

**ARSENIC REMOVAL FROM GROUNDWATER BY FE-MN OXIDATION AND  
MICROFILTRATION**

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# **ARSENIC REMOVAL FROM GROUNDWATER BY FE-MN OXIDATION AND MICROFILTRATION**

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Although arsenic has been classified as human carcinogen and its acute toxicity has long been known, the long term health effects of trace arsenic levels have only recently been realized. The maximum contaminant level (MCL) for arsenic in drinking water was consequently lowered from 50 µg/L to 10 µg/L in 2002, resulting in many water utilities needing upgraded to achieve compliance. In groundwater treatment, Fe-Mn oxidation and microfiltration has been recognized as a cost-effective technology since arsenic removal is facilitated during the removal of iron and manganese.

This study investigated the efficiency of arsenic removal using Fe-Mn oxidation/microfiltration under various process conditions including iron to arsenic ratio, pH, potassium permanganate dose, contact time, oxidation state of iron, and stirring in dead-end filtration cell.

Arsenite removal was relatively insensitive to variations in pH in the range of 6.5-8.0 when only aeration was applied, but the impact of pH was important in the potassium permanganate oxidation. At neutral pH, iron to arsenic ratio of 60 was sufficient to reduce the arsenic concentrations ranging from 25-250 ppb to below 10 ppb (primary MCL for arsenic) with aeration and microfiltration. The oxidation state of iron did not considerably affect the arsenic removal. Oxidation with potassium permanganate facilitated additional arsenite removal

compared to aeration alone. Although higher arsenic removals were observed at pH 7.0 than at pH 8.0, identical residual arsenic concentrations were obtained with 0.5 mg/L permanganate dose at both pH values.

In experiments with various iron levels, concentrations of iron in the permeate remained around 0.01 mg/L, which is far below the secondary MCL for iron (0.3 mg/L), while the manganese standard (0.05 mg/L) was only met when initial concentration of manganese was 0.2 mg/L. Iron and manganese particles were the primary reason for membrane fouling.

The results of this study are important for water treatment systems using groundwater with elevated arsenic and iron concentrations as a raw water source. The proposed technology is much simpler to operate than a conventional coagulation process and chemical requirements are minimized by utilizing existing iron concentration in the raw water.

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## INTRODUCTION

Apart from the lethal effect of arsenic ingested at high doses, it is a known carcinogen when taken in trace amounts over a long period. The maximum contaminant level (MCL) for arsenic was set at 10 ppb in February, 2002, and the compliance deadline was scheduled for January 23, 2006. It is estimated that adopting this new MCL requires at least 300,000 water utilities in the U.S.A to modify their treatment systems to lower the arsenic levels in drinking water. Amongst several methods developed for the removal of arsenic, Fe-Mn oxidation followed by microfiltration has emerged as a promising technology [McNeill and Edwards, 1995]. Removing dissolved iron and manganese along with arsenic has been recognized as a cost-effective method since it can meet both primary MCL for arsenic and secondary MCLs for iron and manganese [Chen et al., 1999].

Microfiltration is an effective technology to remove fine particles and to produce high quality water from raw water in different quality ranges. The sizes of iron and manganese oxide particles are known to vary from 1.5 to 50  $\mu\text{m}$  [Ellis et al., 2000], which allows the efficient use of microfiltration of arsenic bearing particles. The decline in permeate flux due to fouling, however, is one of the most significant issues to be considered in water treatment.

This experimental study investigates the efficiency of arsenic removal from groundwater by Fe-Mn oxidation and microfiltration under various process conditions including iron to arsenic ratio, pH, oxidation state of iron, potassium permanganate dose, contact time, and stirring in dead-end filtration cell. The decline in permeate flux, i.e. membrane fouling, and the removal

of iron and manganese are also examined in order to understand the impacts of variable parameters on process efficiency and thus, to determine the optimum process conditions.

This research is valuable to water utilities, especially those treating groundwaters which have high iron concentrations and significant arsenic levels, since elevated iron concentrations are utilized to remove arsenic and therefore, minimize chemical addition. It is a promising technology for arsenic removal when compared to conventional coagulation method which requires coagulant addition and involves many treatment steps such as coagulation, flocculation, sedimentation, and filtration. Fe-Mn oxidation followed by microfiltration removes arsenic in two simple steps: oxidation and filtration. Therefore, this process helps water treatment facilities lower the cost and save time by reducing treatment process complexity and eliminating chemical addition.

## **1.0 LITERATURE REVIEW**

The literature review mainly emphasized three topics. First, arsenic contamination and occurrence of arsenic in surface waters and groundwaters, and significance of arsenic removal from drinking waters in terms of health concerns were presented. Second, iron-manganese oxidation and coagulation methods as conventional treatment techniques for removal of arsenic, and the impacts of certain process variables on water quality were specified. Finally, the efficiency of membrane filtration technology, particularly microfiltration, for arsenic removal, and the major economical concern – membrane fouling were explained.

### **1.1 ARSENIC IN NATURAL WATERS**

#### **1.1.1 Arsenic Contamination**

Arsenic is a contaminant of well-known toxicity and it is not an uncommon contaminant in groundwaters [Joshi and Chaudhuri, 1996]. It is the twentieth most abundant element in the earth's crust, fourteenth in seawater and it is the twelfth most abundant element in the human body [Shih, 2005]. Although arsenic is necessary as a nutrient to humans in small quantities, it also leads to death in chronic intakes [Kartinen and Martin, 1995].

Arsenic contamination of the surface and subsurface water has been reported in many parts of the world, including South-Western Taiwan, Southern Thailand, Inner Mongolia, China, West Bengal of India, Bangladesh, and Northern Mexico. Although arsenic concentrations in the



U.S. source waters are typically low, elevated arsenic concentrations are also encountered primarily in the northern and southern parts of the western United States, particularly in groundwaters and in surface waters with hydrothermal inputs [AWWA Committee Report, 1985; Wilkie and Hering, 1996].

Organic forms of arsenic that may be present in food are less toxic to humans; however, inorganic forms of arsenic dissolved in drinking water constitute the most significant toxicity. Recent studies conducted to understand the long term health risks associated with ingestion of low levels of arsenic have indicated that arsenic in drinking water is more dangerous than previously suspected. Therefore, the World Health Organisation (WHO) and The U.S. Environmental Protection Agency (USEPA) promulgated more stringent arsenic regulations to minimize these risks [Jiang, 2001].

## **1.1.2 Arsenic in the Environment**

### **1.1.2.1 Sources of Arsenic**

Arsenic is widely distributed in the environment. Ranking twentieth in the abundance of elements in the earth's crust, total amount of arsenic in the upper earth crust is estimated to be  $4.01 \cdot 10^{16}$  kg with an average of 6 mg/kg. In sea water, the concentration of arsenic varies between 0.09 µg/L and 24 µg/L, and in freshwater between 0.15 µg/L and 0.45 µg/L having maximum value of 1 mg/L. The amount increases up to a factor of 300 of the average concentration of arsenic in groundwater in mineral and thermal waters [Bissen and Frimmel, 2003a].

Arsenic is the major constituent of at least 245 different minerals, and in the environment it is mainly associated with sulfide minerals along with copper, nickel, lead, cobalt, or other metals. Orpiment ( $As_2S_3$ ), realgar ( $AsS$ ), mispickel ( $FeAsS$ ), loellingite ( $FeAs_2$ ), niccolite

(NiAs), cobaltite (CoAsS), tennantite (Cu<sub>12</sub>As<sub>4</sub>S<sub>13</sub>) and enargite (Cu<sub>3</sub>AsS<sub>4</sub>) are the most significant arsenic bearing minerals [Bissen and Frimmel, 2003a; Thirunavukkarasu et al., 2005].

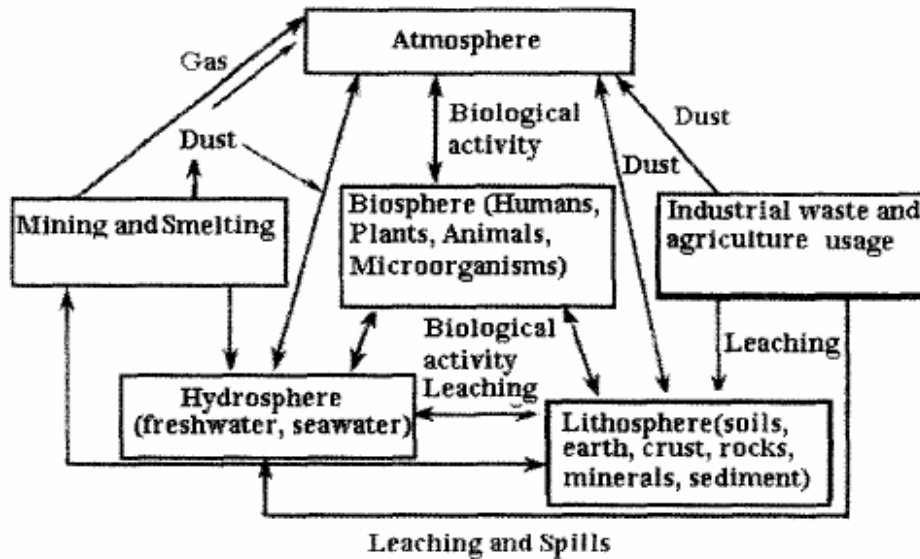
Apart from the natural phenomena such as weathering of sedimentary and igneous rocks, biological activity, and volcanic activity, anthropogenic inputs are also responsible for the emission of arsenic to the environment [Cullen and Reimer, 1989]. Industrial effluents from metallurgical industry, glassware and ceramic industries, dye and pesticide manufacturing industries, petroleum refining, rare earth industry and other organic and inorganic chemical industries are major anthropogenic sources of arsenic. Other industries introducing arsenic to the environment include wood and hide preservative, lead shot manufacture, phosphate detergent builder and presoaks used in many fertilizers [Banerjee et al., 1999; Viraraghavan et al., 1999]. Burning of fossil fuel in households and power plants is another anthropogenic source of arsenic. Mining also exposes arsenic-containing coals or ores, and smelters discharge arsenic wastes into natural water systems [Bissen and Frimmel, 2003a].

#### **1.1.2.2 Mobility of Arsenic**

Arsenic and its compounds are mobile in the environment. Weathering of rocks converts arsenic sulfides to arsenic trioxide, which enters the arsenic cycle by dissolution in rain, rivers, or groundwater or as dust. Arsenic cycle (Figure 1) occurs among land, air, and water after the liberation of arsenic from rocks and soil. Volatile forms of arsenic enter the atmosphere from land and water, and then they are returned by rain or atmospheric fallout. The oxidized forms of arsenic are reduced back to sulfides under anaerobic conditions on land and water sediments [Pontius et al., 1994].

Water is one of the major ways of arsenic transport in the environment. Naturally elevated arsenic concentrations are particularly common in places with high geothermal

activities and groundwaters in mining areas. Although low arsenic levels are usually detected in rivers and lakes, higher concentrations (up to several hundred micrograms per liter) occur in surface waters under the influence of hydrothermal inputs [Hering et al., 1996; Viraraghavan et al., 1999].



**Figure 1** The global arsenic cycle [Shih, 2005].

### 1.1.2.3 Arsenic Chemistry

Arsenic, atomic number 33, is located in the periodic table directly below phosphorus. Arsenic is considered a metalloid and occurs in a variety of forms and oxidation states. The two oxidation states common in drinking water are arsenate, As(V) and arsenite, As(III) [Brandhuber and Amy, 1998].

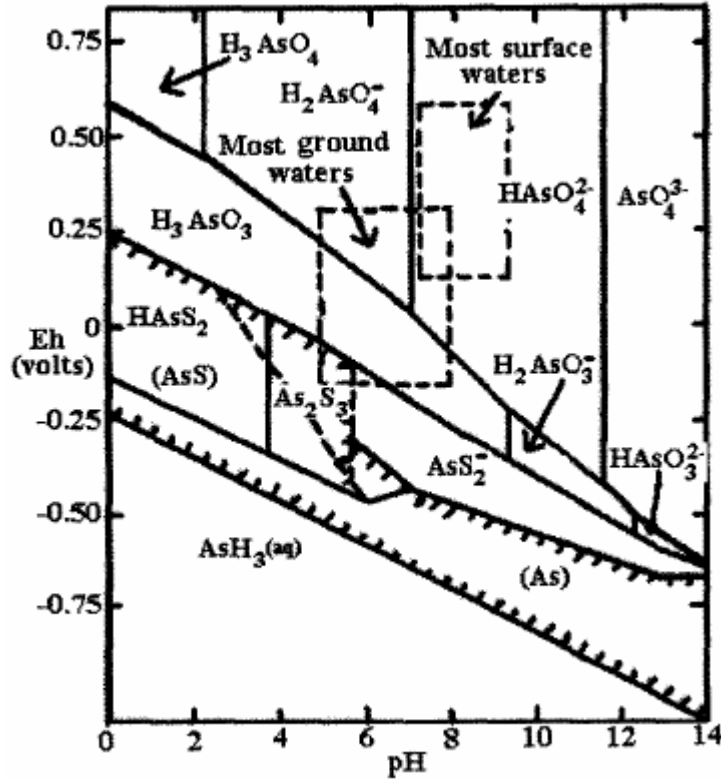
Arsenic occurs in both organic and inorganic forms in natural water. Organic compounds containing arsenic such as monomethylarsonic acid and dimethylarsinic acid may exist in natural waters as a result of the use of organo-arsenical pesticides, as well as through the biomethylation

mechanisms of microorganisms [Zouboulis and Katsoyiannis, 2002]. Microorganisms can oxidize arsenite to arsenate, reduce arsenate to arsenite or even to arsine ( $\text{AsH}_3$ ). Bacteria and fungi can reduce arsenate to volatile methylarsines, and marine algae transform arsenate to non-volatile methylated arsenic compounds.

Organic arsenicals are detected in surface water more often than in groundwater [Ning, 2002], and they are occasionally present at concentrations higher than  $1 \mu\text{g/L}$ . Therefore, organic species are generally considered of little significance compared with inorganic arsenic species in drinking water treatment [Edwards, 1994].

The inorganic arsenic is a result of dissolution from the solid phase, e.g., arsenolite ( $\text{As}_2\text{O}_3$ ), arsenic hydride ( $\text{As}_2\text{O}_5$ ), and realgar ( $\text{As}_2\text{S}_2$ ) [Cheng et al., 1994]. The chemistry of arsenic in aquatic systems is complex, and consists of oxidation-reduction, ligand exchange, precipitation, and adsorption [Banerjee et al., 1999]. In natural environment, arsenic is rarely encountered as the free element, and it is stable in four oxidation states (-3, 0, +3, +5), but the two oxidation states common in drinking water are trivalent arsenic and pentavalent arsenic. The soluble pentavalent (+5) or arsenate species are  $\text{AsO}_4^{3-}$ ,  $\text{HAsO}_4^{2-}$ ,  $\text{H}_2\text{AsO}_4^-$  and  $\text{H}_3\text{AsO}_4$ . The soluble trivalent (+3) or arsenite species include  $\text{AsO}_3^{3-}$ ,  $\text{HAsO}_3^{2-}$ ,  $\text{H}_2\text{AsO}_3^-$ , and  $\text{H}_3\text{AsO}_3$  [Sorg and Logsdon, 1978].

Arsenic is a redox-sensitive element, and its occurrence, distribution, mobility, and forms depend on several factors, such as pH conditions, reduction-oxidation reactions, distribution of other ionic species, aquatic chemistry and microbial activity. In all these factors, oxidation-reduction potential (Eh) and pH are the most important ones controlling arsenic speciation. Figure 2 illustrates the relationships between Eh, pH and aqueous arsenic species.



**Figure 2** The Eh-pH diagram for arsenic at 25 °C and 1 atm, with total arsenic  $10^{-5}$  mol/L and total sulfur  $10^{-3}$  mol/L; solid species are indicated in parentheses in crosshatched area [Shih, 2005].

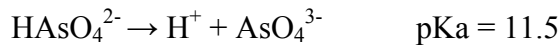
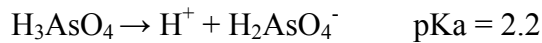
Under oxidizing conditions,  $\text{HAsO}_4^{2-}$  is dominant at higher pH,  $\text{H}_2\text{AsO}_4^-$  predominates at pH less than 6.9, and  $\text{H}_3\text{AsO}_4$  is dominant in extremely acidic conditions [Shih, 2005]. Under anoxic conditions, arsenite is stable, with nonionic ( $\text{H}_3\text{AsO}_3$ ) and anionic ( $\text{H}_2\text{AsO}_3^-$ ) species dominant below and above pH 9.22, respectively. In the presence of sulfides, precipitation of realgar ( $\text{As}_2\text{S}_2$ ) or orpiment ( $\text{As}_2\text{S}_3$ ) may remove soluble arsenite and exert considerable control over trace arsenic levels [Ferguson and Gavis, 1972].

It has been found that dissolved arsenate and arsenite species simultaneously exist in many contaminated groundwaters. Although it is widely believed that arsenate is the major species in groundwater, there is increasing evidence indicating that arsenite might be more prevalent than has been previously thought since groundwater is often reducing (negative Eh

value) [Shih, 2005]. In reducing waters, arsenite is found in some form of arsenious acid which ionizes according to the equations [Kartinen and Martin, 1995]:



In oxygenated waters, generally surface waters, arsenate should strongly dominate over arsenite – at least on the basis of thermodynamic [Cullen and Reimer, 1989]. Pentavalent arsenic is normally found in water as arsenic acid which ionizes according to the equations [Kartinen and Martin, 1995]:



Arsenite and arsenate acid-base reactions can be assumed to occur instantaneously; however, time periods for the changes between oxidation states are uncertain in natural waters. For instance, the conversion of arsenite to arsenate in oxygenated water is thermodynamically favored, but the rate of the transformation may take days, weeks or months, depending on the specific conditions. Strong acidic or alkaline solutions, the presence of copper salts, carbon, unknown catalysts and higher temperatures can increase the oxidation rate. The presence of manganese oxide, chlorine, permanganate and other oxidants can directly transform arsenite to arsenate in the absence of oxygen. The reduction of arsenate to arsenite in anaerobic conditions

may require bacterial mediation since the conversion is chemically slow [Edwards, 1994; Jiang, 2001].

### **1.1.3 Health Impacts of Arsenic**

#### **1.1.3.1 Regulations**

Due to the carcinogenicity of some arsenic compounds, regulatory agencies have established the maximum contaminant level for arsenic in drinking water. The objective is to reduce arsenic exposure to a level as close to zero as possible, considering its health effects and toxicology, occurrence, human exposure, feasibility of the treatment technology, availability of analytical techniques to quantify the lower levels of arsenic, and estimated risk for cancer as a consequence of long term exposure [Viraraghavan et al., 1999].

The World Health Organization (WHO) established an allowable limit of 0.2 mg/L in 1958, and the limit was lowered to 0.05 mg/L in 1963. The United States Public Health Service (1962) recommended a maximum concentration of 0.01 mg/L and the maximum permissible limit of 0.05 mg/L was established for arsenic in public water supplies [Ferguson and Gavis, 1972].

In 1974, the Safe Drinking Water Act (SDWA) introduced maximum contaminant levels (MCL) as national drinking water standards, and the Environmental Protection Agency (EPA) was required to periodically revise the standard. Depending on the standards established by Public Health Service in 1942, the EPA regulated the maximum arsenic level of 50 µg/L in drinking water in 1975. Although WHO adopted the same 50 µg/L recommendation in 1984, recent studies conducted on the carcinogenicity of arsenic and its long term health effects have prompted reevaluation of the arsenic MCL of 50 µg/L. In 1993, WHO lowered the recommended

arsenic level to 10  $\mu\text{g/L}$ , and in 2002, EPA published a revised standard to set the new MCL for arsenic at 10  $\mu\text{g/L}$  [Ning, 2002; Chwirka et al., 2004].

### **1.1.3.2 Toxicity**

Arsenic is considered to be an essential element, but many arsenic compounds are known to be toxic [Bissen and Frimmel, 2003a]. The lethal dose for adults is 1-4 mg As/kg body weight. Humans are exposed to arsenic from air, food, and water. The concentration of arsenic in air is usually only a few ng As/m<sup>3</sup>, and estimated average in the United States is 0.006  $\mu\text{g/L As/m}^3$ . Food is an important source of arsenic. According to the studies in Canada, the arsenic content of many foods is mainly inorganic (typically 65-75 percent), except for fish, fruits and vegetables. The differences in eating habits significantly affect inorganic arsenic intake since some types of foods contain much higher arsenic levels. For instance, marine crabs, lobster, and shrimp contain about 10-40 mg As/kg, while pork, beef, and freshwater fish have arsenic levels less than 1 mg As/kg [Pontius et al., 1994].

The most important source of arsenic exposure is ingestion of drinking water, and the arsenic levels are generally highest in groundwater, especially where geochemical conditions favor the dissolution of arsenic [Pontius et al., 1994]. In six districts of West Bengal, India, the arsenic levels in groundwater, where the source of arsenic is geological, have been found above the maximum allowable limit (50  $\mu\text{g/L}$ ). A survey of groundwater supplies in Halifax county (Nova Scotia, Canada) revealed that the arsenic contamination was in excess of 500  $\mu\text{g/L}$  in at least 10% of the samples and 23% of the samples contained arsenic higher than 250  $\mu\text{g/L}$  [Viraraghavan et al., 1999].

