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Arsenic Removal from Water Using Manganese Greensand: Laboratory Scale Batch and Column Studies

by:

New Mexico State University
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Bates, J., A. Hanson , D. Heil, M. Johnson, G. Rayson, A. Bristol, Batch studies of Arsenic Removal From Drinking Water Using Manganese Greensand, AWWA Annual National Conference, Dallas TX, June 21-25, **1998 (Third Place Poster)**.

A. Hanson , D. Heil, J. Bates, M. Johnson, G. Rayson, A. Bristol, Removal of Arsenic From Drinking Water Using Manganese Dioxide Coated Filter Media, AWWA **Inorganics** Workshop, San Antonio TX, February 23, 1998.

Bates, J., A. Hanson, F. Cadena, B. Thomson, A. Bristol, Technologies for the Removal of Arsenic From Drinking Water in New Mexico, New Mexico Science Journal, 1998.

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EXECUTIVE SUMMARY

Future drinking water regulations for arsenic are expected to be lowered from the present 50 $\mu\text{g/L}$ to somewhere between 2 and 20 $\mu\text{g/L}$. Two recent studies have indicated that manganese greensand could be very effective in removing arsenic. Manganese greensand is a mineral called glauconite that is coated with a manganese oxide coating and used to remove iron and manganese hardness from drinking water.

The purpose of this study is to evaluate several important parameters for arsenic removal using manganese greensand. The parameters chosen to be evaluated were contact time, pH, iron concentration, and potential of sulfate interference. In addition both of the common oxidation forms of arsenic, arsenite and arsenate, were studied.

The experimental procedure was carried out under laboratory conditions. Adjustment of pH was accomplished by the addition of acid or base. Iron-arsenic solutions were mixed for ten minutes. One gram of manganese greensand was added to solution and mixed for the contact time desired. The solution was filtered to separate the liquid phase from the sand. The solution was analyzed by a commercial lab using inductively coupled plasma mass spectrophotometry with a detection limit for arsenic of $\pm 0.4 \mu\text{g/L}$.

A range of pH's from 3 to 9 was evaluated. A pH of 5 was found to be optimal for arsenic removal in the arsenate and arsenite form. For an initial arsenic concentration of 50 $\mu\text{g/L}$, the final arsenic concentration ranged from 1.8 $\mu\text{g/L}$ to 4.2 $\mu\text{g/L}$ for a pH of 5. Two more batch sets were performed at this optimal pH with similar results. Varying ferrous chloride concentrations were added to the solution from zero to 20 times the arsenic concentration in terms of molar ratio of ferrous chloride to arsenic. At all the pHs no significant correlation between iron dose and arsenic removal can be seen. Contact times from 15 minutes to 24 hours were evaluated at a pH of 5. The results indicate that arsenic adsorption to manganese greensand has reached its maximum by 15 minutes of contact time. Sulfate interference was evaluated at a pH to 5. Based on the results from the batch testing, sulfate did not interfere with arsenic removal.

The greensand columns successfully removed arsenic, but only after the media had been pre-treated with dilute acid. A solution of dilute HCl was passed through the media until the influent and effluent pH came to steady state. This allowed the operator to control the operational pH. With the bed properly prepped, 400+ bed-volumes of water were treated with no evidence of impending breakthrough. The bed was regenerated and another 200+ bed-volumes were treated. It appears that the appropriate preparation of the media will allow manganese greensand to act as an effective arsenic removal media. It appears that neither BIRM nor Anthrasand is an adequate replacement for manganese greensand.

There are a number of simple technologies, such as ion exchange, coagulation/microfiltration, iron oxide based filtration, and activated alumina, which are on the market for treatment of arsenic in water. In a situation where only arsenic is to be removed, or where arsenic and fluoride are to be removed, the technology discussed here is probably not cost effective. However, in a situation where Fe & Mn are present with As this technology has great promise. This technology is especially interesting to utilities where Fe and Mn are already being removed using a manganese greensand filter. It is possible that a small pH adjustment from 8+ to 6.5 may be all that is required to bring the facility into compliance.

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1. INTRODUCTION

1.1 Arsenic Background

1.1 .1 Arsenic Chemistry

Arsenic is Group 15 element. It is usually classified as a non-metal with some metallic properties. It has an *atomic* number of 33 and an atomic mass of 74.92. It is odorless, tasteless, and highly toxic. These three characteristics made arsenic the perfect poison in medieval times. Inorganic arsenic can exist in four oxidation states: +5, +3, 0, -3. The two inorganic forms most prevalent in aqueous chemistry are the pentavalent arsenate ion, (As[V]), and the trivalent arsenite ion, (As[III]). Organic forms of arsenic also exist that contribute to total arsenic, but they are probably not significant in most drinking water sources and are therefore not considered in this research.

1 .1.2 Drinking Water Regulations

The regulation of arsenic in drinking water has been continually evolving for half a century. The limits for arsenic in drinking water continue to be hotly debated in scientific and legislative circles because of the potential cost (in terms of treatment or in terms of health care) to the American public. Table 1 summarizes some of the important events relating to arsenic regulation in the United States.

In 1942 the Public Health Service set a maximum permissible concentration for arsenic at 50 $\mu\text{g/L}$, based on existing data on the acute, short-term toxic effects, which were well known because of the use of arsenic as a poison over the past 4000 years (Pontius,1994). This standard was adopted by many of the states, but was relatively unenforceable because the Public Health Service had no national enforcement powers. The standard was reaffirmed by the Public Health Service in the water quality standards adoptions of 1946 and 1962 (Pontius,1994).

The 1974 Safe Drinking Water Act required the recently created U.S. Environmental Protection Agency (EPA) to set enforceable standards for health related drinking water contaminants that were to apply to all public water systems. In 1975, the EPA set the interim maximum contaminant level (MCL) for arsenic at 50 $\mu\text{g/L}$, based in part on the 1962 USPHS standard (Pontius,1994). The standard for arsenic has remained at 50 $\mu\text{g/L}$ since that time, but there has been much debate over whether to lower it.

The Safe Drinking Water Act Amendments of 1996 require a final National Public Drinking Water Regulation (NPDWR) for arsenic must be proposed by January 1, 2000 and promulgated by January 1, 2001. This regulation will be based on current research to “reduce the uncertainty in assessing health risks associated with exposure to low levels of arsenic.” (Pontius, 1997). The range of values under consideration is from 2 $\mu\text{g/L}$ to 20 $\mu\text{g/L}$ as total arsenic.

Table 1: Summary of Arsenic Regulation in the U.S. (summarized from Pontius)

1942	Public Health Service (PHS) sets arsenic standard at 50 µg/L in drinking water.
1946	PHS reaffirms arsenic standard.
1962	PHS reaffirms arsenic standard.
1968	Tsena publishes paper, "Prevalence of Skin Cancer in an Endemic Area of Chronic Arsenicism in Taiwan."
1970	Environmental Protection Agency (EPA) is created.
1974	Safe Drinking Water Act created, require EPA to set and enforce drinking water standards.
1975	Interim Primary Drinking Water Standard MCL for arsenic set at 50 µg/L.
1977	Tsena publishes paper, "Effects and Dose-Response Relationships of Skin Cancer and Blackfoot Disease With Arsenic."
1983	EPA report concludes that studies up to that point lacked sufficient statistical power to definitively determine whether arsenic causes skin cancer.
1985	EPA proposes a recommended MCL of 50 µg/L.
1986	Amendments to the SDWA rename the RMCL as the MCL goal and require EPA to set a MCL and a MCLG for arsenic by 1989.
1988	EPA panel concludes that more research is needed on threshold effects.
1989	Bull Run Coalition files suit against EPA for missing MCL deadline. New deadline set for 1991.
1991	EPA misses deadline. decides no further research is needed, and must propose MCL's by November 1 1992.
1992	Two new studies re-evaluating old data show a high correlation between arsenic in drinking water and cancer. EPA misses deadline.
1994	EPA misses deadline.
1995	EPA misses deadline.
1996	Amendments to the SDWA require a proposed standard for arsenic by January 1, 2000, and a standard be promulgated by January 1, 2001.

International standards have generally been 50 µg/L, but other countries are looking at lowering their standards also. In 1993, the World Health Organization (WHO) recommended a provisional guideline value of 10 µg/L based on both estimated health risks and the practical detection limit (Weston, 1997). Recently the German standard for arsenic has been lowered to 10 µg/L (Weston, 1997).

1.1.3 Health Implications of Arsenic

Arsenic occurs naturally, being the twentieth most abundant element in the earth's crust (Pontius, Brown, and Chen, 1994). Humans are exposed to arsenic primarily through air, food, or water (Pontius, Brown, and Chen, 1994). Exposure through air is negligible unless the area is heavily polluted by smelters or power plants (Pontius, Brown, and Chen, 1994). Exposure to arsenic through food ingestion is significant. "Based on market-basket surveys of the total arsenic content in United States food, the US Food and Drug Administration has estimated that adults ingest an average of about 53 µg/day of arsenic from the diet" (Pontius, Brown, and Chen, 1994). EPA estimates that only twenty percent of the arsenic in food, or 10 µg/day, is inorganic arsenic,

which is the most toxic form of arsenic (Pontius, 1994). Ingestion of inorganic arsenic in drinking water thus possibly becomes the largest source of exposure to the toxic and carcinogenic effects of arsenic if the arsenic concentration in the water is more than 5 $\mu\text{g/L}$, assuming an adult drinks two liters of water per day.

Three possible types of health effects exist for exposure to arsenic. The first effect is toxic effects due to short term, acute exposure to larger amounts of arsenic. The second effect is toxic effects due to long term, chronic exposure to smaller amounts of arsenic. The third effect is increased risk of cancer due to long term, chronic exposure to smaller doses of arsenic. The carcinogenic effect is probably the controlling factor in determining how low to set the drinking water standard for arsenic (Pontius, Brown, and Chen, 1994). Complicating this is the fact that each species of arsenic has a different toxicity.

Studies of organic arsenic excretion suggest that doses of inorganic arsenic up to around 200 $\mu\text{g/day}$ are detoxified, but the validity of the studies was questioned by other scientists (Pontius, Brown, and Chen, 1994). Scientists have suggested that arsenic could actually be a trace nutrient essential to human health. "Studies with minipigs, goats, chicks, hamsters, and rats have indicated that it is an essential nutrient" (Pontius, Brown, and Chen, 1994). Data on humans is insufficient to determine essentiality, but it remains a hotly contested subject. Uthus has suggested that a daily intake of 12 to 40 μg of inorganic arsenic would constitute a safe and adequate dietary intake (Pontius, Brown, and Chen, 1994). Subtracting the 10 $\mu\text{g/day}$ contributed by food, the safe level of arsenic in drinking water would be as high as 15 $\mu\text{g/L}$, assuming an adult would drink 2 liters per day, based on short term toxic effects.

The EPA has used similar reasoning to calculate a maximum level for arsenic based on chronic toxic effects. The value calculated is between 4 to 28 $\mu\text{g/L}$, depending on the safety factor used (Pontius, Brown, and Chen, 1994). Subtracting the 10 $\mu\text{g/day}$ contributed by food, the safe level of arsenic in drinking water would be as high as 9 $\mu\text{g/L}$, assuming an adult drinks 2 liters per day.

The studies in Taiwan linked arsenic with skin cancer. Later studies have also indicated links to internal cancers. One of the most recent studies done in Argentina indicated that people who drank from water wells with an average arsenic concentration of 179 $\mu\text{g/L}$, had an incidence of bladder cancer twice the national average (Raloff, 1996). The data is still being reviewed and restudied in that case.

Statistical studies in the United States and also in Hungary show no positive correlations between arsenic and cancer. Several explanations can be made. One of the more interesting thoughts is that perhaps arsenic acts more as a promoter of cancer, rather than an initiator (Pontius, Brown, and Chen, 1994). This means that other factors in the Taiwanese study, (such as malnutrition, a genetic tendency for cancer, or other contaminants in the water), may have contributed to the high cancer rate, and that the arsenic exposure amplified the number of cancer cases in the presence of these other factors (Pontius, Brown, and Chen, 1994).

The cancer risk is extrapolated from a model which assumes that the dose-response relationship is linear at low doses. Statistically this is invalid because no data exist at low levels and thus no confidence levels exist. Based on the skin cancer studies in Taiwan, the EPA calculated that a

maximum level of 2 $\mu\text{g/L}$ of arsenic would satisfy the risk requirement of one excess death in a lifetime out of ten thousand people (1: 10,000) (Pontius, Brown, and Chen, 1994). One of the questionable assumptions is that the Taiwanese population is similar to the U.S. population. Studies are continuing that mostly focus on the cancer effects of arsenic. These studies will be used to set the arsenic limit for drinking water in 2001.

1.1.4 Occurrences of Arsenic

The occurrence of arsenic can be associated with natural conditions or the industrial practices of mankind. Being a basic element, the occurrence of arsenic is worldwide, but is more concentrated in some geographic regions. Natural arsenic is generally associated with sedimentary rocks of marine origin, weathered volcanic rocks, fossil fuels, and geothermal areas (Korte and Fernando, 1991). Arsenic readily substitutes for silicon, ferric iron, and aluminum in crystal lattices of silicate minerals, and therefore, it is possible for it to occur in all geological materials (Korte and Fernando, 1991). Mankind's activities have caused higher concentrations of arsenic to result in some places. Arsenic is associated with mining wastes, agricultural uses, wood preservation, and irrigation practices (Korte and Fernando, 1991) Some typical concentrations of arsenic in various materials are given in Table 2.

In general, arsenic occurs in higher levels in the southwestern United States and along the western coast. According to Reid (1994), the EPA estimates that 18 percent of the groundwater systems in the United States have arsenic levels greater than 2 $\mu\text{g/L}$. In order to treat the water from these groundwater systems to below 2 $\mu\text{g/L}$ will cost over \$2.1 billion per year according to one EPA estimate (Pontius, 1994). Hanson (1995) showed that 51.3% of existing groundwater systems in New Mexico exceed the 2 $\mu\text{g/L}$ level. A study in Albuquerque, New Mexico, predicted that the annual cost of treating the groundwater of that city to below 2 $\mu\text{g/L}$ using reverse osmosis would cost \$400 million or roughly an extra \$800 per person per year.

Table 2: Typical Arsenic Concentrations in Various Materials

Material	Concentration Range, ppb	Source
Shale, clay	6.4, 9	Weston, 1997
Sandstone, sand	1.1, 4.3	Weston, 1997
Carbonates	0.7 - 2.5	Weston, 1997
Soil	5.5 - 13	Weston, 1997
Loess	8.3	Weston, 1997
Terra rossa	15-21	Weston, 1997
marine crabs, lobster, shrimp	10-40	Pontius, 1994
freshwater fish	0.1 - 3.0	Azcue, 1995
marine fish	1.0 - 100	Azcue, 1995
vegetation	0.01 - 5.0	Azcue, 1995

Most sources indicate that arsenate (+5) is believed to be the prevalent form in surface waters, but the prevalent form in groundwater is not readily apparent. Korte and Fernando, (1991) conclude that arsenite (+3) is more prevalent in groundwater than was previously believed. It exists primarily in alluvial systems with reducing groundwater (Korte and Fernando, 1991). A recent study by McNeil and Edwards (1995) surveyed 13 plants, of which 8 obtained their raw water from groundwater. Only one of these plants had any arsenite (78% arsenite, 22% arsenate), whereas all the other plants had 100 percent arsenate in the raw water. This information is important because each species has a different toxicity and different removal characteristics.

1 .1.5 Arsenic Removal Techniques

Several methods have been investigated for removal of arsenic, including reverse osmosis, ultrafiltration, electrodialysis, ion exchange, adsorption, and chemical precipitation or adsorption by metal hydroxides (Huang and Vane, 1989). Because conventional treatment steps are already in place at many utilities, capital expenses can be minimized if arsenic can be removed using existing processes. The optimization of these conventional treatments has been studied by many sources.

1.1.5.1 Iron Coagulation

Ferric chloride coagulation in addition to chlorination followed by slow sand filtration was investigated by Shen in 1973. Shen determined that this was the best way to remove arsenic, obtaining pilot scale results that achieved better than 90 percent removal of arsenic, (from 790 ppb to 70 ppb) for filter runs of up to 59 days. The ferric chloride dose was varied from 51 to 304 mg/L, the chlorine dosage was varied from 14 to 69 mg/L, and the pH was neutral, at 7.0 to 7.4. Shen noted that the chlorine improved the arsenic removal using ferric chloride coagulation. This might have been due to the oxidation of As(+3) to As(+5). Shen also found an effective way to regenerate the sand in the filters by treating it with a 2,500 mg/L NaOH solution and then washed with arsenic free tap water.

Laboratory experiments by Edwards (1994) indicate that formation of even trace amounts of Fe(OH)₃ precipitate can remove significant concentrations of soluble arsenate during the oxidation of Fe(II). The same study concluded that oxidation of Mn(II) is not expected to remove significant concentrations of soluble arsenic. A full scale study by McNeil and Edwards (1995) supported that research. At the full scale treatment plants, oxidation of Fe^{+*} (>1.5 mg/L Fe⁺²) resulted in 80-95 percent arsenic removal, whereas plants that oxidized only Mn⁺² did not remove significant concentrations of arsenic.

A lab scale study by Kirk (1993) concluded that large concentrations of arsenic could be removed through co-precipitation with ferric hydroxide. The most effective pH was at 5.5 with a mole ratio of iron to arsenic of 7.3 to 1. Similar research was performed by Swanson (1994) that used ferrous hydroxide and allowing it to oxidize. The most effective pH was determined to be 6. Swanson also concludes that lower concentrations of arsenic require larger ratios of iron to arsenic in order to precipitate. Research by Roybal (1997) investigated using carbon dioxide to

lower the pH to 5.3 and precipitation with ferric hydroxide. The removal efficiencies measured in this work were less than theory would have lead one to expect, apparently due to problems with the experimental design.

A lab study by Vogels (1996) explored using ferrous salts followed by the addition of a strong oxidant, (K_2FeO_4) to remove arsenate at an initial concentration of 50 $\mu\text{g/L}$. Removals of greater than 90 percent (from 50 $\mu\text{g/L}$ to 5 $\mu\text{g/L}$) were observed at an optimal pH of 5 and an optimal iron dose of approximately 750 ppb. Vogels speculates that the iron and arsenate combine to form a soluble ion pair, ($FeAsO_4$)⁻. Then the addition of the strong oxidant oxidizes the solution, forming the insoluble $FeAsO_4(s)$, which settles from solution.

1.1.5.2 Alum Coagulation

Alum coagulation followed by slow sand filtration was investigated by Shen in 1973. From laboratory experiments and pilot plant studies, Shen concluded that alum was not helpful in removing arsenic from drinking water for a prolonged period of time. After twelve days, the system was only removing 46 percent of the arsenic, lowering it from 700 ppb to 380 ppb at a dose of 21 mg/L of alum and a pH of about 7.4.

Laboratory experiments by Edwards (1994) indicated that if the alum dose is above 0.1 mM Al^{+3} (or 30 mg/L of alum), the pH is less than 7.8, arsenic removal should exceed 70 percent. A full scale study of five alum coagulation plants by McNeil and Edwards (1995) produced considerably less removal, 6-74 percent. The conclusion of that study was that “when a greater mass of aluminum flocs were captured by the filters, greater percentages of soluble arsenic removal were obtained.”

1.1.5.3 Softening

Lab experiments by Edwards (1994) have indicated that arsenic removal is mediated by calcite or $Mg(OH)_2$ formation during softening. The lab experiments showed that 90 percent removal was possible with the magnesium hydroxide formation, but less than 30 percent removal could be obtained from calcite formation. A full scale study by McNeil and Edwards (1995) produced removals of less than 10 percent for calcite formation and removals of between 60 and 95 percent for calcite and magnesium hydroxide formation, confirming the lab results. McNeil and Edwards (1995) acknowledge that some of the arsenic was probably removed during the precipitation of $Fe(OH)_3$ in that study.

1.1.5.4 Activated Alumina Filtration

A recent study, published by Weston, Inc.(1997), done in conjunction with the Bengal Engineering Department in India, indicates that activated alumina is a satisfactory filter media for removal of arsenate in drinking water. Activated alumina has zero point of charge at a pH of 8.2 (Weston, 1997). Below this pH, the activated alumina has a net positive surface charge, which

allows it to absorb the common arsenate species, HAsO_4^{2-} , and H_2AsO_4^- , by weak base anion exchange (Weston, 1997). The selectivity of activated alumina in the acidic to neutral pH range is as follows (Weston, 1997): $\text{OH}^- > \text{H}_2\text{AsO}_4^- > \text{Si}(\text{OH})_3\text{O}^- > \text{F}^- > \text{HSeO}_3^- > \text{SO}_4^{2-} > \text{CrO}_4^{2-} > \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{Br}^- > \text{I}^-$.

This means that if the concentration of all ions are equal, the arsenate is absorbed to a greater extent than any other ion other than hydroxide, which suggests that little interference from competing ions is expected. It also suggests an obvious method for regeneration of the activated alumina by addition of a strong base, which displaces the arsenate ions with hydroxide ions. Then the activated alumina is treated with a strong acid to return it to a useful state. The weak base anion theory does not work for arsenite because arsenite has a neutral charge at pH's less than 9.2.

Lab mini-columns of activated alumina were able to remove arsenate from de-ionized water for more than 800 bed volumes to a level less than $50\mu\text{g/L}$ from levels ranging from $100\mu\text{g/L}$ to $250\mu\text{g/L}$ (Weston, 1997). Arsenite was initially only removed for 250 bed volumes, but after being regenerated, removed the arsenite for more than 1000 bed volumes (Weston, 1997). Five domestic water filters were tested in homes (Weston, 1997). One unit treated 1685 bed volumes of water containing $100\mu\text{g/L}$ to $250\mu\text{g/L}$ of total arsenic to less than $50\mu\text{g/L}$. The other units worked for more than 2000 bed volumes. The researchers note that high iron content was also removed in the units that worked well (Weston, 1997). Possibly, some iron complexation takes place in this process. One possible drawback could be sulfate ion competition if the concentration of sulfate was much higher than the arsenic.

1.2 Manganese Greensand Filtration Background

Manganese greensand is a zeolite mineral called glauconite processed with manganese sulfide or manganese sulfate, (Ellis, 1996) and potassium permanganate in alternating steps to produce a black precipitate of manganese dioxide on the granules (Knocke, et al, 1990). It is used as a filter media, operated the same as a rapid sand filter except for a regeneration step.

1.2.1 Glauconite Background

Glauconite is a member of a mineral group called illites which are a member of a broader mineral group called phyllosilicates (or zeolites) whose common characteristic is a continuous network of silicon tetrahedral (Nesse,1991). The approximate formula for glauconite is $(\text{K},\text{Na})(\text{Fe}^{3+},\text{Al},\text{Fe}^{2+},\text{Mg})_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$ (Nesse,1991). Glauconite has a similar structure to muscovite, with one dioctahedral sheet sandwiched between two silicon tetrahedral sheets (Nesse, 1991). The tetrahedral sheets are bonded together with potassium and sodium in a 12-fold coordination with oxygen from the tetrahedral sheets (Nesse,1991). The dioctahedral layer in glauconite usually contains more Fe^{3+} along with significant amounts of Fe^{2+} and Mg^{2+} , whereas the primary cation in muscovite's octahedral site is aluminum, Al^{3+} (Nesse,1991). The overall charge deficiency in glauconite caused by the divalent cations replacing trivalent cations in the octahedral layer is balanced by more silicon, Si^{4+} , replacing iron, Fe^{3+} , in the tetrahedral layer

(Nesse,1991). The structure also usually contains layers of expandable-type clay in variable proportions and may contain excess absorbed water (Nesse,1991). A two dimensional representation of the structure of glauconite is shown in Figure 1.

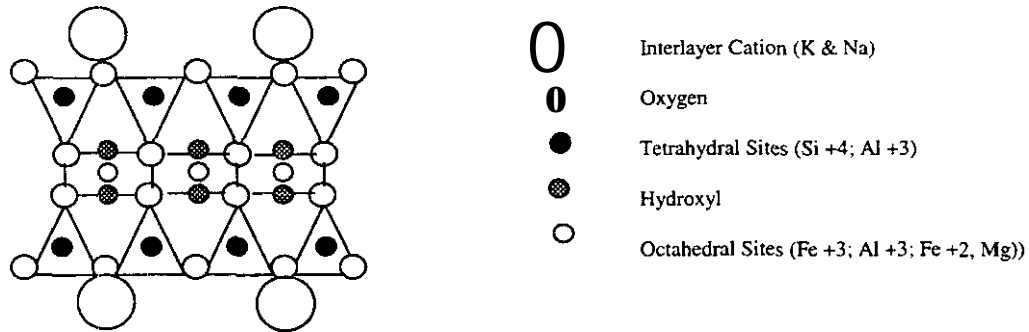


Figure 1: Idealized Structure of Glauconite (Nesse, 1991)

The appearance of glauconite is slightly variable depending on its exact composition but is generally green in color with an earthy or dull luster (Nesse,1991). The general form is small pellets or granules, which usually consist of aggregates of fine, irregular flakes (Nesse,1991). Glauconite has perfect cleavage between the tetrahedral sheets where the bonds are weak (Nesse,1991). Fine grain size may preclude seeing it, however (Nesse,1991). A scanning electron microscope (SEM) photograph of manganese greensand particles is shown in Figure 2. The corresponding elemental analysis of the manganese greensand surface is shown in Figure 3. The elemental analysis is performed using secondary electron backscatter. The elements that make up a material are radiated using the electron beam of the SEM, and the electrons of the atoms will jump up an energy level. The electrons give off a packet of energy when they return to their unexcited state. Each element has a distinct decay signature. If there is less of an element present, more total energy counts need to be collected to produce an equivalent peak area for that element. Thus, if one is viewing a series of these spectrums, the number of counts collected in the upper right hand corner will help the viewer to interpret relative concentrations of the elements in the solid phase. The sample shown in Figure 3, which includes large quantities of silicon (SiKa1), oxygen (O Kal), aluminum (AlKa1), potassium (K Kal), manganese (MnKa1), and iron (FeKa1), is based on 305,667 total counts. Figures 2 and 3 were produced at the New Mexico State University Electron Beam Laboratory.

Glauconite forms small rounded pellets in clastic sediments deposited in marine conditions (Nesse,1991). Along the eastern coast of the United States, the mineral was deposited approximately 75 to 80 million years ago during the Cretaceous period (Ficek,1994). It is generally accepted that glauconites are formed from a variety of starting materials by marine diagenesis in shallow water and at a time of slow or negative sedimentation (Deer, et al., 1969). From their content of both ferric and ferrous iron it may be deduced that they are formed under moderately reducing conditions of the type which may, in some cases at least, occur through the action of sulfur reducing bacteria on decaying organisms (Deer, et al., 1969).



