Removal of arsenic from drinking water using BiolronTech technology

Parvin Zavarei

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Removal of Arsenic from Drinking Water Using BioIronTech Technology

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School of Civil & Environmental Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
Master of Engineering

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Abstract

Arsenic is a known carcinogen to both humans and animals and it has been associated with cancers of the skin, lung, and bladder. Elevated Arsenic concentration has been reported in several countries, including Argentina, Bangladesh, Canada, Chile, China, Hungary, Iran, Japan and Mexico.

Series of methods to remove arsenic from drinking water have been developed and among them removal of arsenic by coagulation with ferric salts was proven to be more effective and safe. However, ferric salts are costly and, therefore, their usage is not an affordable option for developing countries.

The research had two objectives: The first was to investigate the production of biologically produced ferrous coagulant from a cheap source, iron ore. Secondly, the effectiveness of usage of this coagulant for arsenic removal from water was examined.

In the first phase of this research, the effect of different parameters including bacteria and carbon source, iron ore particle size and the amount of cellulose on the ferrous production rate was investigated. Ferrous production rate was higher in the experiments in which bottom sediments were used as the source of bacteria, demonstrating the presence of iron reducing bacteria (IRB) in the bottom sediments.

In the second phase of this study, the efficiency of arsenic removal from water, with the usage of the biologically produced ferrous, as the coagulant, was investigated. Different parameters such as coagulant dosage, pH and presence of an oxidation stage were examined. At natural pH, ferrous to arsenic ratio of 20 was sufficient to result in a 90.4% arsenic removal from water spiked with 50 µg/L arsenic with potassium permanganate oxidation and micro-filtration.

Arsenic removal from water during coagulating with biologically produced ferrous is a feasible and affordable technology for developing countries. With the usage of potassium permanganate as the oxidant, arsenic removal from water is dramatically improved.

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Chapter 1

Introduction

Arsenic is a naturally occurring element. It is known that long-term exposure to low dosage of arsenic may induce serious adverse health effects such as skin and internal cancers, peripheral vascular disease, ischemic heart disease, cerebral infarction, diabetes mellitus and hypertension. Skin, lung, bladder, kidney, liver and uterus are considered as the sites related to arsenic-induced malignancies (Yu et al., 2006).

Studies have indicated that drinking water is a well-recognized pathway of exposure to low levels of arsenic (Mandal et al., 2002). There are two sources of arsenic contamination of drinking water: natural phenomena (such as weathering, biological activity, and volcanic activity), and anthropogenic inputs (such as smelting of metal ores, use of arsenical pesticides and wood preservatives) (Cullen et al., 1989; Jian et al., 2000; Matschullat, 2000).

The maximum contaminant level (MCL) for arsenic was set at 10 $\mu\text{g/L}$ by the United States Environmental Protection agency (USEPA) on the year 2006. The new established MCL requires many water treatment utilities to modify their treatment system to lower the arsenic concentration in water.

There are different categories of treatment technologies to remove arsenic from drinking water. Adsorption-coprecipitation using iron and aluminum salts is one of these technologies. It is also recognized by USEPA as one of the best available technologies for arsenic decontamination from drinking water. Coagulants change surface charge properties of solids to form a flocculated precipitate (USEPA 2000). Another effective technology is adsorption on activated alumina (AA). In this method, arsenic ions in the feed water are sorbed to the oxidized AA surface. A regeneration step (sodium hydroxide is a typical regenerant) is required when adsorption sites on the AA surface become filled (Chwirka et al., 2000). Reverse osmosis and ion exchange are also widely used for arsenic removal from drinking water. Research shows that ion exchange can achieve arsenic reductions of more than 95% and can produce treated water with an arsenic concentration of less than 2 µg/L (Kartinen et al., 1995; Korngold et al., 2001).

BioIronTechTM refers to a set of innovative technologies with sequential reduction of iron (III) and oxidation of iron (II) with the application of iron-reducing and iron-oxidizing bacteria to address several current problems of modern environmental engineering. The principles of BioIronTechTM are as described below:

Soluble iron (II) is produced by iron-reducing bacteria in an anaerobic process from a cheap source of iron (III), for example; iron ore. An effluent from an anaerobic process is oxidized by iron-oxidizing bacteria (the oxidation step can also take place using chemical oxidants or air) and produced iron (III) hydroxide precipitates contaminants, including arsenic.

BioIronTechTM has different applications in water and wastewater treatment plants. However, in the present study its application in the removal of arsenic from water has been examined.

1.1 Research Motivation and Scope

Adsorption-coprecipitation with iron oxide/(hydr) oxide has been shown to be effective in removing arsenic from drinking water. However, the majority of the research has been conducted using ferric salts (Ghurye et al., 2004; Han et al., 2002; Hering et al., 1997; Hering et al., 1996), synthetic ferric (hydr) oxides and ferrihydrite (Jain et al., 1999; Raven et al., 1998; Grossl et al., 1997; Fendorf et al., 1997; Wilkie et al., 1996; Hsia et al., 1994; Pierce et al., 1982; Pierce et al., 1980) or synthetic goethite (Matis et al., 1998). Since these chemicals are expensive, their usage as coagulant/adsorbent might not be the best option for arsenic decontamination from drinking water in developing countries. Hence, production of a less expensive coagulant/adsorbent with high efficiency in removal of arsenic from drinking water yet remains to be a crucial necessity.

Literature has consistently shown that iron-reducing bacteria (IRB) can gain energy for growth by reducing Fe(III) in the crystalline oxides goethite and hematite associated with iron ore. IRB couple the oxidation of organic substrates to the reduction of ferric iron (Fredrickson et al., 1996; Lovely et al., 1991). The biologically produced ferrous has never been applied in water treatment utilities for arsenic removal.

Research was conducted to address two following objectives:

1. The first objective was to investigate parameters such as bacteria and carbon source, iron ore particle size and the amount of cellulose on the ferrous production rate. Experiments were carried out to find the optimum conditions to produce biotic ferrous using iron ore as the main electron acceptor.

2. The second objective was to investigate the application of the biologically produced ferrous as the coagulant/adsorbent in removal of arsenic from drinking water. A set of experiments were conducted to evaluate the effect of coagulant dosage, pH and oxidation with potassium permanganate on the arsenic removal efficiency.

1.2 Thesis Organization

In Chapter 2, arsenic chemistry and its sources are reviewed. Toxic and dangerous effects of exposure to arsenic along with the current exposure guidelines are also discussed.

Treatment processes for arsenic removal from drinking water are discussed. Among the different technologies mentioned, coagulation/filtration, adsorption, ion exchange (IX) and reverse osmosis are elaborated. Efficiency of arsenic removal in these different technologies is presented.

In Chapter 3, the experiments which are carried out in this research are described in detail. Chemical solutions and their preparation methods, different equipments used in this research are documented. Analytical methods to measure iron and arsenic are reviewed.

The results of the experiments are presented in Chapter 4. Plots of arsenic removal efficiency versus parameters such as Fe/As ratio, pH and oxidant dose are constructed. Ferrous production rate with the application of IRB is discussed. The use of micro-filtration to remove ferrous-borne flocs is also examined.

In Chapter 5, conclusions are made with respect to the feasibility of biological production of ferrous from iron ore and its application in removal of arsenic from drinking water. Future work is also discussed in this chapter.

Chapter 2

Literature Review

In this study, arsenic chemistry and its sources are reviewed. Toxic and dangerous effects of exposure to arsenic are also discussed. An overview of different methods of arsenic decontamination is presented followed by a review of the method studied.

2.1 Arsenic in the Environment

Arsenic is a carcinogen to both humans and animals and it has been associated with cancers of the skin, lung, and bladder (Ng et al., 2003). It is the twentieth most abundant element in the earth's crust, fourteenth in the seawater and the twelfth most abundant element in the human body (Shih, 2005). Although as a nutrient, it is necessary to humans in small quantities, chronic exposure to arsenic leads to death (Kartinen et al., 1995). Studies have indicated that drinking water is a well-recognized pathway of exposure to low levels of arsenic (Mandal et al., 2002).

Naturally occurring arsenic in groundwater has become a global problem. Current research shows that arsenic is mobilized in groundwater by natural processes, which is an issue of major environmental health concern. Elevated arsenic concentration in groundwater has been reported in several countries,

including Argentina, Bangladesh, Canada, Chile, China, Hungary, India, Iran, Japan, Mexico, New Zealand, Taiwan, Thailand and the United States, among other parts of the world (Bhattacharya et al., 2004).

The range of arsenic concentrations found in natural waters is large, ranging from less than 0.5 ppb to more than 5000 ppb. Typical concentration in freshwater is less than 10 ppb and frequently less than 1 ppb. Rarely much higher concentrations are found, particularly in ground water (Smedley et al., 2002).

Arsenic is the major constituent of at least 245 different minerals and is mainly present in sulfide minerals (Thirunavukkarasu et al., 2005). Source of arsenic in the environment includes natural and anthropogenic. Long before man's activities had any effect on the balance of nature, arsenic was distributed ubiquitously throughout earth's crust, soil, sediments, water, air and living organisms. Igneous and sedimentary rocks contain varying amounts of arsenic. The average content of arsenic in igneous and sedimentary rocks is 2 mg/kg, and in most rocks it ranges from 0.5 to 2.5 mg/kg. The human exposure of arsenic through air is generally very low and normally arsenic concentrations in air ranges from 0.4 to 30 ng/m³ (Mandal et al., 2002; Thirunavukkarasu et al., 2005).

The most abundant arsenic bearing mineral is arsenopyrite (FeAsS). Other dominant arsenic minerals include realgar (AsS), orpiment (As₂S₃), claudetite (As₂O₃), arsenolite (As₄O₆), arsenic pentoxide (As₂O₅) and scorodite (FeAsO₄·2H₂O). Researchers have demonstrated that high groundwater arsenic concentrations on a regional scale are due to geochemical trigger to mobilise arsenic in water and the hydrogeological regime to preserve it (Smedley et al., 2002).