Arsenic forms both organic and inorganic compounds, and the inorganic compounds are more toxic than the organic compounds. The toxicity of arsenite, the trivalent inorganic species,



is higher than the toxicity of arsenate, the pentavalent species [Sorg and Logsdon, 1978]. The toxicity scale of arsenic can be presented in that decreasing order: arsine > inorganic As(III) > organic As(III) > inorganic As(V) > organic As(V) > arsonium compounds and elemental arsenic [Pontius et al., 1994]. In addition to oxidation state and chemical form of arsenic, its solubility in the biological media also affects the toxicity of arsenic [Viraraghavan et al., 1999].

To evaluate the health protection provided by the current arsenic MCL, the health effects of arsenic are quantified considering acute toxicity (relatively high exposures for a short time period resulting in effects other than cancer), chronic toxicity (relatively low exposures for a long period of time causing diseases other than cancer), and cancer effects (the risk of cancer at different exposure levels) [Pontius et al., 1994]. Arsenical poisoning involves four major areas: (1) digestive system, (2) skin, (3) nervous system, (4) motor paralysis, which causes death upon paralysis of the heart [Gulledge and O'Connor, 1973].

Arsenic in water supplies causes chronic poisoning rather than acute poisoning; therefore, chronic toxicity of arsenic is of main concern in the evaluation of health significance of arsenic in drinking water [Ferguson and Gavis, 1972]. Chronic arsenic poisoning leads to non-specific symptoms including chronic weakness, loss of reflexes, gastritis, anorexia, weight loss, hair loss, and long term exposure results in hyperpigmentation, cardiovascular diseases, disturbance in nervous systems and circulatory disorders. The common signs of acute arsenic poisoning are vomiting, dryness of the mouth and throat, muscle cramps, circulatory disorders, nervous weakness, hallucinations, and fatal shock can develop due to renal failure [Bissen and Frimmel, 2003a].

The most significant consequence is the cancer effect in various organs, especially in the skin, lung, kidney, and bladder. Therefore, arsenic has been classified as human carcinogen and is of public concern due to its natural origin and widespread usage in industry [Shih, 2005].

## **1.2 ARSENIC REMOVAL BY CONVENTIONAL TREATMENT PROCESSES**

The conventional treatment processes for removal of arsenic can be classified based on the mechanisms involved: (1) precipitation, (2) adsorption, (3) ion exchange, (4) membrane technology. Precipitation is a process which involves the combination of anions and cations, and adsorption is a technology that uses materials having a strong affinity for dissolved arsenic. Ion exchange process exchanges arsenic anions for chloride or other anions at active sites on the resin. Membrane technology removes arsenic based on the physical principals by allowing water to pass through special filter media and retaining impurities in water [Shih, 2005].

The USEPA determined seven arsenic removal technologies as the best available technologies (BATs), and these technologies with maximum arsenic removal rates are given in Table 1 [Wickramansinghe et al., 2004].

**Table 1** Best Available Technologies (BATs) and their arsenic removal efficiency. Percent removal figures are for arsenate removal [Wickramasinghe et al., 2004].

<b>Treatment technology</b>	<b>Maximum removal, %</b>
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

Chwirka et al. [2000] evaluated three treatment technologies; ion exchange (IX), iron hydroxide coagulation followed by microfiltration (C/MF), and activated alumina (AA), to remove arsenic from groundwater in Albuquerque, NM. The factors considered in this study included capital costs, operation and maintenance costs, management of hazardous chemicals used during the process, volume and management of residuals, and the amount of water wasted by each treatment option. The C/MF process was found to have the lowest capital and annual operation & maintenance costs amongst these three processes. Chen et al. [1999] also performed a cost analysis to select the lowest-cost arsenic treatment option, and modified conventional treatment was determined as the most cost-effective treatment.

Oxidation, coagulation/precipitation, and adsorption are the most commonly used technologies for the removal of arsenic from surface and groundwaters, achieving residual concentrations of arsenic in the range of 5-10 µg/L against the influent arsenic concentrations in the range of 10-500 µg/L [Jiang, 2001]. There are three mechanisms which may occur during arsenic removal:

- Precipitation (formation of insoluble compounds)
- Coprecipitation (incorporation of soluble arsenic species into precipitates)
- Adsorption (formation of surface complexes between soluble arsenic and external surfaces of insoluble metal hydroxides)

Among all these mechanisms, direct precipitation is of the least importance in arsenic removal, while coprecipitation and adsorption are both active removal mechanisms [MIT, 2001].

Adsorption-coprecipitation with hydrolyzing metals, especially iron(III) is mostly used to remove soluble arsenic [AWWA Committee Report, 1993]. According to several arsenic removal studies, there was no difference in the amount of arsenate adsorbed by ferric chloride or ferric sulfate. Thus, the presence of sulfate ions had little effect on arsenic removal by iron compounds [Han et al., 2002; Wickramasinghe et al., 2004].

Many studies have shown that iron, as a coagulant and as an adsorbent, can remove arsenic efficiently. In water treatment, hydrous ferric oxides can be precipitated in situ during coagulation with iron salts or during oxidation of groundwaters containing iron(II) [Wilkie and Hering, 1996]. Due to its high adsorption capacity, iron oxide-coated sand was recently determined to be a promising technology to achieve very low arsenic levels [Joshi and Chaudhuri, 1996; Thirunavukkarasu et al., 2003, 2005].

Saha et al. used conventional precipitation (alum and iron salt) and adsorption (with various adsorbents) methods for arsenic removal, and observed that iron salt as a coagulant and hydrous granular ferric oxide as a fixed bed adsorbent could remove arsenic efficiently. In their study, iron was found to be more preferable than alum since all the ferric coagulant added forms particulate  $\text{Fe}(\text{OH})_3$ . More than 95% removal of arsenic was achieved using 10 mg/L ferric sulfate at neutral pH for the initial arsenic concentration of 100  $\mu\text{g/L}$ . Hydrous granular ferric

oxide was shown to be an excellent adsorbent for arsenic removal from contaminated drinking water with 99% removal of As(V) and 85% removal of As(III) at neutral pH using the initial arsenic concentration of 1 mg/L [Saha et al.].

### **1.2.1 Coagulation Processes**

Coagulation includes all mechanisms in the overall process of particle growth and aggregation, including in situ coagulant formation, chemical particle destabilization and physical inter-particle contacts. The advantage of coagulation process is that the coagulants (ferric salts) are easily available, cheap, not hazardous and easy to handle [Bissen and Frimmel, 2003b].

The coagulation/filtration process has traditionally been used to remove solids from drinking water supplies; however, it can also remove dissolved species by adsorption onto metal hydroxide particles, which are produced by the addition of metal salts such as ferric chloride and ferric sulfate. Major components of a basic coagulation/filtration facility are chemical feed systems, mixing equipment, basins for rapid mix, flocculation, settling, filter media, filter backwash facilities, and sludge handling equipment [EPA, 2000].

Edwards [1994] conducted bench-scale coagulation studies and revealed that 90 $\mu$ M (5 mg/L) Fe removed higher than 80% arsenite with initial concentration of 300 ppb in the pH range of 5.5 to 8.0. The author also predicted arsenite and arsenate removals with 50 ppb initial concentrations using a diffuse-layer adsorption model and previous data. Arsenate removals were around 100% at neutral pH when 5 mg/L or higher FeCl<sub>3</sub> doses were used, while arsenite removals were about 70% and 89% at neutral pH when 5 mg/L and 20 mg/L FeCl<sub>3</sub> doses were applied, respectively.

Wickramansinghe et al. [2004] investigated the removal of arsenic by coagulation and filtration using groundwater from a city in southern Colorado, U.S.A. and from Sonargaon, Bangladesh. The bench-scale experiments indicated that coagulation with ferric ions followed by filtration is effective for arsenic removal, but the actual efficiency is mostly dependent on raw water quality. Han et al. [2003] also studied arsenic removal by modified coagulation/filtration using groundwater from a small rural city in Colorado, and achieved residual arsenic concentrations lower than 2 ppb with 6 mg/L ferric ion dose at an initial pH of 6.8 for the initial arsenic concentration of 68 ppb.

Pilot tests were conducted in Albuquerque, NM, Naval Air Station, NV, and in El Paso Water Utility, Tx to evaluate the efficiency of arsenic removal from groundwater using coagulation/microfiltration process, and arsenic leakage was reduced to levels below the detection limits when proper pH and  $\text{FeCl}_3$  dose are maintained [Chwirka 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 determined 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 (pH=7.3) or a dose of 1.9 mg/L Fe coupled with sulfuric acid addition to lower the pH to 6.4 for the initial arsenate concentration of 40 ppb.

After performing pilot-scale tests, Cheng et al. [1994] indicated that 0.22 ppb residual arsenic concentration could be achieved by enhanced coagulation when a dose of 10 mg/L  $\text{FeCl}_3$  is used for removal of arsenic with an influent concentration of less than 5 ppb. Scott et al. [1995] evaluated the removal of arsenic in a full-scale conventional treatment plant, and showed

that arsenic removal was 81 to 96 percent when the source water having initial arsenic concentration of 2.1 µg/L was treated with 3 to 10 mg/L ferric chloride.

### **1.2.2 Fe-Mn Oxidation Technology**

Arsenic can be immobilized through adsorption-coprecipitation with iron and manganese hydroxides and mobilized when these solids are dissolved under reducing conditions [Jiang, 2001]. Therefore, in groundwater containing substantial arsenic, iron(II) and manganese(II) also tend to be present in relatively high concentrations [Chen et al., 1999].

Iron-Manganese (Fe-Mn) oxidation is commonly used by facilities using groundwater as a raw water source. The oxidation process used for the removal of iron and manganese leads to the formation of hydroxides that remove soluble arsenic by precipitation or adsorption reactions [EPA, 2000]. The production of oxidized Fe-Mn species and subsequent precipitation of hydroxides are similar to an in situ coagulant addition, with the quantity of Fe or Mn removed translating into a “coagulant dose”. No arsenic removal is expected by soluble Mn(II) or Fe(II) [Edwards, 1994].

Fe(II) salts which are oxidized to Fe(III) during the water treatment process have been used for the removal of arsenic [Bissen and Frimmel, 2003b; Hug and Leupin, 2003], and this is a promising technology to remove arsenic from groundwaters in which reduced forms of iron, i.e. ferrous ions, are dominant. The major steps in the chemical precipitation process are: (1) the oxidation of soluble iron and any As(III), (2) the removal of As(V) by iron hydroxides through adsorption and/or coprecipitation [Fields et al., 2000]. Borho and Wilderer [1996] conducted pilot-scale filtration experiments to remove arsenite from contaminated groundwater, and concluded that iron(II) in combination with oxygen and iron(III) are comparable in terms of arsenic binding capacity.

Even based on the estimates of adsorption alone, arsenic removal during Fe(II) precipitation is highly efficient. Removal of 1 mg/L as Fe(II) is predicted to be capable of sorbing 83 percent of a 22 µg/L arsenate initial concentration. It was reported that 2mg/L Fe(II) removed 60 percent of a 188 µg/L arsenate influent by oxidation and precipitation [Edwards, 1994].

An in-situ process, in which groundwater was aerated and then infiltrated in the subsurface, was developed to remove arsenic from groundwater containing arsenic, iron and manganese, and it was observed that arsenic adsorbs to Fe(OH)<sub>3</sub> and MnO<sub>2</sub> particles formed in the subsurface [Bissen and Frimmel, 2003b]. However, when the effectiveness of iron oxides and manganese oxides is compared, soluble arsenate removals by iron oxides are expected to be very significant. If roughly equal concentrations of iron and manganese were removed, the effects of manganese for arsenic removal could be ignored. It was also suggested that pH is not important in arsenic removal during manganese precipitation [Edwards, 1994].

McNeill and Edwards [1995] obtained arsenic profiles from full-scale treatment (coagulation, Fe-Mn oxidation, or softening) plants to survey arsenic removal. Soluble arsenate removal efficiency was demonstrated to be highly dependent on Fe(II) oxidation and Fe(OH)<sub>3</sub> precipitation during Fe-Mn oxidation process. Insignificant soluble arsenate removal was observed during Mn(II) oxidation-precipitation, whereas oxidation of Fe(II) (>1.5 mg/L) achieved 80-95 percent arsenic removal.

It has also been observed that the iron ores are always enriched with arsenic due to high adsorptive capacity of hydrous iron oxides, whereas manganese ores lacks arsenic. The positive surface charge of iron oxide which preferentially adsorbs anions and the negative charge of



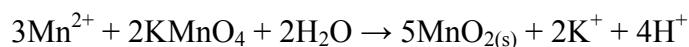
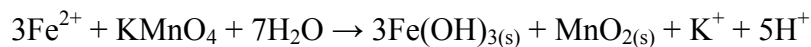
manganese oxide which adsorbs cations have been cited as an explanation for the distribution of arsenic [Ferguson and Gavis, 1972].

### 1.2.2.1 Oxidation of Iron and Manganese

Aqueous iron (Fe) and manganese (Mn) have important roles in the limnological cycles of some key elements in water supplies and water treatment processes [AWWA Committee Report, 1993]. Typical values of dissolved iron and manganese in groundwater are less than 10 mg/L and 2 mg/L, respectively. Since Fe and Mn cause problems in drinking water related to aesthetic concerns such as water discoloration, metallic taste, odor, turbidity, staining of laundry and plumbing fixtures, secondary standards of 0.3 and 0.05 mg/L have been established for Fe and Mn, respectively [Lemley et al., 1999].

Oxidation and precipitation is the most common method to remove iron and manganese from drinking water. Oxidation of Mn(II) by potassium permanganate (KMnO<sub>4</sub>), chlorine dioxide (ClO<sub>2</sub>), and ozone (O<sub>3</sub>) is very rapid provided that pH is between 5.5-9.0 and temperature is higher than 5°C. Oxidation rates increase as solution pH or temperature increases. Similarly, Fe is oxidized almost instantaneously by these oxidants, and it can be readily oxidized by simple aeration when the pH is above 6.0. MnO<sub>2(s)</sub> adsorbs Mn(II) and catalyzes its oxidation, thus increase the overall removal of Mn [AWWA Committee Report, 1993].

In water treatment, potassium permanganate (KMnO<sub>4</sub>) is used primarily to control taste and odor, to remove color, to control biological growth in treatment plants, and to remove iron and manganese. The reactions for the oxidation of iron and manganese are:

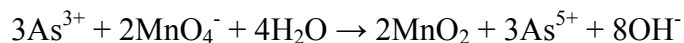


According to the stoichiometry, the potassium permanganate dose required for oxidation is 0.94 mg/mg iron and 1.92 mg/mg manganese; however, in practice, the actual amount of permanganate used for the oxidation is less than the indicated dosage. The possible reason is the catalytic influence of MnO<sub>2</sub> on the reactions. The oxidation time varies generally from 5 to 10 minutes, provided that pH is over 7.0 [EPA Guidance Manual, 1999].

### 1.2.2.2 Oxidation of Arsenite

Arsenate is much more effectively removed than arsenite since arsenic(V) exists in natural waters as monovalent or divalent anions (H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, HAsO<sub>4</sub><sup>2-</sup>) whereas arsenic(III) is predominantly in neutral form (H<sub>3</sub>AsO<sub>3</sub>) [Ferguson and Gavis, 1972]. Unlike arsenate anions, the nonionic arsenite does not adsorb strongly to mineral surfaces [Hug and Leupin, 2003]. Therefore, arsenic removal processes often includes an oxidation step to convert arsenite to arsenate, especially in treatment of groundwaters in which arsenite is the dominant species. Oxidation can be simply the addition of oxygen, i.e. aeration, or it may involve strong oxidizers such as chlorine, hypochlorite, ozone, permanganate, and hydrogen peroxide. The most promising oxidants are permanganate and solid manganese dioxide since they produce no harmful by-products and are easy to apply [Borho and Wilderer, 1996].

Potassium permanganate is one of the most common oxidants applied to remove arsenic in groundwater systems that employ filtration. In order to oxidize 1 part of soluble arsenic, 1.26 parts of potassium permanganate are required. The reaction of arsenic oxidation by permanganate is defined as follows [Carus Chem. Co., 2001]:



Shen [1973] conducted oxidation and coagulation studies with potassium permanganate and chlorine and indicated that both oxidants significantly increased arsenic removal from well-water when compared to arsenic removals in coagulation process alone. The experiments performed with aeration only, aeration combined with coagulation, and aeration combined with oxidation/coagulation showed that aeration had no apparent effect on arsenic removal [Shen, 1973].

Borho and Wilderer [1996] examined the potential of coupled oxidation (with potassium permanganate or manganese dioxide coated quartz sand filter grains), and precipitation (with iron(III) or iron(II) activated by oxygen) processes to eliminate arsenite from contaminated groundwater and to improve the filterability of arsenic-loaded particles in pilot-scale experiments. The results showed that the use of oxidant potassium permanganate causes filtration problems although it is highly effective for the oxidation of arsenite. The oxidation by-product manganese dioxide was only partially removable through sand filtration, and this behavior was most significant when iron(II)/oxygen was used as precipitant.

Bissen and Frimmel [2003b] reported that 19% of arsenite of 69  $\mu\text{g/L}$  was oxidized with pure oxygen in 15 minutes. They also stated that purging groundwater with air and pure oxygen oxidized about 55 percent of arsenite within 5 days.

Although natural oxidation of arsenite to arsenate in the presence of dissolved oxygen is a very slow process, solid-liquid interfaces can catalyze most chemical reactions, including arsenic oxidation. Ferric-iron can facilitate the conversion of arsenite to arsenate both by catalytic effects and by direct reaction [Sarkar and Rahman]. Hug and Leupin [2003] studied the iron-catalyzed oxidation of arsenic(III) by oxygen, and revealed that arsenite was not measurably oxidized by oxygen, dissolved Fe(III), or iron (hydr)oxides as single oxidants; however, partial or complete

oxidation of arsenite was observed in parallel to the oxidation of 20-90  $\mu\text{M}$  Fe(II) by oxygen. Hering et al. [1996] observed constant percent removals of arsenic independent of initial concentrations in coagulation studies; however, increased percent adsorptions were achieved at low initial arsenite concentrations which may be attributed to oxidation of arsenite at ferric hydroxide surface or preferential adsorption of arsenite to strong binding sites on the ferric hydroxide surface.

Manganese oxides have also been shown to oxidize arsenite to arsenate, and it has been observed that  $\delta\text{-MnO}_2$ , amongst the various manganese dioxide modifications, leads to a faster oxidation of arsenite in a time scale of minutes. The oxidation of arsenite to arsenate by manganese dioxide ( $\text{H}_3\text{AsO}_3 + \text{MnO}_2 \leftrightarrow \text{HAsO}_4^{2-} + \text{Mn}^{2+} + \text{H}_2\text{O}$ ) results in the release of  $\text{Mn}^{2+}$  ions. These cations adsorb onto the manganese dioxide and give it a positive surface charge that leads to enhancement in arsenate removal present initially and produced after arsenite oxidation [Bajpai and Chaudhuri, 1999].

Driehaus et al. [1995] also indicated that  $\delta\text{-MnO}_2$  is efficient in arsenite oxidation and adsorption of arsenate, with low soluble manganese releases, and Bissen and Frimmel [2003b] reported that the oxidation of arsenite by  $\text{MnO}_2$  increases the amount of arsenate adsorbed by  $\text{MnO}_2$  surfaces and the adsorption capacity can be enhanced by altering the surface of  $\text{MnO}_2$  particles. Viraraghavan et al. [1999] showed that arsenite concentrations can be reduced from 200  $\mu\text{g/L}$  to below 25  $\mu\text{g/L}$  using manganese greensand system as long as iron to arsenic ratio is 20:1.

### 1.2.3 Effects of Water Quality Parameters on Arsenic Removal

Coagulation and Fe-Mn removal processes can convert soluble arsenic into insoluble reaction products, and thus facilitate their removal from water by filtration or sedimentation. Since the effectiveness of arsenic removal process depends on the removal of soluble arsenic and of the resulting particulates, problems with either process can limit arsenic removal [Edwards, 1994]. Therefore, the impact of water quality parameters on process efficiency should be considered carefully.

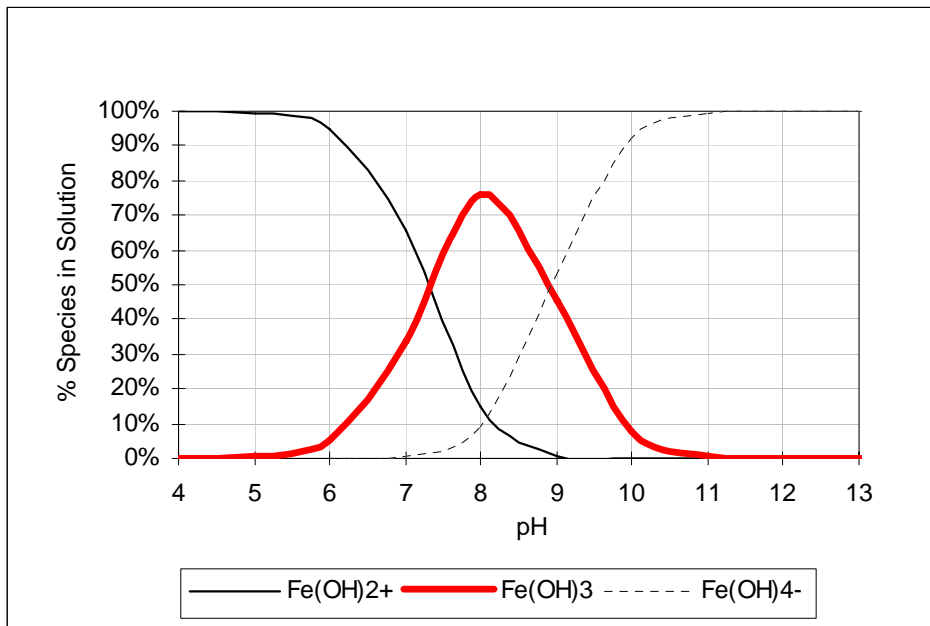
#### 1.2.3.1 pH

The predominance of arsenic(V) acid,  $H_3AsO_4$ , and arsenous(III) acid,  $HAsO_2$ , in natural waters is a significant issue when considering arsenic removal mechanisms. It is apparent that at pH of 7 to 8, arsenic acid is extensively ionized as divalent ion, while arsenous acid remains largely unionized. Due to ionic charge, arsenate can be removed more easily than arsenite [Ning, 2002].