Figure 2: Scanning Electron Microscope Photograph of Greensand Particles

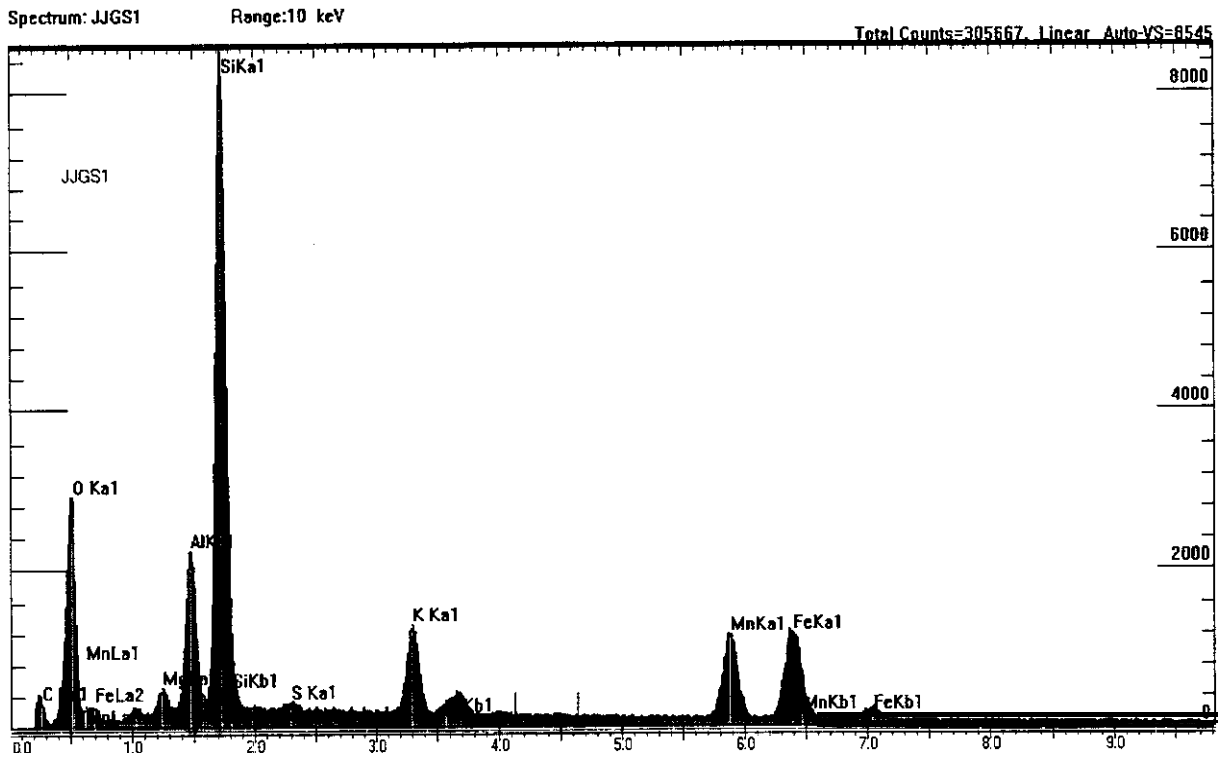


Figure 3 Scanning Electron Microscope Elemental Analysis of Greensand Surface

Greensands are so called because the predominant mineral is glauconite, giving it a green color. Greensands of the coastal plain of New Jersey have been used locally as fertilizer. They are also used as water softeners because they have high base exchange capacities and generally regenerate rapidly (Ficek, 1994). After World War II, synthetic gel-type ion exchange resins were developed that had six to seven times the capacity of glauconite, making them more efficient and reliable for general water softening (Ficek, 1994).

1.2.2 Manganese Dioxide Background

Figure 4 shows a schematic arrangement of the surface atoms for MnO_2 similar to that shown by Posselt, Anderson, and Weber (1968). This schematic illustrates a proposed conceptual model for the manganese oxide coating on a glauconite. It is important to note that manganese dioxide is not really this orderly. Neglecting the varying degrees of hydration, the material may be represented as $\text{MnO}_{(x)}$ where x can vary between 1.1 to 1.95 depending upon the particular conditions of formation (Posselt, Anderson, and Weber, 1968).

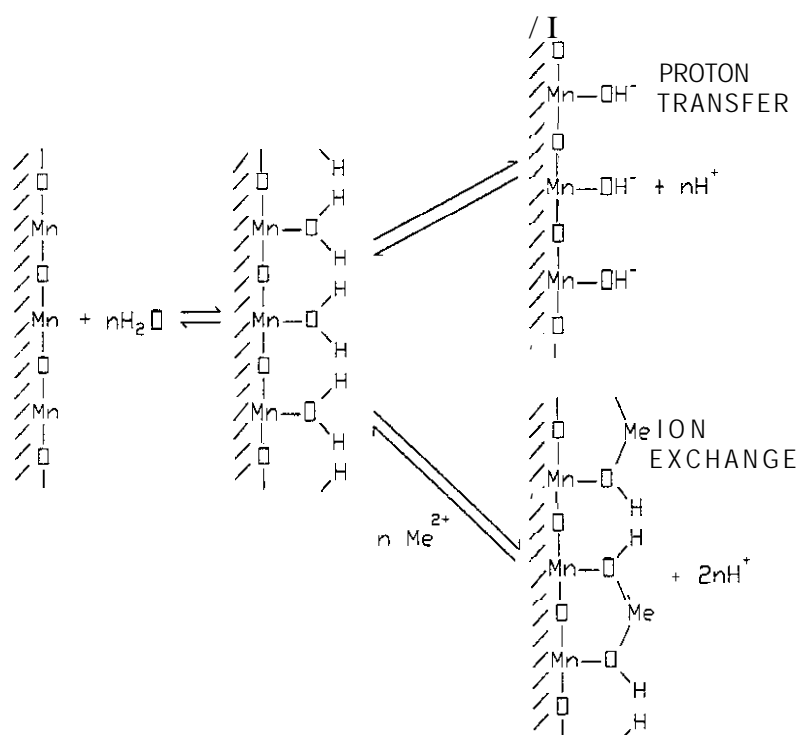


Figure 4: Idealized Schematic of Manganese Dioxide Ion Exchange (Posselt, Anderson, and Weber, 1968)

The surface charge of the MnO_2 is largely determined by the pH of the solution, the charge becoming more negative as pH is increased as a result of the increased ratio of OH^- bound to the H^+ bound (Posselt, Anderson, and Weber, 1968). At very low pH , the H^+ ions bound at the surface predominate, and the colloidal MnO_2 bears a net positive charge (Posselt, Anderson, and Weber, 1968). Less certain is the exact value at which equilibration of the surface bound

hydrogen and hydroxide ions occur-i.e. the zero point of charge (Posselt, Anderson, and Weber, 1968). Posselt, Anderson, and Weber (1968) cite several authors that have given the zero point of charge for manganese dioxide to be from 2.8 to 4.5. From this Posselt, Anderson, and Weber, (1968) conclude that it is clear that manganese dioxide exhibits a net negative surface charge within the pH range (5 to 11) of principle interest for natural waters and for conventional water treatment operations. Therefore, this media is not a candidate for weak base anion exchange removal of arsenic.

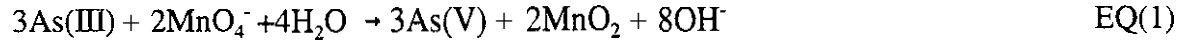
Posselt, Anderson, and Weber (1968) examined many positive metal ions as well as three organic compounds: one an anion, one neutral, and one a cation. The neutral compound and the anion did not absorb to any measurable extent onto the MnO_2 , despite the relatively large surface area of this material. From this Posselt, Anderson, and Weber (1968) concluded that ionic forces of attraction are probably the principal forces involved in the sorption of such organic species on hydrous MnO_2 . The positive metal ions in Posselt, Anderson, and Weber's (1968) research show the following order of decreasing affinity: Ag^+ , Mn^{2+} , Nd^{3+} , Ba^{2+} , Sr^{2+} , Ca^{2+} , and Mg^{2+} . From this the researchers conclude that two factors are important in positive metal ion attraction to hydrous manganese dioxide. The first factor is crystalline ionic radius. For Group II series metals the order of crystalline ionic radius is $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$. After these ions are hydrated, the order of effective size is exactly opposite: $\text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+}$. Thus, the Ba^{2+} is a smaller ion, allowing it to accomplish a closer approach to the active surface of the manganese oxide, resulting in higher capacities and an increased tightness of binding. The other predominant factor is charge. A more charged molecule should absorb more than a less charged molecule, such as $\text{Nd}^{3+} > \text{Ba}^{2+} > \text{Na}^+$. Unfortunately, the silver ion did not follow this order in this study and no reasonable explanation could be found. The Mn^{+2} ion also did not follow this order, but this could be explained by a specific equilibrium between the surface of the MnO_2 and the Mn^{+2} ions in solution.

Waer (undated) found that hydrous manganese oxide was an effective adsorptive media for arsenic, and that it is insensitive at pH values of 6 and 8. Other pHs were not tested. He believed that arsenic was being absorbed rather than co-precipitated with manganese due to the lack of complete removal even at high concentrations of hydrous manganese oxide. He also concluded that only arsenate was being removed and that arsenite was not readily absorbed to hydrous manganese oxides.

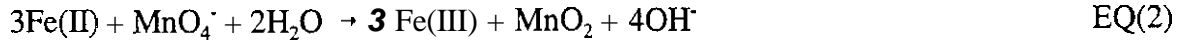
1.2.3 Potassium Permanganate Background

Potassium permanganate is a strong oxidant that is used for a variety of water treatment operations. According to Carus Chemical Company (Form #202), a recent survey shows that 36.8% of surface water treatment plants serving over 10,000 people use potassium permanganate for pre-disinfection, oxidation, and organics removal. This means that only chlorine is used more widely as a oxidant and disinfectant.

Waer performed experiments concluding that arsenic (III) is easily oxidized to arsenic (V) with potassium permanganate at about 1.26 mg KMnO_4 per mg arsenic, about 90 % of the stoichiometric amount, 1.4 mg KMnO_4 per mg arsenic, needed according to the equation:



Oxidation of ferrous iron by potassium permanganate is given by the following equation (Waer):

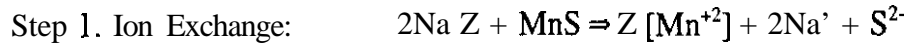


Waer studied the oxidation of arsenic using KMnO_4 at different pH values between 6 and 8, and concluded that the oxidation of arsenite to arsenate is independent of pH in this range. He did not determine the kinetics but states that the reaction times were complete within 60 seconds.

1.2.4 Manganese Greensand Filtration

1.2.4.1 Chemistry

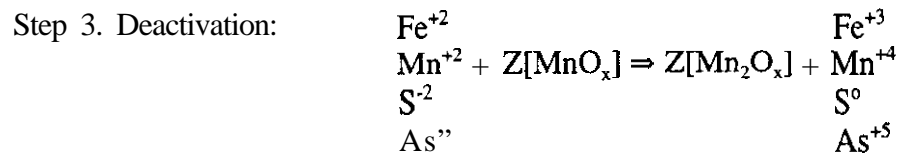
The glauconite and potassium permanganate are used together to produce a process that is very effective at iron and manganese removal. The manganese greensand is prepared by the process below (Ficek, 1994), where Z represents the zeolite base, glauconite.



In this step the glauconite is exposed to manganese sulfide or sulfate (Ellis, 1996). The manganese sulfide dissociates and the manganese (+2) replaces sodium or potassium in the glauconite.



Potassium permanganate is added in this step to oxidize the media to a high oxidation state that will readily remove reduced ions by oxidation. The potassium permanganate also contributes more manganese to the surface. After these two steps are repeated several times, the greensand is ready to be shipped for use in water treatment systems.



The deactivation step represents the actual use of the media to remove common ions that are undesirable in drinking water, through a simple oxidation reduction reaction. The manganese oxide coating of the glauconite oxidizes the ions to a higher charge. The manganese oxide coating is reduced to a lower charge as it accumulates oxygens or electrons. The manganese greensand's surface is re-oxidized through the use of potassium permanganate, as shown below.



1.2.4.2 Typical Physical Characteristics and Operating Parameters

The physical characteristics of manganese greensand are shown below in Table 3 (as given by Inversand).

Table 3: Typical Greensand Physical Properties (Inversand)

Apparent Density:	85 lb./cu.ft.
Shipping Weight:	87 lb./cu.ft.
Screen Grading:	18 x 60 mesh
Effective Size:	0.30-0.35 mm.
Uniformity Coefficient:	Less than 1.60
Specific Gravity:	Approx. 2.4

Typical operating parameters for a manganese greensand filter are given below in Table 4 (from Inversand).

Table 4: Typical Operating Parameters for Manganese Greensand Filters (Inversand)

pH range	6.2~8.6 (for iron & manganese removal)
Maximum temperature	above 80°F. contact supplier
Maximum pressure drop	10 psi.
Backwash rate	minimum 12 gpm/sq.ft.
Service flow rate	2~5 gpm/sq.ft.
Minimum bed depth	24 inches (15~18 inches on dual media beds)

Several sources (Magyar, 1992; Edwards, 1994) recognize that manganese greensand filtration could be used to remove arsenic, but there is little literature available on the subject. Two studies were found that used manganese greensand to treat arsenic, one a full scale study and the other a pilot scale study.

1.2.4.3 Full Scale Arsenic Removal Study

The full scale study by Magyar (1992) concluded that 95% removals of arsenic were possible in a full scale study at a Kelliher, Saskatchewan, treatment plant. The Village of Kelliher had developed a new well that produced an average of 54 µg/L of arsenic during the testing period. Table 5 summarizes the results from Magyar (1992).

Table 5: Arsenic Removal using Manganese Greensand in Kelliher, Saskatchewan (Magyar, 1992)

Sample #	Description	U.S. Gallons Treated	Arsenic Concentration of treated water ($\mu\text{g/L}$)	Percent Removal
3	Filter #1	4248	1.0	98.1
4	Filter #1	12495	1.1	97.9
5	Filter #1	20832	1.3	97.5
6	Filter #1	29155	4.5	91.3
7	Filter #1	37485	5.0	90.3
8	Reservoir	37485	2.2	95.8

The stated diameter of the manganese greensand filters is 54 inches. Assuming a typical depth of 30 inches, the bed volume of one filter is 68,700 cubic inches or 297 gallons. Therefore, about 126 bed volumes were treated, and the average mixed water effluent was treated to 2.2 $\mu\text{g/L}$. This is poor performance in terms of bed volumes if the water quality limit is low, around 2 to 5 $\mu\text{g/L}$, but could still be more economically viable than the other treatment options that are capable of treating to this level. If the water quality limit is higher, around 10 to 20 $\mu\text{g/L}$, manganese greensand filtration will probably become even more viable as many more bed volumes could be treated before regeneration.

The plant was operated as a continuous pressure system at 4.0 to 5.5 PSIG and a flowrate of 76 gpm (4.8L/s). The filtration rate was 2.4 gpm/ft^2 (6 m/h). The system is run for nearly 12 hours, treating 54,021 U.S. gallons (205 m^3). The system is backwashed at 12.73 gpm/ft^2 (32 m/h) for 17 minutes. Potassium permanganate was added in continuous regeneration mode at a rate of about 2.3 mg/L . The average pH was 7.2 to 7.3, typical of groundwater. The total iron concentration of the raw water was 1.79 mg/L and the total manganese concentration was 0.472 mg/L . The average iron removal efficiency was 97.8 percent. The average manganese removal was 74.2 percent.

Magyar (1992) came to several conclusions from this study. In the Kelliher study, arsenic breakthroughs coincided well with iron and manganese breakthroughs. Magyar speculates that the most plausible mechanisms for arsenic removal include “complexing of arsenic with metal salts such as ferric hydroxide ($\text{Fe}(\text{OH})_3$) and manganite (MnOOH) to form precipitates.” These precipitates may then be removed by filter removal mechanisms such as attachment, straining, flocculation, and sedimentation. “Another plausible mechanism is the chemical bonding of arsenic to the: manganese dioxide coating (MnO_2) of the manganese greensand media by chemical adsorption.”(Magyar, 1992). He considers the ion exchange theory, similar to that presented in section 1.2.2, to be possible but less likely.

1.2.4.4 Pilot Scale Arsenic Removal Study

The pilot scale study conducted by West Yost and Associates (1996) tested four small proprietary units supplied by Hungerfield and Terry, Rescue Engineers, Loprest Water Company, and Pureflow Filtration Division. The units supplied by Hungerfield and Terry and by Loprest both

contained traditional beds of manganese greensand in combination with a cover layer of anthracite and bed support layers of gravel and sand. The unit supplied by Pureflow contained 36 inches of unspecified, absorptive, proprietary media, assumed to be somewhat similar to manganese greensand. The unit supplied by Rescue engineers contained medium and coarse silica sand with a cover layer of anthracite.

The water to be treated was produced by a well with an average arsenic concentration of 112 $\mu\text{g/L}$. The raw water also contained the following constituents: 0.1 mg/L of sulfide, 0.25 mg/L of iron, 0.24 mg/L of manganese, 2.5 mg/L of sulfate, a pH of 7.9, and a hardness of 132 mg/L as CaCO_3 . The study primarily varied filtration rates, chlorination rates, and ferric chloride doses. The manufactures were allowed to set the optimum conditions for their unit for sodium hypochlorite feed and ferric chloride dose, but all the units were tested in an initial filtration run with no feed of these two chemicals. Continuous regeneration with potassium permanganate, which is a standard operating mode for the manganese greensand system, was not used in any of the units. No mention of any potassium permanganate being used for intermittent regeneration during the filtration test runs is made. The sodium hypochlorite was assumed to be the only oxidant needed to effectively oxidize the iron, manganese, arsenic, and hydrogen sulfide. The researchers state that generally each manufacturer tried to maintain a chlorine residual of at least 0.5 mg/L in the treated water.

The results were as predicted. Iron and manganese were removed generally at rates higher than 95 percent. Arsenic was only removed at levels less than 20 percent when no additional iron was added, but when ferric chloride was added, arsenic removal increased significantly. The best performance, 93 percent removal of total arsenic to a final concentration range of 12 $\mu\text{g/L}$ to 3 $\mu\text{g/L}$, was achieved by the Loprest unit at a filtration rate of 5 gpm/ft^2 and a ferric chloride dose of 8.12 mg/L . This high performance could be the result of the deepest manganese greensand bed at 36 inches and the highest iron dose of any of the units. The researchers conclude that arsenic removal is primarily a function of iron dose and suggest that co-precipitation with the ferric hydroxide floc is the most reasonable explanation.

1.3 Objectives

The focus of the research presented here is to document the removal of arsenic from water using manganese greensand. This media is used to treat iron and manganese in many water treatment plants around the world. Because it is already in place at many treatment plants, it would be useful to know the optimal conditions for removing arsenic with this media. Previous research has shown that iron concentration is one of the most important factors in arsenic removal. However, the two studies dealing specifically with manganese greensand filtration were conducted with many extraneous factors, such as other media (anthracite and silica sand) and water that contained various other constituents. Because of these extraneous factors, the approximate capacity of manganese greensand and the chemistry involved are difficult to evaluate. A lab scale study with more precisely controlled conditions is more appropriate for these determinations. This thesis will use batch studies for preliminary investigation of the arsenic removal capacity of manganese greensand and to further study the chemistry involved. Lab scale column tests will be examined in another thesis.

Three primary parameters are examined by the batch tests: contact time, pH, and iron to arsenic ratio. These parameters are examined through the use of small batch studies because they are easy and fast to perform. Contact time relates to the flow rate through a filter, as well as the depth of the bed and the configuration. The contact time is important because it indicates whether the reaction kinetics are fast or slow. The pH of the water is very important because it affects the charge of the arsenic, iron, and manganese compounds as well as the surface charge of the manganese greensand.

Because past research by Vogels (1996) indicated that arsenic somehow complexes with iron [III] as it is oxidized to iron [III], a ferrous iron was chosen. Another advantage of adding ferrous compounds over ferric compounds is the economics. The ferrous compounds contain higher iron percentages than the ferric compounds, resulting in more iron added per mass of chemical used. Since an oxidizing agent, such as chlorine or potassium permanganate, has to be added to oxidize the arsenic and other contaminants, the iron will be oxidized to ferric iron anyway, where it is anticipated to precipitate with arsenic. Two typical ferrous compounds are used in water treatment, ferrous sulfate and ferrous chloride. Ferrous chloride was chosen because it will not add sulfates to the system.

A “simulated” water was prepared by adding small amounts of arsenic to de-ionized water to eliminate possible interaction of the arsenic with other chemicals in the water. Most drinking water sources in the United States currently have less than 50 $\mu\text{g/L}$ of total arsenic. Because of the intent to generate isotherms, the initial concentration range of arsenic in this study was chosen to be from 5 to 500 $\mu\text{g/L}$. Both arsenite and arsenate compounds were used as arsenic sources. The arsenite is oxidized to arsenate in any case, but the order in which it is combined with the iron might be important.

2. MATERIALS AND METHODS

2.1 Chemicals and Media Used

2.1.1 Arsenate Solution

Arsenic (V) solutions were made using a commercially available SPEX brand name Plasma standard of arsenic with a 1000 ppm concentration. The arsenic in this standard is made of ultrapure arsenic metal added to nanopure water and acidified with 2 percent HNO₃. Technically it can not be proven that this solution is arsenic in the +5 oxidation state, but it is generally accepted that it is because the solution is exposed to atmospheric oxygen. Two stock solutions were used, one at 1.0 ppm and one at 1 ppm. The 10 ppm standard was prepared by diluting 0.2 mL of the 1000 ppm standard into 19.8 mL of de-ionized water. The 1 ppm standard was prepared by diluting 2 mL of the 10 ppm standard into 18 mL of de-ionized water. Similar dilutions were performed in order to get the initial concentrations of 500, 200, 100, 50, 25, 10, and 5 ppb arsenic.

2.1.2 Arsenite Solution

Arsenic (III) solutions were made from Baker brand arsenic trioxide, (As₂O₃), which is 99.98% arsenic and has a formula weight of 197.82 grams per mole. A 1000 ppm stock solution (as As(III)) was prepared by dissolving 1.320 g of As₂O₃ in 25 mL of 20% (w/v) KOH solution. The solution is neutralized with 20% (v/v) H₂SO₄ to a pH of 8. Then the solution is diluted to 1 liter with 1% (v/v) H₂SO₄ of de-ionized water. From this stock solution, similar dilutions to the ones above were performed to obtain the required initial concentrations of arsenic (III).

2.1.3 Ferrous Iron Solution

Iron solutions were made from Acros brand ferrous chloride, (FeCl₂•4H₂O), which has a formula weight of 198.81 grams per mole. A stock solution of 528.83 mg/L of FeCl₂ was prepared by adding 0.132 grams of FeCl₂•4H₂O to 250 mL of de-ionized water. Two other stock solutions of 52.83 mg/L and 5.283 mg/L were prepared by diluting the original stock solution. The appropriate ferrous chloride concentration for each batch test was determined by a molar factor of the arsenic concentration, and then the appropriate dilution is performed. It should be noted that these stock solutions were probably oxidized to ferric iron by atmospheric oxygen very soon after they were made.

2.1.4 Potassium Permanganate Solution

Technical grade potassium permanganate, (KMnO_4) was donated by Carus Chemical Company. Formula weight of the potassium permanganate is 158.0 grams per mole. A 2 mg/L stock solution was prepared by dissolving 1 mg in 500 mL of de-ionized water. The solution was allowed to sit for 24 hours before use.

2.1.5 Manganese Greensand

Manganese greensand was donated by Res-Kern Company and by Inversand. The media donated by Res-Kern company was used for this study because a greater quantity was available. It is assumed that this media was originally purchased from Inversand since Inversand is the only manufacturer of manganese greensand. For this reason, all manganese greensand is assumed to have similar removal characteristics.

2.2 Experimental Procedure

2.2.1 Pre-Treatment of Glassware and Test Tubes

All glassware, test tubes, and sample bottles were soaked in hot water and Alconox laboratory dish soap for at least 2 hours and then rinsed with de-ionized water. Next they were soaked in a 0.01 M HNO₃ solution for at least 20 hours. The glassware, test tubes, and sample bottles were rinsed with de-ionized water and allowed to air dry.

2.2.2 Optimum pH and Fe Dose

The 15mL centrifuge tubes were filled with the appropriate amount of de-ionized water to give a total volume of solution equal to 10 mL. The calculated amount of arsenic(+5) from the appropriate stock solution was added to the 15 mL centrifuge tube using a pipette. Then the calculated amount of FeCl_2 from the appropriate stock solution was added to the same tube using a clean pipette. Molar ratios of ferrous chloride to arsenic of 0, 1, 2, 5, 10, and 20 were used. Next the correct amount of acid (HCl) or base (NaOH) solution required to adjust the pH to a “target” value was added. The pHs of approximately 3, 5, 7, and 9 were used. A pH of 6 was also explored after some of the data was returned.

The tubes were placed on a rotating shaker which rotated the tubes end over end at 20 rpms for 10 minutes. Then 1.0 gram of manganese greensand was added to the tubes. The tubes were rotated for 24 hours on the rotating shaker. The final pH was measured and recorded when the tubes were removed from the shaker, making sure to rinse the electrode with de-ionized water after each use. The tubes were centrifuged at 3000 rpm for 10 minutes to settle the sand and large suspended solids. Then the solution was poured into a 10 mL syringe and filtered through a 0.2 μm polyvinylidene fluoride filter into high density polypropylene sample bottles. The

samples were preserved with 1-2 drops of concentrated HNO₃, and sent to the Soil, Water and Air Testing Lab (SWAT lab) located on the NMSU campus for analysis using an inductively coupled mass spectrophotometer with a practical minimum detection limit of 0.4 µg/L for arsenic.

2.2.3 Optimum Contact Time

The same general procedure as above was used for this test. The pH was kept constant at 5. The molar ratios of ferrous chloride to arsenic of 0, 5, and 20 were used. The contact times of the manganese greensand in solution were varied at 15 minutes, 30 minutes, 1 hour, 2 hours, 6 hours, and 24 hours. All other procedures were the same.

2.2.4 Sulfate Interference

The same general procedure was used as for optimum pH and iron dose except that the pH was adjusted to a pH of 5 by the use of 0.055 mL of 1N sulfuric acid, H₂SO₄, which dissociates to two hydrogen ions and a sulfate ion, SO₄²⁻. The sulfate concentration in all the test tubes was 266 mg/L. The contact time was 24 hours. The molar ratios of ferrous chloride to arsenic of 0, 5, and 20 were used.