Natural phenomena such as weathering, biological activity, and volcanic activity, are responsible for the emission of arsenic into the atmosphere, however anthropogenic inputs are also a source of it (Cullen et al., 1989). Influx of arsenic from various anthropogenically-induced sources including industrial effluents may

also contaminate both soils and ground water especially under anoxic conditions. Uncontrolled anthropogenic activities such as smelting of metal ores, use of arsenical pesticides and wood preservatives agents may also release arsenic directly to the environment (Jian et al., 2000).

A simplified diagram of arsenic cycle is shown in Figure 2-1.

Figure 2-1 A simplified diagram of arsenic cycle
(Wang et al., 2006).

2.2 Chemistry of Arsenic

Arsenic, atomic number 33, is located in group VA of the periodic table directly below phosphorus. Arsenic is considered a metalloid and occurs in a variety of forms and oxidation states. Arsenic is stable in the +5, +3, -3 and 0 oxidation states. The arsenate species are AsO_4^{3-} , HAsO_4^{2-} and H_2AsO_4^- . The the arsenite species include H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-} and AsO_3^{3-} (Brandhuber et al., 1998; Virarghavan et al., 1999).

Arsenic is a redox-sensitive element, and its occurrence, distribution, mobility, and forms rely on the interplay of several geochemical factors, such as pH conditions, reduction-oxidation reactions, distribution of other ionic species, aquatic chemistry and microbial activity. The pentavalent species are predominant and stable in the oxygen-rich aerobic environments, whereas the trivalent arsenite species are predominant in moderately reducing anaerobic environments such as groundwater (Shih, 2004; Virarghavan et al., 1999).

Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidising conditions, H_2AsO_4^- is dominant at low pH (less than about pH 6.9), whilst at higher pH, HAsO_4^{2-} becomes dominant (H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively). Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species H_3AsO_3 will predominate. The distributions of the species as a function of pH are given in Figure 2-2 (Smedley et al., 2002).

In natural waters, the oxyacids arsenite (H_3AsO_3 ; $\text{pK}_1 = 9.2$; uncharged at neutral pH) and arsenate (H_3AsO_4 ; $\text{pK}_1 = 2.2$; anionic at neutral pH) are the most important arsenic species (Bauer et al., 2006).

The ionization reactions of arsenious acid are according to the equations: (Kartinen et al., 1995)

The ionization reactions of arsenic acid are according to the equations:
(Kartinen et al., 1995)

Methylated arsenic species, such as monomethylarsonous acid [MMA(III)], monomethylarsonic acid [MMA(V)], dimethylarsinous acid [DMA(III)], dimethylarsinic [DMA(V)], trimethylarsine [TMA(III)], and trimethylarsenic oxide (TMAO), can be formed through biomethylation by microorganisms under favorable conditions (Wang et al., 2006).

Figure 2-2 Eh-pH diagram for aqueous arsenic species
(Smedley et al., 2002).

2.3 Toxicity of Arsenic

Arsenic has gained the reputation of a dangerous poison in the Middle Ages, and until the nineteenth century was the preferred poison of most homicidal practitioners. In the nineteenth century, the therapeutic use of arsenicals against trypanosomal or spirochaetal organisms became classical examples of

chemotherapy. These demonstrated the widely differing toxicity and effectiveness of arsenic in different oxidation states and combined with different organic ligands (Ferguson et al., 1972).

The toxicology of arsenic is a complex phenomenon as arsenic is considered to be an essential element also. Two types of toxicity; acute and sub-acute ones are known. The acute arsenic poisoning requiring prompt medical attention, usually occurs through ingestion of contaminated food or drink. The major early manifestation due to acute arsenic poisoning includes burning and dryness of the mouth and throat, dysphasia, circulatory disorders, projectile vomiting, profuse diarrhea, and hematuria. The muscular cramps, facial edema and cardiac abnormalities are among other health effects. Shock can develop rapidly as a result of dehydration (Jain et al., 2000).

Long-term exposure to low dosage of arsenics may induce serious adverse health effects in multiple organs. Chronic health effects of As exposure via drinking water include skin and internal cancers, peripheral vascular disease, ischemic heart disease, cerebral infarction, diabetes mellitus and hypertension. Skin, lung, bladder, kidney, liver and uterus are considered as the sites related to arsenic-induced malignancies (Yu et al., 2006).

Standards for maximum allowable arsenic concentrations have been established by many agencies. The WORLD HEALTH ORGANIZATION (1958) established a permissible limit of 0.2 mg/L; in 1963 the limit was revised to 0.05 mg/L. The UNITED STATES PUBLIC HEALTH SERVICE recommended maximum concentration of 0.01 mg/L and a maximum permissible limit of 0.05 mg/L for arsenic in a public drinking water supply in 1962 (Ferguson et al., 1972). In 1975, USEPA adopted mandatory maximum contaminant level (MCL) for arsenic at 50 µg/L set by USPHS and applied to all public drinking water supplies since this standard has very little impact on the drinking water industry. The need for a revision of this standard value was recognized when a link between skin cancer and arsenic ingestion through drinking water was indicated. In 2001,

USEPA announced it will adopt the new arsenic MCL of 10 µg/L, the year 2002 will be the effective date for this new standard and the year 2006 will be the compliance date for the arsenic MCL of 10 µg/L. USEPA estimated that 5% of all US community water systems will have to take corrective action to lower the current levels of arsenic in their drinking water (Shih, 2005).

The toxicity of arsenic-containing compounds is related to the oxidation state of the arsenic atom. Arsenic acid, H_3AsO_4 , in the +5 oxidation state, is the least toxic of the inorganic forms of arsenic. Arsenious acid, H_3AsO_3 , in the +3 oxidation state is more toxic than arsenic acid. It is reported that arsenate is about 60 times less toxic than arsenite (Ferguson et al., 1972; Knowles et al., 1983). Arsonous acid, $\text{HAS}(\text{OH})_2$, in the + 1 oxidation state, and its organic analogs, $\text{RAs}(\text{OH})_2$, are more toxic than arsenous acid (Knowles et al., 1983).

Organometallic compounds of other heavy metals are reported to be (particularly simple methylated species) more toxic than the corresponding inorganic species. However, organoarsenic compounds represent an exception in this series. Inorganic arsenic compounds are about 100 times more toxic than organic arsenic compounds. The toxicity of different arsenic species varies in the order: (Jian et al., 2000).

arsenite > arsenate > monomethylarsonate (MMA) > dimethylarsinate (DMA)

2.4 Treatment Processes for Arsenic Removal from Drinking Water

The sampling and treatment of arsenic from drinking water has become a growing concern (Gallagher et al., 2001). A community being supplied with water containing an inorganic contaminant such as arsenic higher than the MCL has two possible solutions: change to a new water source, or incorporate treatment methods to meet the contaminant MCL. In many cases treatment of the source water may be

the only option available. The following treatment methods have been adopted to remove arsenic from drinking water under both laboratory and field conditions: adsorption-coprecipitation using iron and aluminum salts; adsorption on activated alumina/activated carbon/activated bauxite; reverse osmosis; ion exchange; and oxidation followed by filtration (Viraraghavan et al., 1999).

The USEPA has identified seven technologies for removal of arsenic from drinking water as the best available technologies (BATs), which are given in Table 1 (Wickramasinghe et al., 2004). BAT can be designated based upon the following criteria: (Saha et al., 2001)

- High removal efficiency
- Affordability (using large system as the basis)
- General geographic applicability
- Compatibility with other water treatment processes, and
- Process reliability

Table 1 Best available technologies (BATs) and their arsenic removal efficiency. Percentage removal figures are for arsenic (V) removal (Wickramasinghe et al., 2004).

Treatment technology	Maximum removal, %
Ion exchange	95
Activated alumina	95
Reverse osmosis	>95
Modified coagulation/filtration	95
Modified lime softening (pH>10.5)	90
Electrodialysis reversal	85
Oxidation/filtration (iron:arsenic = 20:1)	80

Researchers have demonstrated that as a water contaminant, As(III) is more problematic than As(V) (Hering et al., 1997; Hug et al., 2003). Unlike the arsenate anions H_2AsO_4^- and HAsO_4^{2-} , the dominant As(III) species up to pH 8 is the nonionic H_3AsO_3 , which does not adsorb as strongly to mineral surfaces as As(V). As(III) is thus more mobile in ground waters and is also more difficult to remove in arsenic removal treatments. Typically, preoxidation to As(V) is necessary in arsenic removal procedures. Although As(V) is thermodynamically favored under oxic conditions, As(III) is only slowly oxidized by dissolved O_2 (e.g., with a half-life of around 9 d in air-saturated water with low iron contents and pH 7.6-8.5) (Hug et al., 2003).

There are numerous methods of oxidation available, but important factors such as the residual concentrations, availability and running cost of oxidants and oxidation by-products should be considered when selecting an oxidant. Ozone and UV radiation oxidize As(III) normally within about 30–60 seconds. However, it requires a high energy input, which may not be cost effective for small water treatment plants in the developing world. Chlorine is commonly used in the water industry as a disinfectant and is a suitable oxidant. However, the drawback in the use of chlorine is that it will react with natural organic matter to form chlorinated by-products, which are believed to have health concern effects. In addition, it is not so effective for As(III) oxidation if the raw water has high turbidity. The most feasible oxidants to date are either potassium permanganate or Fenton's reagent. These oxidants produce no harmful byproducts, and are easily applied (Jiang, 2001).

Among the technologies mentioned above, coagulation using iron and aluminum salts, adsorption processes including activated alumina(AA) and ion exchange(IX), and reverse osmosis are discussed in this report.