In aerated water, arsenite tends to be oxidized to arsenate, especially at alkaline pH, and arsenate can be reduced to arsenite at low pH ranges [Pontius et al., 1994]. Arsenite removal is expected to be effective in the pH range of 8-11, while arsenate removal is efficient in the pH range of 4-7 [AWWA Committee Report, 1993].

The pH range of the feed water is also significant for the effectiveness of iron oxide particles to remove arsenic. When an iron salt, for instance  $FeCl_3$ , is added to water, it hydrolyzes to form ferric hydroxide [ $Fe(OH)_{3(s)}$ ], which has a net positive charge on the surface of the particles formed. The net positive charge of  $Fe(OH)_{3(s)}$  particles changes depending on the water pH, and as the pH of feed water decreases, the number of positively charged sites on the  $Fe(OH)_{3(s)}$  particles increases. According to ferric hydroxide speciation diagram (Figure 3), a pH around 7.3 is required for  $Fe(OH)_{3(s)}$  particles to have a net positive charge. Since arsenate is an

anion and will adsorb onto positively charged  $\text{Fe}(\text{OH})_{3(s)}$  particles by surface complexation, arsenic removal should be optimized at a pH of 7.3 or less. Arsenic removal may also occur at higher pH levels, but not as effectively as at lower pH values [Chwirka et al., 2004]. It was also reported that better arsenic removal at low pH values is due to decreased concentration of hydroxide anion, which is an excellent ligand that strongly competes with arsenic for adsorption sites [Ghurje et al., 2004].



**Figure 3** Ferric hydroxide speciation (the species are  $\text{Fe}(\text{OH})_{2+}$ ,  $\text{Fe}(\text{OH})_3$  and  $\text{Fe}(\text{OH})_{4-}$ , respectively) [Chwirka et al., 2004].

Increasing coagulation pH was reported to decrease arsenic removal percentage, and optimum pH for arsenic removal with ferric chloride was determined to be 7.0 [Jiang, 2001]. Arsenate adsorption has been shown to decrease with increasing pH in the range of 4-9 [Wickramasinghe et al., 2004] and the decrease is more pronounced at pH values above 8.0 [Gulledge and O'Connor, 1973].

In bench-scale studies, the arsenic removal efficiency from source waters and artificial freshwaters during coagulation with ferric chloride was examined, and approximately 60 percent arsenate removal was observed at higher pH values (particularly at pH 9.0) whereas more than 90 percent arsenic removal was achieved at neutral pH when the source waters were spiked with 20 µg/L arsenate [Hering et al., 1997].

### **1.2.3.2 Fe/As Ratio**

Many studies showed that higher arsenic removal efficiencies can be generally achieved with increased iron concentrations [Gulledge and O'Conner, 1973; Edwards, 1994; Cheng et al., 1994; Scott et al., 1995].

Arsenic adsorption onto ferric hydroxide was investigated for arsenite and arsenate in a pH range of 4-9 at varying iron to arsenic ratios. The extent of arsenite adsorption at pH 4 and 7 was demonstrated to be strongly dependent on total arsenite concentration, and increased adsorption was observed with increasing Fe/As ratios [Wilkie and Hering, 1996].

Sorg and Logsdon [1978] observed that a molar ratio of iron to arsenic of 20 is sufficient for the removal of arsenic in the pH range of 6.1 to 7.2, and Bissen and Frimmel [2003b] reported that a molar ratio of iron to arsenic of 7 is high enough to lower arsenic levels below the current MCL for arsenic of 10 µg/L for raw waters initially containing 50 to 200 µg/L arsenic. Banerjee et al. [1999] achieved soluble arsenic concentrations below 50 µg/L with iron to arsenic ratio of 10 for the type of groundwater studied.

The adsorption and coagulation experiments conducted by Hering et al. [1997] showed similar trends for arsenic removal indicating that adsorption onto freshly precipitated metal hydroxides is an important mechanism during coagulation process and arsenic adsorption become more significant at high iron to arsenic ratios. Mamtaz and Bache performed

experimental studies to evaluate adsorption-coprecipitation with naturally occurring iron in groundwaters. They also revealed that adsorption may be the dominant mechanism when Fe/As weight ratio is equal to or greater than 10 and observed that the effectiveness of arsenite removal is strongly influenced by Fe/As ratio [Mamtaz and Bache].

### **1.2.3.3 Initial As(III)/As(V) Concentration**

The valence and speciation of soluble arsenic are very significant in evaluating arsenic removal since conventional treatment technologies used for arsenic removal rely on adsorption and coprecipitation of arsenic to metal hydroxides [Fields et al., 2000].

In many studies, the extent of arsenic adsorption by iron oxides was reported to be more dependent on its oxidation state than pH within the pH range of 5.5-7.5 [Wickramasinghe et al., 2004]. The removal of arsenite by iron salts was found to be less effective and more strongly dependent on groundwater composition than the removal of arsenate [Shen, 1973; Sorg and Logsdon, 1978; Edwards, 1994; Hering et al., 1997; Jiang, 2001]. If any arsenite is present in the raw water, converting poorly sorbed arsenite to arsenate is the most cost-effective way of improving arsenic removal [Borho and Wilderer, 1996; McNeill and Edwards, 1997].

Ghurye et al. [2004] conducted bench-scale tests to determine the effects of arsenic oxidation state (+3 versus +5) in the iron coagulation and direct microfiltration process, and concluded that arsenate was better removed than arsenite in the pH range of 5.5-8.6, and the initial arsenic concentration in the range of 10-44  $\mu\text{g/L}$  had no effect on the percentage of arsenic removal. Hering et al. [1996] observed better removals with arsenate than with arsenite in both coagulation and adsorption studies. Complete removal of arsenate for the initial concentration of 20  $\mu\text{g/L}$  was observed for coagulant doses above 5 mg/L  $\text{FeCl}_3$  at neutral pH; however, incomplete removal of arsenite was observed under the same range of experimental conditions.



The arsenite removal was about 40% when coagulated with 1 mg/L Fe(III), while about 90% arsenate removal was observed for the same initial arsenate concentration (20 µg/L) and for the same coagulant dose. The highest arsenite removal was around 80% when coagulated with 20 mg/L FeCl<sub>3</sub> at pH of 7.0.

Sorg and Logsdon [1978] reported that the initial arsenic concentration significantly affects the removal of arsenic. For initial arsenate concentrations to about 1 mg/L, a dosage of 30 mg/L of either alum or ferric sulfate achieved higher than 95% arsenate removal; however, the percent removal decreased with increasing concentrations. For initial arsenite concentrations greater than 0.1 mg/L, neither of the coagulants dosed at 30 mg/L could remove arsenite below 0.05 mg/L unless arsenite is preoxidized with chlorine to arsenate.

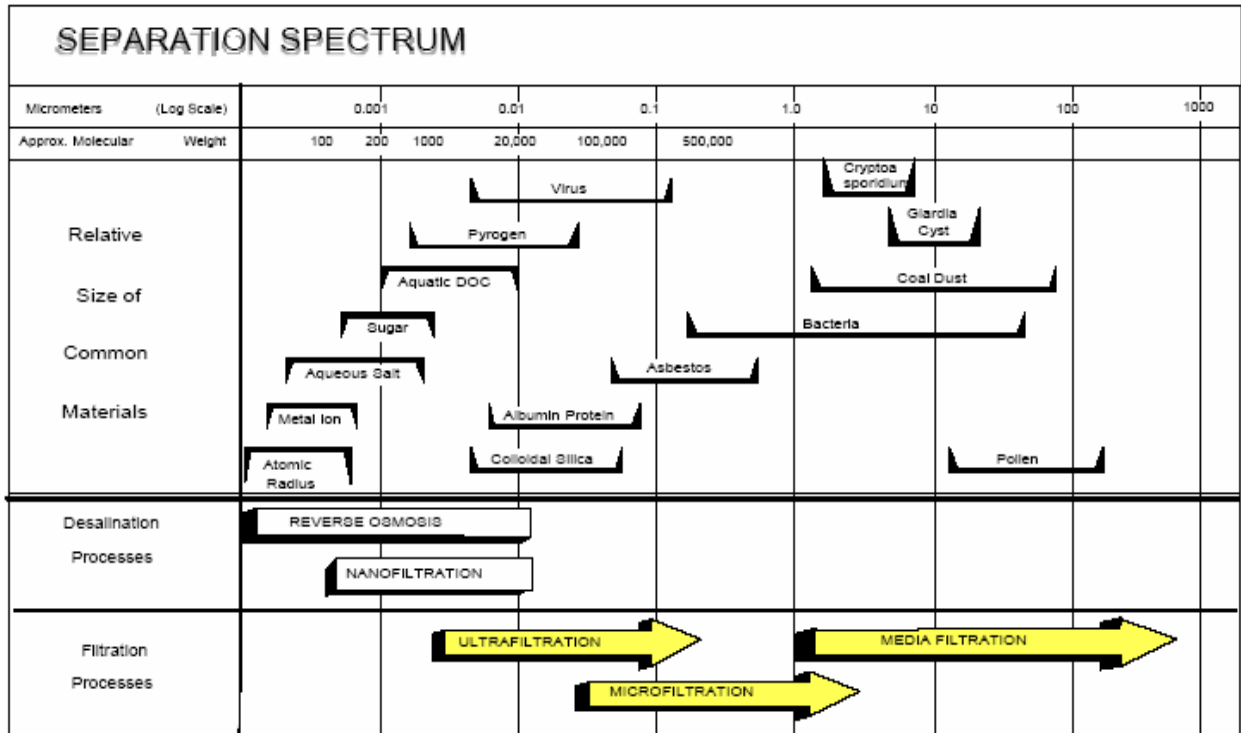
Edwards [1994] evaluated the effects of pH, coagulant dosage, and initial arsenic concentration on arsenate and arsenite removal according to the predictions based on existing data and the use of a diffuse-layer model. At coagulant doses higher than 5 mg/L as FeCl<sub>3</sub>, sorptive removal of arsenate was a relatively strong function of pH and lesser function of coagulant dose or initial arsenate concentration. In contrast, the removal of nonionic arsenite was not dependent on pH, and more strongly influenced by initial concentration of arsenite and coagulant dosage.

Hering et al. [1996] showed that during coagulation experiments with 4.9 mg/L ferric chloride, both arsenite and arsenate removal was nearly constant although the initial arsenic concentrations varied from 2.0 to 100 µg/L. Cheng et al. [1994] also achieved nearly constant arsenic removal percentages with varying influent arsenate spikes from 2.2 to 128 µg/L during the coagulation with 30 mg/L ferric chloride.

### **1.3 ARSENIC REMOVAL BY MEMBRANE PROCESSES**

A membrane process can be defined as splitting a feed stream by a membrane into retentate (or concentrate) and a permeate fraction. Pressure-driven membrane processes use the pressure difference between the feed and permeate side as the driving force for the movement of constituents across the membrane. Particles and dissolved components are retained based on various properties including size, shape, and charge [Bruggen et al., 2003].

Pressure-driven membranes are generally classified according to the pore size into four categories: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). The pore size classification ranges of membrane processes are given in Figure 4. High-pressure processes, i.e. NF and RO, primarily remove constituents through chemical diffusion, while low-pressure processes, i.e. MF and UF, primarily remove constituents through physical sieving. The advantage of NF and RO is the tendency of removing broader range of constituents when compared to MF and UF; however, the increase in energy requirement and decrease in recovery are main disadvantages of these processes [EPA, 2000; Shih, 2005].



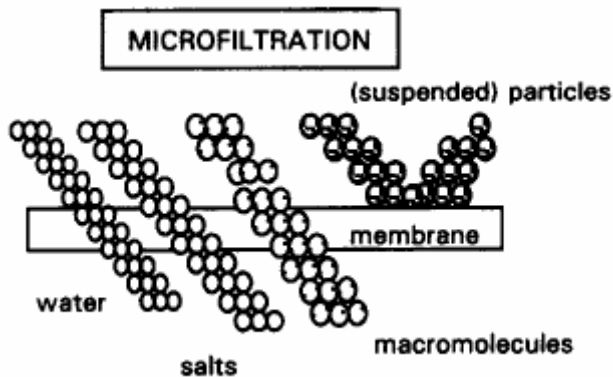
**Figure 4** Pressure Driven Membrane Process Classification [EPA, 2000].

### 1.3.1 Application of Microfiltration in Water Treatment

Membrane technologies have started to play an important role in the treatment of water and wastewater. Several factors, including recent increases in the stringency of water quality regulations that can not be effectively met by conventional treatment processes, decreases in high quality freshwater supplies, better membrane performances and lower costs as a result of technological advances, and development of new applications for membrane processes, have led to the widespread use of membranes [Jacangelo et al., 1997].

Due to high recovery (up to 99%) and low energy requirement, microfiltration process has been used widely in water treatment. MF membranes have the largest pore size, ranging from 0.1  $\mu\text{m}$  to 10  $\mu\text{m}$ . The smallest pore sizes correspond to the size of suspended solids, colloids,

and bacteria. The sieving mechanism of microfiltration process is illustrated in Figure 5 [Bruggen et al., 2003].



**Figure 5** Schematic representation of microfiltration [Bruggen et al., 2003].

Dead-end microfiltration with periodic backwashing is an effective method to remove particles, turbidity, protozoa, and bacteria and is preferred in the municipal applications due to reduction in energy consumption and increase in water recovery. However, the deposition of materials on the membrane surface and in pores, i.e. membrane fouling, is the major impediment for its application. Employing a pretreatment is one approach to increase particle size and to reduce fouling as well as to improve the filtered water quality [Xu et al., 2004].

### 1.3.1.1 Membrane Fouling

During the last 40 years, interest in membrane processes for water and wastewater treatment has increased, and membrane technology constitutes a wide area for research and development effort nowadays. However, fouling, which is the reduction in flux with time, is the most challenging issue in the application of this treatment method. Specific chemical or physical interactions between the various macrosolutes/particles and the membrane are the reason for membrane

fouling, and three major fouling mechanisms are reported as the build-up of a cake layer, pore plugging, and adsorption [Mosqueda-Jimenez et al., 2004].

Particulate matter, which is larger than the nominal pore size of the low-pressure (MF and UF) membranes, forms a cake at the membrane surface. Dissolved matter, some of which can pass through the membrane, causes fouling by various mechanisms such as cake formation, pore clogging, or adsorption within pores that reduces effective size of the pore diameter. Howe and Clark [2002] investigated the fouling of low-pressure membranes by natural waters, and concluded that 94 percent of the flux decline was due to dissolved organic matter whereas only 6 percent was due to particulate matter.

Commercial pressure-driven membranes are available in many types of material and in various configurations. The chemistry of membrane material is an important issue especially for contaminant removals through adsorption. Membrane configuration and pore size are the factors influencing both rejection properties and operational properties to a great extent. Source water quality and water temperature also plays an important role in rejection characteristics of membrane [EPA, 2000]. Operating conditions such as pressure, backwash method, dead-end or cross-flow mode, are other factors affecting membrane performance [Yuasa, 1998].

The particle concentration, particularly after a pretreatment such as coagulation, flocculation, and oxidation, greatly affects membrane fouling rate. When the particle concentration is increased, more particles are brought in contact with the membrane surface and more particles may deposit on the membrane surface, resulting in fouling.

Chemical oxidation as a pretreatment method, e.g., addition of potassium permanganate, has been used in conjunction with microfiltration (MF) membranes for the removal of dissolved iron and manganese in groundwater sources. Ellis et al. [2000] performed lab-scale studies by

using polyethersulfone MF flat-sheet membrane to remove iron and manganese oxide suspensions from groundwater which was previously oxidized by aeration and potassium permanganate addition. The particle size analysis revealed that both iron and manganese oxide particle sizes range from 1.5 to a maximum of 50  $\mu\text{m}$ , which means that MF membranes with an absolute porosity lower than 1  $\mu\text{m}$  should be an effective separation barrier for the removal of iron and manganese oxide particles. This process removed metals in suspension below the MCL for iron and manganese using 0.2  $\mu\text{m}$  pore size with very stable flux, and the fouling was mostly due to oxide particle deposition on the membrane surface.

To understand the fouling issue, researchers have studied the significance of membrane properties such as hydrophobicity, charge, and morphology; solution properties such as pH, ionic strength, and calcium concentration; and organic matter properties such as hydrophobicity, molecular weight, and charge density. Hydrophobic membranes were found to be more prone to fouling than hydrophilic membranes. It has also been noted that both organic and inorganic compounds can induce fouling [Howe and Clark, 2002; Bruggen et al., 2003].

### **1.3.2 Arsenic Removal with Microfiltration**

Membrane processes can remove arsenic-bearing compounds through filtration, electric repulsion, and adsorption. Although size is a very important factor that influences rejection, studies have shown significant rejection of arsenic compounds which are one to two orders of magnitude smaller than membrane pore size. Such observations indicate the presence of removal mechanisms other than physical straining. The chemical characteristics, particularly charge and hydrophobicity, of both membrane material and source water constituents, play an important role in the removal mechanism by membranes [EPA, 2000]. For example, a membrane with a fixed negative charge was found more efficient to remove anionic arsenate than a membrane which is

uncharged, indicating the inhibition of the passage of ions possessing the same charge as the membrane [Brandhuber and Amy, 1998].

Microfiltration can remove particulate forms of arsenic, but this process alone can not provide an efficient arsenic removal unless a considerable percentage of arsenic is in particulate form since MF performance is primarily dependent on pore size.

Brandhuber and Amy [1998] investigated the arsenic size distribution in raw drinking water sources in order to determine the amount of dissolved, colloidal and particulate arsenic in natural waters. In groundwaters, a smaller percentage of particulate/colloidal arsenic was found when compared to surface waters; but, even in groundwaters, approximately 10 to 20 percent of arsenic was in particulate or colloidal form. McNeill and Edwards [1997] also surveyed arsenic speciation in many raw water sources. Particulate arsenic was operationally defined as the metal that can be removed by a 0.45- $\mu\text{m}$ -pore-size filter, and in this study at least 15 percent of the total arsenic was found in the form of particulate arsenic at most plants.

Chen et al. [1999] reported that more than half of the total arsenic could be removed by a filter with a pore size of 0.45  $\mu\text{m}$  at about 30 percent of the facilities treating either surface or groundwater. Furthermore, in extreme cases, as much as 90 percent of the arsenic present in groundwater could be removed by microfiltration or ultrafiltration.

### **1.3.3 Arsenic Removal with Chemical Pretreatment Followed by Microfiltration**

Low-pressure membranes, microfiltration (MF) and ultrafiltration (UF), have been used to remove turbidity, particulate matter, and pathogens, and these membrane filtration systems were the main unit processes with little or no pretreatment. Recently, MF and UF membrane systems have started to be used for the removal of various chemical contaminants such as arsenic, pesticides, taste and odor, iron, and manganese, provided that the contaminants are converted to

a particulate form in a pretreatment step. In addition to increased removal of dissolved contaminants, chemical pretreatment processes can also improve membrane performance by reducing membrane fouling. In the existing conventional water treatment plants, which may involve coagulation, flocculation, solid separation, and filtration, MF and UF membrane systems have replaced sedimentation-filtration or filtration processes due to much higher and more consistent water quality and increased water production in a limited space [Farahbakhsh et al., 2004].

The use of membrane separation is also found more advantageous than conventional clarification techniques since the time required for particle growth is lesser in the former technique. The sub-micron pore size of the filtration membranes requires flocs to grow only to around 2  $\mu\text{m}$  in size in order to be removed from the solution [Judd and Hillis, 2001]. Han et al. [2002] also observed that flocculation followed by microfiltration is significantly better than flocculation followed by sedimentation since microfiltration leads to more rapid and complete arsenic and turbidity removal than sedimentation.

Coagulant dose also impacts the performance of microfiltration systems. It was shown that the conditions for enhanced coagulation (low pH and high coagulant dose) led to the most improved membrane performance, whereas coagulant doses lower than required for enhanced coagulation resulted in membrane fouling higher than without pretreatment [Farahbakhsh et al., 2004].

Brandhuber and Amy [1998] investigated the efficiency of arsenic removal by microfiltration coupled with ferric chloride pretreatment in bench-scale studies. The strategy for arsenic removal from well water was to incorporate arsenic into ferric hydroxide pin flocs of suitable size to be removed with a microfilter. Arsenic removal increased with increasing



coagulant dose, but the increase of coagulant dose above 10 mg/L was much less effective. The size of arsenic bearing flocs remained in the submicron range at all coagulant doses, but only at the highest coagulant dose (25 mg/L) significant portion of arsenic removed was associated with apparent floc size greater than 1 micron [Brandhuber and Amy, 1998].

Chwirka et al. [2004] revealed that the ferric hydroxide particle sizes generated with rapid mixing (eliminating flocculation step) in the pilot tests were typically in the 2-10  $\mu\text{m}$  range, and thus, arsenic bearing particles could be removed efficiently with microfiltration. Iron coagulation and direct microfiltration for removal of arsenic from groundwater was also studied by Ghurye et al. [2004], and a membrane pore size of less than or equal to 0.2  $\mu\text{m}$  was found necessary for efficient removal of arsenic loaded ferric hydroxide precipitate. In all these studies, the ferric ion was added as ferric chloride.