2.2.5 Arsenite Study

The same general procedure was used as for optimum pH and iron dose except that the appropriate amounts of arsenite solution were added from the arsenite stock solution. Then the ferrous chloride was added and the solution pH was adjusted by the appropriate amount of base or acid. Finally, 0.1 mL of the 2 mg/L stock KMnO₄ was added, and the solution was mixed for 10 minutes before adding the manganese greensand. Then the solution was mixed for an additional 15 minutes of contact time. All other procedures were the same.

3. RESULTS AND DISCUSSION

3.1 Optimum pH and Fe Dose

Figures 5, 6, 7, 8, and 9 show the results in graphical form for each of the various pH's. For each of the surface profiles shown in these figures, the pH is the same, and the amount of added base or acid is therefore the same. Figures 10, 11, 12, 13, 14, 15, and 16 are a rearrangement of the same data in order to show the effect of pH and ferrous chloride dose more effectively. For each of the surface profiles shown in these figures, the initial arsenic dose is the same.

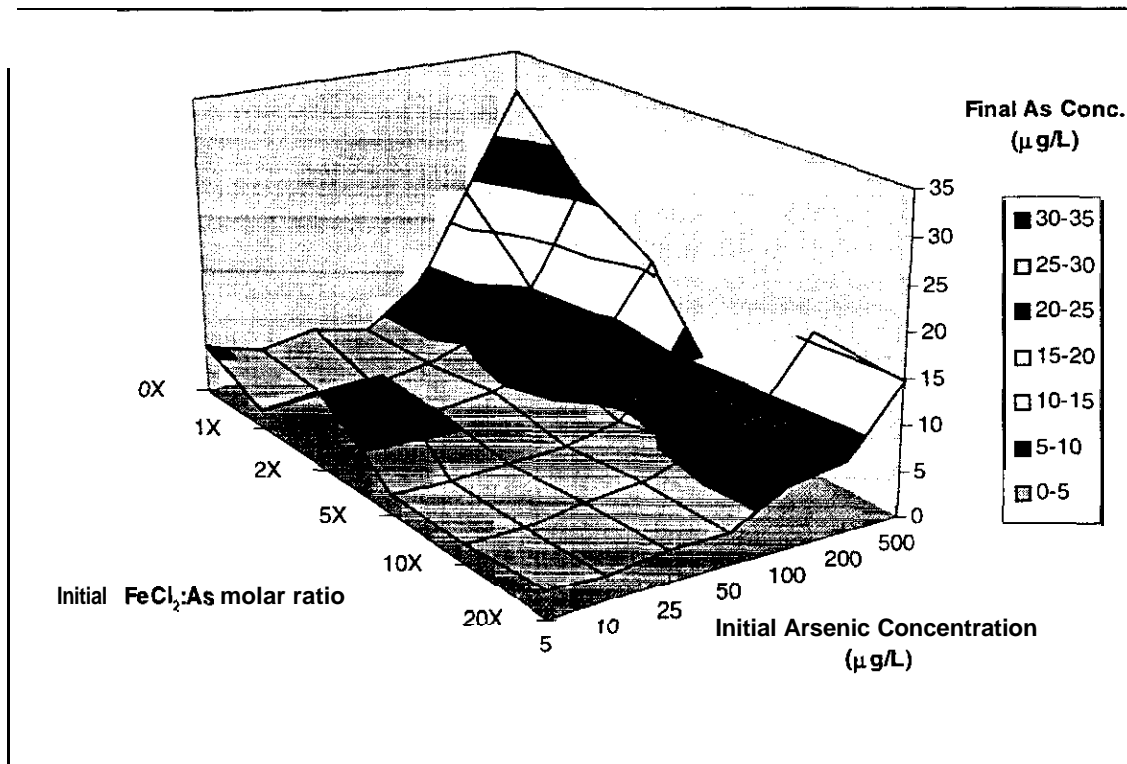


Figure 5: Final Arsenic Concentration (μg/L) at a pH of 3

From the results of the pH and ferrous chloride optimization study, several general points can be observed. An acidic pH seemed to result in the best arsenic removal. Specifically, the pH of 5 performed arsenic removals in the 80 to 95 percent range for all but the lowest initial arsenic concentrations. The solutions with neutral and basic pH's had very little arsenic removal and in some cases seem to be producing more arsenic than was initially added. The solutions with a pH of 3 performed arsenic removals well at high initial arsenic concentrations as shown in Figures 10, 11, 12, and 13 but showed an obvious reduction in removal at lower initial arsenic concentrations as shown in Figures 14, 15, and 16. The ferrous chloride dose doesn't seem to affect the arsenic removal rate to any significant amount at any pH. A possible explanation for these effects are given in section 3.5.