2.4.1 Coagulation/Filtration

Coagulation/filtration (C/F) is a treatment process by which the physical or chemical properties of dissolved colloidal or suspended matter are altered such that agglomeration is enhanced to an extent that the resulting particles will settle out of solution by gravity or will be removed by filtration. Coagulants change surface charge properties of solids to allow agglomeration and/or enmeshment of particles into a flocculated precipitate. In either case, the final products are larger particles, or floc, which more readily filter or settle under the influence of gravity (USEPA 2000).

Water treatment with coagulants, specifically hydrolyzing metal salts such as alum and ferric chloride, has long been recognized as an effective method for removing arsenic from source waters. In the late 1960s, coagulation with ferric chloride was used in Taiwan to treat deep-well water with naturally elevated arsenic concentrations; residual arsenic concentrations in treated water were below 50µg/L (Hering et al., 1996). Hering et al., 1996 describes the coagulation process more precisely:

- 1) Adsorption: Association of the dissolved contaminant with the surface of the precipitate.
- 2) Occlusion: Entrapment of adsorbed contaminants in the interior of the growing particle.
- 3) Solid-solution formation: incorporation of the contaminant into the bulk phase, rather than only onto the surface of the precipitate.

Studies have shown that arsenic in the +V oxidation state, As(V), can be efficiently removed during coagulation with ferric chloride and alum even when present at low concentrations in influent waters (Hering et al., 1996).

Figure 2-3 Schematic of iron CMF (Coagulation-Microfiltration) process
(Ghurye et al., 2004).

Ghurye et al. (2004) performed bench-scale tests and a pilot study in Albuquerque, NM, to determine the impacts of operational variables on arsenic removal using iron coagulation followed by direct microfiltration. The pH and ferric dose were found to be the most significant parameters for arsenic removal. Arsenic concentrations lower than 2 ppb were achieved using either a dose of 7 mg/L Fe without deliberate pH reduction or a dose of 1.9 mg/L Fe after sulfuric acid addition to reduce pH to 6.4 for the initial arsenic concentration of 40 ppb. Figure 2-3 demonstrates the schematic of iron CMF process studied by Ghurye et al. (2004)

Hydrous ferric oxide (HFO) is an important sorbent in both natural and engineered aquatic systems. Authigenic precipitation of HFO has been observed in numerous aquatic environments including stream convergences, hydrothermal vents, sediment pore waters, and at oxic-anoxic boundaries in lakes. Hydrous ferric oxides commonly occur as coatings on the surfaces of suspended sediments, of minerals in soils and sediments, and even of bacteria. In water and wastewater treatment, HFO can be precipitated in situ during coagulation with ferric chloride (or other iron salts) or upon oxidation of groundwaters containing iron(II). Specific, chemical interactions between adsorbed arsenic and iron at the HFO surface have been demonstrated by the adsorption of arsenic under unfavorable electrostatic conditions (Wilkie et al., 1996).

Studies indicate that for As(V), better removal is achieved during coagulation with Fe(III) than with aluminum salts on a weight basis (i.e., mg/L as ferric chloride or alum); removal efficiency however were reported to be similar on a molar basis (i.e., mole Fe(III) or Al(III) per liter) (Hering et al., 1996).

Research was conducted at the Metropolitan Water District of Southern California (MWDSC) to determine arsenic removals using alum and ferric chloride. The average concentration of arsenic in the source water was 2.1 µg/L. When the source water was treated with 3 to 10 mg/L of ferric chloride, arsenic removal was 81 to 96 percent. When the source water was treated with 6, 10, or 20 mg/L of alum, arsenic removal was 23 to 71 percent (USEPA 2000).

It is reported that in general, higher removal efficiencies can be achieved with increased coagulant dosages. Hering et al. (1996) demonstrated in coagulation experiments with ferric chloride at pH 7.0 that both As(III) and As(V) removal were dependent on coagulant dosage. “Complete” removal of As(V) was observed for coagulant dosages above 5 mg/L ferric chloride. “Complete” removal of As(III) was not observed under the range of conditions examined (USEPA 2000).

Meng et al. (2002) has shown that the chemical composition of water such as phosphate and silicate concentrations can significantly affect the removal of arsenic

by iron hydroxides. Silicate decreases the removal of As(III) and As(V) in potassium nitrate solutions by co-precipitation with ferric chloride.

Recent experimental results have shown that arsenic in Bangladesh well groundwater is difficult to remove by iron hydroxides because of elevated phosphate and silicate concentrations. An iron to arsenic mass ratio of greater than 40 is required to remove arsenic to less than 50 µg/l which is the current drinking water standard in Bangladesh. On the other hand, a Fe/As ratio of less than 12 is sufficient to remove greater than 99% of arsenic from groundwater collected from New Hampshire (NH), USA (Meng et al., 2002).

2.4.2 Adsorption

Two adsorption processes have been demonstrated to be effective in removing arsenic from water; activated alumina and ion exchange (Kartinen et al., 1995). Because of the importance of the second process, Ion exchange (IX), it would be discussed in a separate section.

Activated Alumina (AA) is a physical/chemical process by which ions in the feed water are sorbed to the oxidized AA surface. AA is considered an adsorption process, although the chemical reactions involved are actually an exchange of ions. Activated alumina is prepared through dehydration of $\text{Al}(\text{OH})_3$ at high temperatures, and consists of amorphous and crystalline-phase aluminum oxide of approximate composition Al_2O_3 . AA is used in packed beds to remove contaminants such as fluoride, arsenic, selenium, silica, and NOM. The selectivity sequence of AA for absorbing ions is as follows:

As the feed water continuously passes through the bed to remove contaminants, the contaminant ions are exchanged with the surface hydroxides on

the alumina. When adsorption sites on the AA surface become filled, the bed must be regenerated. Regeneration is accomplished through a sequence of rinsing with regenerant, flushing with water, and neutralizing with acid. The regenerant is a strong base, typically sodium hydroxide; the neutralizer is a strong acid, typically sulfuric acid. The alumina loses about 30-40% of its capacity with each regeneration so that it must be replaced after only three or four regenerations. However, its low cost and relatively high capacity for arsenic keep costs at an acceptable level (USEPA 2000; Chwirka et al., 2000; Kartinen et al., 1995).

Many studies have shown that AA is an effective treatment technique for arsenic removal. Factors such as pH, arsenic oxidation state, competing ions, empty bed contact time (EBCT), and regeneration have significant effects on the removals achieved with AA. Other factors include spent regenerant disposal, alumina disposal, and secondary water quality (USEPA 2000).

Kartinen et al. (1995) reported that at higher pH's, the arsenic removal efficiency of activated alumina is considerably less than that obtainable at lower pHs. In addition, at higher pH's even the use of chlorine to oxidize As(III) to As(V) is not too effective at increasing the bed volumes of water that can be treated before "regeneration" of the alumina is needed.

Figure 2-4 demonstrates the activated alumina adsorption process for arsenic removal from water.

Figure 2-4 The activated alumina adsorption process for arsenic removal (Chwirka et al., 2000).

2.4.3 Ion Exchange

Ion exchange (IX) is a physical/chemical process by which an ion on the solid phase is exchanged for an ion in the feed water. This solid phase is typically a synthetic resin which has been chosen to preferentially adsorb the particular

contaminant of concern. To accomplish this exchange of ions, feed water is continuously passed through a bed of ion exchange resin beads in a downflow or upflow mode until the resin is exhausted. Exhaustion occurs when all sites on the resin beads have been filled by contaminant ions. At this point, the bed is regenerated by rinsing the IX column with a regenerant - a concentrated solution of ions initially exchanged from the resin. The number of bed volumes (BV) that can be treated before exhaustion varies with resin type and influent water quality. Typically from 300 to 60,000 BV can be treated before regeneration is required. In most cases, regeneration of the bed can be accomplished with only 1 to 5 BV of regenerant followed by 2 to 20 BV of rinse water.

Important considerations in the applicability of the IX process for removal of a contaminant include water quality parameters such as pH, competing ions, resin type, alkalinity, and influent arsenic concentration. Other factors include the affinity of the resin for the contaminant, spent regenerant and resin disposal requirements, secondary water quality effects, and design operating parameters (USEPA 2000).

IX is currently an EPA-identified best available technology (BAT) for removal of As(V). However, current commercial SBA resins suffer from poor selectivity for As. Due to the strong competition from some ubiquitous anions such as sulfate, the As capacity of SBA resins is prohibitively retarded. For example, the binary arsenate/sulfate separation factor for a typical SBA resin was reported to be ~0.5 (a separation factor of less than one indicates the resin's preference toward the competing ions). As a result, the As breakthrough occurs before sulfate, and chromatographic peaking of As, i.e., effluent concentration exceeds influent concentration, is often observed (Byungryul et al., 2005).

Since the ion exchange is effective only in removing ions from the water, only arsenic that is in an ionic form (has an electrical charge - negative in this case since ionized forms of arsenic are anions) can be exchanged for chloride in this process. Chlorinating the feed water will cause the arsenic to take a (5+) oxidation state. At pH's above about 7.5, most of the arsenic can be expected to be present as either

H_2AsO_4^- or HAsO_4^{2-} , and thus susceptible to removal by ion exchange (Kartinen et al., 1995).

IX removals with strong-base resins, though, are typically not sensitive to pH in the range of pH 6.5 to 9.0. Outside of this range, however, arsenic removal decreases quickly. Groundwaters which are naturally contaminated with arsenic typically exhibit fairly high pH, giving IX a slight advantage for these types of source water. Adjustment of pH prior to IX for arsenic removal is generally not necessary (USEPA 2000).

