the effectiveness from water containing high initial arsenic concentrations (usually >100 ppm) but residual arsenic concentrations exceed the 0.05 ppm water quality standard used in most countries. In rural areas such as in India and Bangladesh, a high technology may not well implement unless it fits into the rural circumstances and is well accepted by the communities. Better technology can be developed when the villagers give commitments. All arsenic removal technologies all have more than one drawbacks, limitations and scope of application (Mohan and Pittman, 2007).

Table 2.3: Major Technologies of Arsenic Removal

Major Technologies of Arsenic Removal	
1. Oxidation/Precipitation	Air Oxidation
	Chemical Oxidation
2. Coagulation/Electrocoagulation/Coprecipitation	Alum Coagulation
	Iron Coagulation
	Lime Softening
3. Sorption and Ion-Exchange Techniques	Activated Alumina
	Iron Coated Sand
	Ion-exchange resin
4. Membrane	Nanofiltration
	Reverse Osmosis
	Electrodialysis
5. Other techniques	Foam Flotation
	Solvent Extraction
	Bioremediation

Adsorption is a traditional process to separate solutes from solvent or gases, where the solute increases on the adsorbent surfaces and decreases in the solvent. Adsorption is a surface-based process where gases, liquids or solutes accumulate. The adsorption method has two categories which are coagulation adsorption and ion exchange adsorption. In the coagulation adsorption process, colloidal solid particles in arsenic-contaminated water first aggregate through the addition of coagulants (Al^{3+} or Fe^{3+} ions) because the ions appear in the Stern layers of the colloidal particles in the form of hydrolysed species. It is the same as the conventional electrolytic coagulation. Then, arsenate ions (As(V)) in water form ferric arsenate (FeAsO_4) or aluminium arsenate (AlAsO_4) with the hydrolysed species in the Stern layers and thus adsorb on the coagulates. This step is also termed as precipitation or co-precipitation.

In ion exchange adsorption, various solid materials, such as iron and aluminium hydroxide flocs, have a strong affinity for dissolved arsenic. Arsenic is strongly attracted to adsorption sites on solid surfaces and is effectively removed from solution. Ion exchange can be considered as a special adsorption, though it is often considered separately. Ion exchange involves the reversible displacement of an ion adsorbed onto a solid surface by a dissolved ion. Other forms of adsorption involve stronger bonds and are less easily reversed

Adsorption process depends primarily on adsorbent. Effective adsorbents have a highly porous structure so that their surface area-to-volume ratio is very large. Various adsorbents (natural and synthetic origin) have been developed for arsenic removal from water, including polymer resins, activated carbon. Adsorption capacity depends on activated carbon properties, adsorbate chemical properties, temperature, pH, ionic strength, etc. However, carbon only removes a few milligrams of metal ions per gram of activated carbon. Regeneration problems exist. Thus, activated carbon use is expensive and will cause a problem (Gallegos-Garcia et al, 2012).

Another method of arsenic removal which is electrocoagulation (EC) process is a promising technology for the effective removal of arsenic from aqueous solution. The present review article (Nidheesh and Singh, 2017) analyses the performance of the EC process for arsenic removal. Electrocoagulation using various sacrificial metal anodes such as aluminium, iron, magnesium, etc. is found to be very effective for arsenic decontamination. A special focus has been made on the mechanism behind the arsenite and arsenate removal by EC process (Nidheesh, and Singh, 2017).

Chemical precipitation technologies like coagulation and precipitation technologies can give instant result and it usually considered as permanent, efficient and easy to handle method. It is not suitable for the removal of arsenic up to 10 ppb as agreed by World Health Organization (WHO) for safe drinking water, though it may be useful to treat large-scale high arsenic water. Major drawbacks of using chemical precipitation method are to handle the large quantity of sludge generated with high maintenance and operating cost (Pal, 2015). This type of arsenic filtration system is a standalone system used to improve overall water quality and was specifically designed to treat wellheads. In addition to effectively removing arsenic, this system will also remove iron and manganese, which are commonly found in drinking and household water supplies. It can also be used in secondary containment systems. Other benefits are: (1) Coagulants and permanganate additives are not required (2) Long service life of around 10 years (3) High performance for a variety of incoming water qualities.