Wickramasinghe et al. [2004] conducted bench-scale experiments to evaluate the removal of arsenic from groundwater by iron coagulation, added as ferric sulfate and ferric chloride, and microfiltration. The authors stated that the degree of rejection of precipitate particles by the membrane at a given ferric ion dose should increase with decreasing pH since increased arsenate adsorption at lower pH will lead to increased particle size. They also observed a lower residual turbidity in the presence of sulfate, suggesting that the sulfate groups are involved in the coagulation reactions. The presence of sulfate groups could lead to larger flocs that are more easily rejected by the membrane, compared to chloride ions.

Han et al. [2002] applied flocculants (ferric chloride and ferric sulfate) before microfiltration to remove arsenic from drinking water, and showed that membranes with a pore size of 0.22  $\mu\text{m}$  remove more arsenic than membranes with a pore size of 1.2  $\mu\text{m}$  for a given ferric ion dose and pH.

After coagulation with ferric chloride, arsenic removal efficiencies were examined with different sizes of membrane filters (0.1, 0.5, and 1.0  $\mu\text{m}$ ) and without filtration. Marked decreases in arsenic removal were observed with unfiltered samples, while variations in filter size had only minor effects on the removal of arsenic [Hering et al., 1996].

## 2.0 MATERIALS AND METHODS

### 2.1 REAGENTS AND STOCK SOLUTIONS

Deionized (DI) water with 17.7 megohm-cm resistivity was produced in environmental lab using a Barnstead Nanopure system, and used for the preparation of all standards and feed waters. All glass and plastic equipment including bottles, flasks, pipettes, and beakers to be used in the experiments were cleaned and acid washed by soaking in nitric acid solution overnight, and then triple rinsed with tap water and triple rinsed with deionized water to prevent any interference during atomic absorption measurements.

The primary arsenite stock solution was prepared from 0.1 N sodium arsenite solution (6.5 g/L as  $\text{NaAsO}_2$  or 3.75 g/L as As) (Labchem Inc) diluting in DI water with 1.5% (v/v) trace metal grade HCl. Secondary standard solution (93.75 mg/L) was prepared by pipetting 10 mL of primary stock solution into a 100 mL volumetric flask, and then the solution was made up to 100 mL with DI water. Secondary arsenite stock solution was prepared every week and stored in acid washed high density polyethylene bottle in 4°C cold storage room, and its concentration was measured during graphite furnace atomic absorption analysis to ensure that the prepared arsenic concentration is preserved during the storage time.

The Fe(II) stock solution containing 2000 mg/L Fe(II) in 1%  $\text{H}_2\text{SO}_4$  (v/v) was prepared from  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (Fisher Scientific), and the Fe(III) stock solution containing 2000 mg/L Fe(III) in 0.1% HCl (v/v) was prepared from  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Fisher Scientific). Manganese stock

solution containing 1000 mg/L Mn(II) was prepared from  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (Fisher Scientific) by dissolving in DI water. The iron and manganese stock solutions were not kept more than three weeks, and the concentrations were checked during atomic absorption analysis. The stock solutions were stored in acid washed high density polyethylene bottles in cold storage room at 4°C.

4.2005 g  $\text{NaHCO}_3$  (Fisher Scientific) was dissolved in 100 mL DI water to make up 0.5 N sodium bicarbonate solution and used to provide required alkalinity. 1000 mg/L  $\text{KMnO}_4$  (J. T. Baker) solution was prepared as a strong oxidizer.

For pH adjustments during feed water preparation or for pH control during the experiments, 1 N and 0.05 N NaOH and 10% (v/v) HCl were used. Measurements of pH were made with a pH electrode and pH meter (Fisher Scientific) calibrated with three buffer solutions at pH 4, 7, and 10.

Nickel nitrate solution (5%) was prepared by dissolving 24.780 g of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Fisher Scientific) in 100 mL DI water, and it was used as a matrix modifier in arsenic analysis during graphite furnace atomic absorption spectrometry (AAS). Plasma grade arsenic standard solution of 1000 ppm (Spex CertiPrep), certified reference iron standard solution of 1000 ppm (Fisher Scientific), and certified reference manganese standard solution of 1000 ppm (Fisher Scientific) were used for the calibration of the AAS during arsenic, iron, and manganese analysis, respectively.

## **2.2 PREPARATION OF FEED WATER**

The purpose of the lab-scale experiments was to investigate the efficiency of arsenic removal from groundwater by Fe-Mn oxidation and microfiltration under a variety of process conditions. Therefore, artificial groundwater containing various amounts of iron, manganese, and arsenite was prepared to simulate natural groundwater.

2 liter DI water was buffered with 4 mL of 0.5 N sodium bicarbonate ( $\text{NaHCO}_3$ ) to provide 1 mM (50 mg/L as  $\text{CaCO}_3$ ) alkalinity. The pH was adjusted to the required value, typically to pH of 7.0, which is representative of the pH range for many groundwaters, by adding necessary amounts of NaOH or HCl solution. Then, calibrated aliquots of arsenite as sodium arsenite from the secondary stock solution (93.75 mg/L), manganous ion as manganese sulfate from primary stock solution (1000 mg/L), and either ferrous or ferric ion as ferrous sulfate or ferric chloride from primary stock solutions (2000 mg/L) were added to buffered DI water to achieve the required concentrations. The solution pH was controlled at a desired pH by the addition of NaOH.

## **2.3 OXIDATION**

The artificial groundwater containing required amounts of iron, manganese and arsenic was oxidized before microfiltration. Two types of oxidation approaches were applied in this study: aeration and oxidation with potassium permanganate.

### 2.3.1 Aeration

The prepared feed water was oxygenated by sparging air (Figure 6) for 10 minutes in all of the experiments. The main purpose of this oxidation step was to completely oxidize ferrous ions, but also to partially oxidize arsenite and manganous ions. The pH of the solution was measured after aeration to make sure that it was in the acceptable range ( $\pm 0.1$  pH unit).



**Figure 6** Aeration of the feed water.

### 2.3.2 Oxidation with Potassium Permanganate

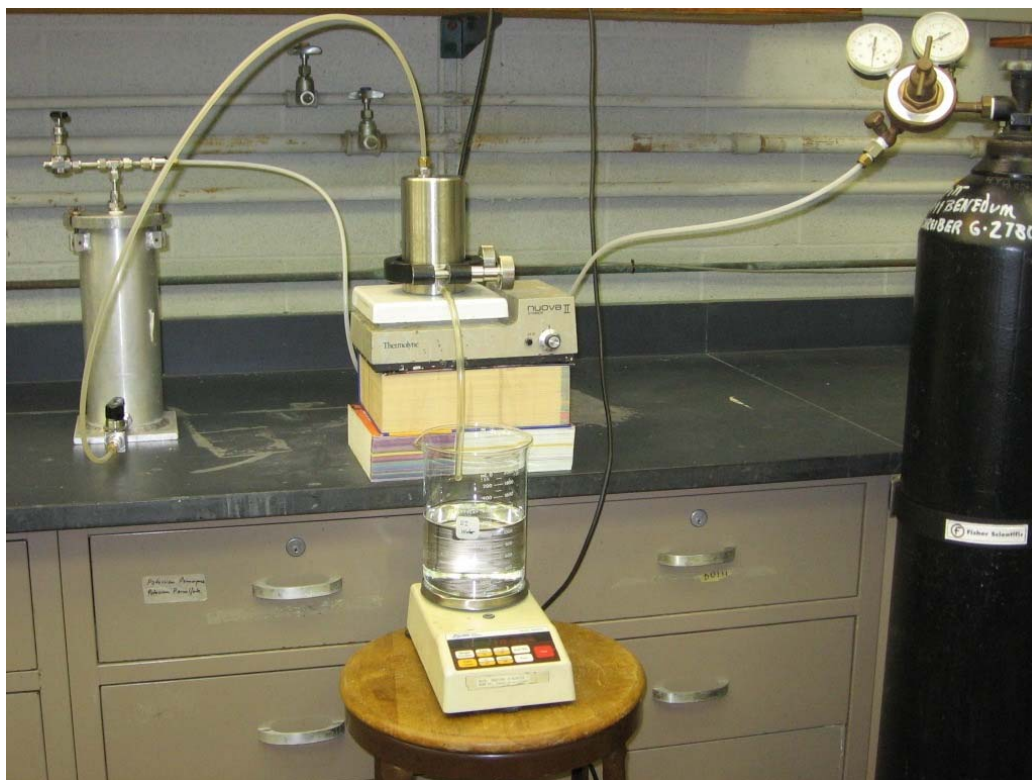
The second oxidation procedure involved the addition of potassium permanganate to oxidize manganous ions and arsenite. The solution was mixed for 30 minutes with a magnetic stirrer to guarantee that the oxidation is complete. In some experiments, this procedure was chosen to achieve complete oxidation of arsenite and manganous ions since their oxidation with oxygen are

slow. The pH was controlled in the range of  $\text{pH} \pm 0.1$  during the oxidation with potassium permanganate.

## **2.4 MICROFILTRATION**

### **2.4.1 Microfiltration Set-up**

Microfiltration was conducted in an unstirred dead-end cell system after the feed water was prepared and oxidized. The experimental set-up of microfiltration unit, shown in Figure 7, consists of a nitrogen gas cylinder which maintains constant-pressure filtration, an external reservoir which is connected between the pressure source and the filtration cell to store feed water to about 2.5 liters, a dead-end filtration cell whose capacity is around 350 mL, 2-L beakers to collect permeate of sample and DI water, and an electronic balance to measure the amount of permeate.



**Figure 7** The experimental set-up of dead-end cell system.

## 2.4.2 Membrane

Supor®200 membrane disc filters with 0.2  $\mu\text{m}$  nominal pore size and 90 mm diameter, supplied by Pall Corporation, were used during the microfiltration experiments. The membrane disc filters were trimmed to 70 mm diameter to fit in the dead-end filtration cell. The technical specification of Supor®200 hydrophilic membrane is given in Table 2.

Supor®200 is generally chosen in microfiltration studies for its resistance to strong acid conditions (nitric acid 10% w/w), to alkaline conditions (sodium hydroxide 10% w/w) and oxidizing conditions (sodium hypochlorite 5.25% w/w) [Ellis et al., 2000].



**Table 2** Technical specification of Supor®200 membrane disc filter [Pall Co. website]

<b>Specifications</b>	<b>Supor®200</b>
Filter media	Hydrophilic polyethersulfone
Pore size (µm)	0.2
Typical thickness (µm)	145
Typical water flow rate at 10 psi (ml/min/cm <sup>2</sup> )	26
Maximum operating temperature-water (°C)	100
Minimum bubble point-water (psi)	51

### **2.4.3 Filtration Procedure**

The microfiltration with Supor®200 membrane was performed at a trans-membrane pressure (TMP) of 10 psi in each run, and a new disc filter was used for each experiment. During filtration, the amount of permeate was measured by an electronic balance, and the time period between two successive data points was recorded with a stop watch.

Each filtration experiment started with an initial permeability test. 2 liters of DI water was filtered through the unstirred dead-end cell filtration system using Supor®200 membrane disc filter for about 4 minutes. The purpose of this initial step was to wet the membrane, to measure pure water permeability, and thus, to ensure that its flux is constant. After the initial permeability test, the feed water was filtrated for a few minutes depending on the fouling rate of the membrane.

## 2.5 WATER QUALITY ANALYSIS

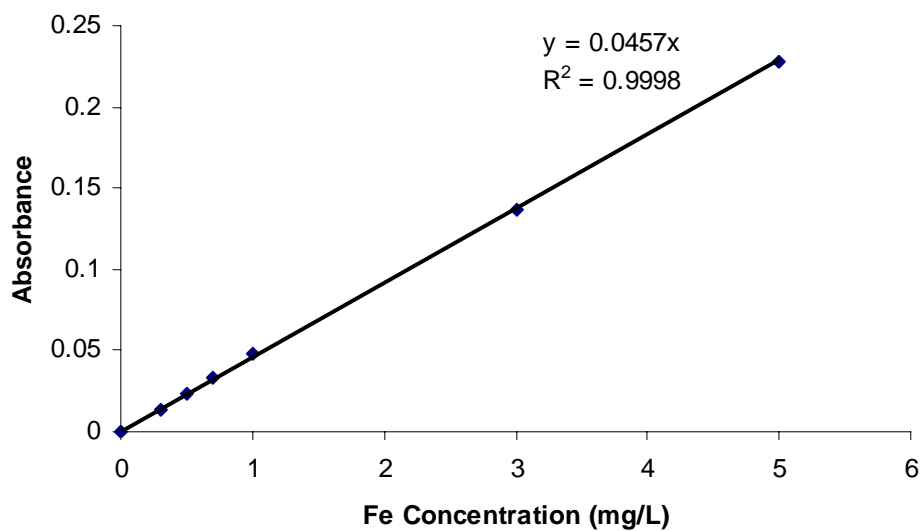
### 2.5.1 Iron and Manganese Analysis

Total iron and manganese analysis was performed by Perkin-Elmer model 1100B flame atomic absorption spectrophotometer (Figure 8) following the Method 3111B of the Standard Methods. Samples were analyzed by direct aspiration into air-acetylene flame, and absorbance was measured at 248.3 nm and 279.5 nm for iron and manganese, respectively. Flow rates were adjusted to 2.5 L/min for acetylene and 8 L/min for air as specified by the manufacturer to give maximum sensitivity for the metal being measured. Operating currents of both hollow-cathode lamps were 20 mA.

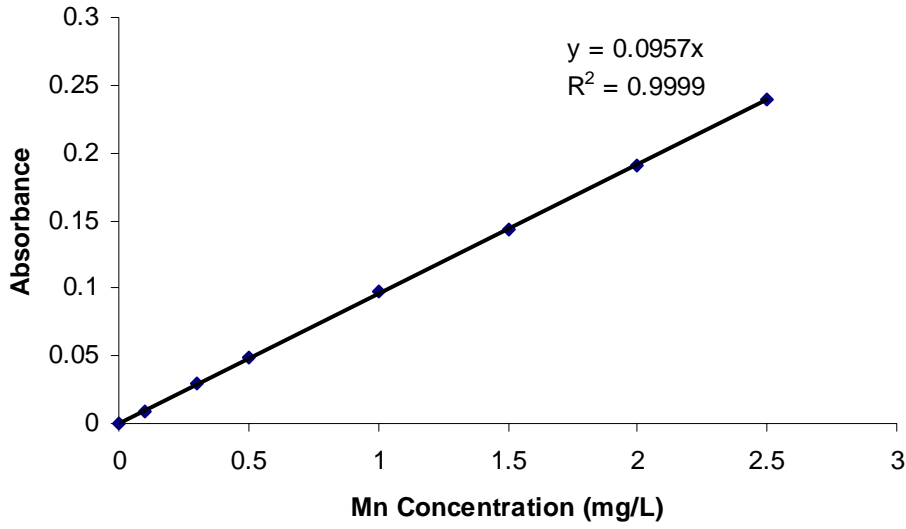
The samples were acidified with concentrated nitric acid to dissolve any iron oxide and manganese oxide suspension before atomic absorption spectrometry analysis. Calibration standards were prepared with the same acid concentration, i.e. 2% HNO<sub>3</sub> (v/v), and in the optimum concentration range of the metals, i.e. 0.3-10 mg/L for iron and 0.1-10 mg/L for manganese. Figures 9 and 10 show the calibration curves used for iron and manganese analysis, respectively. Blank solution was also prepared using DI water and 2% HNO<sub>3</sub> (v/v) in all iron and manganese analysis, and no detectable iron or manganese was observed in the blank.



**Figure 8** Perkin-Elmer model 1100B atomic absorption spectrophotometer used for the analysis of iron and manganese.



**Figure 9** Absorbance as a function of Fe concentration



**Figure 10** Absorbance as a function of Mn concentration

### 2.5.2 Arsenic Analysis

Total arsenic was determined using Perkin-Elmer model 4100ZL Zeeman graphite furnace atomic absorption spectrometer equipped with a graphite tube atomizer and programmable sample dispenser (Figure 11). Argon gas of high purity was used to purge the volatilized matrix materials and protect the heated graphite tube from air oxidation. Arsenic hollow-cathode lamp was used at a wavelength of 193.7 nm with a slit width of 0.7 nm.



**Figure 11** Perkin-Elmer model 4100ZL Zeeman graphite furnace atomic absorption spectrometer used for arsenic analysis.

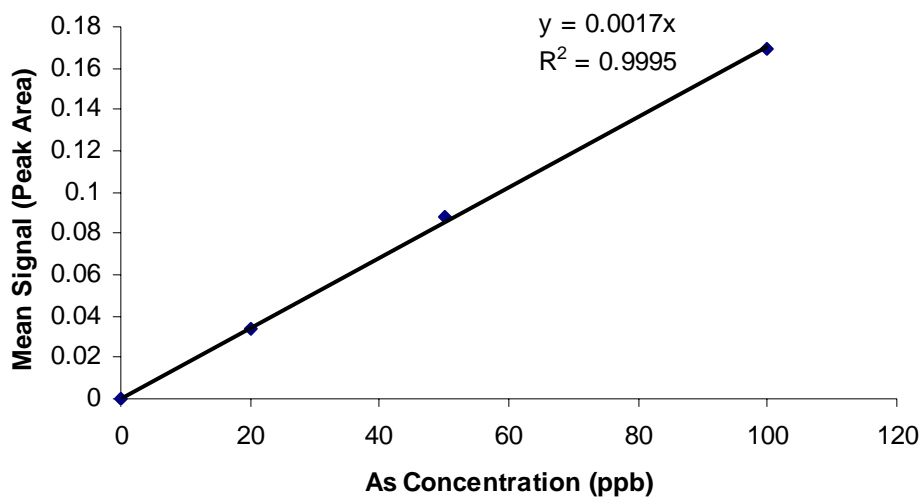
There are generally four steps applied during graphite furnace operation. The drying step is performed to remove any residual solvent from the sample by maintaining the heat of the graphite tube above the boiling point of the solvent. The second step, pyrolysis, volatilizes inorganic and organic matrix components selectively from the sample. The atomization step is used to produce an atomic vapor of the analyte elements, allowing atomic absorption to be measured. The clean out, which is the last step, burns off any sample residue which may remain in the furnace. 6-step graphite furnace program, which is depicted in Table 3, was used for arsenic analysis in this study, and Zeeman background-corrected peak areas due to analyte was obtained for arsenic measurement.

**Table 3** Furnace heating program

<b>Step</b>	<b>Temperature (°C)</b>	<b>Ramp time (s)</b>	<b>Hold time (s)</b>	<b>Internal flow (mL/min)</b>
1	110	1	30	250
2	130	15	30	250
3	200	5	10	250
4	900	15	20	250
5	2200	0	5	0
6	2450	1	5	250

Matrix modification is necessary to allow increased pyrolysis temperatures, and thus to decrease the non-specific absorption signals originating from the matrix [Volynskii, 2003]. Nickel nitrate was selected as the matrix modifier for this study.

Samples and calibration standard solutions were freshly prepared according to approved EPA method (U.S.EPA National Exposure Research Laboratory – NERL Method No. 206.2). Concentrated nitric acid was used for the acidification of samples to prevent analyte losses at high pyrolysis temperatures. The standards were always in the optimum concentration range specified by Method No. 206.2 (5-100 µg/L). The calibration curve used for arsenic analysis is given in Figure 12.



**Figure 12** Calibration curve for arsenic analysis

### 3.0 RESULTS AND DISCUSSION

The purpose of this study was to evaluate the extent of arsenic removal during Fe-Mn oxidation and microfiltration process. Oxidation was achieved with aeration only or aeration and potassium permanganate addition in the lab-scale experiments. Supor®200 with nominal pore size of 0.2 µm was used for the microfiltration of arsenic bearing solution, and each experiment started with an initial permeability test with DI water to ensure that its flux is constant. The permeate quality and flux were investigated as a function of the following process parameters:

- pH
- Iron to arsenic ratio (Fe/As)
- Stirred versus unstirred dead-end filtration cell
- Contact time provided for potassium permanganate oxidation
- Potassium permanganate dose at pH = 7.0 and pH= 8.0
- Oxidation state of iron (ferrous versus ferric iron)



### 3.1 THE EFFECT OF pH

#### 3.1.1 Water Quality

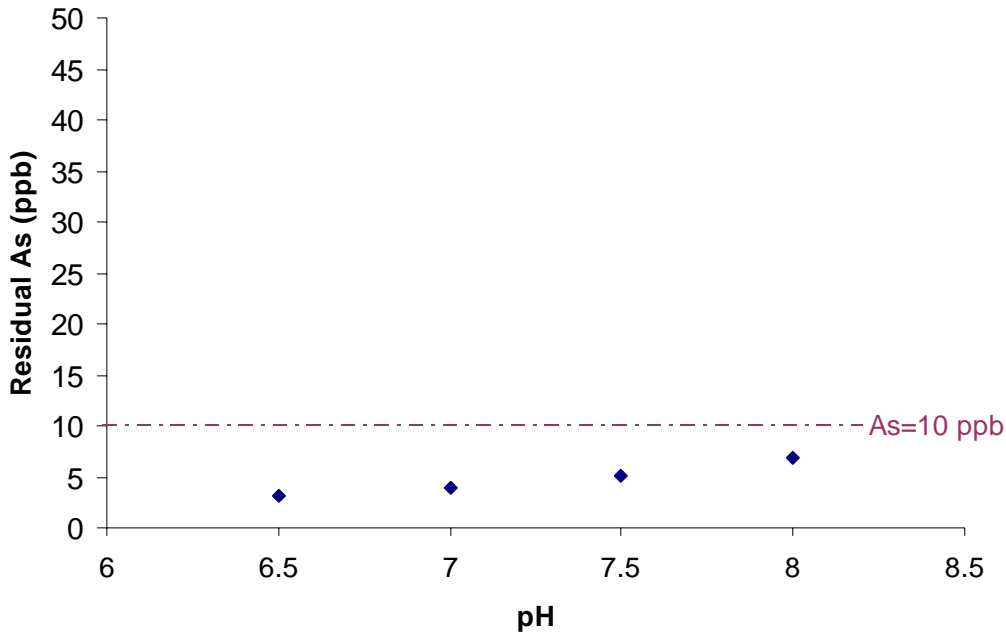
The pH level of natural waters plays an important role in the removal of arsenic since it influences the distribution of arsenic species, tendency of arsenic for adsorption onto iron oxide surfaces, and also the charge and formation of iron oxide particles. The experiments to examine the impact of pH on water quality were conducted with 5 mg/L ferrous ion, 1 mg/L manganous ion and 50 ppb arsenite initial concentrations, and only aeration was applied. Table 4 and Figure 13 show pertinent water quality data and residual arsenic concentration as a function of pH, respectively.