Research shows that ion exchange can achieve arsenic reductions of more than 95% and can produce treated water with an arsenic concentration of less than $2\mu\text{g/L}$ (Kartinen et al., 1995).

2.4.4 Reverse Osmosis

Reverse Osmosis (RO) is the oldest membrane technology. It produces nearly pure water by maintaining a pressure gradient across the membrane greater than the osmotic pressure of the feed water. Osmotic pressure becomes great in RO systems compared to other membrane processes due to the concentration of salts on the feed side of the membrane. The majority of the feed water passes through the membrane, however, the rest is discharged along with the rejected salts as a concentrated stream. Discharge concentrate can be substantial, between 10 and 50 percent of the influent flow depending on influent water quality and membrane properties (USEPA 2000).

RO has been identified as a likely best available technology to help small water treatment systems to remove arsenic from water and meet the new MCL regulation. RO membrane contains extremely small pores ($< 0.001\ \mu\text{m}$) (Shih, 2005).

Literature indicates that reverse osmosis is more effective in removing As(V) than As(III). As(III) removal rates using reverse osmosis have been reported to be 40-80% whereas As(V) removal rates of greater than 97% have been reported. Thus, to achieve the best results, the feed water must be treated with an oxidizing agent to convert As(III) to As(V) in order to achieve substantial arsenic reduction in the permeate (product water). However it should be noted that oxidizing agents, including chloride, are, in general, harmful to reverse osmosis membranes. The life of reverse osmosis membranes can be substantially shortened if an oxidizing agent is injected into the feed water (Kartinen et al., 1995).

Kang et al. (2000) and Ning (2002) reported that elevating the pH of feed water would increase the efficiency of arsenic removal in reverse osmosis.

2.5 Biological Reduction of Iron

It is generally considered that sulphur reduction was one of the earliest forms of microbial respiration, because the known microorganisms that are most closely related to the last common ancestor of modern life are primarily anaerobic, sulphur-reducing hyperthermophiles. However, geochemical evidence indicates that Fe (III) is more likely than sulphur to have been the first external electron acceptor of global significance in microbial metabolism (Vargas et al., 1998).

Microbial Fe (III) reduction is a key biogeochemical process in anaerobic sedimentary environments. Although crystalline minerals such as goethite and hematite are typically the dominant Fe (III) oxide phases in soils and sediments, the apparent resistant of such minerals to enzymatic reduction has led to the view that amorphous Fe (III) oxide is the main form of Fe (III) oxide available for microbial reduction (Roden et al., 2000).

Dissimilatory Fe(III) reduction is being increasingly recognized as an environmentally significant process in both pristine and contaminated sedimentary

environments. On the basis of studies with pure cultures and natural communities in sediments in which Fe(III) reduction was the predominant terminal electron-accepting process, it has been proposed that most of the microbially catalyzed Fe(III) reduction in anaerobic sedimentary environments is due to microorganisms which can completely oxidize acetate and other short-chain fatty acids to carbon dioxide, with Fe(III) serving as the sole electron acceptor. *Geobacter metallireducens* was the first described acetate-oxidizing Fe(III) reducer. 16S rRNA-based phylogeny placed this organism in the delta subdivision of the class *Proteobacteria* (Lonergan et al., 1996).

In addition to the strict anaerobic, Fe(III)-reducing microorganisms in the delta subdivision of the *Proteobacteria*, several H₂-oxidizing isolates in the gamma subdivision of the class *Proteobacteria* have been described. These are *Shewanella putrefaciens*, *S. alga*, and *Pseudomonas* sp. strain Z-731. These organisms have the capacity to use a wide variety of electron acceptors, including oxygen. They can conserve energy to support growth from Fe(III) reduction, but their ability to use organic electron donors is extremely limited. Multicarbon electron donors such as lactate and pyruvate are only incompletely oxidized to acetate (Lonergan et al., 1996).

Sulfurospirillum barnesii, which belongs to the Epsilon subgroup of the proteobacteria, is also capable of reducing iron coupled with oxidation of H₂ or lactate (Stolz et al., 1999).

Substantial advances have been made in the understanding of the phylogeny, physiology, ecology and biogeochemistry of dissimilatory Fe(III)-reducing bacteria. DIRB are now known to be a phylogenetically and physiologically diverse group of microorganisms. Their activities can significantly impact, if not directly control, the biogeochemistry of both pristine and contaminated anoxic environments. With Fe(III) commonly being the most abundant electron acceptor in the subsurface, Fe(III)-reducing bacteria have considerable potential for the direct enzymatic oxidation of organic contaminants and for the indirect chemical transformation of

substituted aromatic and halogenated compounds *in situ*. It is becoming increasingly clear that DIRB can enzymatically reduce Fe(III) associated with a wide range of iron minerals.

In a research conducted by Stabnikov et al., (2004) Fe (III) from cheap iron hydroxides such as wetland iron ore, or iron-containing clay was reduced by the application of iron-reducing bacteria (IRB) to Fe(II), which reacts and precipitates with HPO_4^{2-} .

Chapter 3

Materials and Methods

3.1 Reagent and Stock Solutions

The new polypropylene tubes and caps and pipet tips were soaked in 2N nitric acid overnight. Then they were triple rinsed with deionized water to prevent any interference during measurements. They were dried in a low temperature oven overnight. De-ionized high-purity (DI) water with 18.2 megohm-cm resistivity produced in the environmental lab with a Direct-Q Millipore (USA) was used for the preparation of all standards.

Arsenic stock solution with a concentration of 1000 mg/L was prepared by Perkin- Elmer, Germany. On the stock arsenic solution provided by Perkin-Elmer the percentage of arsenite and arsenate in this solution are not indicated. Therefore in this report, the concentration of arsenic is the concentration of total arsenic. For the preparation of calibration curve, 3 different concentrations of arsenic were used by diluting the original stock solution with de-ionized water. Arsenic solutions with concentrations of 5, 50 and 90 $\mu\text{g/L}$ were prepared as described above for standards of the calibration curve. The standard solutions were kept for one week at 4°C.

The Fe(II) stock solution containing 100 mg/L Fe(II) in 1% H₂SO₄ (v/v) was prepared from FeSO₄·7H₂O and was stored in dark bottles to prevent oxidation due to exposure to the light.

Ammonium acetate buffer solution to be used in Phenanthroline Method (Standard Methods 3500B), was prepared by dissolution of 25 g NH₄C₂H₃O₂ in 15 mL de-ionized water. 70 mL concentrated (glacial) acetic acid was added to the above solution.

Phenanthroline solution was prepared by dissolving 500 mg 1,10-phenanthroline monohydrate, C₁₂H₈N₂·H₂O, in 500 mL de-ionized water and stirring and heating to 80°C.

Nickel nitrate solution with a concentration of 10,000 mg Ni/L was prepared by dissolving 4.96 g of Ni(NO₃)₂·6H₂O (Standard Methods) in DI water and bringing to volume in a 100 mL volumetric flask. It was used as a matrix modifier in arsenic analysis during graphite furnace atomic absorption spectrometry (GFAAS).

As the enrichment culture of Iron-Reducing Bacteria (IRB) was not available at first, anaerobic sludge and sediment from Sungei Buloh Wetland Reserve in Singapore were used as the source of bacteria for reduction of iron.

Cellulose and acetic acid were used as a source of carbon for IRB to investigate the effect of carbon source on the reduction of Fe(III). For obtaining cellulose filter papers were torn into small pieces and dissolved in water to produce pulp.

Potassium permanganate solution with a concentration of 1000 mg/L was prepared by dissolving 0.1 g KMnO₄ in de-ionized water and bringing to volume in a 100 mL volumetric flask. This solution was used as a strong oxidizer in the coagulation process.

For pH adjustments during the experiments, solutions of 1 N and 0.1 N of NaOH and 0.1 N HCl were used. Determination of pH was performed using Orion 3-star refillable pH electrode and pH meter (USA). Daily calibration of the pH meter was done using buffer solutions at pH 4, 7 and 10. After each calibration or measurement, pH electrode was rinsed with de-ionized water and blot dried with lint-free tissue paper.

The feed water for the coagulation experiments was collected at Nanyang Lake. However, as the arsenic determination results with GFAAS show, the concentration of arsenic in Nanyang Lake water is below the detection limits by GFAAS. Therefore, for the coagulation experiments, the feed water was spiked with arsenic from the secondary stock solution of 5 ppm. The secondary arsenic stock solution was prepared by dilution of the original stock solution of 1000 ppm, and was kept at 4°C. Fresh secondary arsenic stock solutions were prepared weekly.

Biologically produced ferrous solution of 80 mg Fe^{2+} /L were used at different dosages as the coagulant/adsorbent in this study.

3.2 Analysis and Measurements

3.2.1 Iron Analysis

The method determining the concentration of ferrous in the samples is phenanthroline method (Standard Methods, Method 3500B). Three molecules of phenanthroline chelate each atom of ferrous iron to produce a deeply colored red complex.

The colored solution obeys Beer's Law and its intensity is independent of pH from 3 to 9. The intensity of the colored solution was measured by spectrophotometer at a wavelength of 510 nm. Calibration curves were prepared with ferrous solutions with concentrations of 1, 2, 3, 4, 5 and 6 mg Fe^{2+}/L respectively. Absorbance was read with a Shimadzu UV-1201 V Spectrophotometer (Japan). Figures 3-1 shows the calibration curve used for Iron analysis.

Figure 3-1 Absorbance as a function of Fe^{2+} concentration

3.2.2 Arsenic Analysis

Total arsenic was determined using Perkin-Elmer model SIMAA 6000 graphite furnace atomic absorption spectrometer. A longitudinal Zeeman-effect background correction system, a graphite tube atomizer and programmable sample dispenser were used (Figure 3-2). An Electrodeless Discharge Lamp was used at a wavelength of 193.7 nm with a slit width of 0.7 nm. Argon gas was used as internal purge gas to volatilize matrix materials and to protect the graphite tube from ambient exposure which would cause degradation at high temperatures.