Alum precipitation technology is effective at pH 5-7. Arsenic ions combine with aluminium ions to form coagulates-precipitates and the combination are easily separated from treated water through downstream sedimentation and filtration (Pal, 2015). However, it may produce sludge and low rate of arsenic removal as it required oxidizing agent chlorine being added ahead flocculator and clarifier.

According to Luong et al (2018), arsenic removal by aeration are shown to be a promising technology with high treatment efficiency that may happen in the future. It offers the advantage of negligible waste production and the potential of being a sustainable treatment option. This aeration technique comprises of three simple steps. The first procedure of aeration technique is aeration system extracted water from the aquifer and oxygenated water. Second, oxygen-enriched water is infiltrated back into the aquifer through an infiltration well forming large oxidation zones in the aquifer. Aqueous Fe(II) is oxidized to solid Fe(III)-hydroxides fomenting the removal of aqueous arsenic onto/into solid phase. The last procedure is water that have low iron content and arsenic will be extracted from the aquifer.

The shortcoming, of pre-oxidation of As(III) to As(V) using toxic oxidants, was resolved by the preparation of metal oxide with reducing properties, doping of other metal in metal oxides or incorporation of oxidant in metal oxides. These constitute the advancement in arsenic remediation. For example, manganese oxide (MnO_2), manganese (Mn^{2+}) doped iron oxide, and H_2O_2 doped metal oxides, have been utilized for the simultaneous oxidation of As(III) to As(V) and adsorption of As(V) species. The water quality constraints such as pH, competing ions, and charge on the arsenic species, affect the adsorption efficiency. Metal oxides are more effective in these constraints as compared to other types of adsorbents.

2.4 Natural and Synthetic Iron Oxyhydroxide

Iron-based oxyhydroxides such as goethite, ferrihydrite and schwertmannite brought interest at many of Acid Mine Drainage (AMD) sites especially in the removal of harmful pollutants such as arsenic. Particularly because they exhibit high surface area and an affinity for arsenic, selenium, and chromium. However, regardless of years of research on both natural and synthetic samples, the actual formation mechanisms of these iron-based hydroxides, as well as their exact chemical and mineralogical properties remain mostly unknown (Bigham and Nordstrom, 2000).

Natural iron oxyhydroxides are commonly derived from the oxidation of Fe(II) sources unlike the laboratory-produced iron oxyhydroxides which precipitates from high concentration Fe(III) sources, certainly higher than natural waters (Thomas et al, 2012). Iron oxides are generally initiated through crystallization of a melt, precipitation from a solution, alteration of a pre-existing mineral phase, or transport as a detrital component. (Favien, 2016) However, iron oxyhydroxides can be produced synthetically by converting Fe^{3+} organic complexes through hydrolytic breakdown which later produced iron oxyhydroxides.

All ferric iron minerals are naturally occurring oxyhydroxides. The FeOOH composition includes four polymorphs based on the spatial arrangement of octahedra. The most common is goethite (α - FeOOH), lepidocrocite (γ - FeOOH), akageneite (β - FeOOH) and feroxyhyte (δ' - FeOOH). Ferrihydrite and schwertmannite are both poorly crystalline hydrated oxyhydroxides. Ferrihydrite occurs exclusively as nanoparticles in either a somewhat more crystallized “six lines” form, so-called because it displays six lines in X-ray diffraction or a more poorly crystalline “two-line” form which exhibits only two broad X-ray diffraction lines. Schwertmannite has the same structure as akageneite but bears a sulfate complex in the tunnel structure instead of chloride ion for akageneite. (Faivre, 2016).

The natural iron oxyhydroxides that occurs as a ferrihydrite sediment fraction in Rifle, Colorado field site was studied to evaluate its potential as U(VI) absorbent compared to synthetic iron oxyhydroxides. Stewart et al (2015) found that natural iron oxyhydroxides have a low reactivity with uranium compared to the synthetic iron oxyhydroxides. This is because the naturally occurring iron oxyhydroxides probably have other elements interference such as Si impurities. The synthetic iron oxyhydroxides displays a good result due to its surface area and significant larger capacity to absorb U(VI).