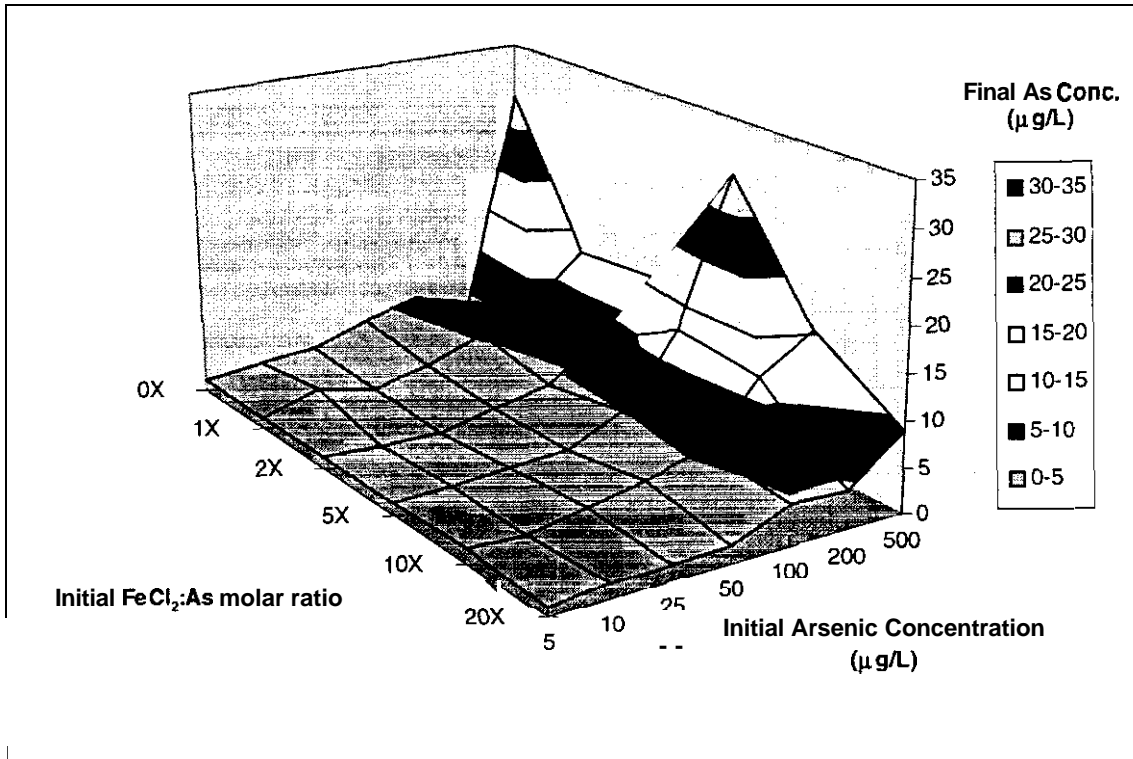


Figure 6: Final Arsenic Concentrations ($\mu\text{g/L}$) at a pH of 5

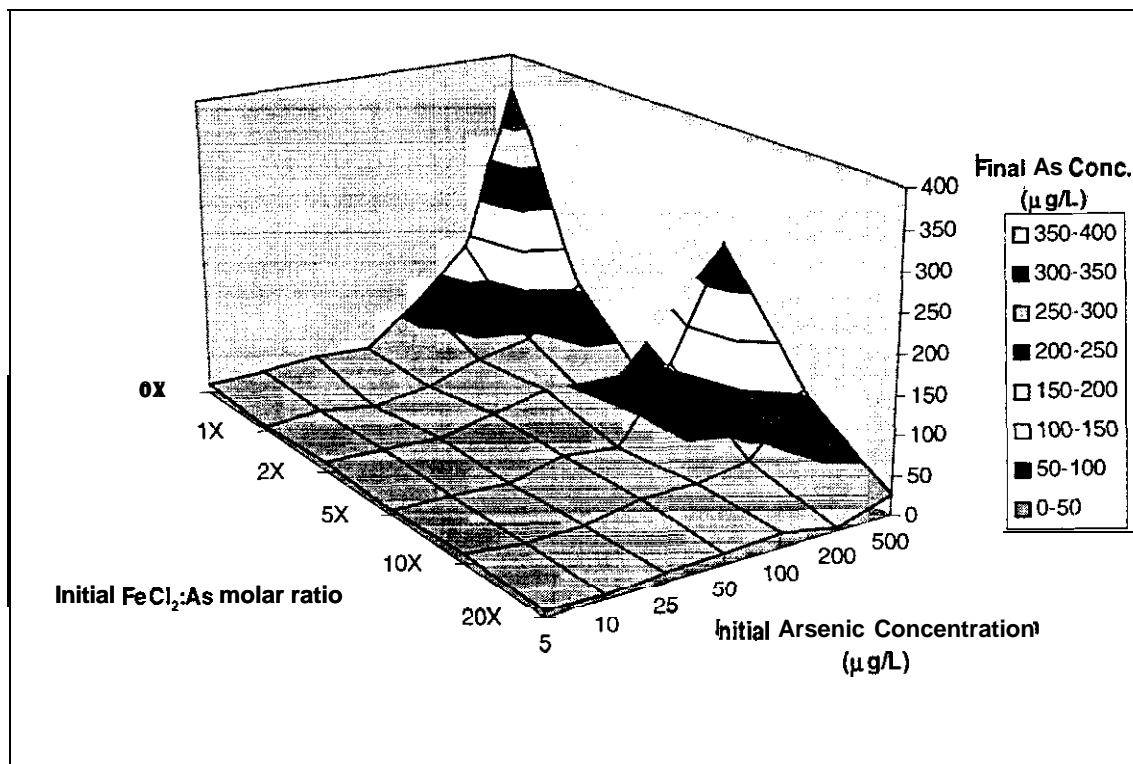


Figure 7: Final Arsenic Concentration ($\mu\text{g/L}$) at a pH of 6

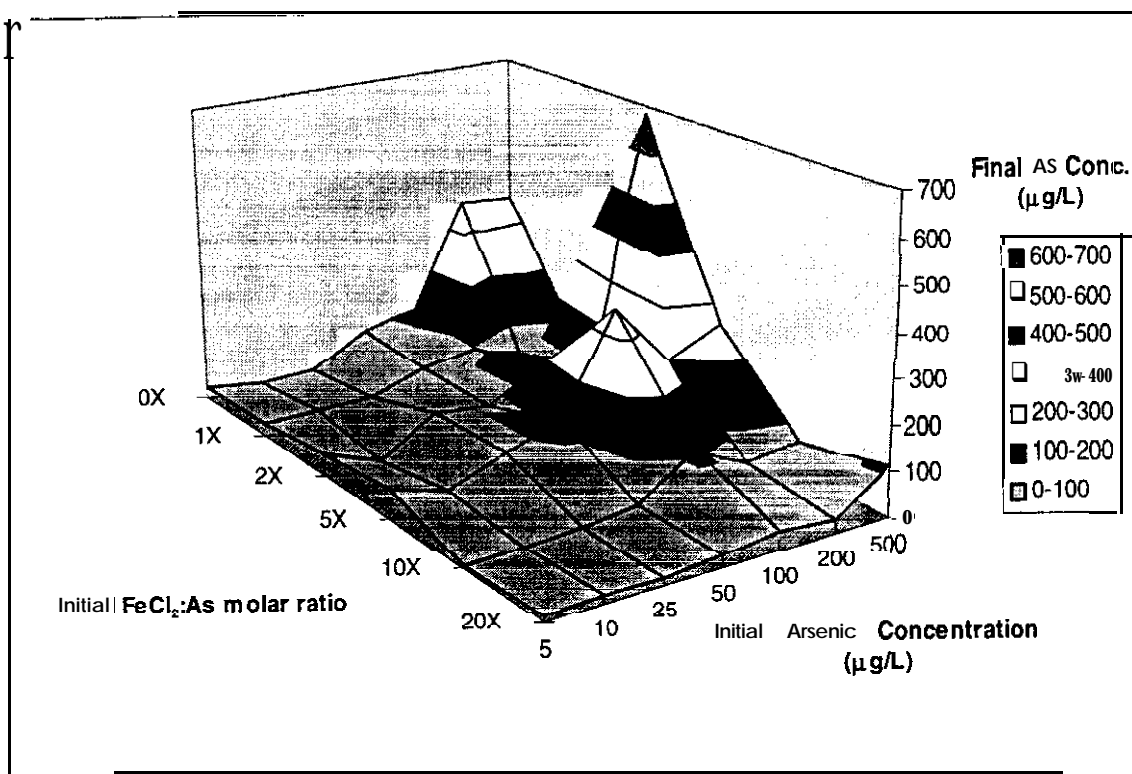


Figure 8: Final Arsenic Concentrations ($\mu\text{g/L}$) at a pH of 7

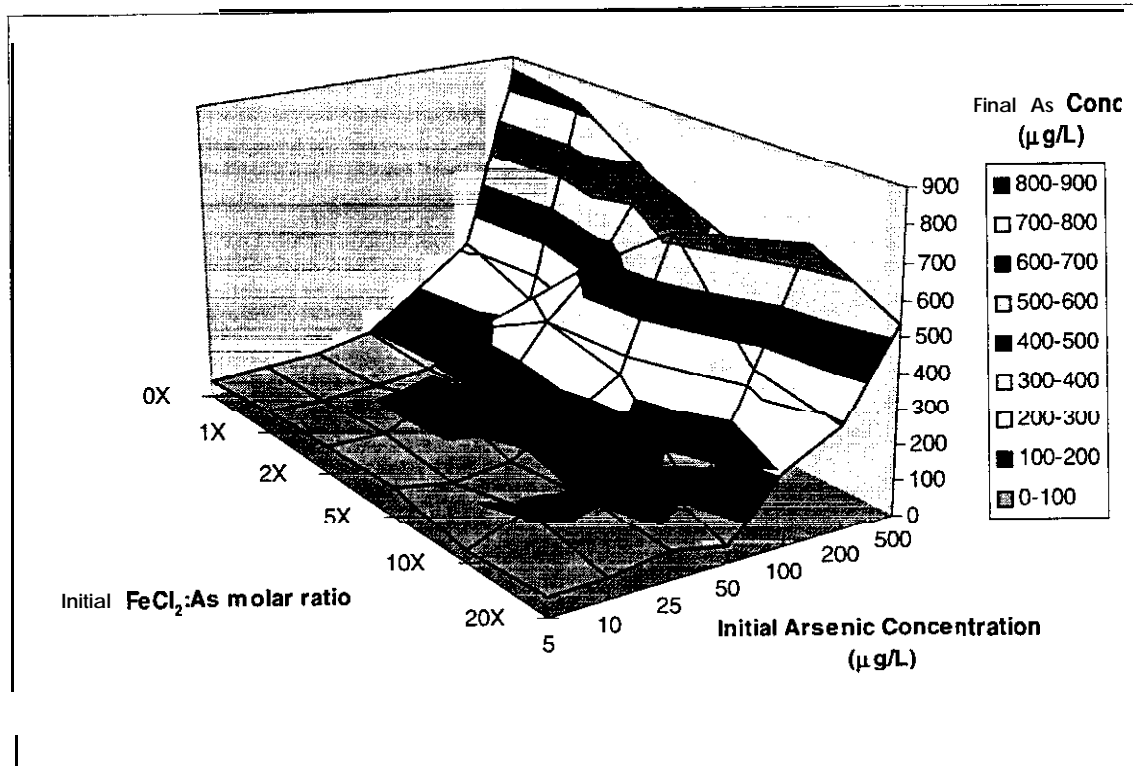


Figure 9: Final Arsenic concentrations ($\mu\text{g/L}$) at a pH of 9

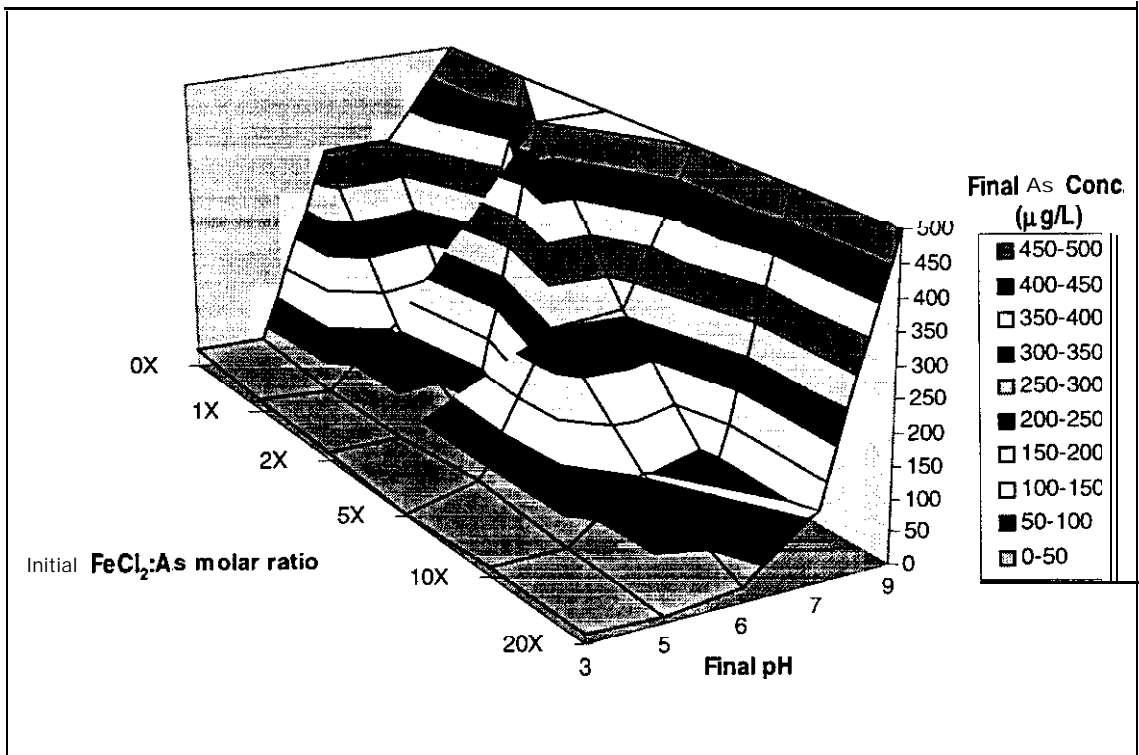


Figure 10: Final Arsenic Conc. at an Initial As Conc. of 500 µg/L

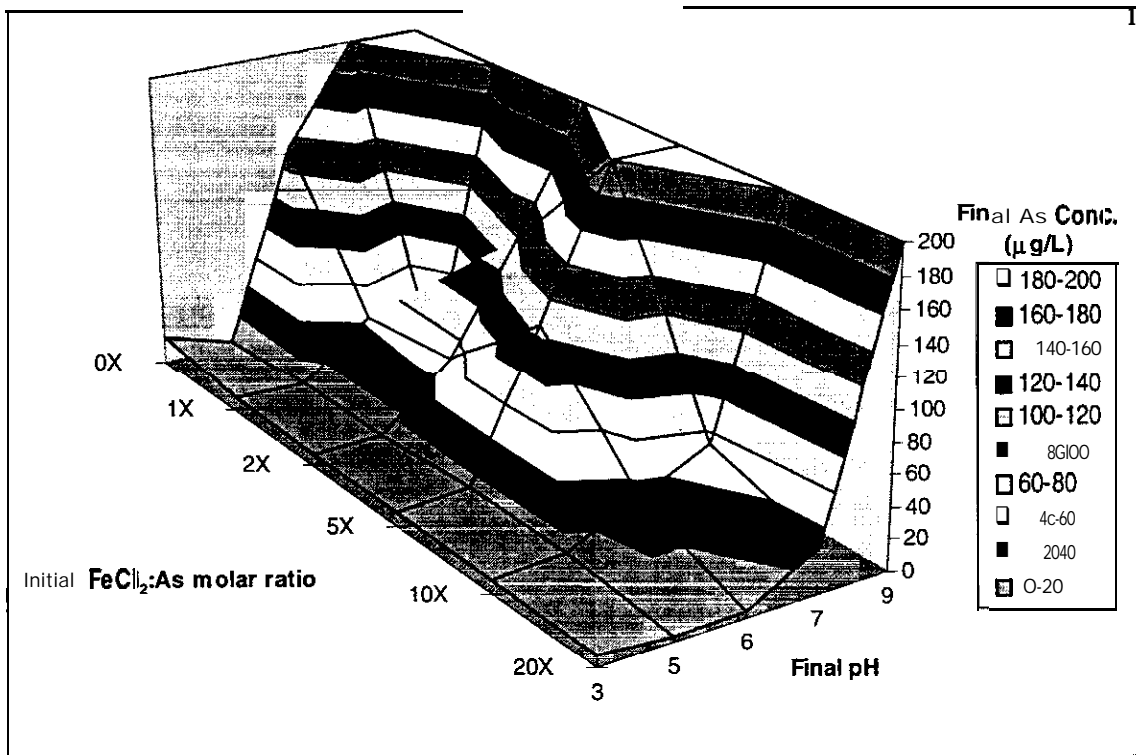


Figure 11: Final Arsenic Conc. at an Initial As Conc. of 200 µg/L

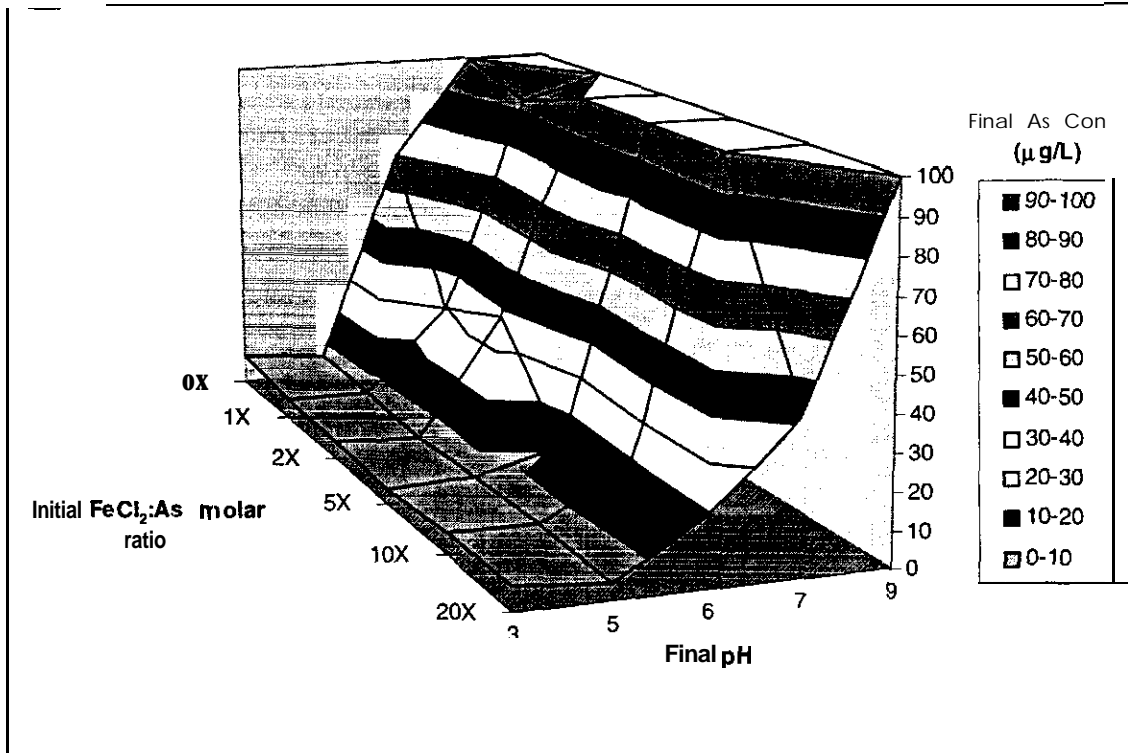


Figure 12: Final Arsenic Conc. at an Initial As Conc. of 100 $\mu\text{g/L}$

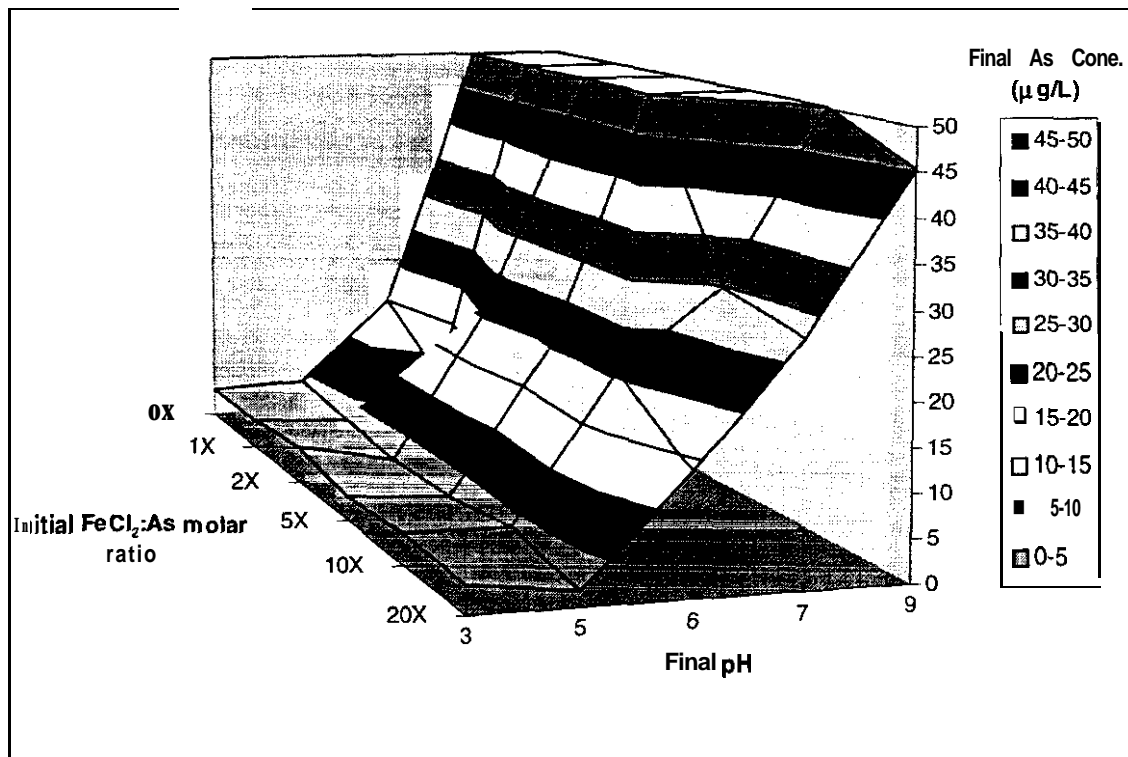


Figure 13: Final Arsenic Conc. at an Initial As Conc. of 50 $\mu\text{g/L}$

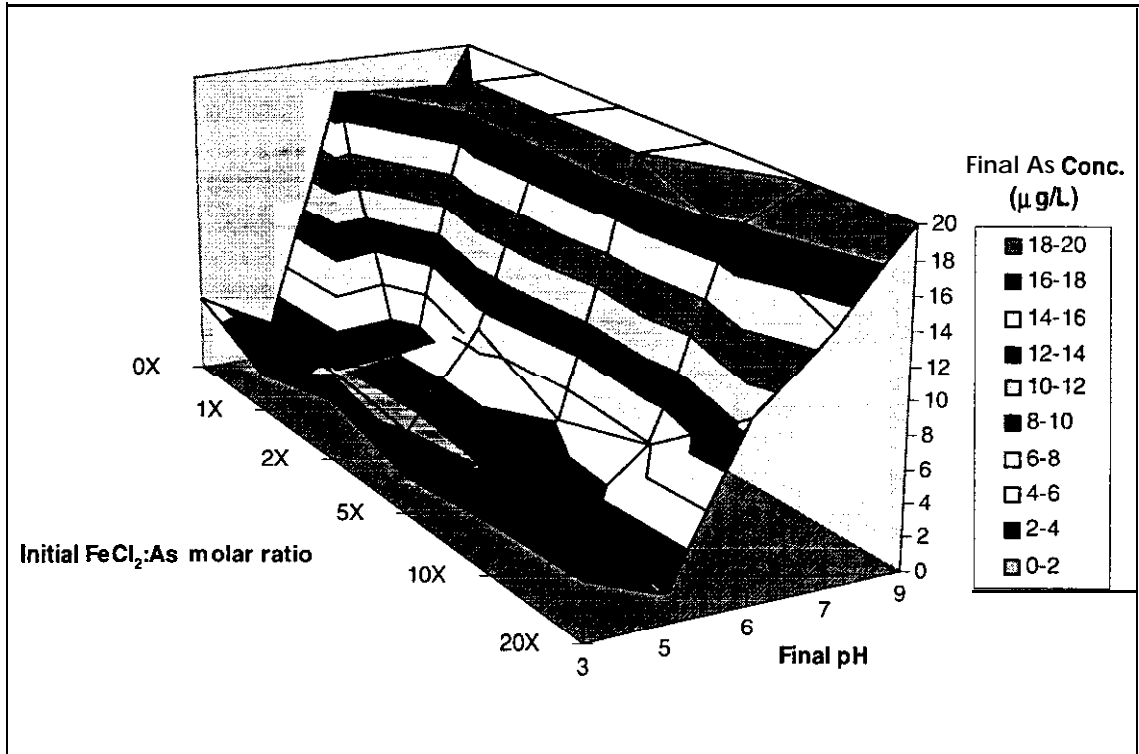


Figure 14: Final Arsenic Conc. at an Initial As Conc. of 25 µg/L

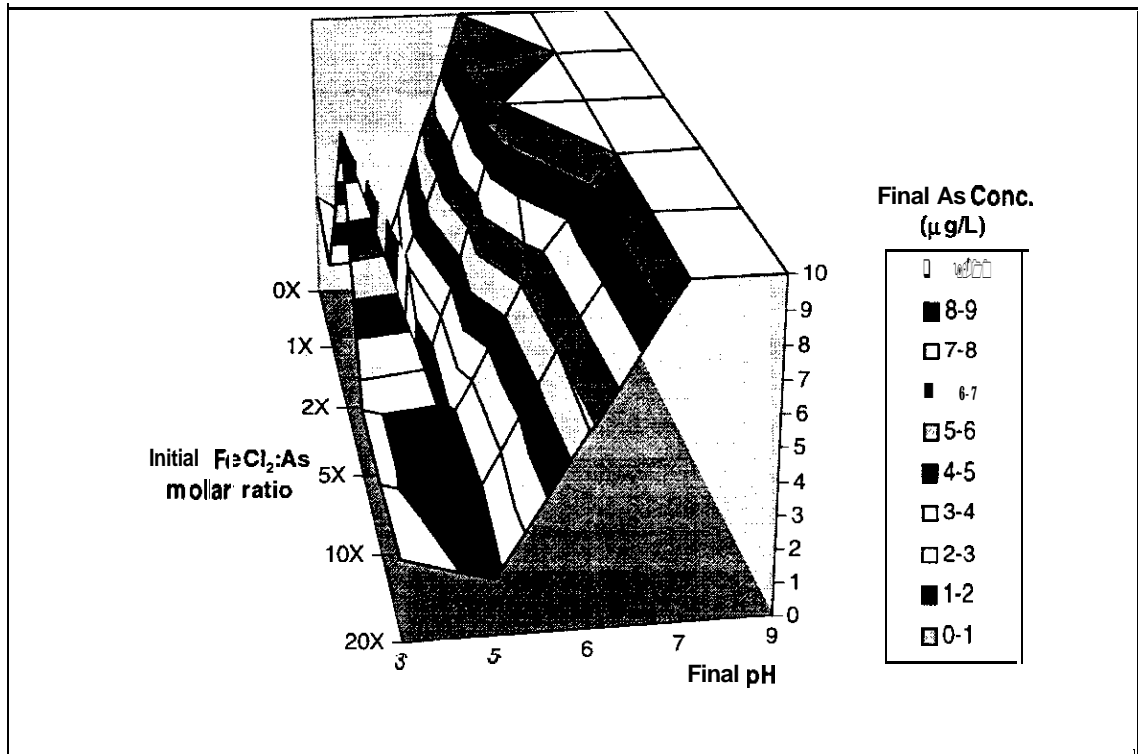


Figure 15: Final Arsenic Conc. at an Initial As Conc. of 10 µg/L

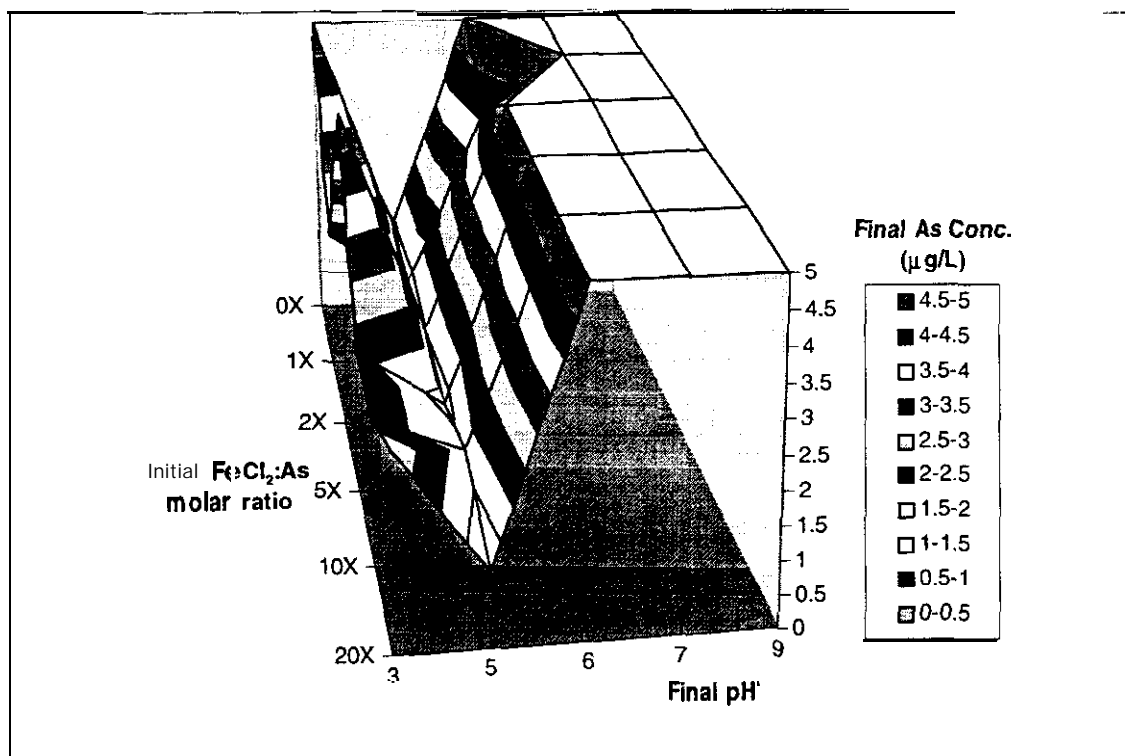


Figure 16: Final Arsenic Conc. at an Initial As Conc. of 5 µg/L

Because a pH of 5 seemed optimum, two more batch sets were run at this pH. The results of this statistical analysis are shown graphically in Figures 17, 18, and 19. The upper and lower lines on these figures represent a 95 percent confidence interval using the Student's t-test, while the middle line is the average of all three sets. From these graphs, several general trends can be observed. As the initial arsenic concentration increases, the percent arsenic removal increases, as well as the predictability of that removal, which is shown by the smaller confidence interval. The inverse is also seen. At an initial arsenic concentration of 5 µg/L, there is very little removal (about 20 to 30%) and no predictability, shown by the fact that the range is from less than zero percent removal to greater than 100 percent removal. Also from these figures, it appears that the FeCl₂ might be having an effect on arsenic removal because Figure 17 seems show a little higher removal than Figure 18 and 19.

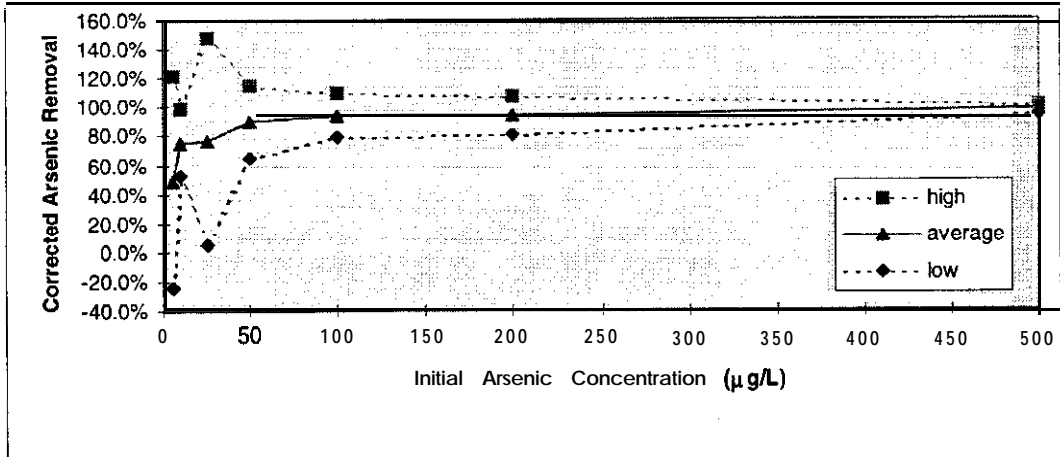


Figure 17: Arsenic Removal Percentages at a pH of 5 (FeCl₂:As molar ratio of 20)

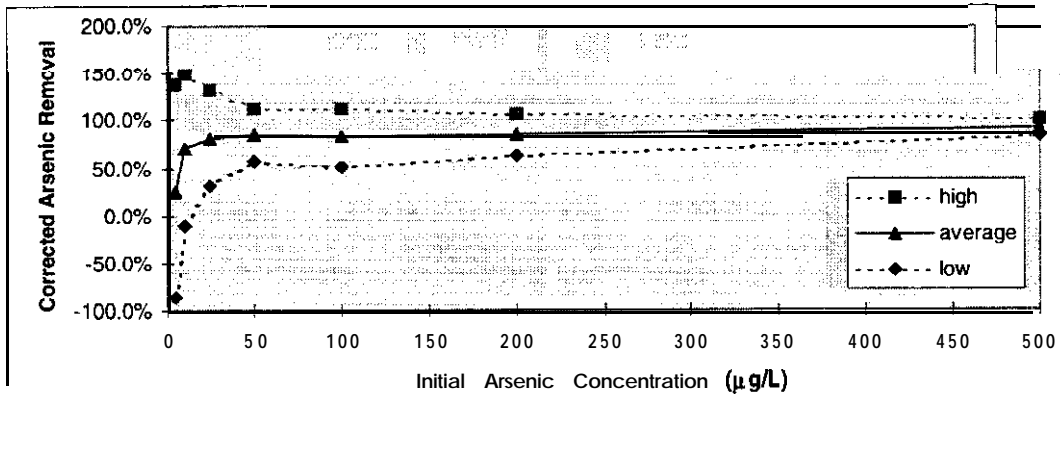


Figure 18: Arsenic Removal Percentages at a pH of 5 (FeCl₂:As molar ratio of 5)

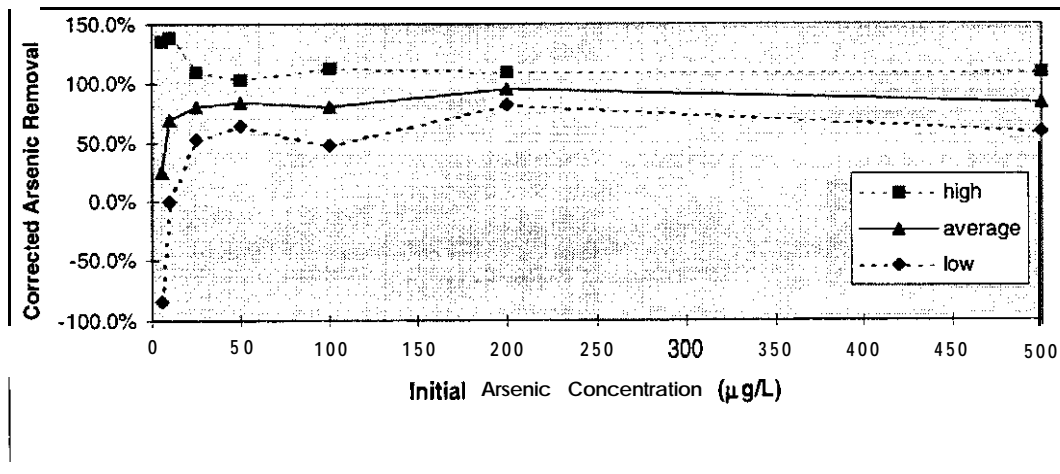


Figure 19: Arsenic Removal Percentages at a pH of 5 (FeCl₂:As molar ratio of 0)

The hypothesis that the data sets represented in Figures 17 and 19 are the same was tested by the using the Student's *t* test for the difference between two means. The result was seven intervals which all contained zero, indicating that difference between the data set with 20 times as much FeCl_2 as arsenic and the data set with no iron added was insignificant at a 95 percent confidence level. Figure 20 shows this test graphically. The differences between the other sets (20x to 5x or 5x to 0x) were not calculated because the largest difference should have been between 20x and 0x

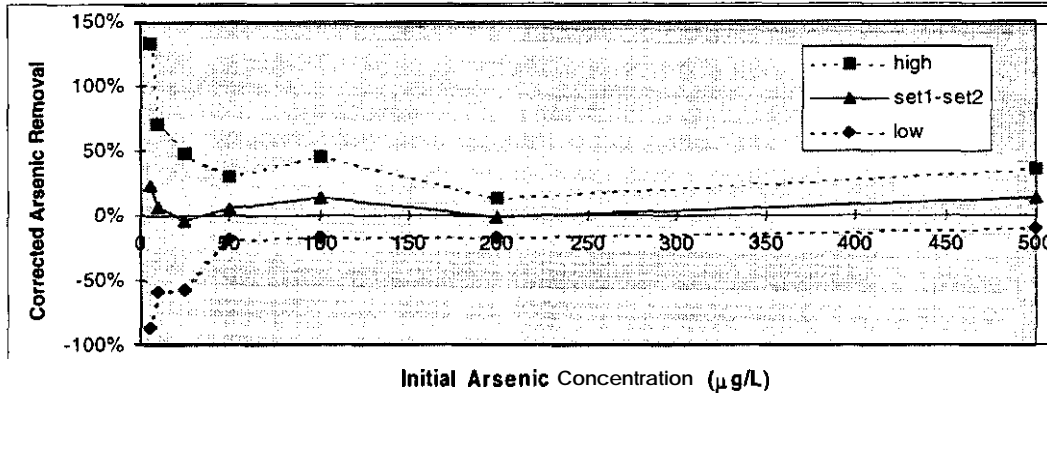


Figure 20: Difference in As Removal Percentages at a pH of 5 between set 1:(FeCl_2 :As molar ratio of 20) & set 2:(FeCl_2 :As molar ratio of 0)

Because the iron ratio has been shown to be insignificant, the data for a pH of 5 shown in Figures 17,18, and 19 were combined into one set with 8 degrees of freedom instead of 2, which should give smaller confidence intervals. This data set is shown in Figure 21. It shows small confidence intervals for all the data sets except the initial arsenic concentration of 5 µg/L.

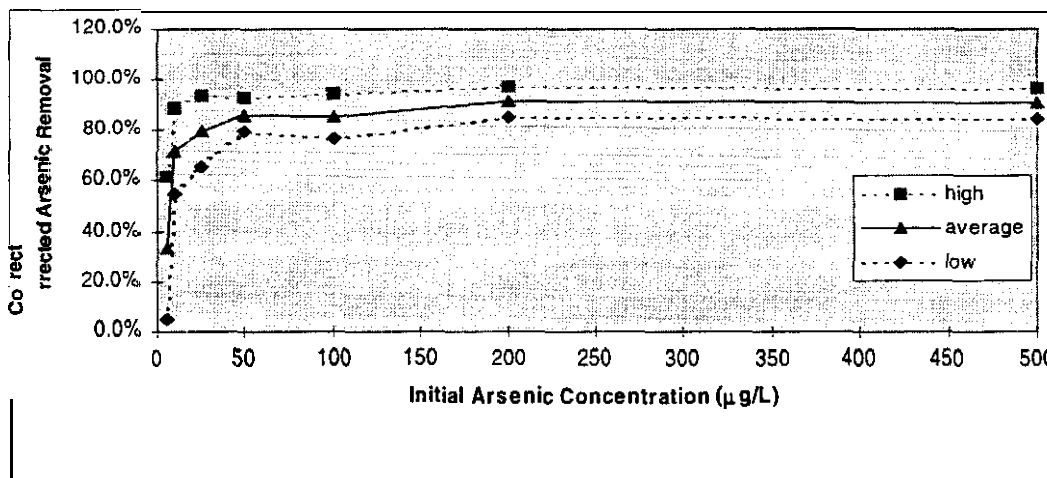


Figure 21: Arsenic Removal Percentages at a pH of 5 (considering iron has no effect, 95% confidence level)

3.2 Optimum Contact Time

Figures 22, 23, and 24 show the results of the batch studies to determine the optimum contact time. From the optimum contact time study, no recognizable effect of arsenic removal performance could be observed with changing contact times in the range studied. From this, it is inferred that whatever removal process is taking place, it is completed within 15 minutes, which is a typical contact time for a low (2 to 3 gallons per minute per square foot of bed) filtration rate in a rapid sand filter. A study of optimum contact times less than 15 minutes would be best accomplished with column studies.

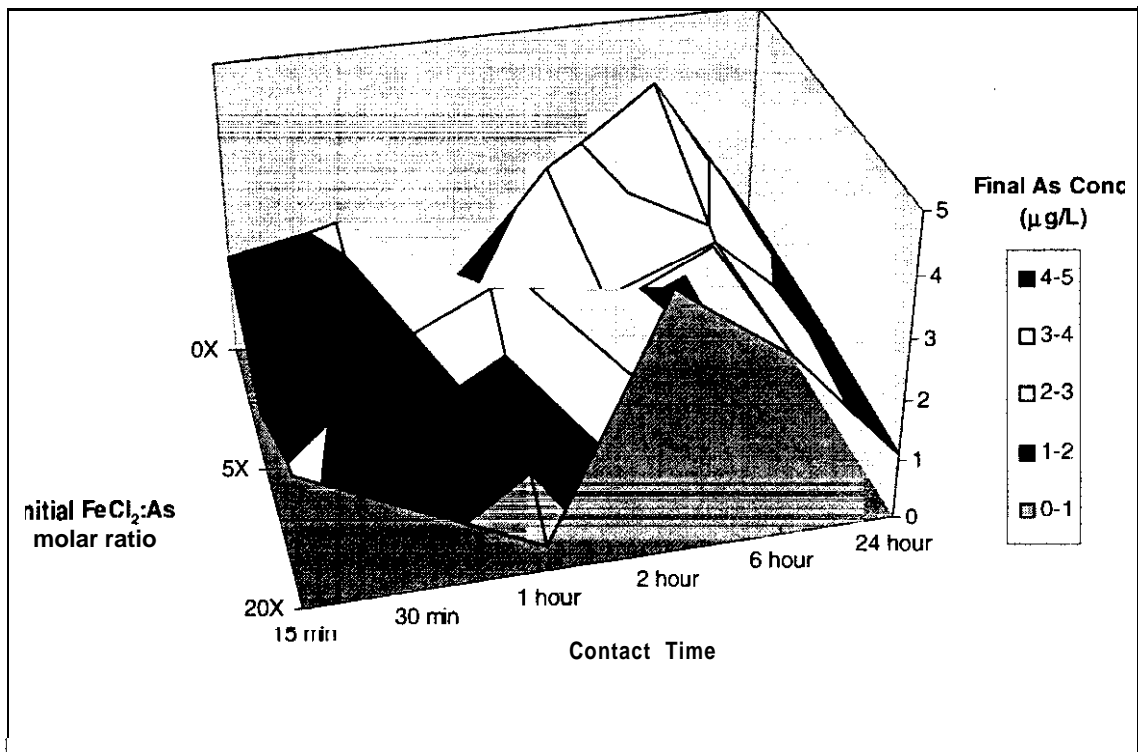


Figure 22: Final Arsenic Conc. for Varied Contact Times (for pH of 5 and initial As conc. of 5 mg/L)

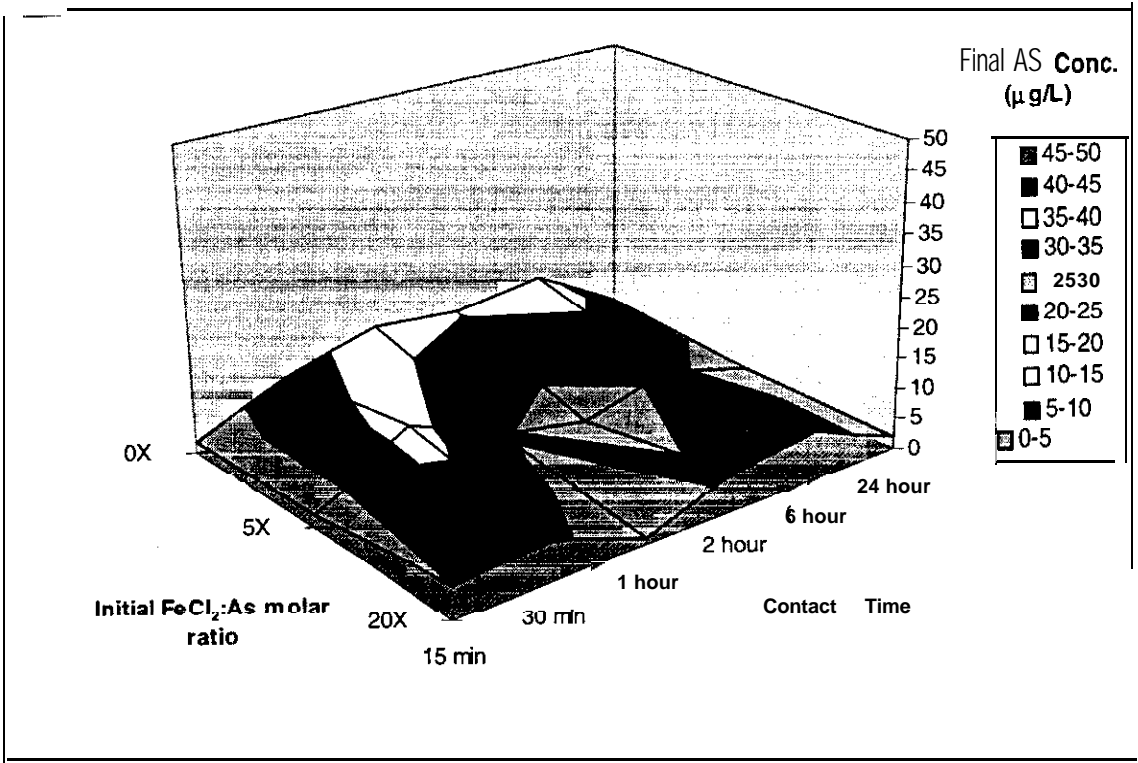


Figure 23: Final Arsenic Conc. for Varied Contact Times (for pH of 5 and initial As conc. of 50 mg/L)

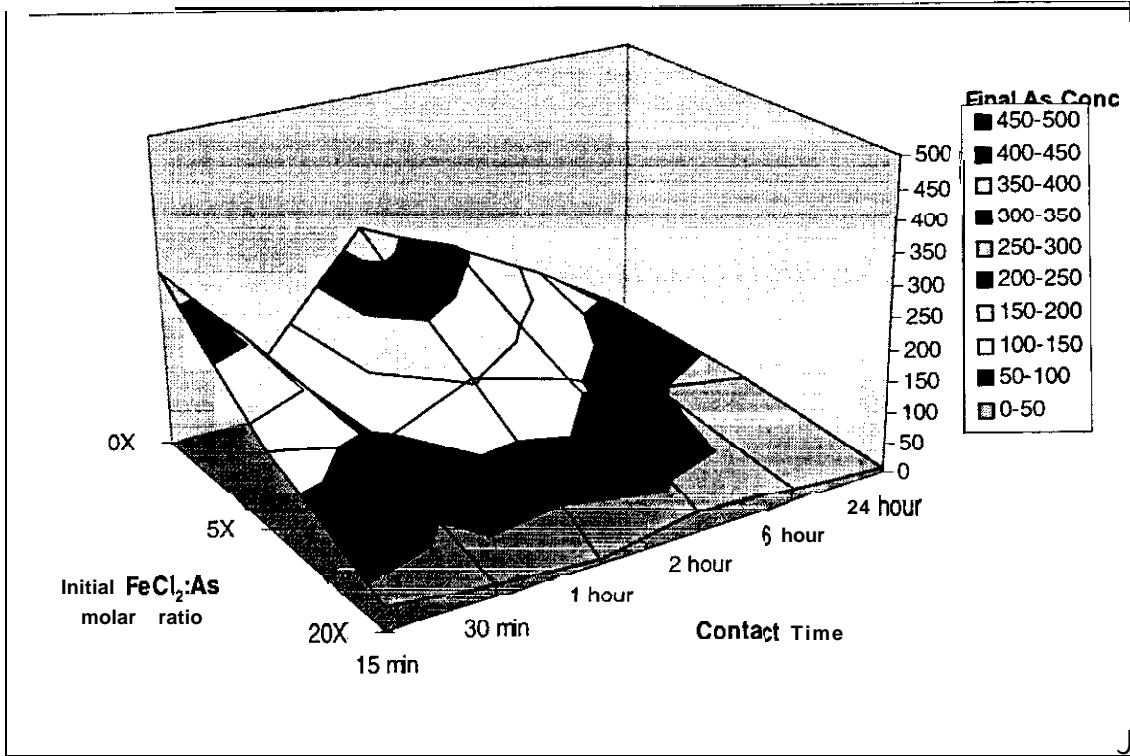


Figure 24: Final Arsenic Conc. for Varied Contact Times (for pH of 5 and initial As conc. of 500 mg/L)

3.3 Sulfate Interference

One set of data was collected at a pH of 5 and contact time of 24 hours to see if sulfate is a competing anion for arsenic oxyanions. The pH adjustment was made with sulfuric acid, which dissociates to form a hydrogen ion and a sulfate ion. Figure 25 is a graphical representation of that data set which shows the final arsenic concentrations. Figure 26, shown for comparison purposes, is a partial representation of the same data set used in Figure 4, with hydrochloric acid used to adjust the pH to 5.