Figure 3-2 Perkin-Elmer model SIMAA 6000 graphite furnace atomic absorption spectrometer

A standard furnace program usually includes the following steps:

- 1) Drying: The solvent is vaporized during the drying step.
- 2) Pyrolysis: The pyrolysis step is used to remove as many matrix components as possible. A matrix modifier can be used to stabilize the analyte or aid in removal of matrix components.
- 3) Atomization: The sample is atomized to form ground state atoms in the path of the radiation beam during this step.
- 4) Clean-out: A high temperature clean-out step after atomization prepares the furnace for subsequent samples.

Figure 3-3 shows a schematic diagram of the basic components of a Graphite Furnace Atomic Absorption spectrometer:

Figure 3-3 A schematic diagram of the basic components of a Graphite Furnace Atomic Absorption spectrometer

The use of a matrix modifier improves the analysis. The modifier salt is added to the sample in high concentration, transforming the analyte element into a more well-defined compound. This makes the thermal pyrolysis more predictable and reproducible for a variety of matrices.

The matrix modifier can either stabilize the analyte element in order to permit a higher pyrolysis temperature or make the matrix more volatile for more effective pyrolysis. In this study Nickel nitrate was chosen as the matrix modifier.

Samples and calibration curves were prepared according to Standard Methods (Figure 3-4). To reduce interference by organic matters nitric acid digestion has been implemented in this work (Standard Method 3030E).

Figure 3-4 Calibration curve for arsenic analysis

3.3 Oxidation

Two types of oxidation were implemented in this study during coagulation experiments. The oxidation step is to ensure oxidation of arsenite to arsenate and also ferrous to ferric ions. This is to enhance the efficiency of arsenic removal during coagulation.

3.3.1 Aeration

Air pumps were used to oxygenate the feed water. Cylinder air diffusers were used to ensure production of fine bubbles. The feed water was aerated for 15 minutes.

3.3.2 Oxidation with Potassium Permanganate

Oxidation via natural aeration is very slow and less effective than applying chemical oxidants. As discussed in chapter 2, oxidation with potassium permanganate is known as one of the most feasible oxidants to date. This oxidant produces no harmful by-products and is easily applied. Potassium permanganate was added to the beakers placed in the flocculator (Stuart Scientific SW1,UK) just before stirring.

3.4 Coagulation Experiments

Coagulation experiments were performed using a Stuart Scientific SW1 Flocculator (UK). In this equipment 6 beakers can be placed and simultaneously stirred at the same speed with flat bladed impellers supported from the upper bulkhead. The stirrer paddles are easily retractable by means of spherical knobs at the upper end of the shaft. Mixing conditions during coagulation were 1 min rapid-mix at 100 rpm followed by 14 min slow mix at 50 rpm. These two speeds were preset using the speed control switch as P1 and P2 in order to facilitate the speed change during coagulation.

3.4.1 Arsenic Removal Using Biologically Produced Ferrous

300 mL Nanyang Lake water was measured with a graduated cylinder and transferred to a beaker. As the concentration of arsenic in Nanyang Lake water is very low, a spike of arsenic from the secondary stock solution was added to the beaker. The ferrous coagulant which was filtered through a 0.45 μm nylon syringe filter was added to the beaker to make desired final concentrations of Fe^{2+} in the solution. The reason to filter the ferrous solution is due to the fact that in this study only dissolved ferrous and its efficiency in the removal of arsenic is examined. The pH of the solution was then adjusted with appropriate amounts of NaOH or HCl with an Orion 3-star pH meter. The beaker was placed in a Stuart Scientific flocculator and necessary amount of KMnO_4 as the oxidant was added to the beaker

simultaneously stirring of the solution started at 100 rpm for 1 min and followed by 14 min slow mix at 50 rpm. Ferrous-borne flocs were formed at this stage. The stirring was stopped and the stirrer paddle was lifted up with the spherical knob. The procedure was followed by 15 min settling time. After the settling period, 10 mL of the supernatant was collected using a 10 mL disposable syringe from 1.5 cm below the liquid surface. It was then filtered through a 0.22 μm nylon syringe filter. The filtration step is to physically remove ferrous-borne flocs from water. The efficiency of the usage of these filters to remove ferrous-borne flocs is discussed in the next chapter.

Appropriate amounts of concentrated HNO_3 , 30% H_2O_2 and Nickel nitrate were added to the sample and the digestion method was followed as described earlier. Although acid preserved and stored at 4°C, samples were analyzed not later than one week after preparation.

3.4.2 Turbidity Measurement

Turbidity of the treated water with biologically produced ferrous was determined by using a HACH 2100 N Turbidimeter (USA). After the treatment 30 mL of the supernatant was collected and transferred to a tube for the measurement of turbidity. The turbidity of Nanyang Lake water was measured prior to the treatment.

3.4.3 Structural Characterization of Ferrous-Borne Flocs

After the coagulation experiment, the contents of the beaker were stirred using a rubber spatula and transferred to a 30 mL tube. This tube was centrifuged using a KUBOTA 8410 (Japan) at 3300 rpm for 8 min, and the clear supernatant was disposed. The remaining mud which was the ferrous-borne flocs were scattered on a filter paper and put in a petry dish and dried over night using a Christ Alpha 1-4 LD (UK) freeze-dryer. Observation of the samples was then carried out using a Leica Stereoscan 420 Scanning Electron Microscope (SEM). The samples were mounted on a double-side adhesive disc and coated with a thin layer of gold to prevent

sample charging problems. Figure 3-5 shows the SEM used in Environment Laboratory at NTU.

Figure 3-5 Scanning Electron Microscope, Leica Stereoscan 420

3.4.4 Particle Size Analysis

In order to gain data on the size distribution of the Ferrous-borne flocs and also evaluation of the micro-filtration efficiency in removing the flocs after treatment with ferrous solution, particle size distribution of the flocs was measured using a particle size analyzer Malvern Mastersizer 2000 (UK).

Chapter 4

Results and Discussion

4.1 Effects of Bacteria Source and Carbon

The first set of cultivation examines the effects of anaerobic sludge and bottom sediment. This cultivation contains three controlling samples to examine the results without carbon and bacteria. The detail constituents and the cultivation results of each sample are listed in Table 2.

In the first set of cultivation, three controlling samples (Sample No. 1, 2 and 5) were involved. Sample 1 (both A1 and B1) only contained raw water without any iron ore or cellulose. Sample 2 contained 1.4286 g of iron ore without addition of cellulose. Sample 5 contained additional 15 ml of 10% ethanol, as the abiogenic controlling sample.

From the final product concentration listed in the last two columns of the Table 2, no production of ferrous is observed in samples A1 and B1. Sample 2 and Sample 5 showed very low production of ferrous, which could be ignored. Based on this it can be concluded that the three basic growth factors for the bacteria are: cellulose (carbon source), ferric (iron-ore) and bacteria (IRB).

Chapter 4 Results and Discussions

It is interesting to note that, ferrous produced from the usage of bottom sediments is much higher than that of anaerobic sludge. The difference observed might be due to the difference of initial bacteria concentration in the two different media. A better option for the bacteria source can be the enrichment culture of iron-reducing bacteria cultivated in the lab.

Table 2 First set of Production of ferrous coagulant.

Sample No.	Raw water (ml)	Cellulose (g)	Fe ³⁺ (g)	Bacteria source	Ethanol	Dissolved Ferrous (mg/l)	Total Ferrous (mg/l)
A1	300	-	-	-	-	-	-
A2	300	-	1	Anaerobic sludge	-	0.005	0.043
A3	300	0.13	1	Anaerobic sludge	-	0.283	0.448
A4	300	0.39	1	Anaerobic sludge	-	0.385	0.405
A5	300	0.39	1	Anaerobic sludge	15ml, 10%	0.01	0.004
B1	300	-	-	-	-	-	-
B2	300	-	1	Bottom Sediment	-	0.008	0.023
B3	300	0.13	1	Bottom Sediment	-	0.263	0.37
B4	300	0.39	1	Bottom Sediment	-	0.201	0.211
B5	300	0.39	1	Bottom Sediment	15ml, 10%	0.006	0.006

Chapter 4 Results and Discussions

In order to evaluate the effect of different carbon source on the production of ferrous, both cellulose and acetic acid were selected in the second set of cultivation. The chemical reactions occurred as follows:

Based on these two equations, 1 g of Fe^{3+} requires minimum 0.13 g of either carbon source. Eight samples with different ratio of Fe^{3+} to C source (either CH_2O or CH_3COOH) were prepared. They were divided into two groups according to the carbon utilized. The mass ratios of Fe^{3+} to C were 1:0.13, 1:0.26, 1:0.39, and 1:0.52 respectively.

Table 3 Ferrous concentration and maximum ferrous production rate by adding cellulose and acetic acid as C source

Sample No.	Carbon Source	Mass of C source (g)	Maximum Dissolved Ferrous (mg/L)	Maximum Total Ferrous (mg/L)	Maximum Ferrous Production rate (Total) (mg/L/day)	Maximum Ferrous Production rate (Dissolved) (mg/L/day)
C1	Cellulose	0.13	14.05	18.79	2.76	2.50
C2	Cellulose	0.26	16.23	24.43	2.95	2.35
C3	Cellulose	0.39	36.78	55.65	4.46	3.68
C4	Cellulose	0.52	46.46	62.96	4.22	3.03
D1	Acetate Acid	0.13	1.01	6.25	1.04	0.17
D2	Acetate Acid	0.26	0.86	6.74	1.29	0.14
D3	Acetate Acid	0.39	0.71	7.63	1.56	0.10
D4	Acetate Acid	0.52	5.80	21.25	1.23	0.30

As shown in Table 3, all the critical parameters measured for samples with cellulose as C source were higher than those with acetic acid as C source under the

same condition. Cellulose is more effective as C source than acetic acid. Iron-reducing bacteria produced larger amount of ferrous with the presence of cellulose than that of acetic acid. The biological reaction was also faster since the maximum production rates of both dissolved and total ferrous were at least 17 times higher for C samples in which cellulose was added.