**Table 4** The effect of pH on the permeate quality for artificial groundwater with initial Fe(II), Mn(II) and As(III) concentrations of 5 mg/L, 1 mg/L and 50 ppb, respectively. Only aeration was applied for the oxidation of the contaminants.

<b>Feed Water</b>	<b>Residual Fe</b>	<b>Residual Mn</b>	<b>Residual As</b>	<b>%As Removal</b>
<b>pH</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(ppb)</b>	
6.5	0.02	0.73	3.1	93.8
7.0	0.01	0.48	4.0	92.0
7.5	0.02	0.48	5.1	89.8
8.0	0.01	0.38	6.8	86.4

As shown in Table 4, residual iron and arsenic levels at all pH values were well below the MCL (0.3 mg/L for iron and 10 ppb for arsenic), while manganese concentrations below the secondary MCL for manganese (0.05 mg/L) could not be achieved under these experimental conditions. The decrease in the residual manganese levels from 0.73 mg/L at pH = 6.5 to 0.38 mg/L at pH = 8.0 clearly shows the enhanced oxidation of manganese and increased

formation of manganese dioxide particles with increasing pH. However, manganese typically requires chemical oxidation and in the absence of a strong oxidant it is unlikely to be able to reduce residual manganese concentrations to trace levels with aeration only.



**Figure 13** Residual arsenic concentrations achieved with an initial Fe/As ratio of 100 as a function of pH.

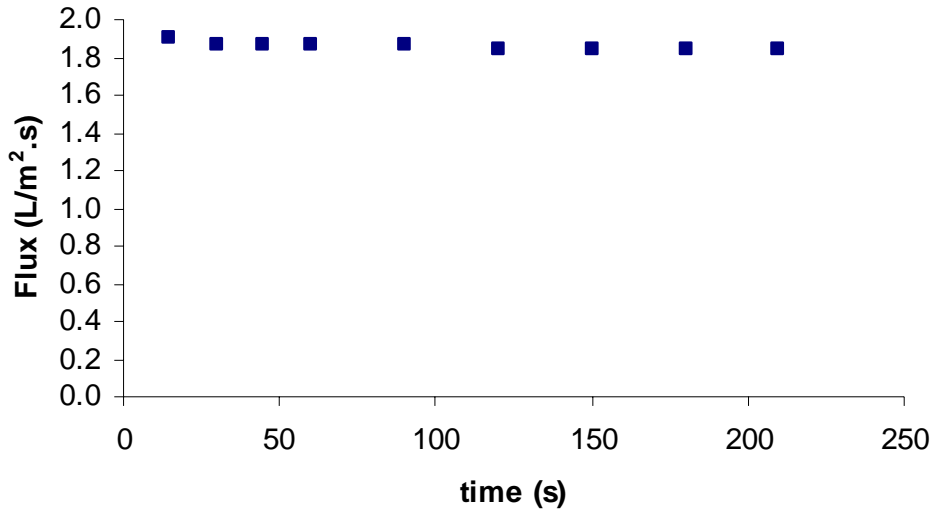
The percent arsenic removal is supposed to remain constant with increasing pH within the range applied in these experiments (pH 6.5-8.0) since arsenite is found in the neutral form ( $\text{H}_3\text{AsO}_3$ ) up to pH of 9.22 ( $\text{pK}_{a1}$  of arsenite). Edwards [1994] studied the effect of pH on arsenate and arsenite removal, and determined that arsenate removal is strongly dependent on pH while it is not important for the removal of arsenite. Therefore, the removal of arsenite is not a function of pH unlike arsenate which exists in anionic forms in this pH range.

Complete oxidation of arsenite to arsenate is not expected under the experimental conditions used in this study since only aeration was applied. The observed arsenite removal rates were not as high as those predicted for arsenate (about 100%) [Edwards, 1994; Hering et al., 1996], but the slight increase in residual arsenic concentrations with increasing pH (Figure 13) (the behavior that is typical for arsenate) can be explained by partial oxidation of arsenite. As explained by Hug and Leupin [2003], catalytic influence of iron surfaces in the presence of oxygen can partially convert arsenite to arsenate. Since adsorption of arsenate decreases with increasing pH in the range of 4-9 [Wickramasinghe et al., 2004], the slight reduction in arsenic removal observed in this study may be attributed to partial oxidation of arsenite to arsenate during aeration. In addition, the net positive charge of  $\text{Fe}(\text{OH})_{3(s)}$  changes depending on the water pH, and the number of positively charged sites on ferric hydroxide particles increases as the pH of feed water decreases [Chwirka et al., 2004]. Since arsenate is an anion and adsorbs on positively charged particles, better arsenic removals are achieved at lower pH. In summary, slightly reduced arsenic removal rates at high pH values is due to partial conversion of arsenite to arsenate.

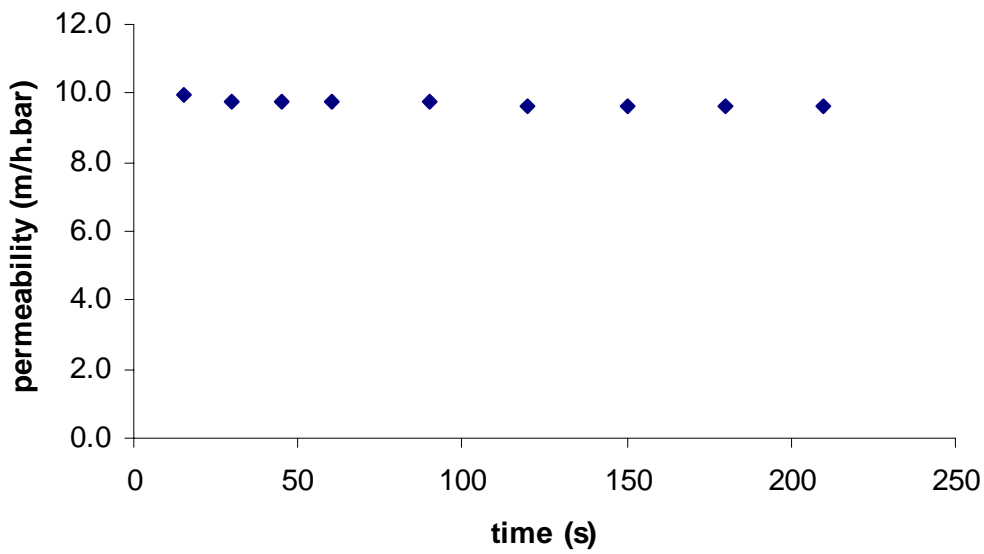
### **3.1.2 Permeate Flux**

Microfiltration experiments started with a blank test with DI water to wet the membrane, to measure the pure water permeability, and thus, to make sure that its flux is constant before the filtration of feed water. The typical flux rate and permeability of DI water with Supor®200 membrane at 10 psi were about 1.9 L/m<sup>2</sup>.s and 9.7 m/h.bar, respectively, as shown in Figures 14 and 15. No significant flux decline was observed during the initial tests, indicating that there was no contribution to membrane fouling coming from DI water. In the technical specification of the membrane (Table 2), the water flux for Supor®200 was given as 4.33 L/m<sup>2</sup>.s (26 mL/min.cm<sup>2</sup>)

which is higher than the measured flux rate, but the difference between these flux rates might be due to the type of filtration process (batch or continuous) applied.

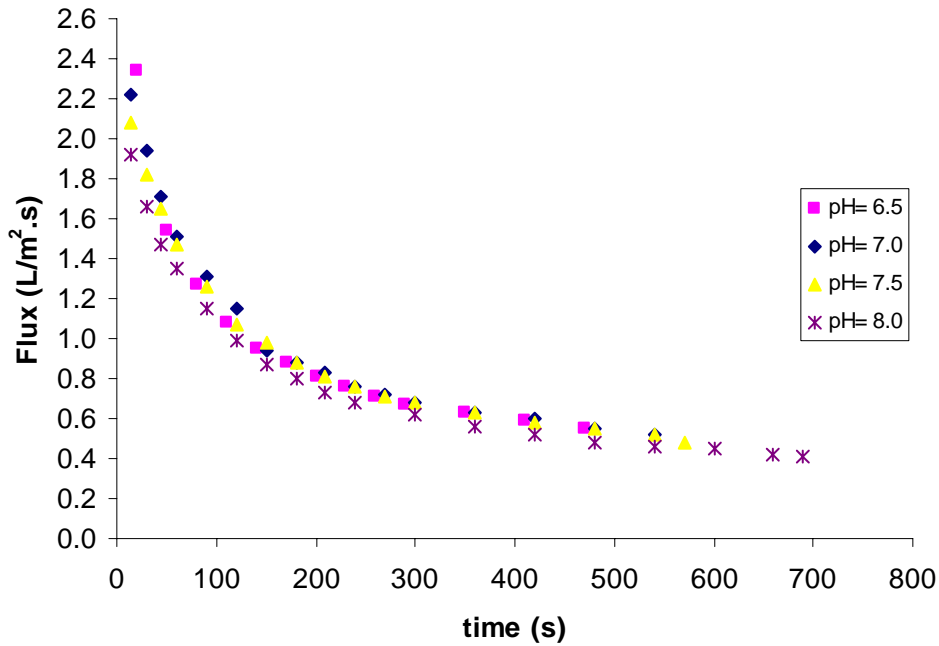


**Figure 14** Typical flux rate of DI water with Supor®200 membrane at 10 psi (blank test).



**Figure 15** Typical permeability of DI water with Supor®200 membrane at 10 psi (blank test).

Microfiltration of feed water at different pH levels was performed with Supor®200 polyethersulfone membrane with nominal pore size of 0.2  $\mu\text{m}$  at 10 psi (Figure 16). Although flux rates were very similar at all pH values since the amount of iron removed from feed water was roughly same, the membrane fouling rate for the feed water at pH of 8.0 was slightly higher when compared to feed waters at other pH levels. This was probably due to the increased removal of manganese which deposited on the membrane surface at high pH values. Aeration was clearly not sufficient to oxidize all manganous ions and to form manganese dioxide particles greater than the pore size of the membrane (0.2  $\mu\text{m}$ ); therefore partial removal of manganese was achieved at the pH levels studied. With a strong oxidant, for example, potassium permanganate, more efficient manganese removal can be accomplished as demonstrated by Ellis et al. [2000] since the particle sizes for both iron and manganese oxides formed in the presence of potassium permanganate were reported to be between 1.5 to 50  $\mu\text{m}$  which should easily be removed by a membrane with 0.2  $\mu\text{m}$  pore size.



**Figure 16** Effect of different pH values on permeate flux for artificial groundwater with initial Fe(II), Mn(II) and As(III) concentrations of 5 mg/L, 1 mg/L and 50 ppb, respectively.

### 3.2 THE EFFECT OF IRON TO ARSENIC RATIO

#### 3.2.1 Water Quality

In many studies, enhanced arsenic removals have been observed with increased iron concentrations in water [Gulledge and O’Conner, 1973; Edwards, 1994; Cheng et al., 1994; Scott et al., 1995]. To evaluate the efficiency of arsenic removal with different iron to arsenic ratios, a set of experiments was performed with feed water containing various concentrations of arsenite and ferrous ion and 1 mg/L manganous ion. Feed water was prepared at neutral pH and only aeration was performed.

As can be seen in Table 5, increasing iron concentrations for a given arsenic dosage resulted in lower arsenic residual concentrations due to increasing adsorption of arsenic ions onto iron oxide particles or coprecipitation of arsenic with iron oxide particles. As shown in the permeate quality data (Table 5), percentage removals of arsenic increased from 53.2% to 100%, from 50.2% to 96.6%, from 38.1% to 100%, from 35.7% to 99% and from 56.8% to 99.3% for the initial arsenite concentrations of 25 ppb, 50 ppb, 100 ppb, 150 ppb, and 250 ppb, respectively, with increasing initial iron levels.

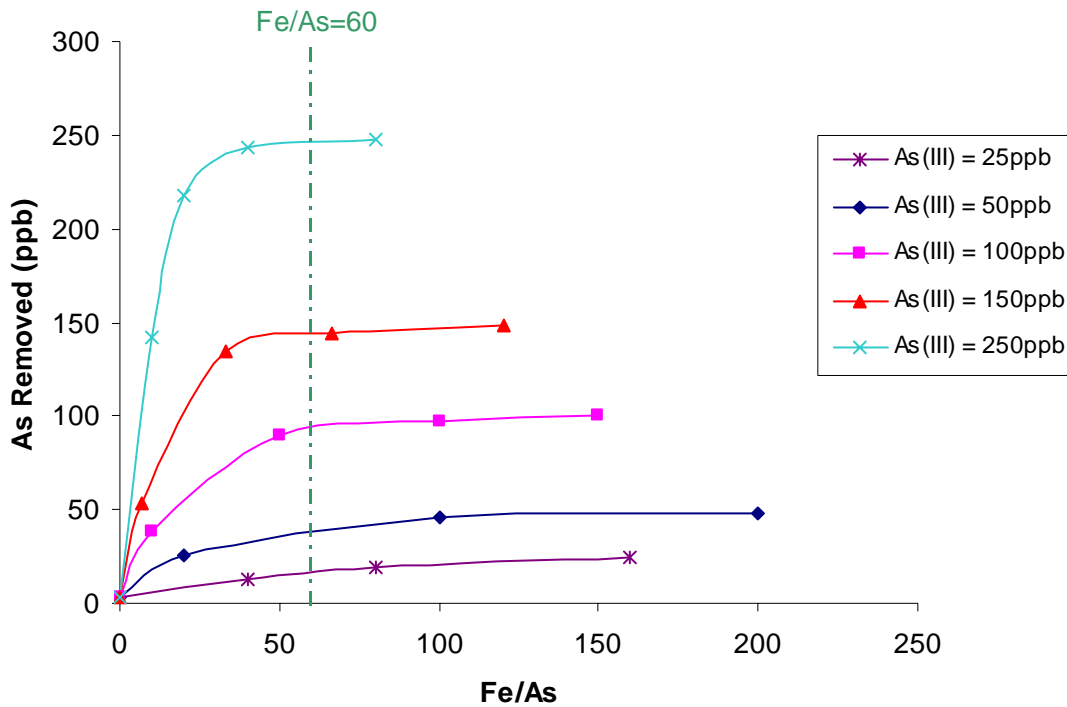
**Table 5** Permeate quality data of artificial groundwater prepared with different iron to arsenic ratios and 1 mg/L manganese at neutral pH. Only aeration was applied.

<b>Initial Fe and As Concentrations</b>	<b>Fe/As Ratio</b>	<b>Residual Fe (mg/L)</b>	<b>Residual Mn (mg/L)</b>	<b>Residual As (ppb)</b>	<b>%As Removal</b>
Fe(II) = 1 mg/L As(III) = 25 ppb	40	0.01	0.69	11.7	53.2
Fe(II) = 2 mg/L As(III) = 25 ppb	80	0.01	0.60	5.9	76.4
Fe(II) = 4 mg/L As(III) = 25 ppb	160	0.02	0.54	0	100
Fe(II) = 0, As(III) = 50 ppb	0	0	0.78	46.7	6.6
Fe(II) = 1 mg/L As(III) = 50 ppb	20	0.01	0.65	24.9	50.2
Fe(II) = 5 mg/L As(III) = 50 ppb	100	0.01	0.48	4.0	92.0
Fe(II) = 10 mg/L As(III) = 50 ppb	200	0.01	0.47	1.7	96.6
Fe(II) = 1 mg/L As(III) = 100 ppb	10	0.01	0.72	61.9	38.1
Fe(II) = 5 mg/L As(III) = 100 ppb	50	0.01	0.47	10.7	89.3
Fe(II) = 10 mg/L As(III) = 100 ppb	100	0.01	0.41	2.4	97.6
Fe(II) = 15 mg/L As(III) = 100 ppb	150	0.01	0.32	0	100
Fe(II) = 1 mg/L As(III) = 150 ppb	6.67	0.01	0.71	96.4	35.7
Fe(II) = 5 mg/L As(III) = 150 ppb	33.3	0.01	0.59	16.0	89.3
Fe(II) = 10 mg/L As(III) = 150 ppb	66.67	0.01	0.38	5.4	96.4
Fe(II) = 18 mg/L As(III) = 150 ppb	120	0.01	0.35	1.3	99.1
Fe(II) = 2.5 mg/L As(III) = 250 ppb	10	0.01	0.61	108	56.8
Fe(II) = 5 mg/L As(III) = 250 ppb	20	0.01	0.52	32.0	87.2
Fe(II) = 10 mg/L As(III) = 250 ppb	40	0.01	0.33	6.7	97.3
Fe(II) = 20 mg/L As(III) = 250 ppb	80	0.01	0.32	1.8	99.3



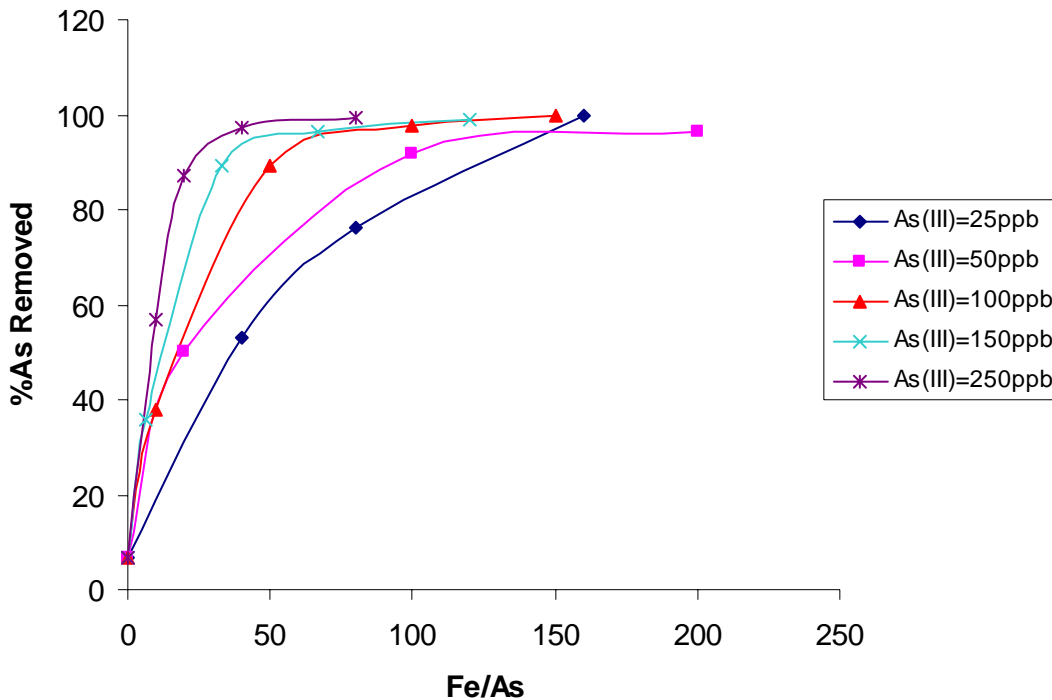
Initial arsenite concentrations did not have a significant effect on arsenic removal rates for a given iron dose. This finding is in agreement with Hering et al. [1996]. For example, 5 mg/L of ferrous ion removed 92% and 89.3% of arsenic with initial arsenite concentrations of 50 ppb and 100 ppb, respectively. Furthermore, 89.3% and 87.2% arsenic removal was observed when the initial concentrations of arsenite were increased to 150 ppb and 250 ppb, indicating that very similar arsenic removal percentages were achieved by increasing initial arsenic levels from 50 ppb to 250 ppb. Initial iron concentrations above 5 mg/L also provided similar arsenic removal percentages with increasing arsenite concentrations. However, this situation was different when lower iron concentrations were used in the experiments. Initial ferrous ion dose of 1 mg/L removed 53.2% and 50.2% of arsenic for the initial arsenic concentrations of 25 ppb and 50 ppb. However, the percentage arsenic removal decreased to 38.1% and 35.7% when the initial levels of arsenic increased to 100 ppb and 150 ppb, respectively. The decrease in arsenic removal percentages at low iron concentrations might be due to the lack of available iron surfaces for adsorption of arsenic, or due to insufficient oxidation capacity of iron for conversion of arsenite to arsenate. Hering et al. [1996] suggested that arsenite can be oxidized on ferric hydroxide surfaces at low initial arsenite concentrations and Hug and Leupin [2003] observed the partial or complete oxidation of arsenite in parallel to the oxidation of 20-90  $\mu\text{M}$  (1.18-5.03 mg/L) Fe(II) by oxygen. Since high amounts of iron can oxidize arsenite to arsenate in the presence of oxygen and since arsenate removal is not a function of initial arsenic concentration [Cheng et al., 1994; Edwards, 1994], the arsenic removal did not change at high iron levels. These studies also explain why adsorption may be the dominant arsenic removal mechanism at high iron to arsenic ratios as proposed by Hering et al. [1997] and Mamtaz and Bache.