The results seem to show an effect of the sulfate ion on arsenic removal performance. However, it was noted that the quality control arsenic spikes for this data set were roughly twice their expected value. Assuming these values are correct and recalculating the removal efficiencies results in significantly enhanced removal performance. The difference between the data set of Figure 25, and all the data from the three sets of data at pH of 5 adjusted by hydrochloric acid, were evaluated. This evaluation was performed by comparing corrected arsenic removal efficiencies, assuming the quality control spikes were a true representation of the initial arsenic concentration for both sets of data. The average corrected removal efficiencies were compared using the Student's *t* test to see if the two data sets were significantly different at a 95% confidence level. Figure 27 shows the results, which indicate that the two data sets are not significantly different. This leads to the conclusion that sulfate is not a competing ion at this concentration level and should have little effect on the removal performance of arsenic using manganese greensand.

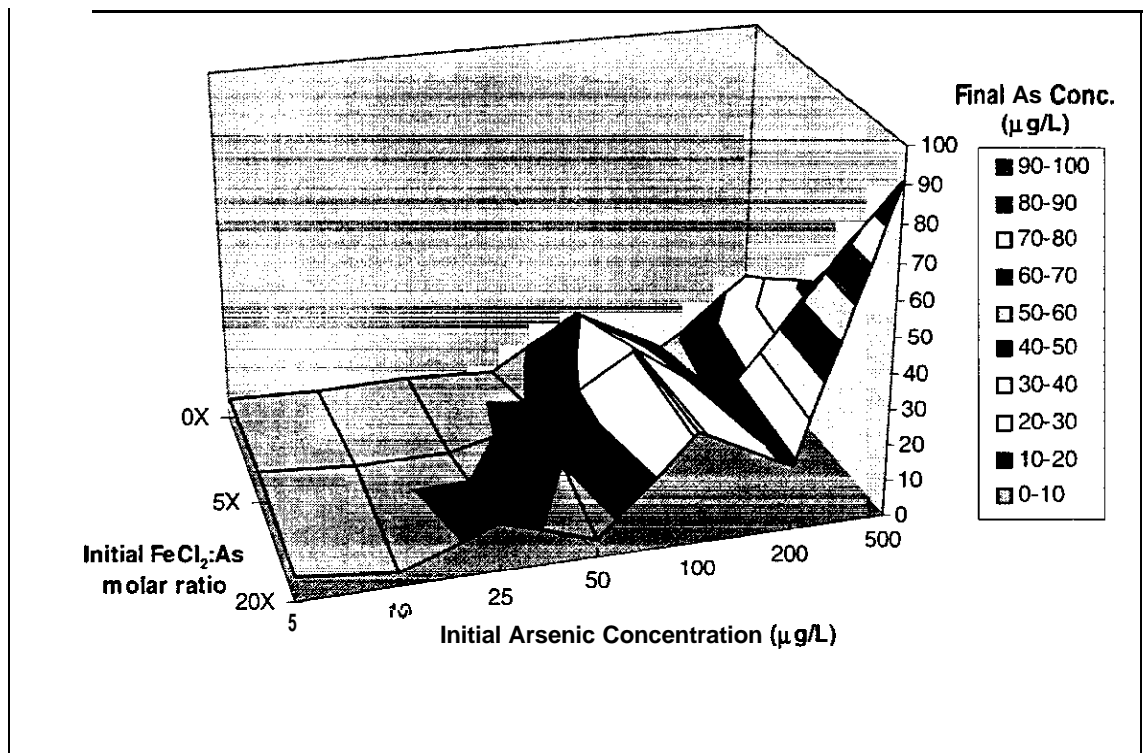


Figure 25: Final Arsenic Concentrations (mg/L) at a pH of 5 (competing sulfate ion present)

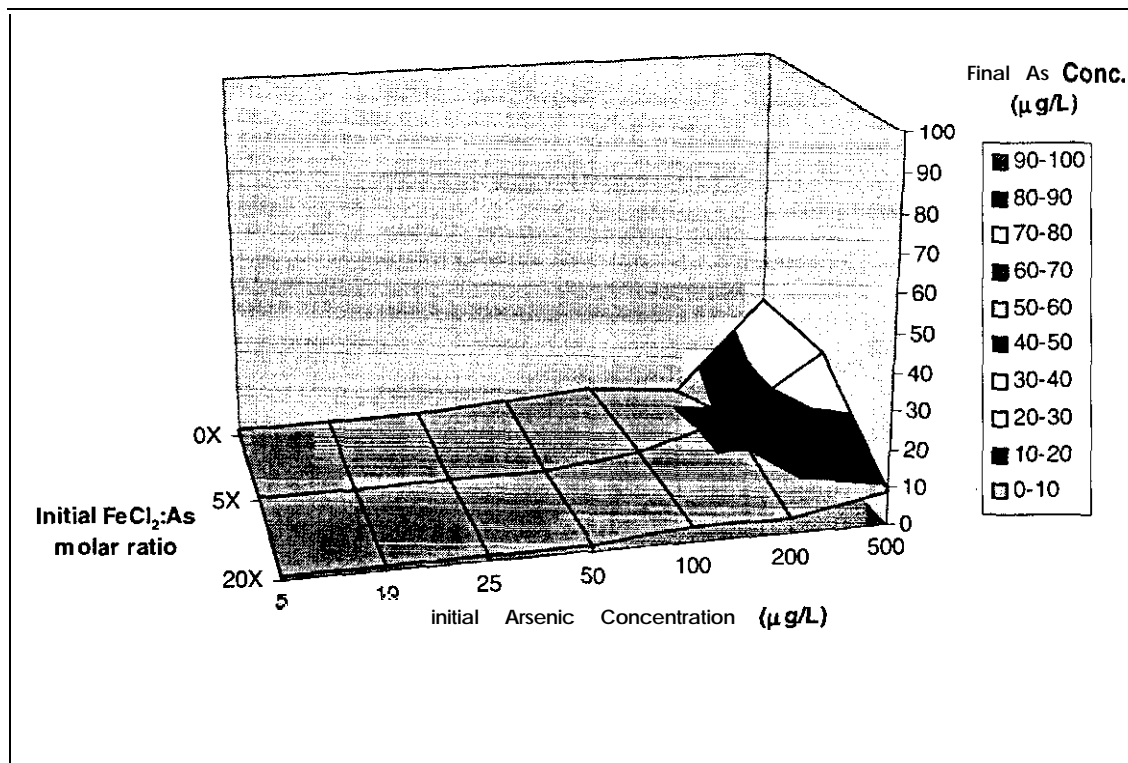


Figure 26: Final Arsenic Concentrations (mg/L) at a pH of 5 (chloride ion present)

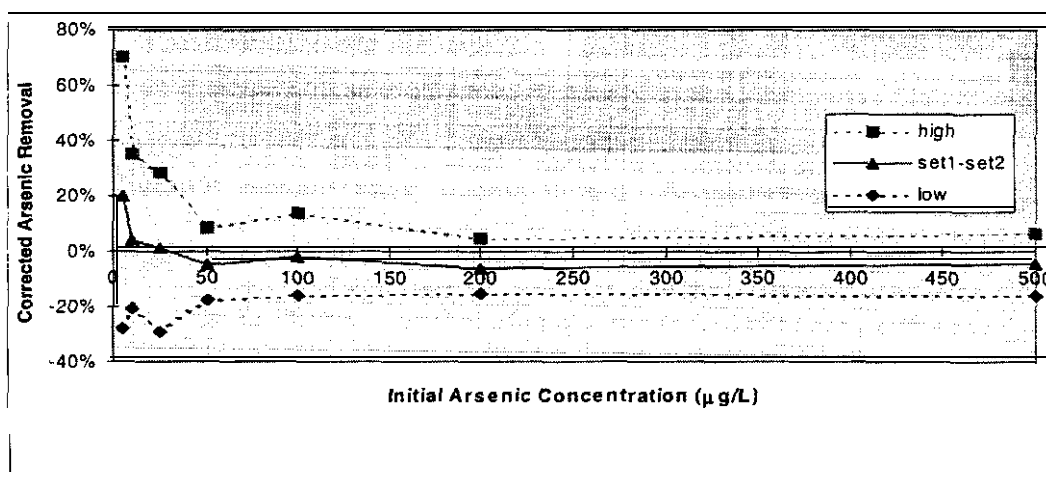


Figure 27: Difference in Arsenic Removal % at a pH of 5 between set 1:(chloride ion present) & set 2:(sulfate ion present)

3.4 Arsenite Study

Figures 28 through 30 show the arsenite removal study the data. This small data set shows a large effect due to pH and seems to also show an effect of iron dose. Again, a pH of 5 to 6 seems to be optimum. As shown by Figure 29 and 30, when more iron is added at any pH, a slightly better arsenic removal seems to occur. Figure 28 does not show this effect because the initial arsenic concentration is only 5 $\mu\text{g/L}$. At this low concentration, whatever removal mechanisms are occurring have probably begun to reach their capacity for removing arsenic. No statistical comparisons are possible with these data sets because of limited data. No duplicates were performed because of cost and time limitations.

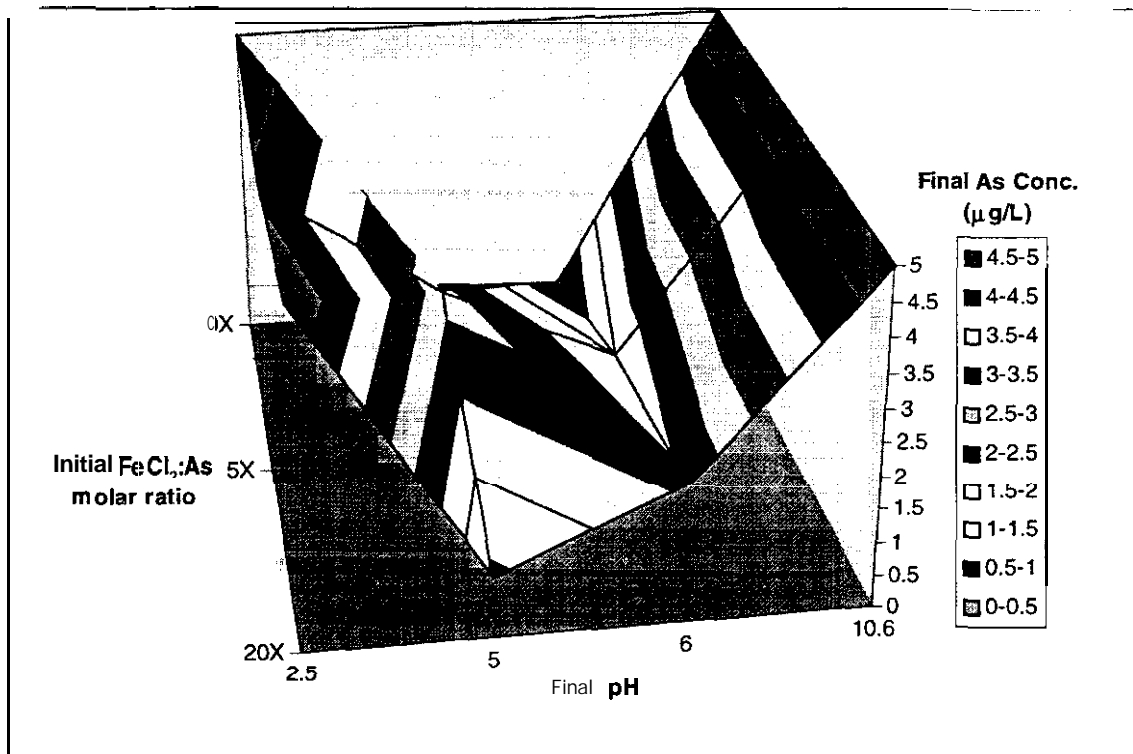


Figure 28: Arsenite Study (Initial Arsenic Conc. of 5 mg/L)

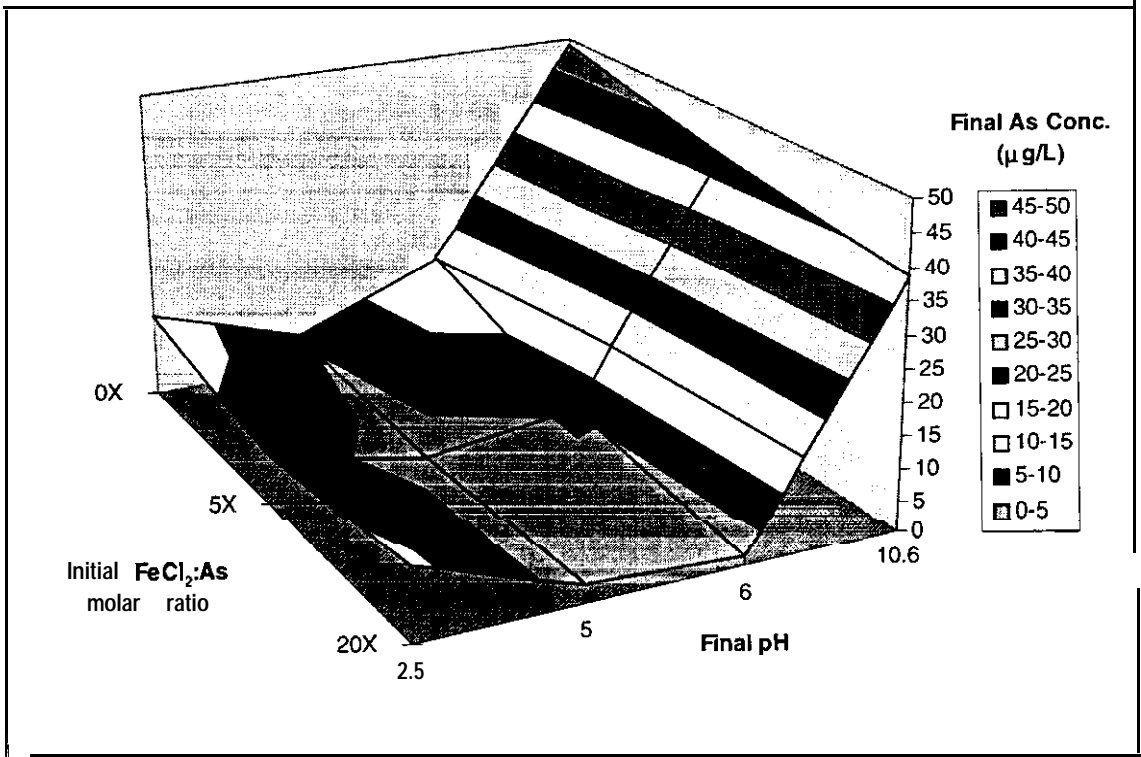


Figure 29: Arsenite Study (Initial Arsenic Conc. of 50 mg/L)

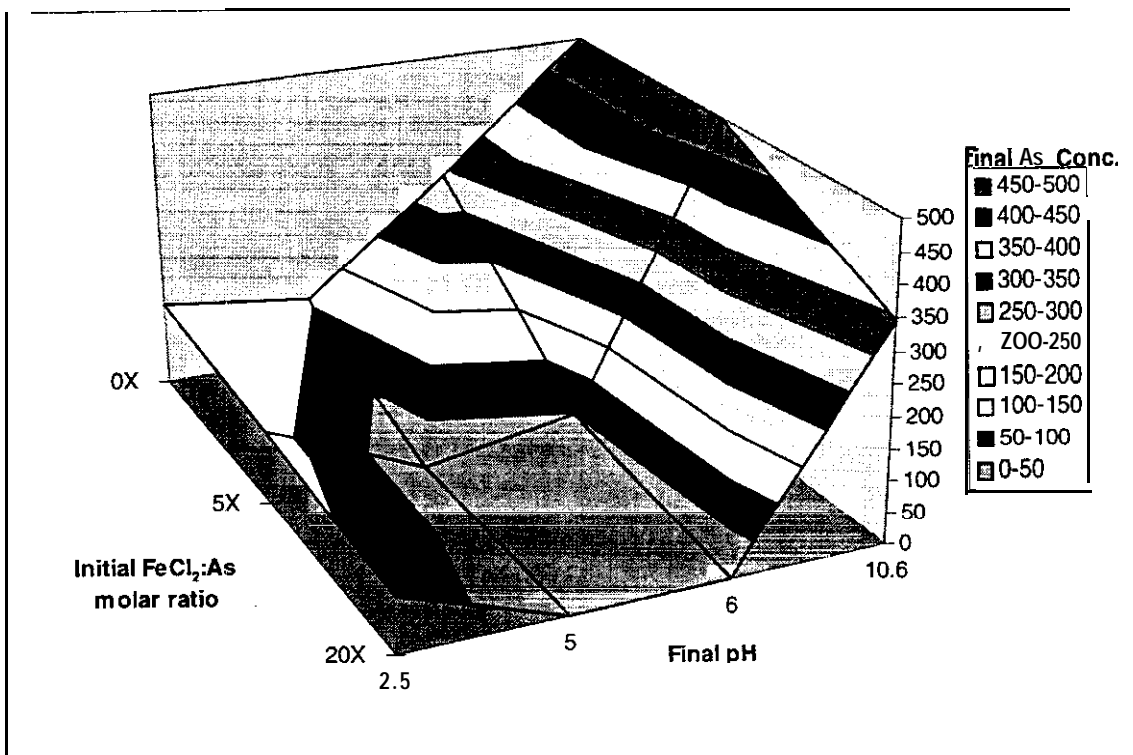


Figure 30: Arsenite Study (Initial Arsenic Conc. of 500 mg/L)

3.5 Chemical Models

Several methods are available for analyzing this data. Adsorption isotherms are a popular method of quantifying removals using various media. An adsorption isotherm is a relationship determined at a constant temperature between the amount of adsorbant used and the amount of chemical absorbed at varied ratios. The two most often used are the Langmuir isotherm and the Freundlich isotherm, each with its different assumptions. Another way of analyzing this data is to assume some sort of ionic exchange and try to explain attractions based on chemical charges.

3.5.1 Freundlich Isotherm

The Freundlich equation is an empirical equation that is very useful because it accurately describes much adsorption data. The equation is an exponential equation of the form:

$$\frac{X}{M} = KC_e^{1/n} \quad \text{EQ(3)}$$

which can be linearized as follows:

$$\log\left(\frac{X}{M}\right) = \log K + \frac{1}{n} \log C_e \quad \text{EQ(4)}$$

$$y = \text{intercept} + \text{slope} \times x$$

where X is the mass of absorbed arsenic, M is the mass of greensand, C_e is the equilibrium concentration of arsenic in solution after absorption, K is a constant, and n is a constant. The constant K is related primarily to the capacity of the manganese greensand to absorb arsenic. Larger values of K mean larger capacities of absorption. The constant $1/n$ is a function of the strength of adsorption. Larger values of $1/n$ mean the adsorption bond is weak because the value of X/M experiences large changes for small changes in C_e . Smaller values of $1/n$ mean the adsorption bond is strong. As $1/n$ becomes very small, the isotherm plot approaches horizontal, and the isotherm is termed *irreversible*.

Figure 3 1 shows the Freundlich isotherms calculated for the original data sets from section 3.1. The iron concentration was assumed to have no effect, so each line represents six combined data sets at each pH. Any data that resulted in negative removals was left out of the calculations. The set of data at a pH of 9 was not included because there was no significant removal shown at that pH. A pH of 5 performs the best adsorption and a pH of 7 performs the worst adsorption of arsenic.

Figure 32 shows the Freundlich isotherm for the three sets of data at a pH of 5, where the best removal occurred. The data was plotted for each iron concentration (0, 5, and 20X) for visual effect. The three linearized plots are very close to each other, representing the insignificance of iron addition in this study.

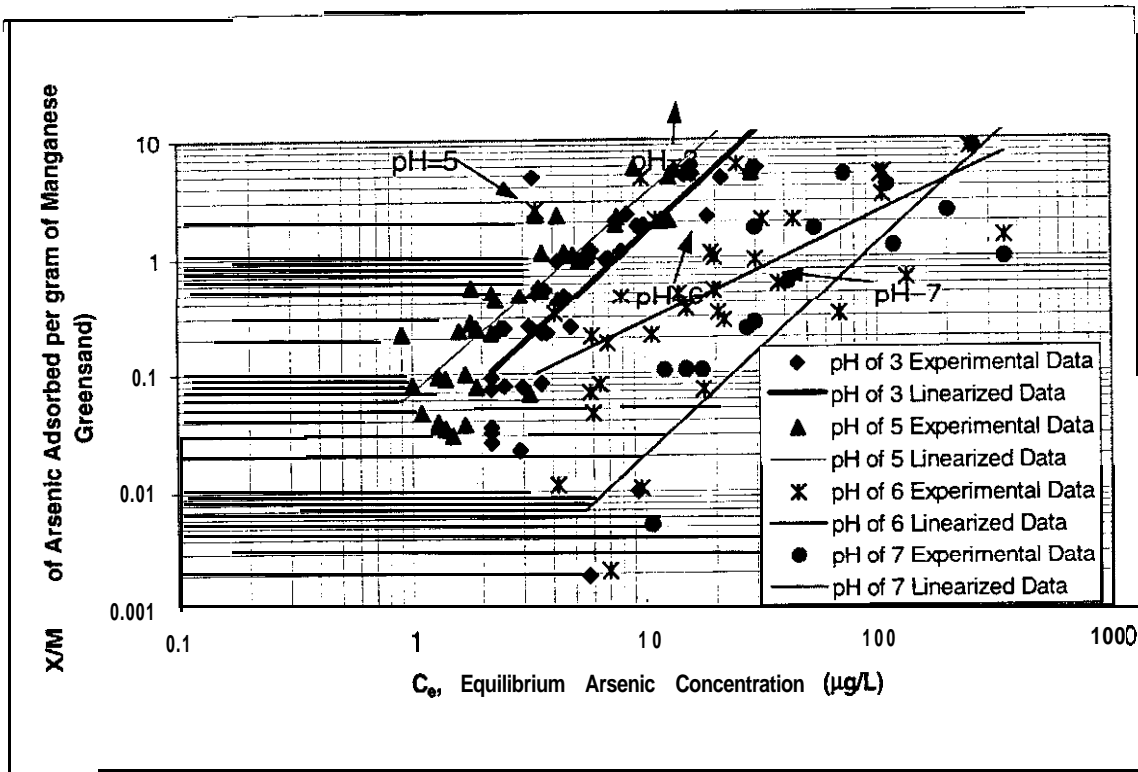


Figure 31: Freundlich Isotherms for Varied pHs

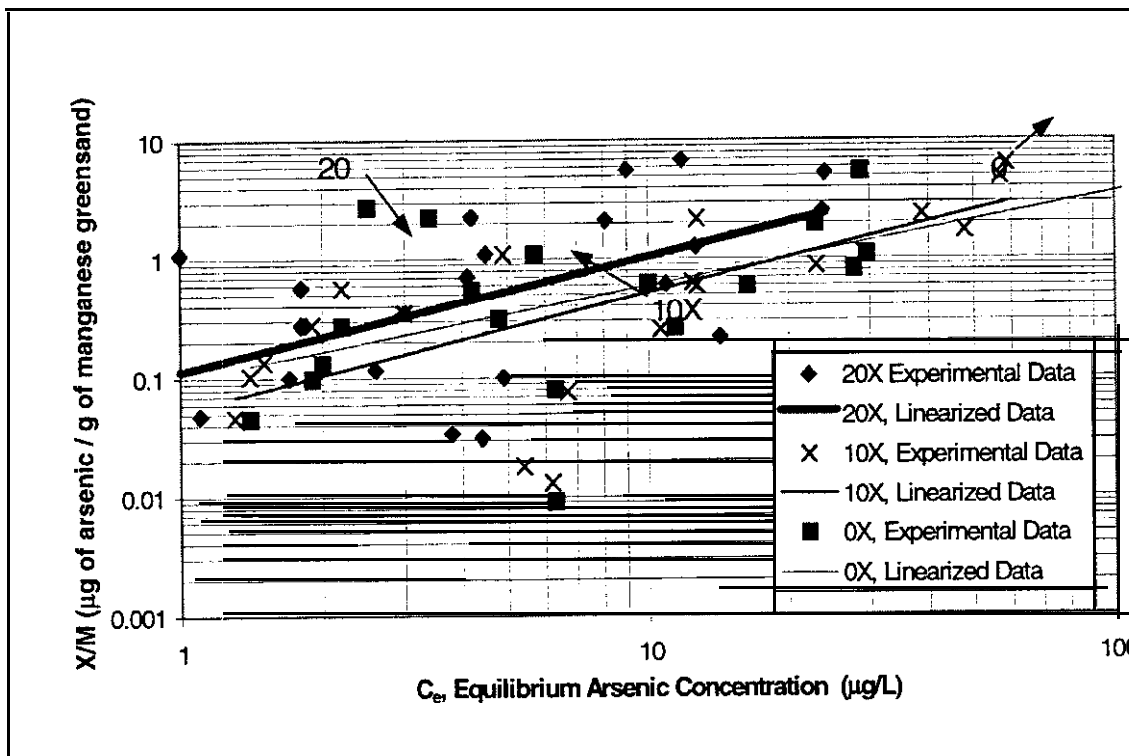


Figure 32: Freundlich Isotherms, pH=5 for three sets

Table 6 and Table 7 contain the constants obtained from the Freundlich equation analysis and the square of the correlation coefficient, r^2 , for each set of data. The r^2 term indicates a strong linear relationship for values close to 1 and a weaker linear relationship for values closer to zero. Thus, a high r^2 term would indicate that the Freundlich isotherm fits the data well.