Theoretically, acetic acid should be easier for iron-reducing bacteria to utilize under anaerobic condition since it is not required to take the hydrolysis and fermentation processes. The reason why the experiment results did not present the effective outcomes was that the amount added to the batch cultivation samples was mass-based and the raw water in the sample was around 400 ml. The small mass of acetic acid added did not produce a desired concentration in the samples for bacteria to consume. On the other hand, the cellulose added was in the solid phase and before being added to the samples, it was pre-treated into fine particles and therefore it produced a larger site for bacteria and iron particles. Thus, on the reaction site, more C source was available for IRB to consume and hence samples with cellulose presented more effective production results.

4.2 Effects of Iron Ore Particle Size

The contact surface or the reaction site for iron-reducing bacteria to undertake the oxidation-reduction reaction is very important in the production of ferrous. The third set of batch cultivation was conducted to determine the effect of iron ore particle size on the biological production of ferrous. Three particle size ranges were selected: $X < 1$ mm, 1 – 2.8 mm, and 2.8 – 6.7 mm. The average length, width, height and corresponding surface area, volume and surface to volume ratio are listed in Table 4. The height of a single particle is assumed to be 1/2 of its length. The shape of the particle is assumed to be cubical.

Table 4 Parameters for iron ore particle size

Particle size (mm)	Length (mm)	Width (mm)	Height (mm)	Surface (mm ²)	Volume (mm ³)	Surface-Volume ratio
3.8-6.7	6.0854	4.4232	3.0427	117.7842	81.9015	1.4381
1-2.8	2.6315	2.0278	1.3158	22.9333	7.0210	3.2664
<1	0.7541	0.5582	0.3771	1.8315	0.1587	11.5394

The following two figures show the correlations between the size of the iron ore particles and the maximum ferrous concentration produced and the maximum production rate of ferrous.

Figure 4-1 Maximum concentration of ferrous vs. surface-volume ratio of iron ore.

Batch cultivation with 1 g of iron ore (< 1 mm, 1-2.8 mm, and 2.8-6.7 mm),
1.95 g of cellulose and 4 g of bottom sediment.

The third set of batch cultivation also included three different groups with different iron/carbon ratio. Results in Figure 4-1 and 4-2 were selected from one group of them ($\text{Fe}^{3+}/\text{Cellulose} = 1:1.95$) in order to show the effect of iron ore particle size on the production of ferrous. The results of the other two groups demonstrated the similar relations between ferrous production and iron ore particle size.

From Figure 4-1, we found that particles with larger surface to volume ratio produced solutions with higher ferrous concentration and faster ferrous production rate (Figure 4-2). That means small size particles have a better effect to produce ferrous coagulants since small size particles would provide more reaction site or surface for bacteria and cellulose to attach and therefore more metabolism reactions would occur and hence, the production rate would be faster.

Figure 4-2 Maximum Fe^{2+} production rate vs. surface to volume ratio of iron ore particle. Batch cultivation with 1 g of iron ore (< 1 mm, 1-2.8 mm, and 2.8-6.7 mm), 1.95 g of cellulose and 4 g of bottom sediment.

4.3 Effect of amount of cellulose

The whole three batch cultivation results showed the maximum ferrous concentration produced was proportional to the amount of cellulose added. Cellulose in the batch cultivation served as carbon source for the metabolism of iron-reducing bacteria. They provided “food” for the bacteria and worked as electron donors in the redox reactions. More cellulose in the cultivation means more nutrients in the environment and bacteria would grow faster. The relationship between maximum ferrous concentrations and amount of cellulose is presented in Figure 4-3.

Figure 4-3 Maximum ferrous concentration (mg/L) vs. mass of cellulose(g)

From Figure 4-3, a general increasing maximum ferrous concentration with the increase in mass of cellulose can be observed. The largest value produced by largest mass of cellulose was almost 4 times higher than the lowest concentration.

Figure 4-4 Maximum ferrous production rate vs. mass of cellulose

Figure 4-4 shows the effects of amount of cellulose on the ferrous production rate. Generally, there was an increasing trend. However, some exceptions occurred. The maximum production rate of dissolved ferrous with 1.95 g of cellulose even decreased. This is because when the amount of cellulose reached a certain level (note: all the batch cultivations in this project use 1 g of Fe^{3+}), the excess cellulose covered on the surface of the iron ore particles and prevented the direct contact between iron ore particles and bacteria, therefore the reactions were negatively affected. The same phenomena could also be found in the ferrous production curve for last set of batch cultivation (Figure 4-5). The mass ratio of Fe^{3+} to cellulose in this case was 1:1.95. And during the early days of cultivation, no production of ferrous was observed until the test on Day 13.

Figure 4-5 Ferrous production curve: batch cultivation with 1 g of Fe^{3+} , 1.95 g of cellulose; iron ore particle size < 1 mm

The other samples in the third set of cultivation showed the similar results since the cellulose amount is at excessive level. Figure 4-5 is selected for the presentation purpose.

4.4 Coagulation Experiments with Biologically Produced Ferrous

The first step of this study was to evaluate the possibilities of biological production of ferrous from a cheap source of Iron; Iron ore. In the previous sections the effect of different parameters on the production of ferrous were studied. These studies provide the knowledge to choose and prepare suitable conditions for the biological production of ferrous.

The second step of this study is the evaluation of the arsenic removal efficiency during coagulation with biotic ferrous. Literature indicates that different parameters affect the adsorption of arsenic on ferric (hydr) oxides. Among these parameters are initial arsenic concentration, dosage of the coagulant, oxidation and pH. Different conditions were obtained to evaluate the effect of these parameters. In this section the extent of arsenic removal with respect to these parameters are discussed.

4.4.1 The Effect of Different Dosage of Ferrous

Adsorption and co-precipitation using coagulants for sequencing arsenic from drinking water has been studied by different workers and its economic feasibility established. Coagulation is the most common arsenic removal technology (Singh, 2007). This is due to the fact that some anions and cations have a specific affinity for the surface metal atoms and adsorb out of all proportion to their concentration in solution (Pierce et al., 1980). The sorption of arsenic on hydrous ferric oxides has been extensively studied (Wilkie et al., 1996). When aeration is applied to a dissolved Fe(II) containing aqueous solution, Fe(II) oxidizes via Fe(III) into Fe(hydr)oxides and ferrihydrite (Wolthoorn et al., 2003).

In this study, after addition of biotic ferrous solution to feed water (either raw or spiked with arsenic) a pale yellow color appeared which gradually turned into a more intense yellow color. This might be an indication of formation of goethite (α -

FeOOH). Hamzaoui et al. (2002) describes the goethite crystallization from ferrihydrite in two steps:

- dissolution of ferrihydrite
- reprecipitation of the Fe as goethite

Nagano et al. (1992) studied the reaction mechanism for the crystallization of ferrihydrite to goethite and conducted a laboratory experiment to quantify colors of precipitates and to relate their changes to goethite crystallization. The color change associated with the goethite crystallization was easily observed with the naked eye and varied from brown to yellow as a function of time.

Literature indicates that ions such as PO_4^{3-} , Ca^{2+} or SO_4^{2-} bind specifically to singly coordinated surface groups of goethite (Wolthoorn et al., 2003). The surface complexation of goethite with arsenate anions has been examined. Both monodentate, such as XH_2AsO_4 , XHASO_4^- or XHASO_4^{2-} and bidentate (X_2HASO_4 or X_2AsO_4^-) surface species have been observed (Matis et al., 1998).

Formation of inner-sphere monodentate arsenate/goethite surface complexes are according to the equation: (Grossl et al., 1997)

Formation of inner-sphere bidentate arsenate/goethite surface complexes are according to the equation: (Grossl et al., 1997)

Previous studies show that increasing iron concentration in water leads to the higher removal efficiencies of arsenic (Hering et al., 1996; Ghurye et al., 2004). In this study, a set of experiment was performed to evaluate the effect of different dosages of biotic ferrous on the arsenic removal efficiency. 300 mL of the Nanyang lake water spiked with arsenic was poured into 4 beakers with a graduate cylinder. It was previously observed that the addition of ferrous coagulant decreases the pH of the feed water. Different ferrous doses of 1, 5, 10 and 20 mg Fe^{2+} / L was added to the beakers resulting in the decrease of pH from 7.6 to 7.3, 6.72, 6.46 and 6.25 respectively. This might be due to the hydrolysis of oxidized ferrous iron. Also the initial pH of the biotic ferrous solution was 5.9. The pH was adjusted to 7, which is representative of the pH range for many ground waters, with the addition of pre-determined amounts of solutions of 1 N and 0.1 N of NaOH and 0.1 N HCl as necessary. This experiment was performed with the addition of 1 mg/L KMnO_4 to improve the arsenic removal efficiency.

Table 5 Data obtained from the treatment of Nanyang Lake water spiked with arsenic to 50 ppb at pH=7, with the addition of potassium permanganate.

Initial Fe^{2+} Concentration (ppm)	Initial As concentration (ppb)	Fe/As Ratio	Residual As (ppb)	As Removal Percentage
0	50	0	41.1	17.8
1	50	20	4.8	90.4
5	50	100	<4.7	>95
10	50	200	<4.7	>95
20	50	400	<4.7	>95

It should be noted that the detection limit established for the GFAAS was 4.7 ppb. The method for determination of detection limit is to run the graphite furnace for the method blank in 10 replicates, detection limit is three times the standard

deviation obtained. Therefore the results for the concentration of arsenic below 4.7 are not accurate. However, it can be observed that an increase in the Fe/As ratio decreases the peak area and the results are of some value.