Arsenic removal at different iron to arsenic weight ratios is given in Figure 17. Increasing iron to arsenic ratios resulted in lower residual arsenic concentrations and thus, higher removals of arsenic, as observed by Wilkie and Hering [1996]. Although the increase in arsenic removals at low iron to arsenic ratios (from 0 to 50) was more pronounced, nearly constant arsenic removals were achieved after the Fe/As ratio of 60, which was sufficient to reduce arsenic concentrations below the primary MCL of arsenic (10 ppb) at all initial arsenite levels (from 25 ppb to 250 ppb) with aeration alone.



**Figure 17** Arsenic removal at pH = 7.0 for different initial arsenite concentrations as a function of iron to arsenic ratio. Only aeration was applied.

Because iron concentration in the feed water is more important than arsenite concentration with respect to arsenic removal efficiency, higher arsenic removal rates can be achieved in waters with high iron and high arsenic levels when compared to waters with low iron and low arsenic levels for the same iron to arsenic weight ratio (Figure 18). For example, for Fe/As ratio of 20, 1 mg/L ferrous ion removed 50.2% of 50 ppb arsenite initial concentration while 5 mg/L ferrous ion achieved 87.2% removal of 250 ppb arsenite influent. Therefore, lower Fe/As ratios might be required for waters with high initial arsenic levels. As illustrated in Table 5, 250 ppb initial arsenite concentration was reduced below 10 ppb with Fe/As ratio of 40, while the Fe/As ratio required to meet the standard for lower initial arsenic levels was 60.



**Figure 18** Arsenic removal efficiency at pH = 7.0 with 10-min aeration only for different initial arsenite concentrations as a function of iron to arsenic ratio.

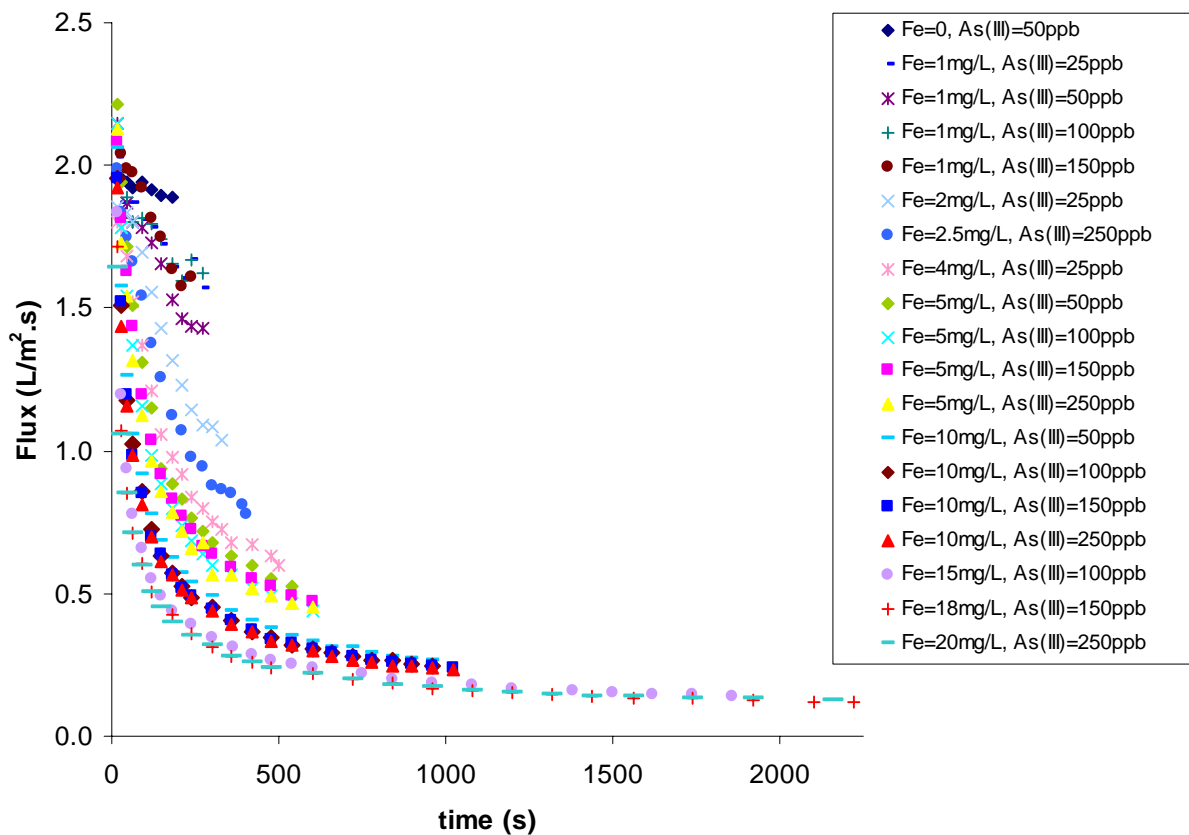
The residual iron and manganese concentrations were also measured after Fe-Mn oxidation and microfiltration process. Soluble iron levels were much lower than the secondary MCL (0.3 mg/L), whereas residual manganese concentrations were higher than 0.05 mg/L (secondary MCL of Mn). A decrease in manganese concentration was observed in the permeate with an increase in initial iron concentration. Ellis et al. [2000] explained this phenomenon by the adsorption of manganous ions on iron oxide particles or the co-precipitation of iron and manganese.

The removal of soluble arsenic during manganese removal was of lesser importance compared to iron as observed by McNeill and Edwards [1995]. Removal of 0.22 mg/L manganous ion achieved 6.6% removal of 50 ppb initial arsenite concentration at pH of 7.0 when the experiment was conducted in the absence of iron and only aeration was applied. Higher arsenic removals may be achieved if a strong oxidizer was used to remove all manganese particles from the feed water.

### **3.2.2 Permeate Flux**

The permeate flux rates for a feed water prepared with 1 mg/L manganous ion and different ferrous ion and arsenite concentrations were measured during the filtration through unstirred dead-end cell system with Supor®200 microfiltration membrane. As shown in Figure 19, the membrane fouling was primarily due to iron in the feed water. The initial iron level in the prepared artificial groundwater was highly significant in terms of membrane fouling for three reasons. First, high iron concentration can create more iron oxide particles which deposit on the membrane surface. Second, manganous ions can also be removed by adsorbing onto iron oxide particles or by co-precipitating with iron. Finally, oxidation of arsenite to arsenate is promoted at high iron concentrations, which enhances its adsorption onto iron oxide particles and removal

from the feed water. Therefore, higher membrane fouling rates were observed with higher initial iron concentrations. The decrease in permeate flux rates observed in the experiments were also comparable with the results of the membrane fouling study conducted by Ellis et al. [2000]. However, the exact match of the results was not possible due to the difference in the applied trans-membrane pressures.



**Figure 19** Effect of different initial ferrous iron and arsenite concentrations on membrane fouling rate for artificial groundwater with initial Mn(II) concentration of 1 mg/L and at pH of 7.0.

When the effects of initial arsenite concentrations on membrane fouling were examined, it can be concluded that arsenite levels do not create a significant difference in terms of permeate flux. A slight decrease in permeate flux was observed with an increase in arsenite levels due to the adsorption of arsenic onto iron oxide particles, but this effect is negligible since the arsenic levels are too low (in the range of parts per billion) to significantly influence the membrane fouling rate.

### **3.3 STIRRED VERSUS UNSTIRRED DEAD-END FILTRATION CELL**

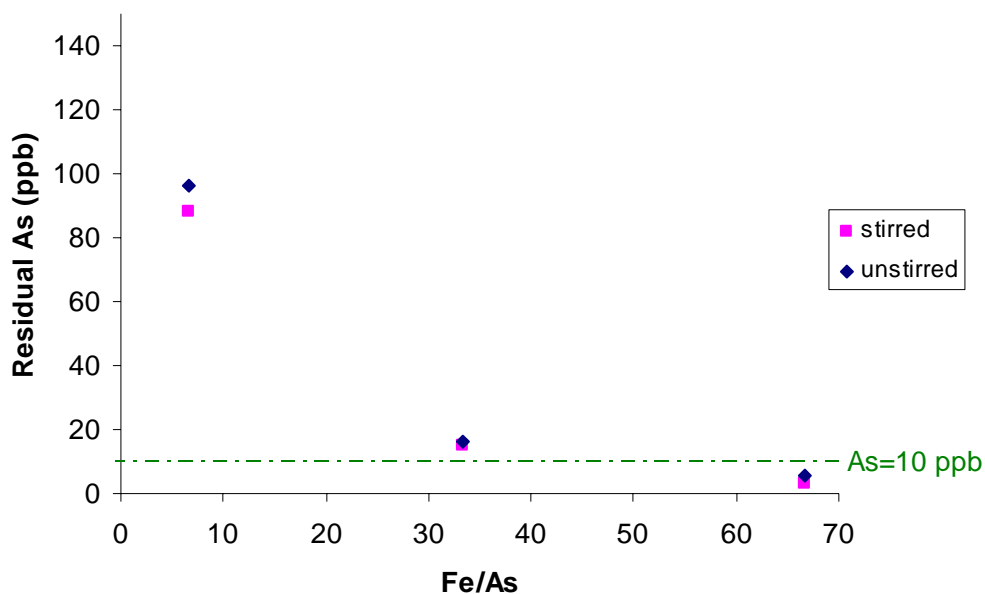
#### **3.3.1 Water Quality**

To investigate the effect of stirring in a dead-end cell filtration unit on water quality and membrane fouling rate, feed water with 150 ppb of arsenite, 1 mg/L of manganous ion, and 1, 5 and 10 mg/L of ferrous ion was prepared at neutral pH, and 10-min aeration was applied for the oxidation of ions. As demonstrated in Table 6, the experimental results showed that using stirring in a dead-end filtration cell does not lead to a significant difference with respect to water quality. All residual iron concentrations were equal to or less than 0.01 mg/L since ferrous ions are readily oxidized to ferric ions to form ferric hydroxide particles at neutral pH. Manganese concentrations decreased significantly with increasing initial iron concentrations, but there was no marked difference in the permeate manganese concentrations obtained from stirred and unstirred dead-end cell filtration.

**Table 6** The effect of unstirred and stirred dead-end cell filtration systems on the permeate quality for artificial groundwater with initial arsenite of 150 ppb, manganous ion of 1 mg/L and ferrous ion of 1, 5, and 10 mg/L at neutral pH. Only aeration was applied.

<b>Condition of dead-end cell</b>	<b>Fe/As Ratio</b>	<b>Residual Fe (mg/L)</b>	<b>Residual Mn (mg/L)</b>	<b>Residual As (ppb)</b>	<b>%As Removal</b>
unstirred	6.67	0.01	0.71	96.4	35.7
stirred	6.67	0.01	0.69	88.3	41.1
unstirred	33.33	0.01	0.59	16.0	89.3
stirred	33.33	0.01	0.50	14.9	90.1
unstirred	66.67	0.01	0.38	5.4	96.4
stirred	66.67	0.01	0.40	3.3	97.8

Arsenic removal efficiency increased with increasing iron to arsenic weight ratio, as explained in the previous section (Section 3.2.1). Figure 20 shows the decreased permeate arsenic levels with the increasing iron to arsenic ratios. Both filtration processes, stirred or unstirred dead-end cell filtration, reduced residual arsenic concentrations to about the same level. Although there was a slight improvement in the arsenic removal at all Fe/As ratios when stirring was employed, this was probably due to the improved contact of arsenic ions with iron oxide particles during filtration. Primary MCL for arsenic was only met at Fe/As ratio of 66.67 in both conditions.

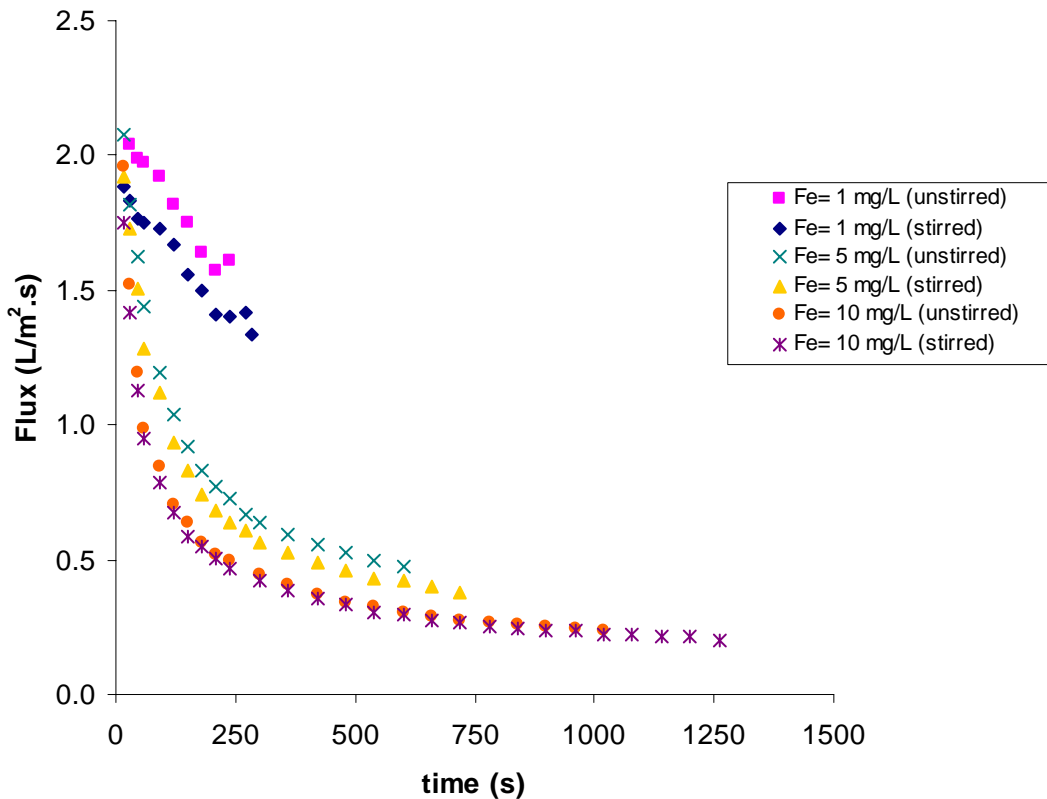


**Figure 20** Residual arsenic concentrations achieved after the filtration of artificial groundwater with initial arsenite of 150 ppb, manganous ion of 1 mg/L and ferrous ion of 1, 5 and 10 mg/L at neutral pH with stirred and unstirred dead-end cell filtration cells as a function of iron to arsenic ratio.

### 3.3.2 Permeate Flux

Figure 21 shows the effect of stirring on membrane fouling rate. Feed water with different initial ferrous ion concentrations, 150 ppb arsenite and 1 mg/L manganous ion were filtered at a TMP of 10 psi. As shown in Table 6, all residual iron concentrations were equal to or less than 0.01 mg/L, but manganese and arsenic removals were slightly better when the experiments were with stirring. Stirring during the filtration of feed water probably led to lower permeate flux rates due to increased contact of arsenic and manganous ions with iron oxide particles, thus leading to slightly better removal of the contaminants.





**Figure 21** Effect of stirred and unstirred dead-end cell filtration on permeate flux for artificial groundwater with initial Fe(II) concentrations of 1, 5 and 10 mg/L, Mn(II) concentration of 1 mg/L and As(III) concentration of 150 ppb at pH of 7.0.

In conclusion, unstirred dead-end cell filtration system was used in the microfiltration experiments since there was no significant difference in terms of both water quality and permeate flux.

### 3.4 THE EFFECT OF CONTACT TIME FOR POTASSIUM PERMANGANATE OXIDATION

#### 3.4.1 Water Quality

It is known that arsenate is much more effectively removed than arsenite since arsenate exists in natural waters as monovalent and divalent anion ( $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ ) while arsenite is predominantly in neutral form ( $\text{H}_3\text{AsO}_3$ ). Unlike arsenate anions, arsenite does not adsorb strongly to mineral surfaces [Thirunavukkarasu et al., 2003]. Therefore, an oxidation step is generally applied to convert arsenite to arsenate, and thus, increase the removal efficiency. In groundwaters, apart from arsenite, reduced forms of iron and manganese, i.e. ferrous and manganous ions, should also be oxidized for efficient removal of these contaminants.

Aeration is one alternative for oxidation, and its effects on the process efficiency were explained in the previous sections. Although iron particles were effectively removed from the feed water by aeration and microfiltration, high arsenic removals with low iron concentrations (about 1 mg/L) and manganese concentrations below the secondary MCL for manganese (0.05 mg/L) could not be achieved with aeration alone. Therefore, a strong oxidizer, potassium permanganate ( $\text{KMnO}_4$ ) was applied to enhance the removal of arsenic and manganese.

To determine the required contact time that should be provided after the addition of potassium permanganate, feed water with 1 mg/L ferrous ion, 1 mg/L manganous ion and various concentrations of arsenite (50, 100 and 150 ppb) were prepared at pH 7.0 and aerated for 10 minutes. Aeration was applied before permanganate oxidation to reduce the consumption of  $\text{KMnO}_4$  for oxidation of ferrous ion and for partial oxidation of arsenite and manganous ions. After this initial oxidation step, 1 mg/L of  $\text{KMnO}_4$  was added and mixed for 15 or 30 minutes

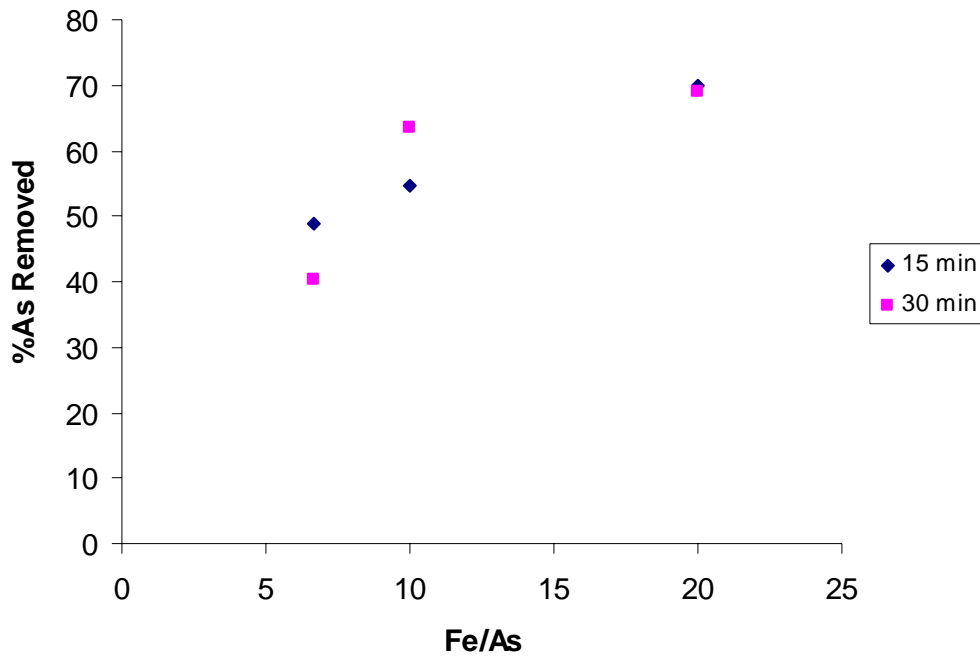
with a magnetic stirrer. The pH of feed water was controlled in the range of  $7.0 \pm 0.1$  by adding NaOH during the oxidation with permanganate. Permeate water quality data are given in Table 7.

**Table 7** The effect of contact time provided after potassium permanganate addition on the permeate quality for artificial groundwater with initial ferrous and manganous ions of 1 mg/L and arsenite of 50, 100, and 150 ppb at neutral pH.

<b>Contact time (min)</b>	<b>Fe/As Ratio</b>	<b>Residual Fe (mg/L)</b>	<b>Residual Mn (mg/L)</b>	<b>Residual As (ppb)</b>	<b>%As Removal</b>
15	20	0.01	0.73	15.1	69.8
30	20	0.01	0.73	15.5	69.0
15	10	0.01	0.78	45.3	54.7
30	10	0.01	0.81	36.5	63.5
15	6.67	0.01	0.72	76.8	48.8
30	6.67	0.01	0.81	89.7	40.2

Higher removal rates of arsenic with increasing contact time is expected since 10-15 minutes are required for oxidation and about 30 minutes are suggested for the coagulation of the oxidation by-products [Carus Chem. Co., 2001]. As shown in Table 7, higher percent arsenic removals were observed for 50 ppb and 100 ppb arsenite influent with 30 minutes contact time compared to 15 minutes. However, the percent removal of 150 ppb arsenite with 15 minutes contact time was found higher than the percent removal of the same arsenite concentration with 30 minutes contact time, which might be due to an experimental error during preparation of feed water or analysis of arsenic. Therefore, in the experiments conducted with potassium permanganate, 30 minutes contact time was provided to guarantee complete oxidation.

Figure 22 shows the relation between arsenic removal efficiency and iron to arsenic ratio. Increasing Fe/As ratios provided better arsenic removal, and the percent removal of arsenic was about 70% when Fe/As ratio of 20 was provided. As shown in Table 1, USEPA determined 80% maximum removal efficiency for arsenate with Fe/As ratio of 20, which is close to the arsenic removal efficiency observed in this study, showing that a comparable efficiency was achieved with the potassium permanganate oxidation. This efficiency may increase when high iron and high arsenic concentrations with the same Fe/As ratio is provided, as discussed in section 3.2.1, since the increased iron concentrations can provide higher removals of arsenic even when the ratio of iron to arsenic remains the same.