Table 6: Summary of Freundlich Constants From Figure 31

pH	K	n	r^2
-	($\mu\text{g/g}$)	-	-
3	0.0248	0.5515	0.347
5	0.0700	0.5918	0.748
6	0.0318	1.0709	0.295
7	0.0003	0.5563	0.586

Table 7: Summary of Freundlich Constants From Figure 32

FeCl ₂ :As molar ratio	K	n	r^2
	($\mu\text{g/g}$)	-	-
20X	0.1130	1.0384	0.292
5X	0.0532	1.0147	0.499
0X	0.0967	1.2744	0.36

Table 6 shows that at a pH of 5, the K value is the highest, which indicates that the manganese greensand has the largest capacity to absorb arsenic at this pH. The highest correlation coefficient is also produced at this pH, indicating a fair predictability using the Freundlich isotherm. The n values, which correspond to the strength of the adsorption bond, are approximately the same for all the pH's except for a pH of 6. This is probably a result of the low correlation shown by an r^2 value of only 0.295 at a pH of 6.

Table 7 shows how similar the constants are at a pH of 5 for varied iron ratios. Because the correlation coefficient is so low, these three lines are virtually indistinguishable. Also of note is the fact that the first data set at a pH of 5, shown in Table 6 with an r^2 value of 0.748, is much better defined by the Freundlich equation than all three sets of data at a pH of 5 shown in Table 7 with an r^2 value of less than 0.5. This is because the second two sets didn't perform as much removal as the first set. For each pH, the K and $1/n$ are taken from the linearized equations. Using these values the X/M ratio is calculated according to the Freundlich equation

3.5.2 Langmuir Isotherm

The Langmuir isotherm is derived assuming the following: a limited area available for adsorption, arsenic is absorbed in a mono-molecular layer, adsorption is reversible, and equilibrium is achieved. The fact that experimental data for sorption of arsenic on manganese greensand can be described by an equation of the Langmuir type should not be construed as

validation of the applicability of the Langmuir model for description of the process. It is apparent that not all of the basic assumptions of the Langmuir model are satisfied. Nonetheless, the equation itself is useful for describing data. The equation is of the form:

$$\frac{x}{M} = \frac{x_m k C_e}{1 + k C_e} \quad \text{EQ(5)}$$

which can be linearized as follows:

$$\frac{M}{X} = \frac{1}{x_m} + \left(\frac{1}{x_m k} \right) \frac{1}{C_e} \quad \text{EQ(6)}$$

$$y = \text{intercept} + \text{slope} \times x$$

where M is the mass of greensand, X is the mass of absorbed arsenic, x_m is the limiting value for x (monolayer capacity), k is a constant relating to the energy of sorption, and C_e is the residual concentration of the sorbate in solution phase at equilibrium. For data which may be described by the Langmuir equation, a plot of M/X versus $1/C_e$ should yield a linear trace with an intercept of $1/x_m$ and a slope of $1/x_m k$.

Figure 33 shows the Langmuir isotherms calculated for the original data sets from section 3.1. The iron concentration was assumed to have no effect, so each line represents six combined data sets for each pH. Any data that resulted in negative removals or a M/X ratio greater than 80 was left out of the calculations. The set of data at a pH of 9 was not included because there was no significant removal shown at that pH. Figure 33 shows that the data does not fit this isotherm as well as the Freundlich isotherm. A pH of 5 performs the best adsorption and a pH of 7 performs the least adsorption of arsenic.

Figure 34 shows the Langmuir isotherm for the three sets of data at a pH of 5, where the best removal occurred. Iron concentration is still insignificant, but the data was plotted for each iron concentration (0, 5, and 20X) for visual effect. The three linearized plots are very close to each other, representing the insignificance of iron addition in this study.

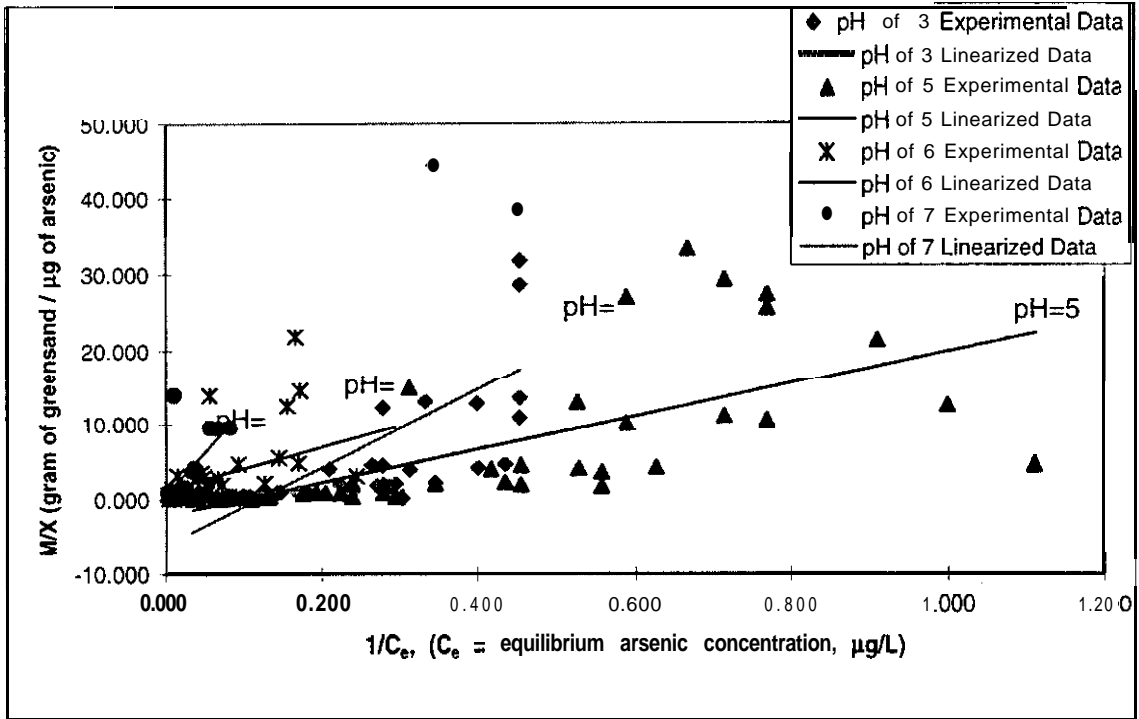


Figure 33: Langmuir Isotherm for Varied pHs

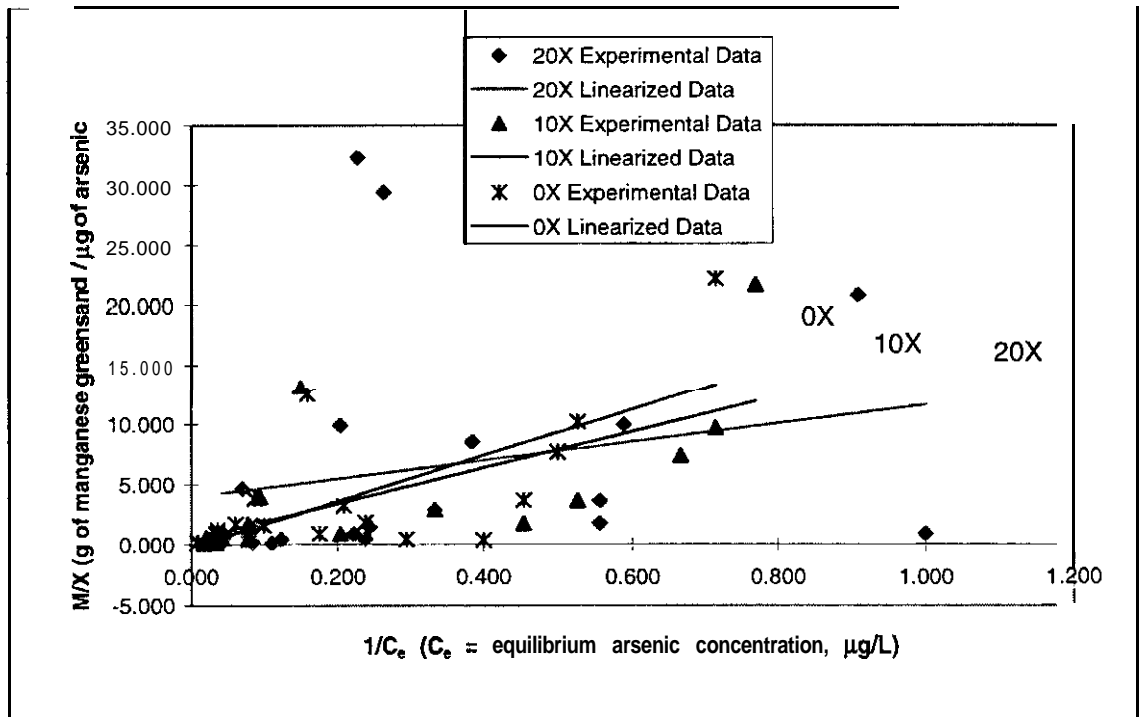


Figure 34: Langmuir Isotherms, pH=5 for three sets

Table 8 and Table 9 contain the constants obtained from the Langmuir equation analysis and the square of the correlation coefficient, r^2 , for each set of data. The r^2 term indicates a strong linear relationship for values close to 1 and a weaker linear relationship for values closer to zero. Thus, a low r^2 term indicates that the Langmuir isotherm fits the data poorly.

Table 8: Summary of Langmuir Constants From Figure 33

pH	X_m	k	$k \cdot X_m$	r^2
-	(g/mg)	-	(g/ μ g)	-
3	-0.166	-0.12	0.0194	0.41
5	-0.485	-0.094	0.0457	0.44
6	0.752	0.047	0.0351	0.10
7	1.483	0.006	0.0088	0.37

Table 9: Summary of Langmuir Constants From Figure 34

FeCl ₂ :As molar ratio	X_m	k	$K \cdot X_m$	r^2
	(g/mg)	-	(g/mg)	-
20X	0.255	0.512	0.130	0.05
5X	2.494	0.027	0.067	0.49
0X	-4.122	-0.013	0.052	0.50

Table 8 shows that at a pH of 3 and 5, a negative x_m value was obtained. This can be seen in Figure 33 by observing that the lines for these two pHs have negative intercepts. The k value is then also negative so that the slope, which is $1/(x_m \cdot k)$, will be positive. The result is a Langmuir isotherm which predicts negative removals at high concentrations of arsenic and good removals at lower concentrations of arsenic. This peculiarity is the result of the linearization of the data, where the removal is very good at lower concentrations, but not as good, relatively, at higher concentrations. The highest ($x_m \cdot k$) product is at a pH of 5, indicating the best removal at this pH. The highest correlation coefficient, 0.5 is also produced at this pH, indicating a poor predictability using the Langmuir isotherm.

3.5.3 ion Exchange Model

The following general hypothesis, based on ion exchange is proposed to explain the results of this experiment. Even though the amount of iron added to solution in this experiment appeared to have no effect on arsenic removal, it is felt that the presence of iron must play an important role, which is discussed below. The two studies summarized in sections 1.2.4.3 and 1.2.4.4 both concluded that iron was an essential element for removing arsenic on greensand. By careful study of Figure 1 and Figure 3, it is noted that glauconite contains significant amounts of both ferrous and ferric iron in its octahedral site. After 24 hours of mixing in the test tube, the solution water would be greenish-brown, similar to backwash water. It is quite possible that iron was being

released into solution during the mixing process, so that even the solutions with no external iron added ended up with iron in the ppb concentration level, which would be significant for arsenic removal in the low ppb concentration level.

Assuming this hypothesis is true, much of the pH effect observed in this experiment can be explained by ion exchange. The zero point of charge of ferric hydroxide is about 7 according to Peng and Di (1994). Figure 35, recreated from Peng and Di (1994), shows the zeta potential of ferric hydroxide versus pH. Below a pH of about 7, the surface of ferric hydroxide flocs become positively charged. Above a pH of about 7, the surface of ferric hydroxide flocs become negatively charged. So below a pH of 7, a negatively charged ion should be attracted to ferric hydroxide.

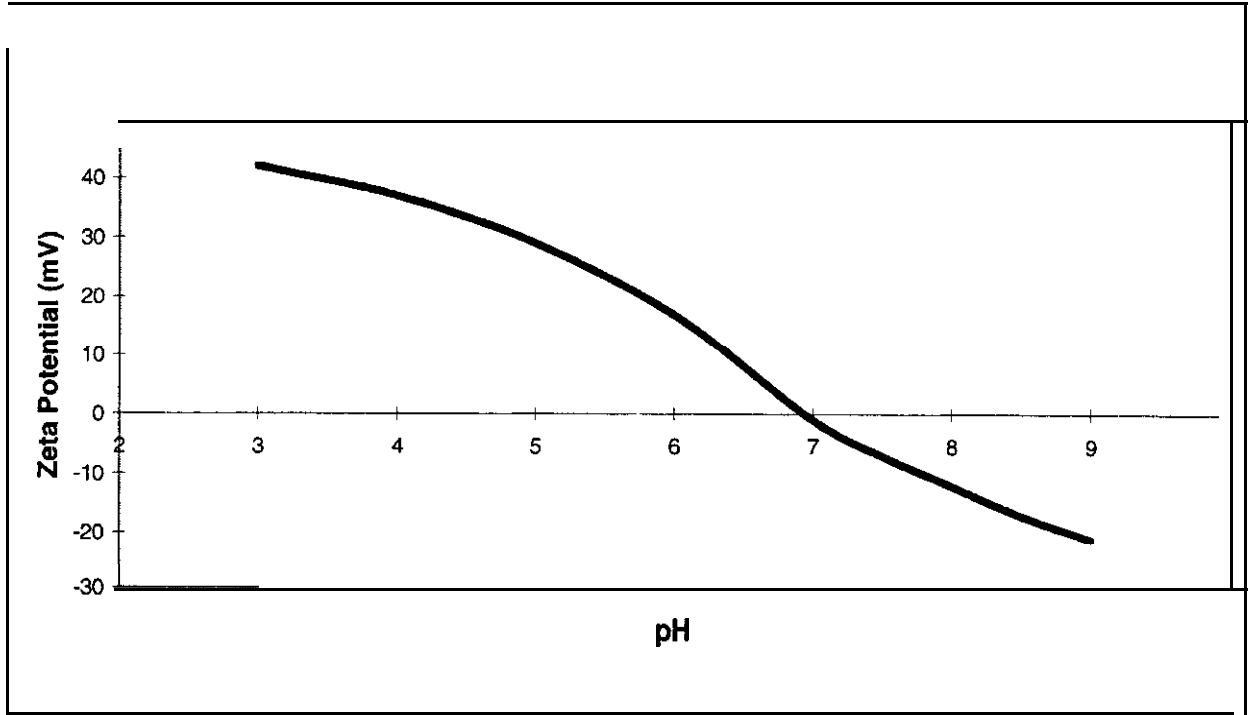


Figure 35: Zero Point of Charge of Ferric Hydroxide (Peng and Di,1994)

Depending on the pH, four species of arsenate ion can exist in a pure aqueous solution. The derived equations for each species are shown in the four equations below (Snoeyink and Jenkins, 1980):

$$[\text{H}_3\text{AsO}_4] = C_{\text{T,As(V)}} \left[\frac{1}{1 + (K_{a1} / [\text{H}^+]) + (K_{a1}K_{a2} / [\text{H}^+]^2) + (K_{a1}K_{a2}K_{a3} / [\text{H}^+]^3)} \right] \quad \text{EQ(7)}$$

$$[\text{H}_2\text{AsO}_4^{-1}] = C_{\text{T,As(V)}} \left[\frac{1}{([\text{H}^+ / K_{a1}] + 1 + (K_{a2} / [\text{H}^+]) + (K_{a2}K_{a3} / [\text{H}^+]^2)} \right] \quad \text{EQ(8)}$$

$$[\text{HAsO}_4^{-2}] = C_{\text{T,As(V)}} \left[\frac{1}{([\text{H}^+]^2 / K_{a1}K_{a2}) + ([\text{H}^+] / K_{a1}) + 1 + (K_{a3} / [\text{H}^+])} \right] \quad \text{EQ(9)}$$

$$[\text{AsO}_4^{3-}] = C_{T,\text{As(V)}} \left[\frac{1}{([\text{H}^+]^3 / K_{a,1}K_{a,2}K_{a,3}) + ([\text{H}^+]^2 / K_{a,2}K_{a,3}) + ([\text{H}^+] / K_{a,3}) + 1} \right] \quad \text{EQ(10)}$$

where $K_{a,1} = 10^{-2.2}$, $K_{a,2} = 10^{-7.08}$, and $K_{a,3} = 10^{-11.5}$ at 25° C (Gulledge and O'Connor, 1972). Figures 36 and 37 show the speciation of arsenate for each pH graphed from these equations.

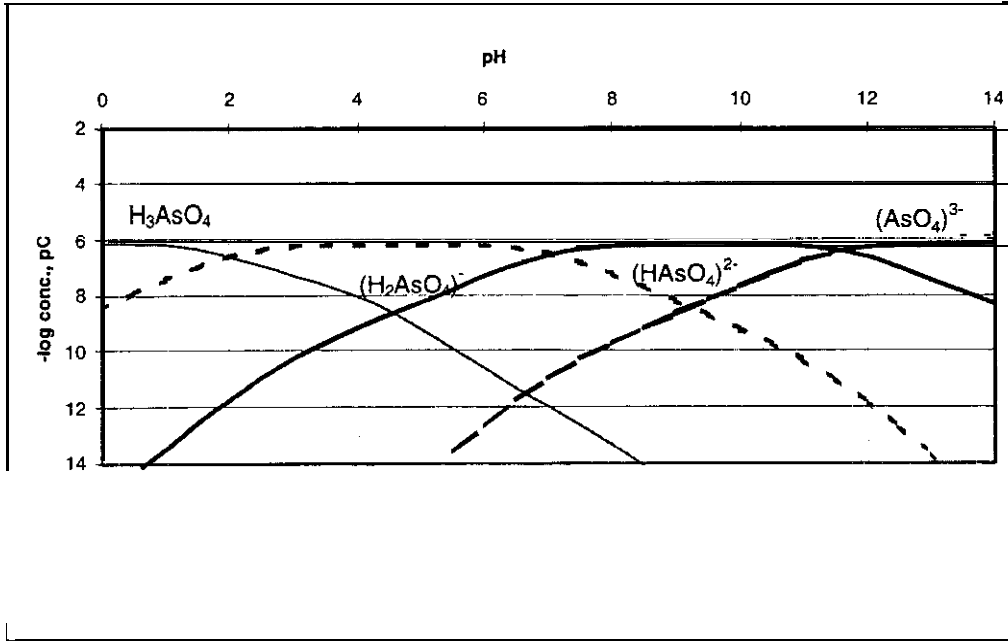


Figure 36: pC-pH diagram for a $10^{-6.1}$ M ($50\mu\text{g/L}$) solution of Arsenate

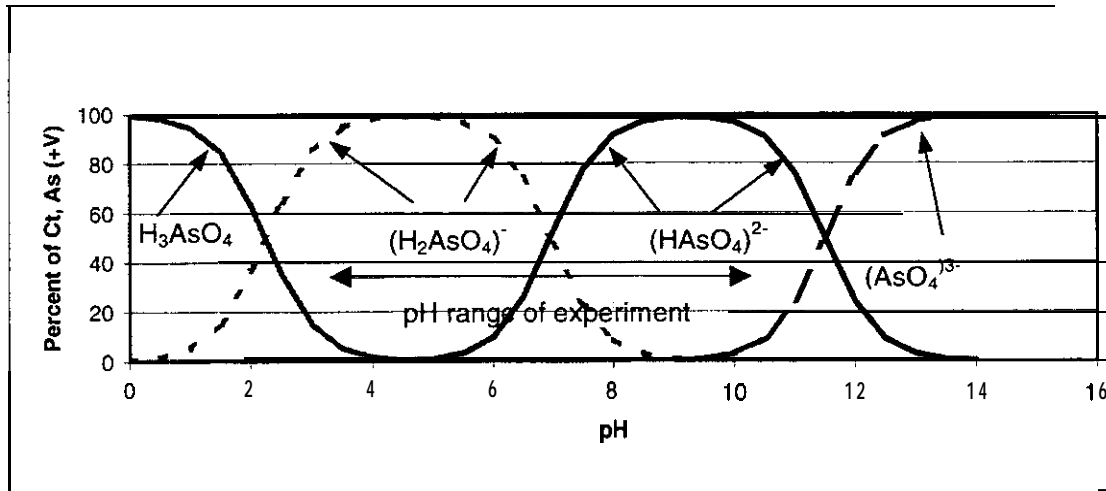


Figure 37: Distribution Diagram for Arsenate

Three arsenite species exist in aqueous solution at a normal pH. The derived equations for each species are shown below (Snoeyink and Jenkins, 1980):

$$[\text{H}_3\text{AsO}_3] = C_{\text{T,As(III)}} \left[\frac{1}{1 + (K_{a1} / [\text{H}^+]) + (K_{a1}K_{a2} / [\text{H}^+]^2)} \right] \quad \text{EQ(11)}$$

$$[\text{H}_2\text{AsO}_3^-] = C_{\text{T,As(III)}} \left[\frac{1}{([\text{H}^+ / K_{a1}] + 1 + (K_{a2} / [\text{H}^+])} \right] \quad \text{EQ(12)}$$

$$[\text{HASO}_3^{2-}] = C_{\text{T,As(III)}} \left[\frac{1}{([\text{H}^+]^2 / K_{a1}K_{a2}) + ([\text{H}^+] / K_{a2}) + 1} \right] \quad \text{EQ(13)}$$

where $K_{a1} = 10^{-9.2}$ and $K_{a2} = 10^{-12.3}$ at 25° C. (Gulledge and O'Connor, 1972). Figures 3X and 39 show the speciation of arsenite for each pH graphed from these equations.

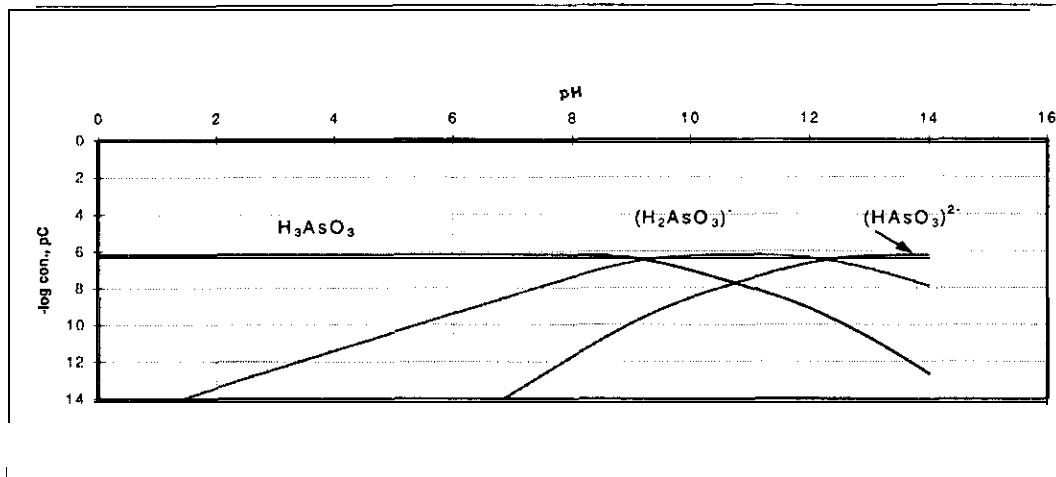


Figure 38: pC-pH diagram for a $10^{-6.1}\text{M}$ ($50\mu\text{g/L}$) solution of Arsenite

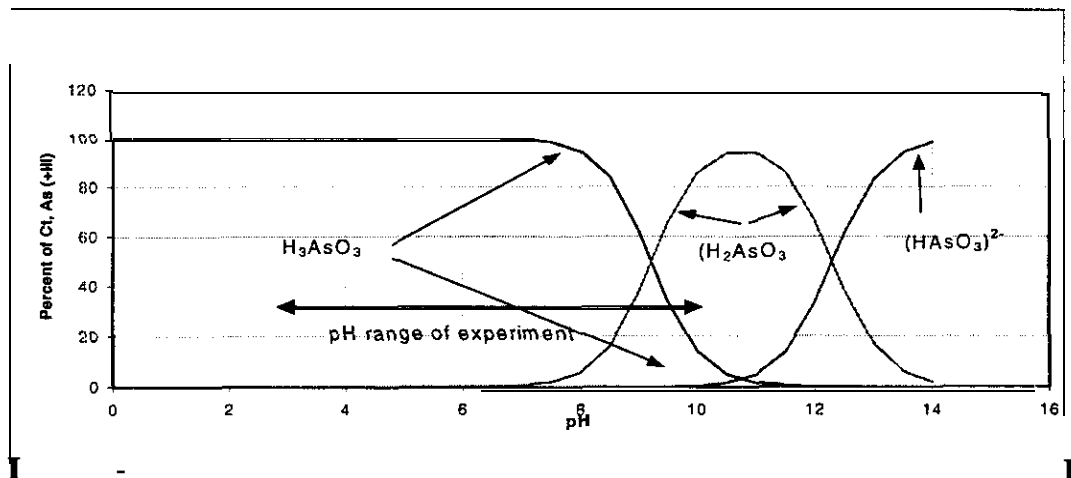


Figure 39: Distribution Diagram for Arsenite

From this discussion, it is shown that seven species of arsenic exist in aqueous solution, each with a charge ranging from zero to negative 3. The concentration of each species depends on pH and oxidation potential. Because the manganese greensand is a strong oxidizer itself and is usually pre-fed with either chlorine or potassium permanganate, all the arsenite ions will be oxidized to arsenate ions.

From Figure 37 the predominant arsenate species in this experiment are $\text{H}_2\text{AsO}_4^{-1}$ from a pH of 2.2 to 7.08 and HAsO_4^{-2} from a pH of 7.08 to 11.5. Also a small amount, (less than 20%), of uncharged H_3AsO_4 exists in the pH range from 3 to 4.3. From Figure 39 the predominant arsenite species in this experiment is the neutrally charged H_3AsO_3 , which exists below a pH of 9.22.