It can be noted from Table 5 that an increase in the biotic ferrous concentration increases the arsenic removal efficiency. This might be due to the adsorption of arsenic ions onto ferrihydrite or goethite particles. Co-precipitation with the mentioned particles might be another reason for the improved arsenic removal efficiency. With the increase of ferrous dosage from 1 to 20 mg Fe²⁺/L the arsenic removal efficiency increased from 90.4% to more than 95% at neutral pH. This result is in agreement with the findings of Ghurye et al. (2004) that the increase in the ferric dosage from 4 to 7 mg/L Fe yields to residual arsenic concentrations of <10 and 2 ppb, respectively. Figure 4-6 shows the arsenic removal at different ferrous to arsenic weight ratios.

Figure 4-6 Arsenic removal at pH 7 as a function of iron to arsenic ratio. 1 mg/L KMnO₄ was added as the oxidant.

The slight removal of arsenic at no addition of ferrous conditions is observed. As described in the previous chapter the samples were filtered through a 0.22 μm nylon filter. The decrease observed in the arsenic concentration might be due to adsorption of arsenic to the partially oxidized ferrous particles. Ferrous can be readily oxidized and from the findings of this experiment it can be concluded that the initial dissolved oxygen concentration in Nanyang Lake water was enough for partially oxidation of ferrous. Therefore the reason for decrease in residual arsenic concentration might be due to the removal of the arsenic adsorbed particles with the 0.22 μm filters.

An increase in the intensity of the yellow color, after the addition of the biotic ferrous to the water was observed as a function of the concentration of ferrous in water and time. After a few minutes of the addition of ferrous solution to water, the pale yellow color associated with the formation of goethite changed to a strong yellow color. In the feed water with a pH of more than 7, required amount of 0.1 N HCl was added to the water to decrease the pH, hence formation of FeCl_3 which also has a yellow color. However the amount of HCl added for pH adjustment was little and the dominant yellow color might be mostly due to the formation of goethite.

Table 5 clearly shows that at neutral pH and with the initial arsenic concentration of 50 ppb, addition of biotic ferrous could decrease the concentration of arsenic below the MCL which is 10 ppb.

It is observable that the lowest dosage of biologically produced ferrous, 1 mg Fe^{2+} /L could bring down the arsenic concentration below the MCL set by USEPA. However, due to the carcinogenic and mutagenic characteristics of arsenic and its severe toxicity which is elaborately discussed in Chapter 2, it can be deduced that the total removal of arsenic from drinking water, wherever costs permit, can be a better option with lower health risks. As previously discussed, maximum allowable arsenic concentrations set by WHO and USEPA has decreased from 200 $\mu\text{g/L}$ in

1958 to 10 µg/L in 2006. Therefore, with the new findings in the adverse effects of arsenic on health, future revisions on the MCL and decrease in it can be predictable.

4.4.2 The Effect of Aeration versus Chemical Oxidation

It is known that arsenious acid, H_3AsO_3 , in the +3 oxidation state is more toxic than arsenic acid. It is reported that arsenate is about 60 times less toxic than arsenite (Ferguson et al., 1972; Knowles et al., 1983). Therefore a pre-oxidation step is important to oxidize As(III) to As(V). The oxidation step is also crucial in this study as biological ferrous is added to the water and natural oxidation of ferrous without any chemical oxidation or aeration applied is not efficient.

As discussed previously there are numerous methods of oxidation available, but important factors such as the residual concentrations, availability and running cost of oxidants and oxidation by-products should be considered when selecting an oxidant. The most feasible oxidants to date are either potassium permanganate or Fenton's reagent. These oxidants produce no harmful byproducts, and are easily applied (Jiang, 2001).

In this set of experiments, arsenic removal efficiency without any pre-oxidation step, with 15 min aeration while stirring and also with the chemical oxidation using potassium permanganate was examined. Aeration was applied during mixing. In the case of chemical oxidation, 1 mg/L KMnO_4 was added immediately after mixing started. Data obtained from this set of experiment is shown in Table 6. These experiments were conducted at the initial ferrous and arsenic concentration of 20 mg Fe^{2+} /L and 50 mg/L, respectively. Ph was controlled at 7 with addition of 0.1 N NaOH.

Table 6 Data obtained from the treatment of Nanyang Lake water spiked with arsenic to 50 µg/L and ferrous dosage of 20 mg Fe²⁺/ L at pH=7 with the addition of 1 mg/L potassium permanganate as the oxidant.

Sample status	Fe/As Ratio	Residual As (ppb)	As Removal Percentage
No aeration applied	400	35.1	29.8
15 min aeration applied	400	<4.7	>95
1 mg/L KMnO ₄ added	400	<4.7	>95

From the data obtained, the effect of oxidation in arsenic removal is observed. In the sample with no aeration applied, no flocs were formed after the rapid mixing at 100 rpm and slow mixing at 50 rpm, hence only 29.8% arsenic removal was observed and the residual arsenic concentration in the sample after treatment is much higher than the MCL of 10 µg/L. The decrease of arsenic concentration after treatment might be the result of the partial adsorption of arsenic ions on ferrous hydroxides.

In the samples in which oxidation was applied through aeration or chemical oxidation with potassium permanganate, more than 95% removal of arsenic was observed which might be due to the high Fe/As mass ratio of 400. However in the sample in which aeration was applied, the ferrous-borne flocs observed were finer than the flocs formed after the addition of KMnO₄ and the formation of the flocs was slower in comparison with the usage of chemical oxidation.

4.4.3 The Effect of pH

Experiments to evaluate the effect of pH on arsenic removal efficiency were conducted with ferrous iron dosage of 20 mg Fe²⁺/ L, and initial arsenic concentration of 50 µg/L. Potassium permanganate with a dosage of 1 mg/L was

added with the start of the stirrer, as the oxidant. Table 7 shows the data obtained in this set of experiments.

Table 7 Data obtained from the treatment of Nanyang Lake water spiked with arsenic to 50 ppb and ferrous dosage of 20 mg Fe^{2+} / L, with the addition of 1 mg/L potassium permanganate as the oxidant.

pH	Fe/As Ratio	Residual As (ppb)	As Removal Percentage
6.0	400	<4.7	>95
7.0	400	<4.7	>95
8.0	400	<4.7	>95

It can be observed in Table 7 that the addition of biotic ferrous solution with a dosage of 20 mg Fe^{2+} / L at the pH range examined can result in a more than 95% arsenic removal from water and that the percent arsenic removal remained constant in this range (pH 6.0-8.0).

Figure 2-2 in Chapter 2, demonstrates the effect of pH on different arsenic species. It can be seen that arsenite (H_3AsO_3) is found in the neutral form up to pH more than 9. Therefore in this range of pH arsenic removal efficiency is not affected by the changes in pH.

Raven et al. (1998) studied the kinetics and equilibria of the adsorption of arsenite and arsenate on ferrihydrite, at pH 4.6 and 9.2. In addition he studied the effect of pH on the adsorption of arsenite and arsenate within the pH range of 3-11 at different arsenic concentrations. The results of his studies showed that arsenite adsorption was higher than arsenate adsorption through the pH range of 3-11. The lower adsorption of arsenate at high pH values is attributable to an increased repulsion between the more negatively charged arsenate species and negatively

charged surface sites. Since arsenite species have less negative charge character as compared to arsenate species at the same pH value, they do not exhibit as much repulsion, and as a result, the adsorption decreases less with increasing pH.

Ankomah (1991) determined the zero point of charge (ZPC) for some iron oxides including goethite. ZPC is the pH value of a solution in equilibrium with a particle whose net charge from all sources is zero. The ZPC of oxides serves as a convenient reference for predicting how the surface charge and potential on oxides depend on pH. A ZPC of 7.9 was obtained for the synthetic goethite (α -FeOOH) by Ankomah (1991). Therefore it can be deduced that high adsorption on goethite surface can be observed at pH below 7.9 and this is in agreement with the findings of this set of experiments. The pH range studied in this set of experiments can be an optimum pH range for the removal of both arsenite and arsenate.

4.4.4 The Effect of Dosage of Chemical Oxidant

Since the oxidation rate of dissolved As(III) by oxygen is extremely slow, oxidants such as chlorine, ozone or permanganate need to be used. Chlorine has traditionally been the oxidant of choice, but there are growing concerns regarding the generation of organochloride byproducts from the naturally occurring organic matter which may also be present (Zaw et al., 2002).

Permanganate effectively oxidizes arsenite. It is a poor disinfectant, though it can produce a bacteriostatic effect. Potassium permanganate (KMnO_4) is widely available in developing countries. It is relatively stable with a long shelf life (Johnston et al.). Potassium permanganate is more expensive than chlorination; \$2700 per ton compared with \$350 to \$400 per ton. However, unlike chlorination, potassium permanganate is not known to form measurable DBPs. Raw water and downstream process considerations should be made when selecting a pre-oxidation technology (USEPA 2000).

Oxidation of arsenite ion by potassium permanganate is according to the equation: (Lauf et al., 1993)

Oxidation of ferrous ion by potassium permanganate is according to the equation: (Lauf et al., 1993)

The typical dosage of potassium permanganate in most conventional coagulation treatments for arsenic removal is 0.7-2 mg/L.

In the previous section, it was shown that aeration alone is not sufficient for the oxidation of arsenic (ferrous is more readily oxidized with aeration). It was observed that aeration brought down the residual arsenic concentration to 35.1 µg/L and therefore the arsenic concentration below the MCL for arsenic (10 µg/L) could not be achieved.