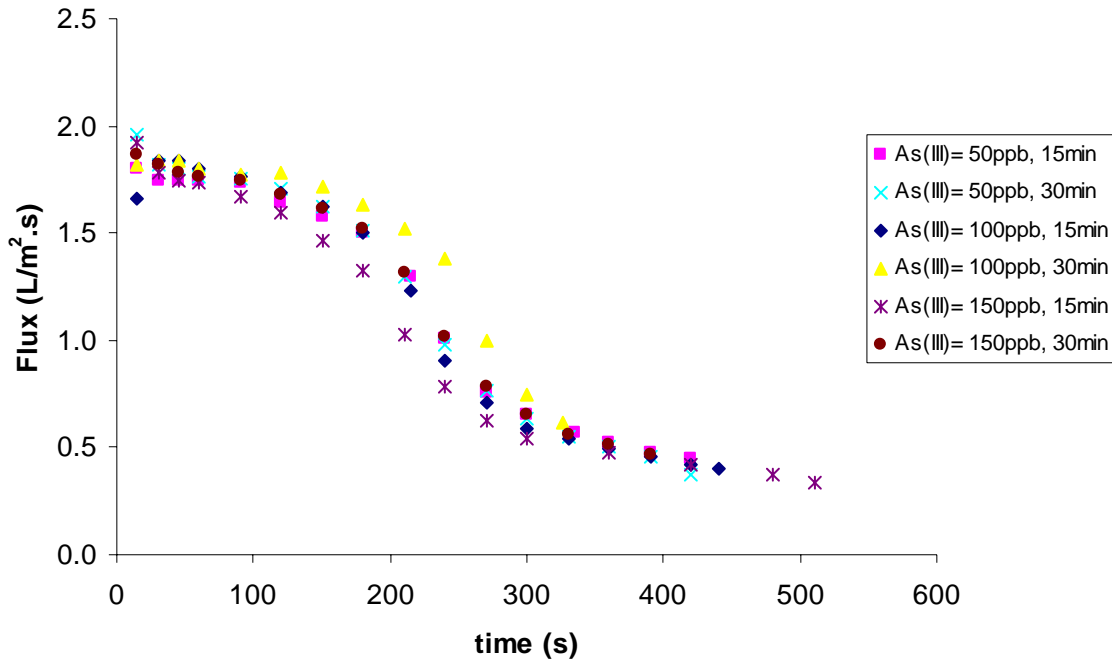


**Figure 22** Arsenic removal efficiency for different contact times provided after potassium permanganate addition as a function of iron to arsenic ratio.

Ferrous ions were readily removed from the feed water, but residual manganese levels after potassium permanganate oxidation (Table 7) were nearly identical to the manganese concentrations found in the permeates when only aeration was applied (Table 5). Such observation indicates that the potassium permanganate dose or experimental conditions (pH, initial manganese concentration, etc.) were not favorable for manganese removal. The effects of potassium permanganate dose and pH on the removal efficiency of manganese are discussed in section 3.5.

### **3.4.2 Permeate Flux**

The permeate fluxes with 15 or 30 minutes of contact time for potassium permanganate oxidation are compared in Figure 23. The permeate fluxes decreased from 1.8 L/m<sup>2</sup>.s to about 0.4 L/ m<sup>2</sup>.s in approximately 8 minutes in all experiments conducted with initial ferrous ion of 1 mg/L, manganous ion of 1 mg/L, arsenite concentrations of 50, 100 and 150 ppb and potassium permanganate dose of 1 mg/L. Minor differences in the flux rates were probably due to variations in manganese removal since all residual iron concentrations were less than or equal to 0.01 mg/L. The flux decline for feed water with 150 ppb initial arsenite concentration and with 15 minutes contact time is slightly higher than the flux decline for other samples due to higher manganese removal achieved in that experiment. However, membrane fouling was generally the same for both conditions (15 min or 30 min contact time).



**Figure 23** Effect of different contact times allowed for potassium permanganate oxidation on membrane fouling rate for artificial groundwater with initial Fe(II) concentrations of 1 mg/L, Mn(II) concentration of 1 mg/L and As(III) concentrations of 50, 100 and 150 ppb at pH of 7.0.

### 3.5 THE EFFECT OF POTASSIUM PERMANGANATE DOSE AND pH

#### 3.5.1 Water Quality

In the treatment of groundwaters, which include high amounts of manganous ions, i.e. reduced forms of manganese, a strong oxidizer is used to form manganese dioxide particles since the oxidation of manganous ions with oxygen is very slow. If there is any arsenite in the source water, the strong oxidizer can also convert arsenite to arsenate and increase the arsenic removal efficiency.

To determine the required potassium permanganate dose for efficient removal of arsenic and manganese, 1 or 2 mg/L permanganate was added to the feed water including 1 mg/L ferrous ion, 1 mg/L manganous ion, and different arsenite concentrations at pH 7.0. The same experimental procedure as the one explained in the previous section (section 3.4.1) was applied and 30 minutes contact time was provided after potassium permanganate addition. The residual iron, manganese and arsenic concentrations, and the percent arsenic removal for each experiment performed with a different iron to arsenic ratio are given in Table 8.

**Table 8** The effect of potassium permanganate dose on the permeate quality for artificial groundwater with initial ferrous ion of 1 mg/L, manganous ion of 1 mg/L and arsenite of 50, 100, and 150 ppb at pH 7.0.

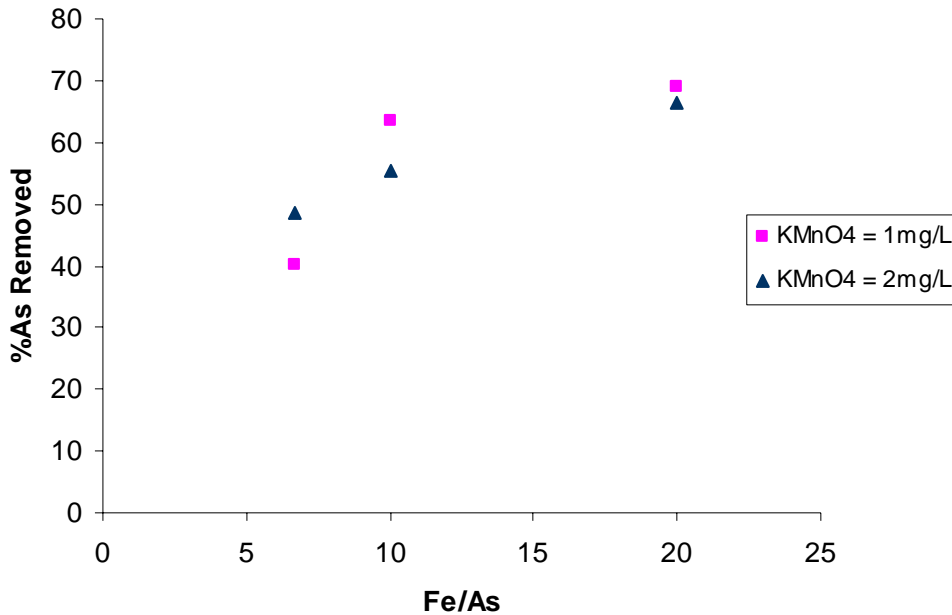
<b>KMnO<sub>4</sub> Dose</b> <b>(mg/L)</b>	<b>Fe/As</b> <b>Ratio</b>	<b>Residual Fe</b> <b>(mg/L)</b>	<b>Residual Mn</b> <b>(mg/L)</b>	<b>Residual As</b> <b>(ppb)</b>	<b>%As</b> <b>Removal</b>
1.0	20	0.01	0.73	15.5	69.0
2.0	20	0.01	1.34	16.8	66.4
1.0	10	0.01	0.81	36.5	63.5
2.0	10	0.01	1.34	44.7	55.3
1.0	6.67	0.01	0.81	89.7	40.2
2.0	6.67	0.01	1.37	77.2	48.5

As shown in Table 8, the residual manganese concentrations increased with increasing potassium permanganate dose. It is obvious that the required size of manganese dioxide particles, which can be removed by Supor®200 microfiltration membrane with 0.2 µm pore size, did not form in these tests. Although the stoichiometric amount of 1.92 mg potassium permanganate is required per 1 mg manganese ( $3\text{Mn}^{2+} + 2\text{KMnO}_4 + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_{2(s)} + 2\text{K}^+ + 4\text{H}^+$ ), 2 mg/L permanganate dose was very high for the removal of 1 mg/L manganese. The potassium

permanganate addition actually increased the residual manganese levels. The actual amount of permanganate used for the oxidation is less than the dosage calculated from the stoichiometry probably due to the catalytic influence of  $MnO_2$  on the reactions [EPA Guidance Manual, 1999].

The inadequate removal of manganese also affected the efficiency of arsenic removal. As shown in Figure 24, the percent arsenic removal was generally higher when 1 mg/L permanganate dose was applied in comparison with 2 mg/L permanganate dose. Since 1 mg  $KMnO_4$  includes 0.35 mg manganese, manganese levels in the feed water that involves initial manganese concentration of 1 mg/L were increased to 1.35 mg/L and 1.70 mg/L with the addition of 1 mg/L and 2 mg/L potassium permanganate, respectively. However, the manganese concentration removed from the feed water was higher (in terms of mg/L of manganese) when 1 mg/L permanganate dose was applied, considering the total manganese concentration provided after the addition of potassium permanganate (1.35 mg/L as manganese). About 0.6 mg/L manganese was removed from the feed water when 1 mg/L permanganate was used, while approximately 0.35 mg/L manganese removal was achieved with the addition of 2 mg/L permanganate dose. Therefore, arsenate which did not adsorb to iron oxide particles might be adsorbed to manganese dioxide particles and since manganese was more efficiently removed from the feed water with 1 mg/L permanganate dose, arsenic removal was higher at this dosage.





**Figure 24** Arsenic removal efficiency achieved with different potassium permanganate doses as a function of iron to arsenic ratio.

The pH of the feed water also influences the removal of arsenic and manganese. Artificial groundwaters with 1 mg/L of ferrous ion, 1 mg/L of manganous ion and 50 ppb of arsenite were first aerated followed by the potassium permanganate addition at pH 7.0 and pH 8.0 to determine the effect of pH on arsenic and manganese removal. As shown in Table 9, lower residual manganese concentrations were obtained at pH 8.0 than at pH 7.0 since the oxidation rate of manganous ions increases with increasing pH. The difference in the manganese removal at pH 7.0 and pH 8.0 was much more emphasized at potassium permanganate dosage of 0.5 mg/L when compared to the manganese removals observed with 1 and 2 mg/L of permanganate at these pH values. The manganese concentration was reduced to 0.18 mg/L at pH 8.0 with 0.5 mg/L permanganate dose while 0.70 mg/L residual manganese was obtained at pH 7.0 with the same dosage. The potassium permanganate concentration of 0.2 mg/L was not sufficient to

remove manganese efficiently. In summary, under the range of experimental conditions used in this study, 0.5 mg/L potassium permanganate dose provided the lowest residual manganese concentration (0.18 mg/L) at pH 8.0.

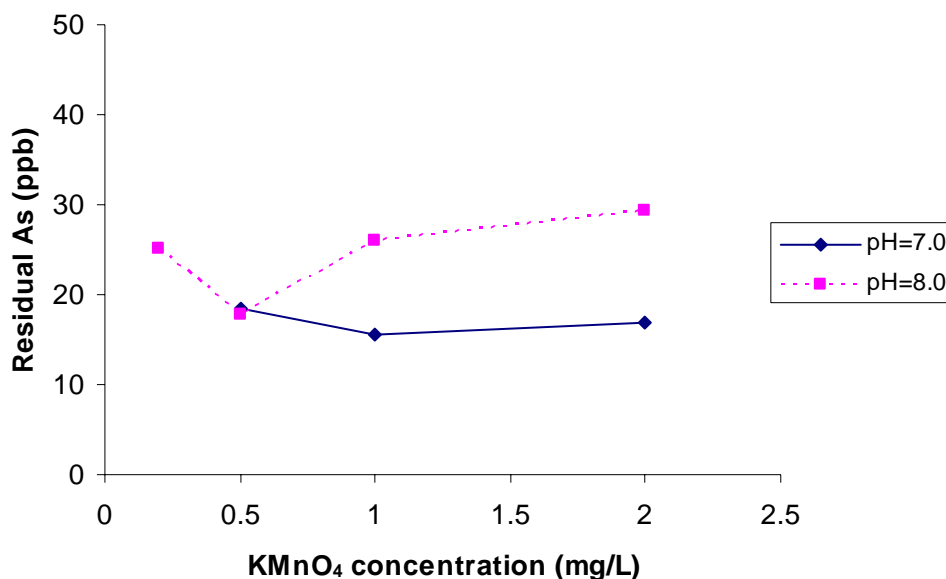
**Table 9** The effect of pH and potassium permanganate dose on the permeate quality for artificial groundwater with initial ferrous ion of 1 mg/L, manganous ion of 1 mg/L and arsenite of 50 ppb.

<b>Feed Water</b>	<b>KMnO<sub>4</sub> Dose</b>	<b>Residual Fe</b>	<b>Residual Mn</b>	<b>Residual As</b>	<b>%As</b>
<b>pH</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(mg/L)</b>	<b>(ppb)</b>	<b>Removal</b>
8.0	0.2	0.01	0.44	25.1	49.8
7.0	0.5	0.01	0.70	18.4	63.2
8.0	0.5	0.01	0.18	17.8	64.4
7.0	1.0	0.01	0.73	15.5	69.0
8.0	1.0	0.01	0.58	26.0	48.0
7.0	2.0	0.01	1.34	16.8	66.4
8.0	2.0	0.01	1.27	29.3	41.4

The pH level of feed water and the applied potassium permanganate doses also affected the arsenic removal rates. As illustrated in Figure 25, residual arsenic concentrations were higher at pH 8.0 than at pH 7.0 since arsenite was oxidized to arsenate with permanganate addition and arsenate adsorption decreases with increasing pH in the range of 4-9 [Wickramasinghe et al., 2004]. However, the arsenic concentrations at pH 7.0 and pH 8.0 were identical when 0.5 mg/L permanganate dose was applied due to efficient removal of manganese at this dosage.

Arsenic removals at pH 8.0 were 49.8% and 48.0% with permanganate doses of 0.2 mg/L and 1.0 mg/L, in which manganese removals were 0.63 mg/L and 0.62 mg/L, respectively. Arsenic removal decreased to 41.4% with the addition of 2.0 mg/L permanganate when

0.43 mg/L manganese was removed. These results indicate that similar arsenic and manganese removals are observed under the experimental conditions of this study. Also, arsenic removal decreases with a decrease in manganese removal at pH 8.0. However, since adsorption of arsenic onto iron oxide particles is much more efficient at pH 7.0, arsenic concentrations do not significantly change with increasing manganese removals. For example, 69% of arsenic was removed at 0.62 mg/L manganese removal with 1 mg/L permanganate dose and the arsenic removal just decreased to 66.4% when 2 mg/L permanganate was applied in which only 0.36 mg/L manganese was removed. When a significant removal of manganese was achieved at pH 8.0 (1 mg/L manganese removal with 0.5 mg/L permanganate addition), manganese dioxide particles can provide additional arsenic removals that are comparable to arsenic removals at pH 7.0. In conclusion, high manganese removals that can be achieved at pH 8.0 enhance arsenic removal. However, more effective mechanism of arsenate adsorption onto iron oxide particles provides efficient arsenic removal at pH 7.0 regardless of manganese removal.



**Figure 25** Residual arsenic concentrations achieved after the filtration of artificial groundwater with initial arsenite of 50 ppb, ferrous ion of 1 mg/L, and manganous ion of 1 mg/L at pH 7.0 and pH 8.0 as a function of potassium permanganate concentration.

Residual manganese concentrations were always higher than the secondary MCL for manganese of 0.05 mg/L for the initial manganese concentration of 1.0 mg/L. Aeration alone or aeration followed by potassium permanganate addition did not decrease the manganese levels below 0.05 mg/L. Since the removal of manganese at pH 8.0 was more efficient than at pH 7.0, some experiments were conducted at pH 8.0 with initial manganese concentration of 0.2 mg/L with aeration alone and aeration with oxidation by potassium permanganate in order to determine if the manganese standard can be met with lower initial manganese levels. Initial ferrous ion and arsenite concentrations were 1 mg/L and 50 ppb, respectively. The experiments performed with 1 mg/L initial manganese concentration showed that the half of this concentration, i.e. 0.5 mg/L, was the optimal potassium permanganate concentration. Therefore, permanganate dose of

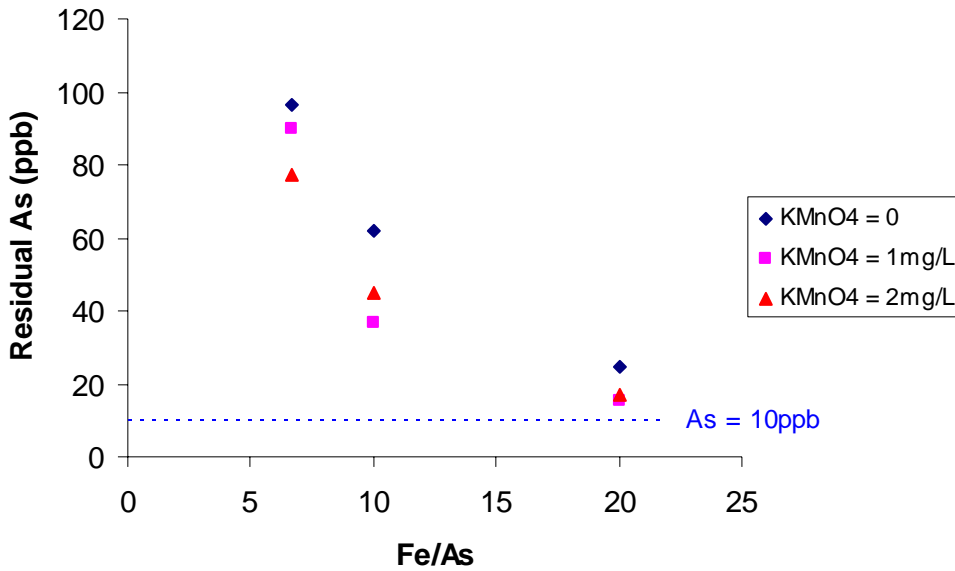
0.1 mg/L was applied when 0.2 mg/L initial manganese concentration was provided to maintain that optimum condition for manganese removal.

As shown in Table 10, the residual manganese levels were lower than the secondary MCL for manganese (0.05 mg/L) with both aeration alone and aeration followed by potassium permanganate addition. However, 35.4% of arsenic was removed when just aeration was applied while 55.4% arsenic removal was achieved when permanganate dose of 0.1 mg/L was used since oxidation of arsenite to arsenate is facilitated in the presence of a strong oxidizer.

**Table 10** The permate quality data for artificial groundwater with initial ferrous ion of 1 mg/L, manganous ion of 0.2 mg/L and arsenite of 50 ppb obtained after aeration alone and aeration followed by potassium permanganate oxidation at pH 8.0.

<b>Oxidation Procedure</b>	<b>Residual Fe (mg/L)</b>	<b>Residual Mn (mg/L)</b>	<b>Residual As (ppb)</b>	<b>%As Removal</b>
Aeration alone	0.01	0.04	32.3	35.4
Aeration + KMnO <sub>4</sub> of 0.1 mg/L	0.01	0.03	22.3	55.4

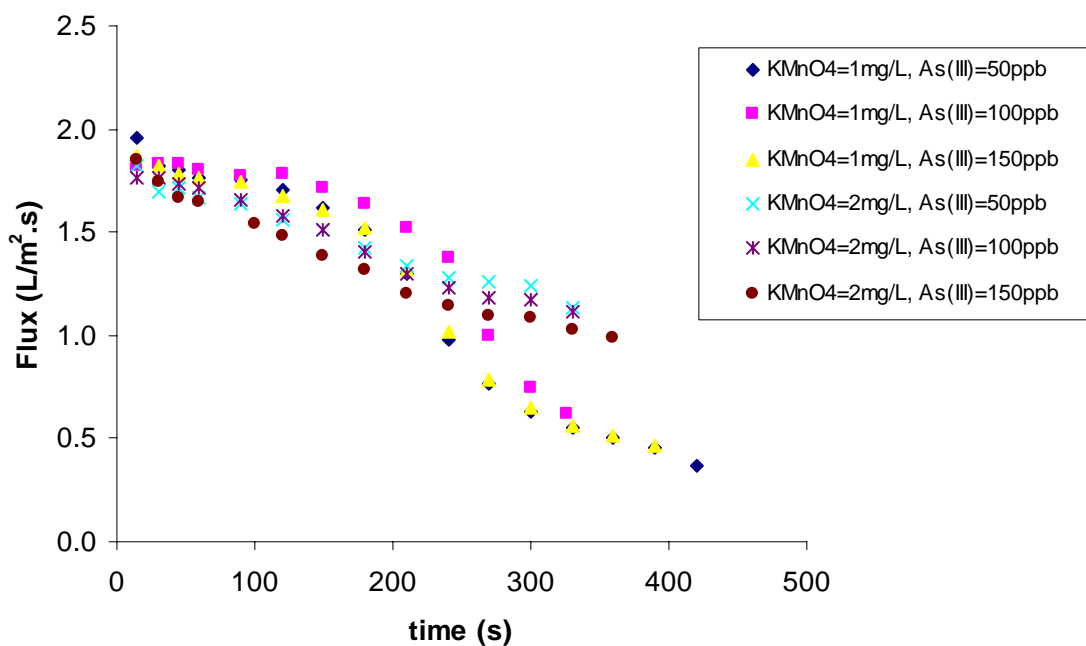
The effect of potassium permanganate on the removal of arsenic at pH of 7.0 can also be seen when the residual arsenic concentrations in Table 5 (aeration alone) and Table 8 (aeration followed by potassium permanganate oxidation) are compared in Figure 26. The residual arsenic concentrations achieved with aeration alone were always higher than the concentrations obtained with the addition of either 1 or 2 mg/L of potassium permanganate. However, the primary MCL for arsenic (10 ppb) was not met even when effective potassium permanganate oxidation was achieved, since 1 mg/L iron concentration was not sufficient to remove arsenic from 50, 100 or 150 ppb to less than 10 ppb.