The scenario for arsenate removal on greensand might be as follows. The arsenate and ferrous ions remain separate in solution. As the ferrous ions are oxidized to ferric hydroxides, the negative charge of the predominant arsenate species would be attracted to the positive surface charge of the ferric hydroxide. If more ferric hydroxide ions were present than arsenate ions, the net charge would still remain positive and this combined ferric hydroxide-arsenate micro floc would be attracted to the negatively charged manganese oxide coating of the manganese greensand. To examine this theory, all the component's theoretical charges can be examined at each pH to see if the predicted relative removal performance is the same as the experimental relative removal performance.

At a pH of 3, arsenate ions have mostly negative one charges (greater than 70%) and a few neutral charges (less than 30%). Ferric hydroxide is very positively charged and the manganese oxide coating has a small negative charge. Moderate to good removal performance would probably be expected due to the roughly thirty percent of the neutrally charged arsenate ions that would not be attracted to any of the other chemical components based on charge.

At a pH of 5, arsenate ions have mostly negative one charges. Ferric hydroxide is still very positively charged, although less so than at a pH of 3. The manganese oxide coating has a larger negative charge. Therefore, good removal performance would be expected, because the components have all the needed charges to combine in the way hypothesized.

At a pH of 6, arsenate ions have mostly negative one charges and a few negative two charges (less than 10%). Ferric hydroxide is still positively charged, although less so than at a pH of 5. The manganese oxide coating has an even larger negative charge than at a pH of 5. Therefore, good removal performance would be expected, because the components have all the needed charges to combine in the way theorized. The expected removal might be more than at a pH of 5 if the surface charge of the arsenate and manganese oxide is more important in the removal mechanism. The expected removal might be less than at a pH of 5 if the surface charge of the ferric hydroxide is more important in the removal mechanism.

At a pH of 7, arsenate ions have half negative one charges and half negative two charges. Ferric hydroxide is neutrally charged. The manganese oxide coating has an even larger negative charge than at a pH of 6. Therefore, poor removal performance would be expected, because all the components have negative or neutral charges.

At a pH of 9, arsenate ions have mostly negative two charges. Ferric hydroxide is negatively charged. The manganese oxide coating has an even larger negative charge than at a pH of 7. Therefore, very poor removal performance would be expected, because all the components have negative charges and would thus repel each other.

The experimental data seems to agree with this theory. Experimentally at a pH of 5 the manganese greensand performed the best arsenic removal. At a pH of 3, the manganese greensand performed the next best removal. At a pH of 7 and 9, no significant arsenic removal occurred. At a pH of 6, moderate removal was seen, perhaps indicating that the positive charge of the ferric hydroxide was weaker and thus less attractive to the negative arsenic oxyanions.

4. COLUMN STUDIES

The adsorption step associated with this process is probably fast, but the oxidation (surface precipitation) step, may be slow. This means the system may be kinetically limited and the batch studies, while quick to perform, may be misleading. Pilot scale column studies were performed to confirm the results of the batch studies. A series of seven columns tests were performed. Selected columns were exhausted, regenerated, and then loaded again.

Figure 40 is representative of early column tests which were performed. The columns were run both with and without iron in the feed stream, there seemed to be no impact on the performance of the system with regard to As removal. The breakthrough pattern shown in Figure 40 seems to indicate that there may have been column short-circuiting and insufficient contact time. Notice that the concentration of As in the effluent starts to increase as soon as the column is placed in use. If there is treatment occurring, one would expect that there would be a lag prior to the onset of breakthrough.

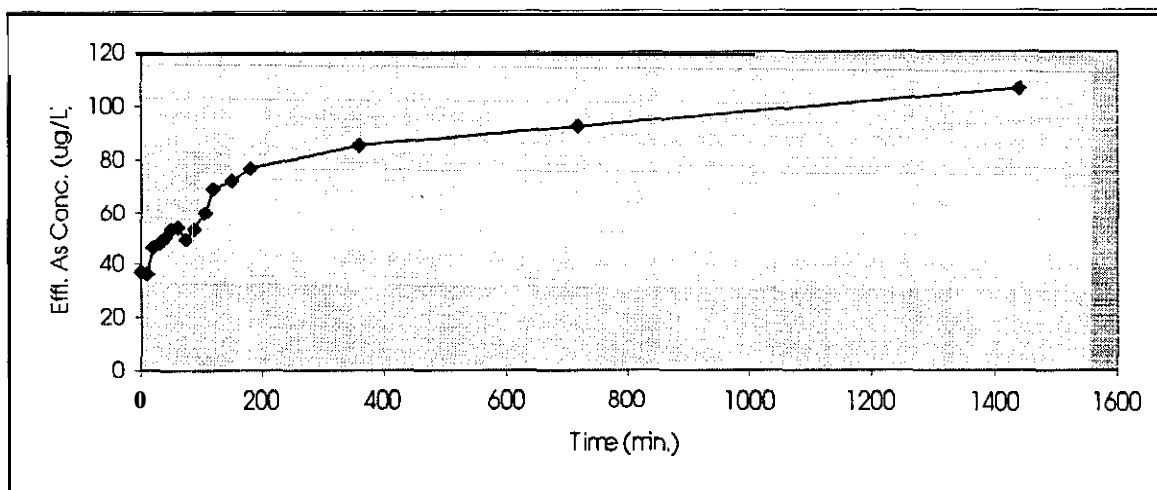


Figure 40: Manganese greensand filter used to treat As contaminated water. No special column preparation. Influent pH adjusted to 6.0. Filter rate 2 gpm/ft². Filter media depth 6 inches.

Figure 41 contains data from a column used to test the impact of detention time and short circuiting by increasing the filter media depth from 6 in. to 13 in. Because the column to particle diameter ratio was already greater than 25: 1, the researchers believed the problem was likely to be detention time rather than short circuiting.

It is clear that increasing the depth of media did not improve column performance, indicating that the performance is an operational problem not a column geometry problem. A review of the operational data showed that the influent pH was climbing as much as a full pH unit as the water passed through the column. The column operations was modified to preadjust the pH of the column by passing dilute HCl through the column until the influent and effluent pH were stable at the desired operational pH (5-5.5).

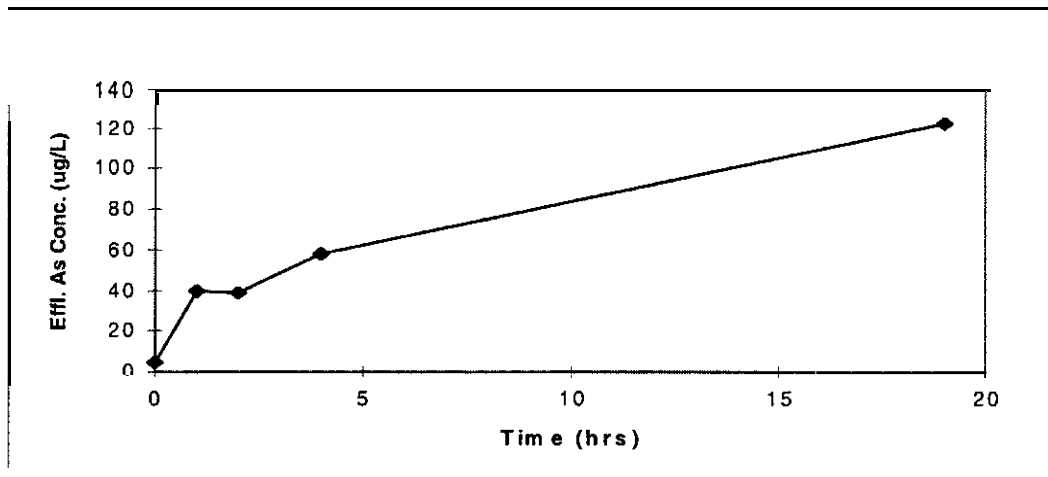


Figure 41: Manganese greensand filter used to treat As contaminated water. No special column preparation. Influent pH adjusted to 6.0. Filter rate 2 gpm/ft². Filter media depth 18 inches.

Figure 42 and 43 contain data from typical column runs performed with the filter pH brought to steady-state prior to treating water. The columns in both cases are achieving a continuous removal of approximately 80% of the As(III) for 200+ bed volumes.

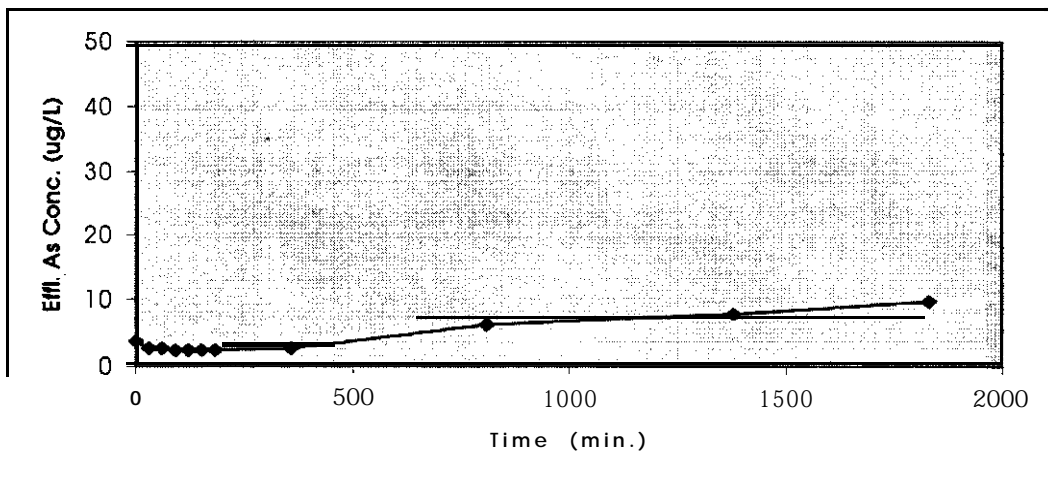


Figure 42: Manganese greensand filter used to treat As contaminated water. Column pH pre Adjusted prior to As removal. Influent and Effluent pH adjusted to 5.5. Filter rate 2 gpm/ft². Filter media depth 13 in.

The column represented by Figure 42 was run for 400 bed volumes and then terminated. Termination was not the result of increased As concentration, but rather an arbitrary decision based on a combination of factors including lab analysis time, and an anticipation that a process which was successful for 400 bed volumes would be economically viable. It is interesting to note that the concentration of As in the column effluent is very nearly the same as the equilibrium concentration in the 50 µg/l, pH 5.5 batch tests (Figure 13). After the column shown in Figure 42 was terminated, it was backwashed, regenerated with potassium

permanganate, and put back into production. The data from this test is shown in Figure 43. Note that the effluent concentration starts at 20 $\mu\text{g/l}$ and quickly drops to 10 $\mu\text{g/L}$, and then stays at 10 $\mu\text{g/L}$ for roughly 200 bed volumes with no change. From this it appears that the columns can be easily regenerated using traditional methods of backwash followed by permanganate regeneration. No attempt was made to operate the column in continuous regeneration mode.

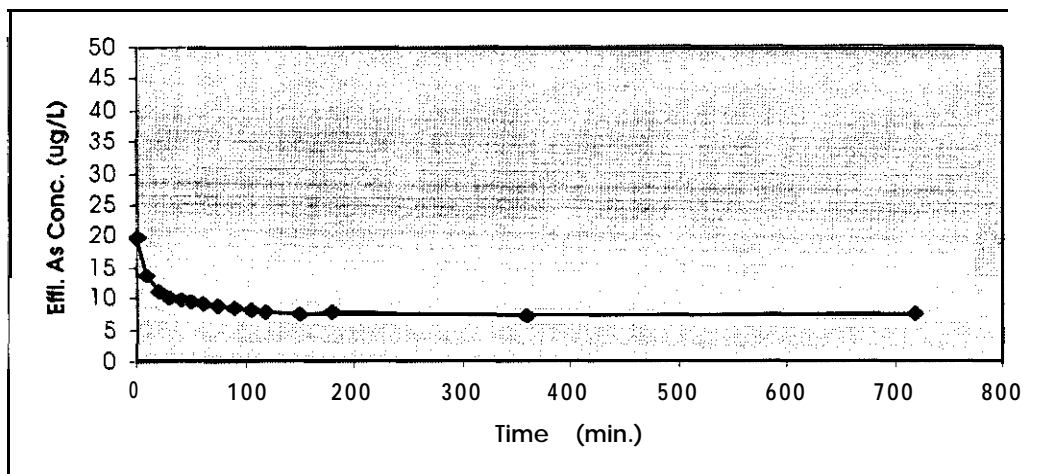


Figure 43: Regenerated manganese greensand filter used to treat As contaminated water. Column pH pre Adjusted prior to As removal. Influent and Effluent pH adjusted to 5.5. Filter rate 2 gpm/ft². Filter media depth 13 in.

Clearly, at the appropriate pH and with the appropriate bed preparation, this technology can achieve significant reduction of either As(III) or As(V). An arsenic concentrations of 10 $\mu\text{g/l}$ appears relatively easy to achieve. If the regulations require a total arsenic concentration of less than 5 $\mu\text{g/L}$, it may be problematic.

In addition to the Manganese greensand, two other medias have been suggested for testing: BIRM and Anthrasand (General Filter Company). Anthrasand is similar to BIRM, but the manganese dioxide coating is on an anthracite base. These media are of interest because they may act differently than the M.G.S.

5. ALTERNATE MANGANESE DIOXIDE COATED MEDIA

There are several manganese dioxide coated proprietary filter media available, which are marketed as iron and manganese removal media. Two of these media, **BIRM** and **ANTHRASAND**, were evaluated using elemental analysis; EDAX secondary electron back-scatter analysis.

5.1 BIRM Media

BIRM stands for Burgess Iron Removal Media, and it can be used as a replacement media for manganese greensand in an iron and manganese removal filter. This media is a manganese

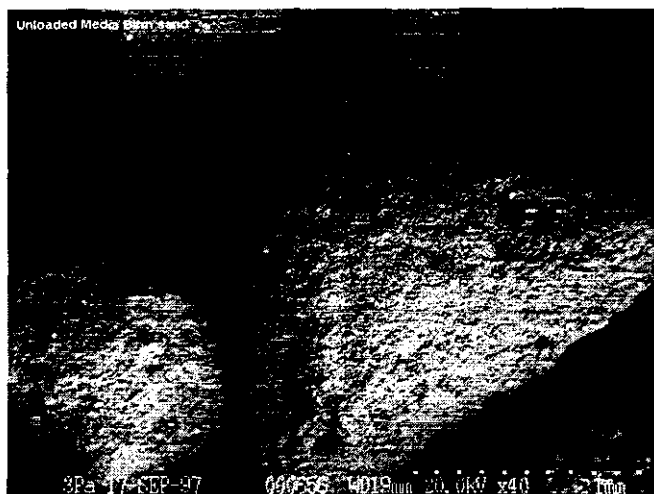


Figure 44: Photomicrograph of the BIRM media.

dioxide coated alumina silicate, with the following physical properties:

- color: black
- density: 47-50 lbs./ft³
- effective size: 0.61 mm
- uniformity coefficient: 1.72

The following SEM micrograph illustrates the angularity of the **BIRM**.

When used as an iron removal media, **BIRM** acts as a catalyst to enhance the reaction between dissolved oxygen (D.O.) and the iron compounds found in many groundwater supplies. Because of the excess free carbon dioxide often found in groundwater, the iron is in the ferrous bicarbonate form and is soluble up to pH = 8.5. The media acts as a catalyst and enhances the reaction between the oxygen and the ferrous iron to form ferric hydroxide, which precipitates and is easily filtered. After a period of time it is necessary to backwash the filter to clean the bed of the material which has been removed from the water.

The following operating conditions apply to the this media when it is used to remove iron and manganese:

- raw water pH:
 - iron removal 6.8+
 - manganese removal 8.0-9.0
- service flow rate 5 gpm/ft²
- backwash flow rate 8-10 gpm/ft²
- min. D.O. 15% of iron and manganese content expressed as mg/l
- max. H₂S 0 mg/l
- max. organic matter 4-5 mg/l
- oil concentration 0 mg/l

The following spectrum is an elemental analysis performed using an EDAX. Based on the model proposed for the removal of arsenic using the manganese greensand, one would anticipate that the BIRM might also be an acceptable media. If one looks at the peak located at 65, it is clear that there is a significant amount of iron in this media. From the apparent area under the peak and the relative number of counts required to form the peak, one might expect that there is 1/6 of the iron in the surface of the BIRM compared to the manganese greensand.

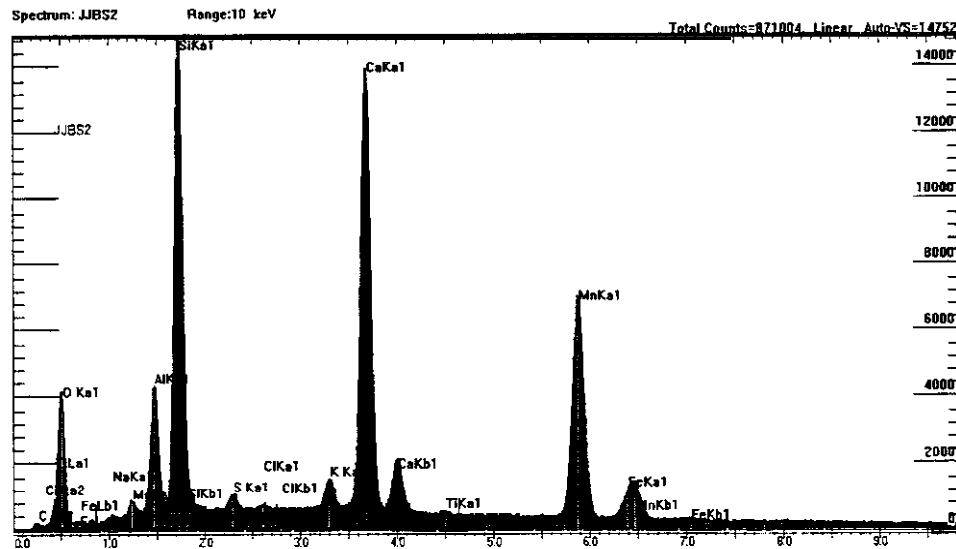


Figure 4.5: EDAX spectrum for the BIRM media.

If one is to use BIRM in an arsenic removal application, the operational pH range would need to be 5 to 6.5. The adjustment of the solution pH turned out to be problematic with this media. Upon addition of acid to this media, the pH immediately begins to climb and eventually returns to levels greater than 7.5. An attempt to titrate the media and determine the buffer capacity indicated that it was impractical to adjust the pH of this media. It was abandoned as an arsenic removal media because of the pH adjustment difficulty.

5.2 Anthrasand Media

In addition to these two media, a third proprietary media produced by General Filter Company with the trade name Anthrasand, was tested. This media is manufactured by putting a manganese dioxide coating on either a sand or an anthracite-base. A SEM photo micrograph of the Anthrasand is shown below.

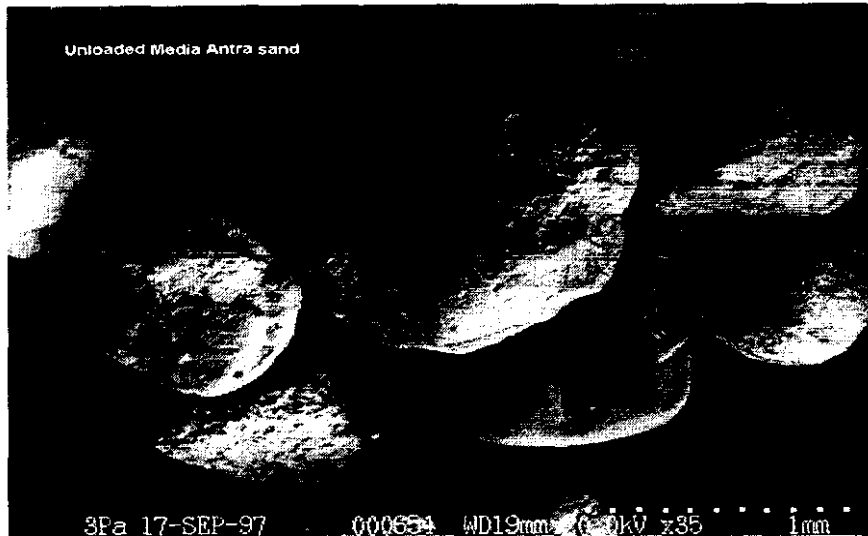


Figure 46: Photomicrograph of Anthrasand media, a proprietary General Filter Product.

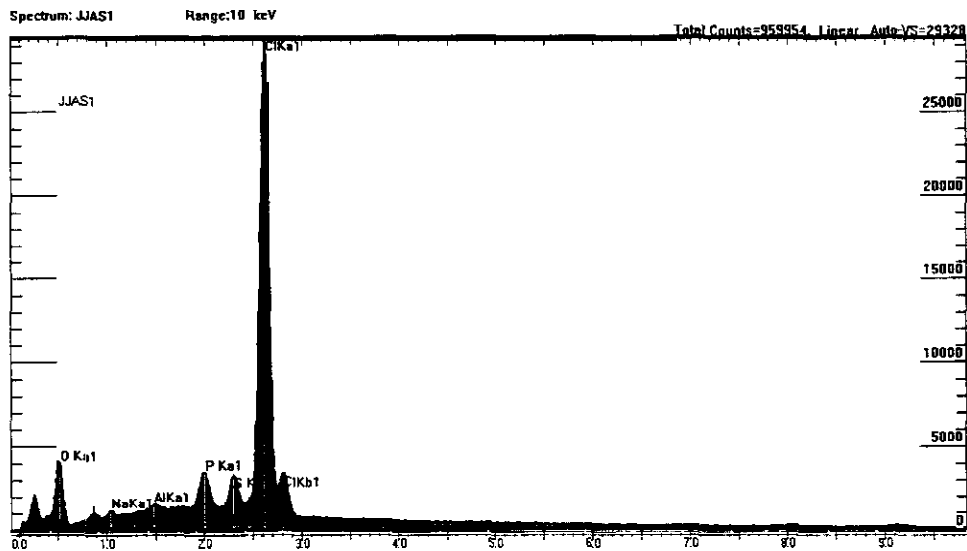


Figure 47: EDAX spectrum for the Anthrasand media, a proprietary General Filter Product.

From the EDAX spectrum of this media it is apparent that there is very little iron present. Note that the number of total counts used to develop this elemental analysis is over three times the counts used to develop the manganese greensand analysis. Information provided by Thomson

(1998) indicates that a media with a similar surface make-up was not successful in removing arsenic from water at a pH of 7-3. The authors are currently performing batch studies to demonstrate that this media performs in a manner similar to the laboratory scale media Thomson manufactured.

6. CONCLUSIONS

The following specific conclusions can be drawn:

1. Manganese greensand is a viable alternative for removing small concentrations of arsenic, possibly to levels as low as 2 $\mu\text{g/L}$ arsenic.
2. Manganese greensand filtration to remove arsenic works best at a pH of 5, probably because the positive charge of the ferric hydroxide is higher than at a pH of 6 and the arsenate ions are more negatively charged than at a pH of 3.
3. The optimal iron concentration in a manganese greensand filtration system was undetermined in this experiment, probably because the glauconite released enough iron into the system as it was being mixed to provide an adequate supply for any co-precipitation process taking place.
4. Sulfate was not expected to be a significant competing anion. One set of data was collected at a pH of 5 and contact time of 24 hours. The results indicated no significant effect of the sulfate ion on arsenic removal performance.
5. The arsenite removal results appear very similar to the arsenate removal results. Arsenite appears to be oxidized to arsenate very rapidly by the manganese dioxide. This is probably because the manganese oxide coating on the manganese greensand bed oxidizes the arsenite to arsenate, and it is then removed by the same process as the arsenate.
6. A general ion (exchange co-precipitation theory was proposed in section 3.5.3 and the theory seems to explain the results of this experiment in a general way, but the lack of fit using the ion exchange isotherms gives one little confidence in this explanation.
7. The arsenic removal data of this experiment was fitted to Langmuir and Freundlich isotherms. Both isotherms fit the data poorly. The Freundlich isotherms fit the data better but the linear correlation was not strong, as measured by the correlation coefficient, r^2 . This indicates that the removal mechanism is probably something other than simple ion exchange.
8. Changing contact times from 15 minutes to 24 hours had no impact on arsenic removal. From this, it is inferred that the removal process is completed within 15 minutes, which is a typical contact time for a low (2 to 3 gallons per minute per square foot of bed) filtration rate in a rapid sand filter.
9. The column studies showed great promise. A contact time of 15 minutes was adequate in the batch tests which indicated a 30 inch deep bed with a 2 gpm/ft^2 filtration rate will allow the reaction to come to completion in the filter bed. The greensand columns successfully removed arsenic, but only after the media had been pre-treated with dilute acid. A solution of dilute HCl was passed through the media until the influent and effluent pH came to steady state. This allowed the operator to control the operational pH . With the bed properly prepared, 400+ bed-volumes of water were treated with no evidence of impending breakthrough. The bed was regenerated and another 200+ bed-volumes were treated. It

appears that the appropriate preparation of the media will allow manganese greensand to act as an effective arsenic removal media.

10. An existing manganese greensand filter plant designed to remove Fe and Mn, can be easily and inexpensively modified to remove arsenic. This is done by simply lowering the pH of the filter bed. However, the manufacturer of the manganese greensand cautions against lowering the bed pH below 6.2.
11. It appears that, if manganese greensand is to be used to remove arsenic, neither BIRM media nor Anthrasand media is an adequate replacement for the manganese greensand media.