In order to determine the required potassium permanganate dose for efficient arsenic removal 0.5, 1 and 2 mg/L permanganate was added to water including 20 mg Fe²⁺/L and 50 µg/L arsenic at PH 7. The experimental procedure is the same as discussed in the previous chapter. Potassium permanganate is added at the same time as mixing started at 100 rpm. Table 8 shows the data obtained in this experiment.

Table 8 Data obtained from the treatment of Nanyang Lake water spiked with arsenic to 50 ppb and ferrous dosage of 20 mg Fe^{2+} / L, with the addition of different dosage of potassium permanganate as the oxidant at pH=7.

KMnO₄ Dose (mg/L)	Fe/As Ratio	Residual As (ppb)	As Removal Percentage
0.5	400	<4.7	>95
1.0	400	<4.7	>95
2.0	400	<4.7	>95

It can be noted from Table 8 that at the conditions provided for this experiment almost total removal of arsenic can be achieved. The reason might be due to the high ratio of ferrous to arsenic in this experiment. It is interesting to note that the dosage of 0.5 mg/L of permanganate could result in the more than 95% removal of arsenic and therefore permanganate dosage above that is in excess for the oxidation required. This can lower the operational costs in water treatment plants.

The different dosage of permanganate applied in this experiment does not particularly affect the arsenic removal efficiency. However from the experiments formation of considerably bigger flocs was observed for the usage of 2.0 mg/L permanganate and therefore higher settling rates of the flocs could be seen. In this case settling time less than 15 min is sufficient for the total settling of the particles.

One concern about the usage of permanganate in water treatment plants is the remaining pink color which is a nuisance for drinking water. In this experiment however, the application of above mentioned dosages of permanganate left no color to the treated water for the three dosages.

4.4.5 Particle Size Distribution

Figure 4-7 shows the size distribution of ferrous-borne flocs from the coagulation of Nanyang Lake water spiked with 50 µg/L arsenic with the application of 20 mg Fe^{2+} /L at pH 7. There were approximately 3% (volume percentage) particles smaller than 1.4 µm and 97% smaller than 0.45 µm. As it can be seen in Figure 4-8 there are no particles smaller than 0.22 µm. Therefore, it can be deduced that filtration of treated water using filter membranes with a nominal pore size of 0.22 µm proves to be qualified for the total removal of ferrous-borne particles in this experiment.

On the other hand, as a large portion of the ferrous-borne flocs are in the colloid size range, total removal of the flocs can not be achieved by gravitational sedimentation and implementation of a micro-filtration step is necessary. The effectiveness of the micro-filtration step depends on the floc size distribution.

Figure 4-7 Size distribution of ferrous-borne flocs from the coagulation of arsenic spiked water with Fe/As mass ratio of 400 at pH 7.

Figure 4-8 shows the SEM micrographs of the ferrous-borne flocs. The coagulation was performed at Fe/AS mass ratio of 400 at pH 7. In this micrographs the highly porous particles can be observed.

Figure 4-8 SEM micrographs of ferrous-borne flocs

4.4.6 The Effect of Coagulation on Turbidity

Turbidity is a measure of the cloudiness of water. It is quantified with a turbidimeter which measures the intensity of light scattered at 90 degrees as a beam of light passes through a water sample. The EPA Interim Primary Drinking Water Regulations recommend that turbidity of potable water be less than 1 Nephelometric Turbidity Units (NTU) and less than 5 NTU under special conditions.

To evaluate the effect of coagulation with biotic ferrous on the water turbidity a set of experiments were conducted with different Fe/As mass ratios and an initial arsenic concentration of 50 mg/L at pH 7. Potassium permanganate was added at a dosage of 1 mg/L as the oxidant. After the settling of the ferrous-borne flocs, turbidity of the treated water was measured. Table 9 demonstrates the data obtained in the above mentioned experiment.

Table 9 Data obtained from the treatment of Nanyang Lake water spiked with arsenic to 50 ppb and different Fe/As ratios, with the addition of 1 mg/L potassium permanganate as the oxidant at pH 7.

Fe/As Ratio	As Removal Percentage	Turbidity (NTU)
0	17.8	56.6
20	90.4	10.2
100	>95	5.54
200	>95	5.07
400	>95	2.78

Figure 4-9 Turbidity as a function of Fe/As with initial arsenic concentration of 50 µg/L at pH 7.

As it can be observed in Figure 4-9, treated water turbidity decreases as the Fe/As ratio increases during coagulation. It can be seen that with the addition of ferrous solution with a dosage of 1mg Fe²⁺/L, water turbidity drops dramatically from an initial value of 56.6 to 10.2 NTU. Further increase in the dosage of the coagulant, results in a removal of suspended matter in water hence a decrease in turbidity. The highest dosage of ferrous solution leads to a turbidity of 2.78 which is still above the recommended level (1 NTU) set by USEPA and WHO.

The remaining turbidity in the treated water is partly due to the fact that some flocs remain attached to the water surface and will not settle as a result of high surface tension of water. It can be deduced that the higher dosage of ferrous leads to form flocs which can settle faster.

Figure 4-10 Turbidity versus arsenic removal efficiency with initial arsenic concentration of 50 $\mu\text{g/L}$ at pH 7.

Figure 4-10 demonstrates turbidity of the treated water versus arsenic removal efficiency. It can be observed that a reduction in residual arsenic concentration also reduces the turbidity. A more than 95% removal of arsenic from water leads to 95% removal of the suspended matter. As a result, addition of ferrous coagulant not only removes arsenic from water but also removes suspended matter which are considered nuisance for drinking water.

Chapter 5

Conclusions

5.1 Conclusions

Arsenic is a known carcinogen and occurs naturally in groundwater in many parts of the world. Coagulation/adsorption of arsenic on iron particles is known to be an effect technology to remove arsenic from drinking water. However, due to the relatively high costs of this technology, it is not affordable for developing countries. Biologically produced ferrous was applied in this study to remove arsenic from drinking water. Research was conducted to evaluate the effect of different parameters on the production of ferrous and its efficiency in arsenic removal. Based on this research the following conclusions are made:

- The usage of bottom sediments produced significantly higher ferrous production rate in comparison with the usage of anaerobic sludge.
- The usage of cellulose, as the main electron donor, resulted in higher ferrous production rate in comparison with the use of acetic acid. A ferrous

production rate of 0.126 mg/L.h was resulted at the presence of 0.52 g cellulose and 1 g Fe^{3+} as iron ore.

- The production rate of ferrous is sensitive to iron ore particle size. Iron ore with the least particle size of less than 1 mm had a surface to volume ratio of 11.54 mm^{-1} . The higher the surface to volume ratio, the higher the ferrous production rate, as this surface acts as the reaction site for the bacteria. Application of the iron ore particles with the above mentioned size in the amount of 1 g Fe^{3+} as iron ore and 1.95 g cellulose, resulted in 85 mg Fe^{2+} /L.
- Addition of biologically produced ferrous solution to Nanyang Lake water spiked with arsenic, resulted in the formation of ferrihydrite and goethite.
- Fe/As mass ratio of 20 was sufficient to decrease the arsenic concentration from 50 $\mu\text{g/L}$ to below 10 $\mu\text{g/L}$ (USEPA recommended MCL for arsenic) with the addition of 1 mg/L KMnO_4 as the oxidant at neutral pH.
- Fe/As mass ratio of 400 resulted in the total removal of arsenic at pH 7. KMnO_4 with a dosage of 1 mg/L was added as the oxidant.
- Low residual arsenic concentration (less than 5 $\mu\text{g/L}$) was achieved with the usage of all the implemented Fe/As ratios in these experiments and at a pH range of 6.0-8.0 with the addition of 1 mg/L KMnO_4 as the oxidant.
- The application of 15 min aeration alone yielded to the almost total removal of arsenic at pH 7 with the Fe/As mass ratio of 400.
- The pH range studied (pH 6-8) did not affect the arsenic removal efficiency with the application of Fe/As mass ratio of 400.

- Arsenic removal efficiency was insensitive to the different potassium permanganate dosages applied, with Fe/As ratio of 400 at neutral pH.
- No pink color was remained in the treated water with the application of different permanganate dosages tested in this study.
- Micro-filtration of the treated water after settling of the flocs, with a 0.22 μm membrane filter, was sufficient to remove the ferrous-borne flocs from water and thus decrease the residual arsenic concentration.
- Treated water turbidity decreased as the Fe/As mass ratio increased. A turbidity of 2.78 NTU was resulted at the addition of Fe/As mass ratio of 400.

These observations indicate that the biological production of ferrous with the use of iron ore, is a viable technology for removal of arsenic from drinking water. Due to the low costs of iron ore, this technology can be a suitable option for developing countries with high groundwater arsenic contamination. Therefore, this is an important finding with potentially far-reaching economic and social consequences.

5.2 Future Work

Future work should include data about the arsenic speciation in the feed water and also in the treated water. According to the literature, As (III) is more toxic than As (V). This difference in the toxicity and also the effect of arsenic oxidation state on the treatment efficiency, suggests a necessity for measurements being carried out regarding the arsenic speciation.

In this study, the effect of pH on the arsenic removal was examined in a pH range of 6 to 8. However, due to the fact that groundwaters of more acidic or basic pH have been reported in different countries, it would be desirable to examine the

effect of pH on a wider range to study the efficiency of the proposed technology in arsenic removal at different pH levels.

Although several experiments were carried out to investigate the optimum conditions for the biological production of ferrous, it would be informative to explore the effect of the parameters studied more thoroughly in order to reach a higher rate of ferrous production.

The experiments conducted in this study used a batch reactor for the biological production of ferrous, however it would be desirable to conduct similar experiments in a continuous reactor and design an economically feasible plant for arsenic removal from water.

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