Synthetic iron oxyhydroxides can be synthesized using various method such as novel epoxide precipitation route (Cui et al, 2013), leaching of natural clay (Chaudhary et al, 2016), neutralization technique (Houngaloune et al, 2014) and facile polystyrene (PS) microspheres-templated method (Cao et al, 2014). In this research, synthetic iron oxyhydroxide samples were obtained from the previous researcher (Ikhwan, 2016). He used the neutralization technique proposed by Houngaloune et al, 2014 to synthesize the iron oxyhydroxides. However, the synthetic iron oxyhydroxide that has been produced can be classified as schwertmannite as he found that the iron oxyhydroxided bears sulfate complex about 10.55% analysed by Energy-dispersive X-ray spectroscopy (EDX).

As reported by Chaudhary et al (2016), the iron oxyhydroxide nanoparticles were synthesized using micro-emulsion technique from natural clay in acid solution such as hydrochloric acid, HCL to obtain iron precursor consist of ferrous and ferric ions to prepare the iron oxyhydroxide nanoparticles. Figure 2.1(a) shows the SEM image of the fresh synthetic iron oxyhydroxide nanoparticle before the adsorption experiment. The nanoparticles are said to be clearly visible in the size range of 6 to 20 nm and have high porosity that may contribute to the impact of the removal of pollutants such as fluoride in wastewater. The result of SEM image however showed a significance difference after the adsorption of fluoride compare to the fresh adsorbent nanoparticles. Figure 2.1(b) showed the reduction of

agglomeration in the synthetic iron oxyhydroxide nanoparticles after adsorption of fluoride. Chaudhary mentioned that under high agitation during fluoride adsorption experiment, the breakage of agglomeration could not be prevented. The removal of dangerous fluoride ions in water using synthetic iron oxyhydroxide particle were successful by concluding that higher specific surface area and pore volume contributes to a higher Langmuir maximum adsorption capacity in the range of 229.5 ± 7.5 .

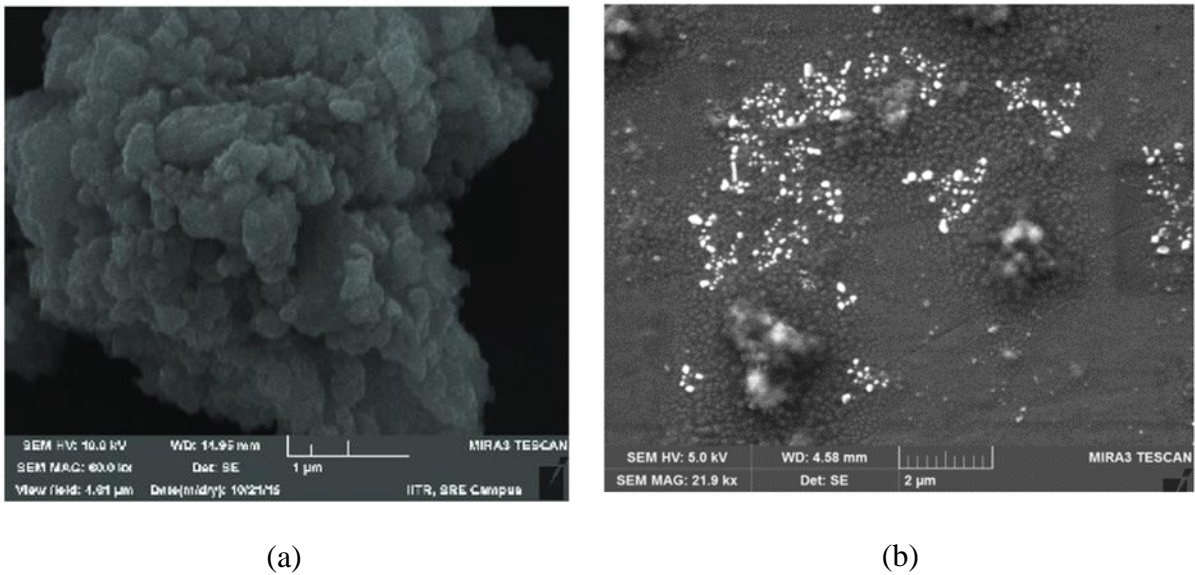


Figure 2.1: SEM Image of The Iron Oxyhydroxide Nanoparticles (a) before fluoride removal (b) after fluoride removal (Chaudhary et al, 2016)