**Figure 26** The effect of potassium permanganate dose on the removal of arsenic as a function of iron to arsenic ratio. Initial concentrations of ferrous ion of 1 mg/L, manganese ion of 1 mg/L and arsenite of 50, 100, and 150 ppb were provided at pH 7.0.

### 3.5.2 Permeate Flux

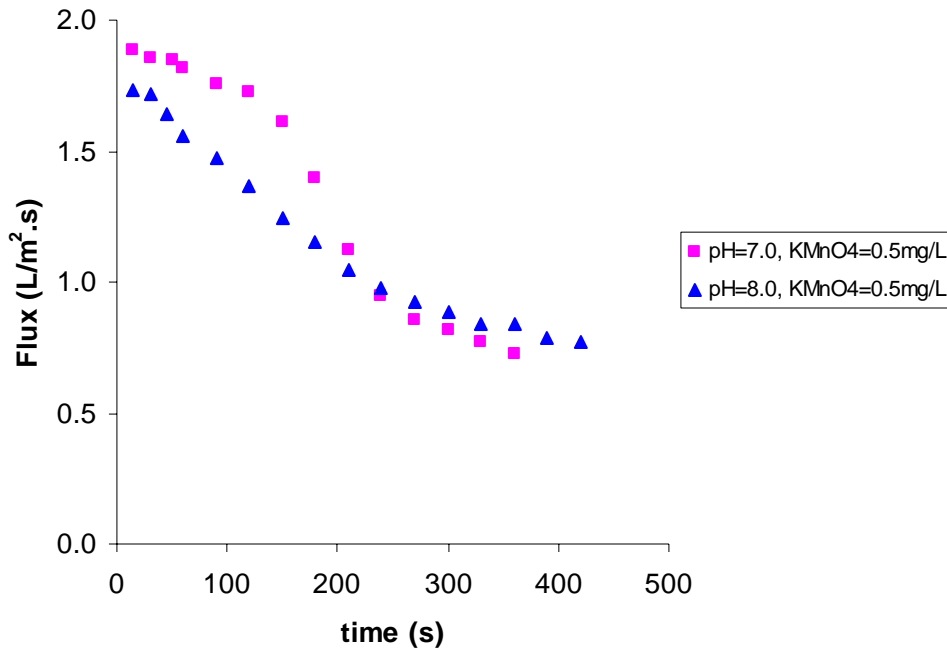
The effect of various potassium permanganate doses on water quality can also be figured out from the extent of membrane fouling. As shown in Figure 27, lower permeate fluxes were obtained after the oxidation of feed water with 1 mg/L potassium permanganate compared to the permeate fluxes of the feed water oxidized with 2 mg/L permanganate at pH 7.0. Higher manganese removal with 1 mg/L permanganate addition, as shown in Table 8, resulted in deposition of more manganese dioxide particles on the membrane surface since 2 mg/L permanganate dose was very high for the efficient removal of manganese and for the formation of particles larger than the membrane pore size (0.2  $\mu\text{m}$ ).



**Figure 27** Effect of potassium permanganate dose on permeate flux for artificial groundwater with initial Fe(II) concentration of 1 mg/L, Mn(II) concentration of 1 mg/L and As(III) concentration of 50, 100 and 150 ppb at pH 7.0.

When the effect of various potassium permanganate doses at pH 7.0 and pH 8.0 was compared with respect to arsenic removal, residual arsenic concentrations were higher at pH 8.0 since arsenate adsorption decreases with increasing pH. However, identical arsenic removals were observed at both pH 7.0 and pH 8.0 when potassium permanganate dose of 0.5 mg/L was applied. Water quality data in Table 9 shows that the highest manganese removal was achieved with 0.5 mg/L permanganate at pH 8.0. The difference between residual manganese concentrations at pH 7.0 and 8.0 at this dosage was much higher (0.52 mg/L) than the difference between manganese levels achieved at 1 mg/L permanganate dose (0.15 mg/L) or 2 mg/L permanganate dose (0.07 mg/L). Therefore, this marked difference in manganese removal provided high arsenic removal at pH 8.0. The permeate fluxes at pH 7.0 and pH 8.0 with

potassium permanganate dose of 0.5 mg/L also shows the difference in the amount of manganese removed from the feed water (Figure 28). High manganese removal at pH 8.0 leads to lower permeate flux than at pH 7.0.



**Figure 28** Effect of potassium permanganate dose of 0.5 mg/L on membrane fouling rate for artificial groundwater with initial Fe(II) concentration of 1 mg/L, Mn(II) concentration of 1 mg/L and As(III) concentration of 50 ppb at pH 7.0 and pH 8.0.

Although the permanganate dose of 0.5 mg/L achieved the highest removal of manganese, complete removal of 1 mg/L manganese could not be accomplished under the range of experimental conditions used in this study. Since manganous ions remained in the permeate, it can be concluded that microfiltration may not be the best method for the removal of high concentrations of manganese compared to sand filtration in which dissolved ions are removed by adsorption onto the manganese dioxide that forms on the surface of filter media.



## 3.6 THE EFFECT OF OXIDATION STATE OF IRON

### 3.6.1 Water Quality

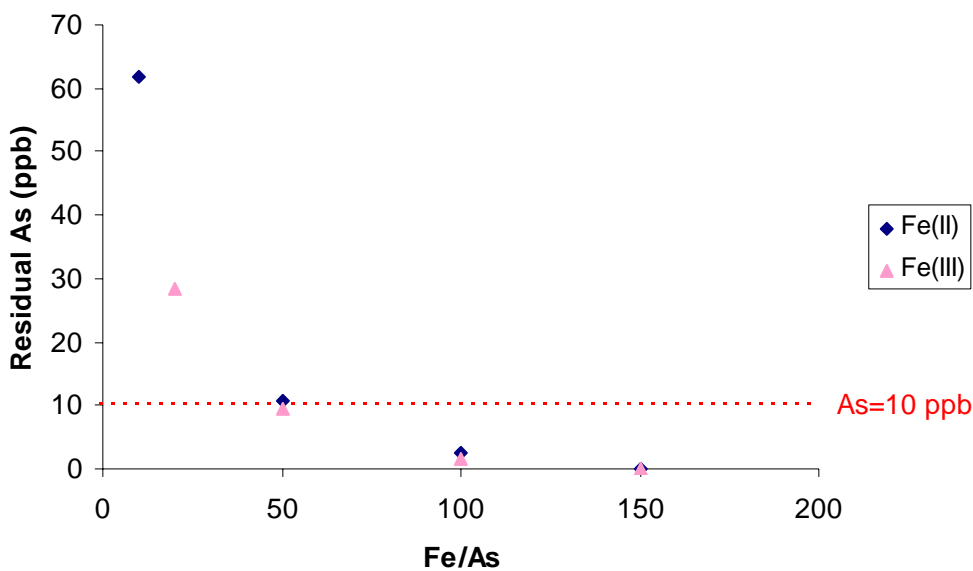
Iron concentration in source waters is a key parameter that determines the extent of arsenic removal in both Fe-Mn oxidation and coagulation processes. Ferric hydroxides can be precipitated in situ during coagulation with iron salts, generally ferric chloride, or during oxidation of groundwaters containing ferrous iron. To determine if there is any difference in terms of arsenic removal when the iron is added in ferrous or ferric form, experiments were conducted with feed waters containing initial concentrations of manganous ion of 1 mg/L, arsenite of 100 ppb and various concentrations of ferrous or ferric ions, which were added as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ , respectively. The feed water was aerated for 10 minutes and the pH was adjusted to 7.0.

As shown in Table 11, residual iron concentrations were about 0.01 mg/L, while manganese concentrations in the permeate correlated with initial iron concentrations. Increased iron concentrations resulted in decreased residual manganese levels due to adsorption of manganous ions onto iron oxide particles or the coprecipitation of iron and manganese as explained by Ellis et al. [2000].

**Table 11** The effect of oxidation state of iron on the permeate quality for artificial groundwater with initial concentrations of manganous ion of 1 mg/L, arsenite of 100 ppb and various concentrations of iron at pH 7.0. Only aeration was applied for the oxidation of the contaminants.

<b>Initial Fe Concentrations</b>	<b>Fe/As Ratio</b>	<b>Residual Fe (mg/L)</b>	<b>Residual Mn (mg/L)</b>	<b>Residual As (ppb)</b>	<b>%As Removal</b>
Fe(II) = 1 mg/L	10	0.01	0.72	61.9	38.1
Fe(III) = 2 mg/L	20	0.01	0.62	28.3	71.7
Fe(II) = 5 mg/L	50	0.01	0.47	10.7	89.3
Fe(III) = 5 mg/L	50	0.02	0.56	9.4	90.6
Fe(II) = 10 mg/L	100	0.01	0.41	2.4	97.6
Fe(III) = 10 mg/L	100	0.01	0.38	1.7	98.3
Fe(II) = 15 mg/L	150	0.01	0.32	0	100
Fe(III) = 15 mg/L	150	0.02	0.33	0	100

Residual arsenic concentrations also decreased with increasing iron concentrations and primary MCL for arsenic (10 ppb) was accomplished for iron to arsenic ratio above 50 (Figure 29). Slightly lower arsenic removals were observed with ferrous sulfate than with ferric chloride. Sulfate ions added as ferrous sulfate may lead to decreased arsenic removals, but low concentrations of sulfate ions have negligible effect on arsenic removal [Han et al., 2002; Wickramasinghe et al., 2004].



**Figure 29** The effect of oxidation state of iron on the removal of arsenic as a function of iron to arsenic ratio. Initial concentrations of manganous ion of 1 mg/L and arsenite of 100 ppb were provided at pH 7.0, and only aeration was applied.

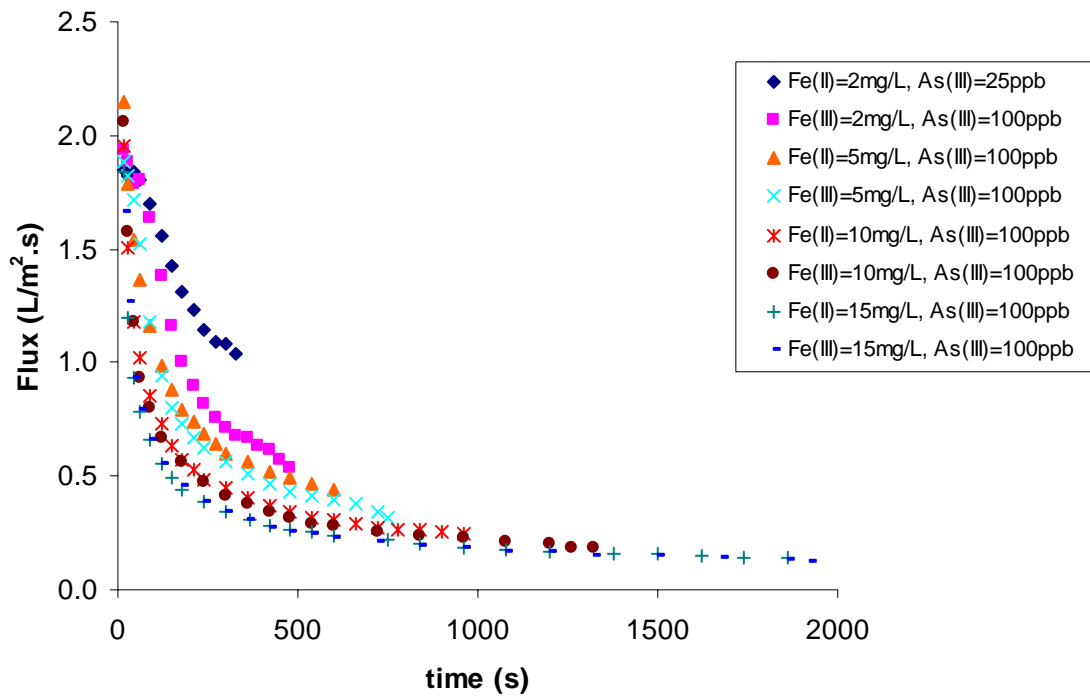
Overall, arsenic removal efficiencies provided by ferrous and ferric iron were very similar. Similar findings were reported by Borho and Wilderer [1996]. If there is insufficient iron concentration in the source water for the reduction of arsenic below the MCL, iron can be added as either ferrous or ferric iron without a significant difference in water quality. The choice of chemical can be made based on the cost alone.

### 3.6.2 Permeate Flux

In the experiments conducted with various initial concentrations of iron, manganese and arsenite, the membrane fouling rate was mainly dependent on the amount of iron particles formed during the oxidation process since the size of iron oxide particles was efficiently removed by Supor®200 membrane filter discs with 0.2 µm pore size. Apart from the initial concentration, the

oxidation state of iron or other dissolved ions present in the feed water could impact the membrane fouling rate.

As shown in Figure 30, lower permeate fluxes were obtained with the addition of ferric chloride than ferrous sulfate. The first reason may be the size of ferric hydroxide particles formed from ferrous or ferric ions. Ellis et al. [2000] investigated particle size distribution of iron oxides after the oxidation of ferrous ions, and revealed that the particle sizes ranged from 1.5 to 50  $\mu\text{m}$ . However, in coagulation studies performed with ferric chloride, the size of arsenic loaded ferric hydroxide particles were found generally in the submicron range for a coagulant dose up to 25 mg/L [Brandhuber and Amy, 1998] or in the 2-10  $\mu\text{m}$  range [Chwirka et al., 2004]. Another reason for the difference in the permeate flux during the filtration of feed water including ferric chloride or ferrous sulfate is the presence of sulfate and chloride ions. As suggested by Wickramasinghe et al. [2004], sulfate groups may be involved in the coagulation reactions to form larger flocs that are more easily rejected by the membrane compared to chloride ions. This effect is particularly significant in the filtration of feed waters with low iron concentrations, e.g. 2 mg/L in Figure 30, since more iron oxide particles formed in waters with high iron levels can mask the effect of other dissolved ions on permeate flux. Higher removals of arsenic by adsorption or coprecipitation with iron hydroxides may also lead to lower permeate fluxes, which is particularly valid for the filtration of feed water with 2 mg/L iron and 100 ppb arsenite influent compared to 25 ppb arsenite influent with the same iron dosage (Figure 30).



**Figure 30** Effect of oxidation state of iron (ferrous vs. ferric iron) on permeate flux for artificial groundwater with initial Mn(II) concentrations of 1 mg/L and different initial iron and arsenite concentrations at pH 7.0.

#### 4.0 SUMMARY AND CONCLUSIONS

Arsenic is classified as a human carcinogen and is a common contaminant in groundwaters in many parts of the world. Amongst the conventional treatment processes, Fe-Mn oxidation is an attractive method for the removal of arsenic from groundwaters since arsenic can be effectively removed with iron that is already present in groundwater. The arsenic loaded particles formed by adsorption or coprecipitation reactions are easily removed with microfiltration process. Therefore, the main objective of this study was to investigate the efficiency of arsenic removal from groundwater by Fe-Mn oxidation and microfiltration under a variety of process conditions, including iron to arsenic ratio, pH, potassium permanganate dose, contact time, oxidation state of iron and stirring in dead-end filtration cell.

Artificial groundwater containing various amounts of iron, manganese, and arsenite was prepared using DI water and the pH was adjusted to the required value (typically to pH of 7.0). Two types of oxidation approaches were applied: aeration and oxidation with potassium permanganate. Aeration was applied in all of the experiments to oxidize mainly ferrous ions, and potassium permanganate was added after aeration in some experiments to further oxidize arsenite and manganous ions. The filtration of the oxidized feed water was conducted in the unstirred dead-end cell filtration system using Supor®200 membrane disc filters with 0.2 µm nominal pore size at a trans-membrane pressure of 10 psi. The iron and manganese analysis were performed with flame atomic absorption spectrophotometry, and total arsenic was determined using graphite furnace atomic absorption spectrometry.

The Fe-Mn oxidation and microfiltration lab-scale study yielded the following significant findings and conclusions:

- pH does not significantly influence arsenic removal when only aeration is applied, but its impact is important in the potassium permanganate oxidation. Similar residual arsenic concentrations were obtained in the experiments carried out with aeration alone in the pH range from 6.5 to 8.0 since arsenite is mostly in the neutral form up to pH of 9.22 (pK<sub>a1</sub> of arsenite); however, the difference in the arsenic removal was more pronounced when a strong oxidizer, i.e. potassium permanganate, was added due to much more efficient conversion of arsenite to arsenate and thus the predominance of anionic forms of arsenic whose adsorption is enhanced at lower pH values.
- Fe/As ratio of 60 is sufficient to reduce the arsenic concentrations ranging from 25-250 ppb to below 10 ppb (primary MCL for arsenic) simply with aeration and microfiltration at pH of 7.0.
- Ferrous iron and ferric iron are comparable in terms of their ability to remove arsenic. If the iron concentration is not sufficient to lower the arsenic level below the standard, iron in either ferrous or ferric form can be added to the source water without any significant difference in the arsenic removal efficiency.
- Initial arsenite concentrations did not have a significant effect on the removal of arsenic over a wide range for high initial iron concentrations ( $\geq 5$  mg/L). However, increasing arsenite levels decreased the arsenic removal when low iron dosages were applied.
- Oxidation with potassium permanganate facilitates additional arsenite removal compared to aeration alone. Aeration process in the presence of high iron concentrations can

partially oxidize arsenite to arsenate, but complete oxidation of arsenite can be achieved with potassium permanganate addition. Since arsenate, which is the anionic form of arsenic, can be removed much more effectively than arsenite, which is the neutral form of arsenic, oxidation with potassium permanganate provides lower residual arsenic levels.

- Although higher arsenic removals are observed at pH 7.0 than at pH 8.0, identical residual arsenic concentrations are obtained with 0.5 mg/L permanganate dose at both pH 7.0 and 8.0 due to the effect of pH on manganese oxidation and arsenic adsorption. Higher manganese removals that can be achieved at pH 8.0 enhance the arsenic removal, while more effective adsorption of arsenate, thus efficient removal of arsenic occurs at pH 7.0 regardless of manganese removal.
- Stirred and unstirred dead-end filtration cells yielded similar results in terms of water quality and permeate flux.
- Low residual iron concentrations ( $\sim 0.01$  mg/L) were obtained at all initial iron levels; however, residual manganese concentrations were always higher than the secondary MCL for manganese (0.05 mg/L) when 1 mg/L of manganese was added to the feed water. Although manganese levels in the permeate decreased with increasing initial iron concentrations due to adsorption of manganous ions onto iron oxide particles or the coprecipitation of iron and manganese, the residual manganese levels below the standard were achieved using this treatment approach only when the initial manganese concentration was 0.2 mg/L.
- Iron hydroxide and manganese oxide particles are the primary reason for membrane fouling. Arsenic removal also decreases permeate flux, but its impact is not significant



since the concentration of arsenic in the feed water is very low (ppb levels) compared to iron and manganese.

## 5.0 RECOMMENDATIONS FOR FUTURE STUDIES

Fe-Mn oxidation and microfiltration process for the removal of arsenic from groundwaters was shown as a promising technique. Artificial groundwater including various concentrations of iron, manganese, and arsenic was prepared and used in the experiments. However, in natural groundwaters sulfate, phosphate, carbonate, chloride, silicate or natural organic matter may affect the removal of arsenic by ferric hydroxides, particularly during the adsorption reactions in which anions can compete with arsenate for surface sites and reduce the surface potential. Therefore, it is suggested to use natural groundwater in future studies to evaluate the effects of other inorganic contaminants on the removal of arsenic during the oxidation process.

In this study, microfiltration was performed with unstirred dead-end filtration cell. The filtration rate can decrease rapidly in a dead-end cell due to cake formation on the membrane surface that causes high resistance to flow. Therefore, cross-flow filtration, in which feed water flows parallel to the membrane surface, thereby minimizing the cake formation by providing shear at the surface of the membrane and thus permitting higher filtration rate for a long period of time, is generally employed in full-scale systems. In further studies, cross-flow filtration can be used as the microfiltration unit to represent continuous systems instead of dead-end cell filtration. Membrane fouling in cross-flow filtration systems should be investigated during the prolonged use, and the process parameters, such as cross-flow velocity, trans-membrane pressure and membrane cleaning methods, should be optimized to obtain increased permeate flux rates.

Another recommendation for future studies is to examine the effects of different membrane materials on membrane fouling. In this study, Supor®200 polyethersulfone (PES) microfiltration membrane was used after Fe-Mn oxidation process. Other common membrane materials, such as polysulfone (PS), cellulose acetate (CA), polypropylene, and polyvinylidene fluoride (PVDF), can be employed for microfiltration of iron and manganese oxide particles, and the rejection of these particles by different membrane materials should be evaluated. Since membranes with smaller pore sizes provide higher water quality, another type of low-pressure membrane, ultrafiltration membranes, can also be used for the removal of arsenic bearing particles, but the trade-off between water quality and water quantity should be established in laboratory scale studies before deciding on which membrane technology is best suited for field trials.

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