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Appendix A

BATCH TESTS: Effect of Fe and pH

Table A-1: Raw Data for Optimum pH and Iron Dose

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio											
		20X		10X		5X		2X		1X		0X	
		final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	2.9	3.2	2.2	3.2	2.2	3.1	8.7	2.7	2.2	3.2	5.7	3.1	
10	2.5	3.2	2.2	3.2	2.2	3.2	9.3	2.7	3	3.1	3.6	3.1	
25	3.6	3.2	3.2	3.2	2.3	3.1	3.8	2.7	2.5	3.1	4.8	3.1	
50	3.4	3.2	3.7	3.2	2.9	3.2	4.5	2.7	3.6	3.2	3.5	3.1	
100	6.8	3.2	5.9	3.2	4.2	3.2	7	2.7	5.6	3.1	7.9	3.1	
200	7.6	3.2	8.4	3.2	9.3	3.2	7.5	2.7	9.9	3.1	18.5	3.1	
500	14.8	3.2	15.7	3.2	3.3	3.2	15.9	2.7	21.3	3.1	30.3	3.2	
controls													
500	514.4	-	598.5	-	484	-	521.6	-	492.8	-	599.4	-	
50	51.5	-	57	-	48.1	-	51.5	-	53.4	-	58.9	-	
5	-	-	-	-	-	-	-	-	-	-	-	-	
DI blank	0.3	-	0	-	-	-	-	-	-	-	-	-	
system blank	-	-	-	-	2.9	3.2	9.5	7.0	3	3.2	2.6	3.2	

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio											
		20X		10X		5X		2X		1X		0X	
		final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	1.1	5.3	1.7	5.6	1.3	5.2	1.5	5.9	1.3	5.2	1.4	4.8	
10	1.7	5.2	1.3	5.4	1.4	5.0	1	4.9	3.2	5.2	1.9	4.8	
25	1.8	5.1	2.4	5.3	1.9	4.9	0.9	4.5	1.6	5.1	2.2	4.6	
50	1.8	5.0	3.6	5.2	2.2	5.1	2.3	4.6	2.9	5.1	4.2	4.7	
100	4.5	5.1	5.5	5.2	4.9	5.0	3.6	4.6	5.2	5.1	5.7	4.7	
200	4.2	5.1	11.7	5.1	12.7	5.0	7.6	4.6	7.5	5.1	3.4	4.7	
500	9	5.0	15.3	5.1	28.8	5.1	13.4	4.6	12.7	5.1	28.6	4.7	
controls													
500	-	-	-	-	547.9	-	569.4	-	-	-	598.4	-	
50	57.8	-	58.8	-	52	-	45	-	49.5	-	48.1	-	
5	5.9	-	5.4	-	-	-	-	-	5.7	-	5	-	
DI blank	-	-	-	-	-	-	-	-	-	-	-	-	
system blank	1.4	5.2	1.3	5.2	1.5	5.4	1	4.6	1.4	5.5	-	-	

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio											
		20X		10X		5X		2X		1X		0X	
		final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	7.2	5.9	12.4	6.2	7	6.0	13.1	6.0	4.2	6.2	11.6	5.5	
10	5.8	5.8	6	5.9	6.4	5.8	11.8	5.7	9.6	6.1	13.4	5.7	
25	10.7	5.8	5.9	5.7	4.1	5.5	6.9	5.7	-	-	17.8	6.6	
50	13.9	5.8	20.6	5.8	19.6	5.8	21.9	5.7	7.9	5.9	15	5.8	
100	19.1	5.8	19.8	5.8	11.1	5.7	37.4	5.8	29.8	5.9	68.8	5.8	
200	3.4	5.5	31.9	5.8	105.9	5.8	-	-	43.6	5.7	134	5.8	
500	24.9	5.7	104.1	5.7	250.3	5.7	9.7	5.7	107.6	5.7	351	5.8	
controls													
500	637	-	596.5	-	1096.4	-	483.8	-	625.3	-	-	-	
50	63.4	-	52.8	-	72.1	-	49.6	-	53.3	-	-	-	
5	-	-	-	-	-	-	-	-	-	-	-	-	
DI blank	-	-	-	-	-	-	0	-	-	-	0	-	
system blank	6.3	5.8	3.5	5.7	10.4	5.8	-	-	5.4	5.8	9.8	5.7	

Table A-1 (cont.): Raw Data for Optimum pH and Iron Dose

pH = 7

Initial As Concentration (ppb) or (µg/L)	Initial FeCl ₂ :As molar ratio											
	20X		10X		5X		2X		1X		0X	
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	10.1	7.3	5.6	7.4	65.4	7.0	50.7	7.8	29.9	6.8	26.1	7.1
10	15.2	7.1	10.7	7.2	27.8	7.2	-	-	28.8	6.8	11	6.9
25	15	7.1	17.6	7.4	78.7	7.2	81.7	7.3	27.6	6.9	12.1	6.7
50	27.5	7.1	29.8	7.2	125.8	7.1	66.3	7.2	72.5	7.0	84.2	6.9
100	41.3	7.1	174.1	7.1	351.4	7.3	135.3	7.1	92.8	7.0	112.3	7.1
200	29.8	6.9	53.9	6.9	202.2	6.9	118.3	7.1	2.4	5.9	362.6	7.1
500	111.2	7.0	72.1	6.9	258.6	7.4	681.4	6.7	68.7	6.9	352.3	7.0
controls												
500	514.4	-	567.8	-	1109.4	-	-	-	-	-	-	-
50	51.1	-	56.1	-	0.5	-	85.7	-	58.4	-	48.7	-
5	-	-	-	-	-	-	6	-	5	-	4.5	-
DI blank	0	-	-	-	-	-	-	-	-	-	-	-
system blank	-	-	5.4	7.0	47.8	7.7	25.9	7.2	21.8	6.9	23.7	7.6

pH = 9

Initial As Concentration (ppb) or (µg/L)	Initial FeCl ₂ :As molar ratio											
	20X		10X		5X		2X		1X		0X	
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	51.2	8.8	38.4	8.8	84.9	9.1	75.7	9.1	68.1	8.9	49.2	8.9
10	55.4	9.0	108	9.1	57.7	10.9	72.1	9.0	60.8	8.9	60	9.0
25	80.8	8.9	103.6	9.1	73	9.4	144	9.1	69.6	8.9	61.6	8.8
50	45.3	8.6	144.3	9.3	159.8	8.7	99.4	9.3	84.6	8.9	96.6	8.9
100	214	9.0	-	-	248.7	8.9	298.2	8.9	174.7	8.8	201.4	8.9
200	290.9	9.0	339.9	9.1	628.1	9.3	448.8	9.2	235	8.9	316.7	8.1
500	537.3	8.7	658.2	8.8	581.8	11.1	676.5	9.1	825.1	8.7	860.1	8.8
controls												
500	-	-	-	-	-	-	-	-	-	-	-	-
50	56.9	-	-	-	61.9	-	69.5	-	56.7	-	56.7	-
5	5.4	-	5.9	-	5.9	-	6.1	-	5.4	-	7.1	-
DI blank	-	-	0	-	-	-	-	-	-	-	-	-
system blank	52	8.6	42.9	9.1	90.1	9.6	31.9	9.3	49.5	8.8	30.3	9.0

Table A-2: Removal Efficiencies for Optimum pH and Iron Dose Test at 24 Hour Contact Time

pH = 3		Initial FeCl ₃ :As molar ratio for pH=3																
Initial As Concentration (ppb) or (µg/L)	20X			10X			5X			2X			1X			0X		
	final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency	
5	2.9	42.0%		2.2	56.0%		2.2	56.0%		8.7	0%		2.2	56.0%		5.7	0%	
10	2.5	75.0%		2.2	78.0%		2.2	78.0%		9.3	7.0%		3	70.0%		3.6	64.0%	
25	3.6	85.6%		3.2	87.2%		2.3	90.8%		3.8	84.8%		2.5	90.0%		4.8	80.8%	
50	3.4	93.2%		3.7	92.6%		2.9	94.2%		4.5	91.0%		3.6	92.8%		3.5	93.0%	
100	6.8	93.2%		5.9	94.1%		4.2	95.8%		7	93.0%		5.6	94.4%		7.9	92.1%	
200	7.6	96.2%		8.4	95.8%		9.3	95.4%		7.5	96.3%		9.9	95.1%		18.5	90.8%	
500	14.8	97.0%		15.7	96.9%		3.3	99.3%		15.9	96.8%		21.3	95.7%		30.3	93.9%	

pH = 5		Initial FeCl ₃ :As molar ratio for pH=5																
Initial As Concentration (ppb) or (µg/L)	20X			10X			5X			2X			1X			0X		
	final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency	
5	1.1	78.0%		1.7	66.0%		1.3	74.0%		1.5	70.0%		1.3	74.0%		1.4	72.0%	
10	1.7	83.0%		1.3	87.0%		1.4	86.0%		1	90.0%		3.2	68.0%		1.9	81.0%	
25	1.8	92.8%		2.4	90.4%		1.9	92.4%		0.9	96.4%		1.6	93.6%		2.2	91.2%	
50	1.8	96.4%		3.6	92.8%		2.2	95.6%		2.3	95.4%		2.9	94.2%		4.2	91.6%	
100	4.5	95.5%		5.5	94.5%		4.9	95.1%		3.6	96.4%		5.2	94.8%		5.7	94.3%	
200	4.2	97.9%		11.7	94.2%		12.7	93.7%		7.6	96.2%		7.5	96.3%		3.4	98.3%	
500	9	98.2%		15.3	96.9%		28.8	94.2%		13.4	97.3%		12.7	97.5%		28.6	94.3%	

pH = 6		Initial FeCl ₃ :As molar ratio for pH=6																
Initial As Concentration (ppb) or (µg/L)	20X			10X			5X			2X			1X			0X		
	final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency	
5	7.2	0%		12.4	0.0%		7	0.0%		13.1	0.0%		4.2	16.0%		11.6	0.0%	
10	5.8	42.0%		6	40.0%		6.4	36.0%		11.8	0.0%		9.6	4.0%		13.4	0.0%	
25	10.7	57.2%		5.9	76.4%		4.1	83.6%		6.9	72.4%		-	-		17.8	28.8%	
50	13.9	72.2%		20.6	58.8%		19.6	60.8%		21.9	56.2%		7.9	84.2%		16	70.0%	
100	19.1	80.9%		19.8	80.2%		11.1	88.9%		37.4	62.6%		29.8	70.2%		68.8	31.2%	
200	3.4	98.3%		31.9	84.1%		105.9	47.1%		-	-		43.6	78.2%		134	33.0%	
500	24.9	95.0%		104.1	79.2%		250.3	49.9%		9.7	98.1%		107.6	78.5%		351	29.8%	

pH = 7		Initial FeCl ₃ :As molar ratio for pH=7																
Initial As Concentration (ppb) or (µg/L)	20X			10X			5X			2X			1X			0X		
	final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency	
5	10.1	0%		5.6	0%		65.4	0%		50.7	0%		29.9	0%		26.1	0.0%	
10	15.2	0%		10.7	0%		27.8	0%		N/A	N/A		28.8	0%		11	0.0%	
25	15	40.0%		17.6	29.6%		78.7	0%		81.7	0%		27.6	0%		12.1	51.6%	
50	27.5	45.0%		29.8	40.4%		125.8	0%		66.3	0%		72.5	0%		84.2	0.0%	
100	41.5	58.5%		114.1	0%		351.4	0%		135.3	0%		92.8	7.2%		112.3	0.0%	
200	29.8	85.1%		53.9	73.1%		202.2	0%		118.3	40.9%		2.4	98.8%		362.6	0.0%	
500	111.2	77.8%		72.1	85.6%		258.6	48.3%		681.4	0%		68.7	86.3%		352.3	29.5%	

pH = 9		Initial FeCl ₃ :As molar ratio for pH=9																
Initial As Concentration (ppb) or (µg/L)	20X			10X			5X			2X			1X			0X		
	final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency		final As Conc.	removal efficiency	
5	51.2	0%		38.4	0%		84.9	0%		75.7	0%		68.1	0%		49.2	0%	
10	55.4	0%		108	0%		57.7	0%		72.1	0%		60.8	0%		60	0%	
25	80.8	0%		103.6	0%		73	0%		144	0%		69.6	0%		61.6	0%	
50	45.3	9.4%		144.3	0%		159.8	0%		99.4	0%		84.6	0%		96.6	0%	
100	214	0%		N/A	N/A		248.7	0%		298.2	0%		174.7	0%		201.4	0%	
200	290.9	0%		339.9	0%		628.1	0%		448.8	0%		235	0%		316.7	0%	
500	537.3	0%		658.2	0%		581.8	0%		676.5	0%		825.1	0%		860.1	0%	

Table A-3: Raw Data for Duplicates of Best Results at a pH of 5.
(CONTACT TIME = 24 HOURS)

Set 1: pH=5 (partial representation of initial set shown in tables A-1 and A-2)

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5X		0X	
uncorrected	corrected	final As Conc.	final pH	final As Conc.	final pH	final As Conc.	final pH
5	5.9	1.1	5.3	1.3	5.2	1.4	4.8
10	11.7	1.7	5.2	1.4	5.0	1.9	4.8
25	29.3	1.8	5.1	1.9	4.9	2.2	4.6
50	58.7	1.8	5.0	2.2	5.1	4.2	4.7
100	114.4	4.5	5.1	4.9	5.0	5.7	4.7
200	228.8	4.2	5.1	12.7	5.0	3.4	4.7
500	571.9	9	5.0	28.8	5.1	28.6	4.7
controls							
target value	actual ave.						
500	571.9	547.9	-	569.4	-	598.4	-
50	58.7	57.8	-	58.8	-	59.4	-
5		-	-	-	-	-	-
DI blank		-	-	-	-	-	-
system blank		6.6	5.0	7.5	5.0	4.3	5.0

Set 2: pH=5

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5X		0X	
uncorrected	corrected	final As Conc.	final pH	final As Conc.	final pH	final As Conc.	final pH
5	7.5	4.4	5.1	6.2	4.9	8.3	4.9
10	15.0	4.9	5.1	1.5	4.9	2	4.5
25	37.5	3	5.2	3	5.1	11.4	5.1
50	75.0	4.1	5.2	12.4	5.2	16.3	5.2
100	109.8	1	5.0	23	5.3	27.7	5.1
200	219.6	8.1	5.1	47.8	5.3	22.9	5.1
500	549.0	24	5.1	57	5.3	112.7	5.1
controls							
target value	actual ave.						
500	549.0	563.9	-	564.1	-	519	-
50	75.0	70.7	-	66.8	-	87.5	-
5		-	-	-	-	-	-
DI blank		-	-	-	-	-	-
system blank		6.6	5.0	7.5	5.0	4.3	5.0

Set 3: pH=5

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5X		0X	
uncorrected	corrected	final As Conc.	final pH	final As Conc.	final pH	final As Conc.	final pH
5	7.2	3.8	4.9	5.4	5.0	6.3	4.8
10	14.3	2.6	4.9	6.7	5.1	6.3	5.1
25	35.8	14.2	5.0	10.6	5.2	4.8	5.0
50	71.6	10.9	4.9	12.7	5.2	10	4.9
100	138.1	12.6	4.9	29.2	5.1	29.5	5.1
200	276.3	23.7	4.9	38.8	5.1	2.5	4.8
500	690.7	11.8	4.7	58.8	5.0	119.9	5.0
controls							
target value	actual ave.						
500	690.7	784.8	-	764.2	-	523.2	-
50	71.6	66.1	-	77	-	-	-
5		-	-	-	-	-	-
DI blank		-	-	-	-	-	-
system blank		6.6	5.0	7.5	5.0	4.3	5.0

Table A-4.; Removal Efficiencies for Duplicates of Best Results at a pH of 5.
(CONTACT TIME =24 HOURS)

Set 1: pH=5 (partial representation of initial set shown in tables A-1 and A-2)

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As ratio					
		20X		5X		ox	
uncorrected	corrected	final As removal Conc.	efficiency	final As removal Conc.	efficiency	final As removal Conc.	efficiency
5	5.9	1.1	61.3%	1.3	77.0%	1.4	76.1%
10	11.7	-1.7	85.5%	1.3	86.1%	1.9	83.8%
25	29.3	1.8	93.9%	1.4	93.5%	2.2	92.5%
50	58.7	1.8	96.9%	2.2	96.3%	4.2	92.8%
100	114.4	4.5	96.1%	4.9	95.7%	5.7	95.0%
200	228.6	4.2	98.2%	12.7	94.4%	3.4	98.5%
500	571.9	9	98.4%	28.8	95.0%	28.6	95.0%
controls							
target value	actual ave.						
500	571.9	547.9	-	569.4	-	598.4	-
50	58.7	57.8	-	58.8	-	59.4	-
5		-	-	-	-	-	-
DI blank		-	-	-	-	-	-
system blank		6.6	5.0	7.5	5.0	4.3	5.0

Set 2: pH=5

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5 x		ox	
uncorrected	corrected	final As removal Conc.	efficiency	final As removal Conc.	efficiency	final As removal Conc.	efficiency
5	7.5	4.4	41.3%	6.2	0.0%	8.3	0.0%
10	15.0	4.9	67.3%	1.5	90.0%	2	86.7%
25	37.5	3	92.0%	3	92.0%	11.4	69.6%
50	75.0	4.1	94.5%	12.4	83.5%	16.3	78.3%
100	109.8	1	99.1%	23	79.1%	27.7	74.8%
200	219.6	8.1	96.3%	47.8	78.2%	22.9	89.6%
500	549.0	24	95.6%	57	89.6%	112.7	79.5%
controls							
target value	actual ave.						
500	549.0	563.9	-	564.1	-	519	-
50	75.0	70.7	-	66.8	-	87.5	-
5		-	-	-	-	-	-
DI blank		-	-	-	-	-	-
system blank		6.6	5.0	7.5	5.0	4.3	5.0

Table A-4 (cont.)

Set 3: pH=5

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5X		0X	
		final As Conc.	removal efficiency	final As Conc.	removal efficiency	final As Conc.	removal efficiency
uncorrected	corrected						
5	7.2	3.6	24.0%	5.4	0.0%	6.3	0.0%
10	14.3	2.6	74.0%	6.7	33.0%	6.3	37.0%
25	35.8	14.2	43.2%	10.6	57.6%	4.6	60.6%
50	71.6	10.9	78.2%	12.7	74.6%	10	80.0%
100	139.1	12.6	67.4%	29.2	70.6%	29.5	70.5%
200	276.3	23.7	88.2%	38.8	60.6%	2.5	98.8%
500	690.7	11.8	97.6%	56.6	66.2%	119.9	76.0%
controls							
target value	actual ave.						
500	690.7	784.8	-	764.2	-	523.2	
50	71.6	66.1	-	77	-		
5							
DI blank							
system blank		6.6	5.0	7.5	5.0	4.3	5.0

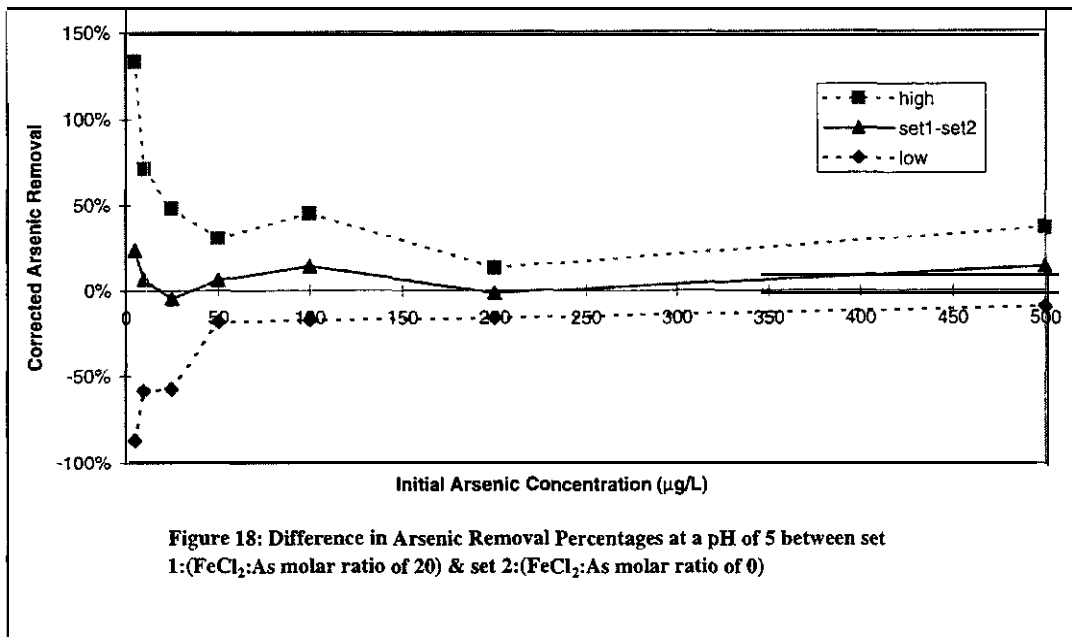


Table A-5: t-test for means of two data sets

Intended Initial As Concentration (ppb) or (µg/L)	set 1	set 2	set1-set2	t-test for means 95% conf. level	
	removal efficiency average	removal efficiency average		high	low
	20X	0X			
5	48.9%	25.4%	23.5%	134%	-87%
10	75.6%	69.2%	6.5%	71%	-58%
25	76.4%	81.0%	-4.6%	48%	-57%
50	89.9%	83.7%	6.2%	31%	-18%
100	94.2%	80.1%	14.1%	45%	-17%
200	94.2%	95.6%	-1.4%	13%	-16%
500	97.2%	83.5%	13.7%	37%	-9%

Table A-6: Combination of Data Sets Assuming added Iron has no effect
Average of **the three sets** of three

Intended Initial As Concentration (ppb) or (µg/L.)										removal		t-test interval	
	20X	5X	0X	20X	5X	0X	20X	5X	0X	efficiency	α = 95%		
	set1	set1	set1	set2	set2	set2	set3	set3	set3	average	low	high	
5	81%	78%	76%	41%	0%	0%	24%	0%	0%	33.4%	5.3%	62%	
10	86%	88%	84%	67%	90%	87%	74%	33%	37%	71.7%	55%	89%	
25	94%	94%	93%	92%	92%	70%	43%	58%	81%	79.5%	65%	94%	
50	97%	96%	93%	95%	83%	78%	78%	75%	80%	86.1%	79%	93%	
100	96%	96%	95%	99%	79%	75%	87%	71%	71%	85.4%	76%	94%	
200	98%	94%	99%	96%	78%	90%	88%	81%	99%	91.4%	85%	97%	
500	98%	95%	95%	96%	90%	79%	98%	88%	76%	90.6%	84%	97%	

APPENDIX B

BATCH TESTS: Effect of Contact Time

Table B-I: Optimum Contact Time Raw Data

(at pH = 5)

15 min		Initial FeCl ₂ :As molar ratio						controls	
Initial As Concentration (ppb) or (µg/L)	20X		5x		ox		system blank	50 ppb spike	500 ppb spike
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH			
5	2.2	4.53	1	4.49	1.7	4.32			2.2
50	5	5.08	2.2	4.62	1.6	4.53			
500	37.5	4.48	126.2	4.53	280.2	4.57			*

30 min		Initial FeCl ₂ :As molar ratio						controls	
Initial As Concentration (ppb) or (µg/L)	20X		5X		OX		system blank	50 ppb spike	500 ppb spike
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH			
5	1.3	4.44	1.7	4.65	2.1	4.72			1.1
50	6.2	4.63	11.8	4.73	7.9	4.67			52.6
500	20.4	4.56	87.7	4.66	107.7	4.69			527.1

1 hour		Initial FeCl ₂ :As molar ratio						controls	
Initial As Concentration (ppb) or (µg/L)	20x		5x		ox		system blank	50 ppb spike	500 ppb spike
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH			
5	0	4.8	2.6	4.84	0.6	4.9			3.7
50	0.9	4.5	5.4	4.74	12.3	4.88			58.8
500	6.5	4.54	153.5	4.86	279.5	4.89			795.7

2 hour		Initial FeCl ₂ :As molar ratio						controls	
Initial As Concentration (ppb) or (µg/L)	20X		5x		ox		system blank	50 ppb spike	500 ppb spike
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH			
5	4.3	4.94	2.2	4.91	2.8	4.78			4.3
50	6.2	4.9	2.4	4.73	10.3	4.82			-
500	33.4	4.87	108.9	4.48	213.8	4.85			

6 hour		Initial FeCl ₂ :As molar ratio						controls	
Initial As Concentration (ppb) or (µg/L)	20X		5x		ox		system blank	50 ppb spike	500 ppb spike
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH			
5	3	5.16	2.9	5.09	3.9	5.03			5.07
50	7.8	5	6.1	5.03	12.5	5.09			61.4
500	20.1	5	51.6	5.06	129.5	5.07			617.7

24 hour		Initial FeCl ₂ :As molar ratio						controls	
Initial As Concentration (ppb) or (µg/L)	20X		5x		ox		system blank	50 ppb spike	500 ppb spike
	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH			
5	1.1	5.3	1.3	5.2	1.4	4.8			1.5
50	1.8	5	2.2	5.1	4.2	4.7			5.2
500	9	5	28.8	5.1	28.6	4.7			547.9

**Table B-2: Removal Efficiencies for Contact Time Varied Batch Tests
(at pH \approx 5)**

15 min		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		initial As Concentration (ppb) or (µg/L)	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.
5	2.2	56.0%	1	80.0%	1.7	66.0%	
50	5	90.0%	2.2	95.6%	1.6	96.8%	
500	37.5	92.5%	126.2	74.6%	280.2	44.0%	

30 min		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		initial As Concentration (ppb) or (µg/L)	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.
5	1.4	74.0%	1.1	86.0%	2.1	58.0%	
50	6.2	07.6%	11.8	76.4%	7.9	64.2%	
500	20.4	95.0%	87.7	82.5%	107.7	78.5%	

1 hour		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		initial As Concentration (ppb) or (µg/L)	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.
5	0	100%	2.6	48.0%	0.6	88%	
50	0.9	98%	5.4	69.2%	12.3	75.4%	
500	6.5	98.7%	153.5	69.3%	279.5	44.1%	

2 hour		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		initial As Concentration (ppb) or (µg/L)	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.
5	4.3	14.0%	2.2	56.0%	2.6	46.0%	
50	6.2	87.6%	2.4	95.2%	10.3	79.4%	
500	33.4	93.3%	108.9	76.2%	213.6	57.2%	

6 hour		Initial FeCl ₂ :As molar ratio					
		20x		5x		ox	
		initial As Concentration (ppb) or (µg/L)	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.
5	3	40.0%	2.9	42.0%	3.9	22.0%	
50	7.8	04.4%	6.1	67.8%	12.5	75.0%	
500	20.1	96.0%	51.6	69.6%	129.5	74.1%	

24 hour		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		initial As Concentration (ppb) or (µg/L)	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.
5	1.1	78.0%	1.3	74.0%	1.4	72.0%	
50	1.8	96.4%	2.2	95.6%	4.2	91.6%	
500	9	98.2%	26.6	94.2%	26.6	94.3%	

Table 3: Removal Efficiencies for Mixing Time Varied Batch Tests						
15 min	Initial FeCl ₂ :As molar ratio					
Initial As	20X		5X		0X	
50	5	90.0%	2.2	95.6%	1.6	96.8%
30 min	Initial FeCl ₂ :As molar ratio					
Initial As	20X		5X		0X	
50	6.2	87.6%	11.8	76.4%	7.9	84.2%
1 hour	Initial FeCl ₂ :As molar ratio					
Initial As	20X		5X		0X	
50	0.9	98%	5.4	89.2%	12.3	75.4%
2 hour	Initial FeCl ₂ :As molar ratio					
50	6.2	87.6%	2.4	95.2%	10.3	79.4%
6 hour	Initial FeCl ₂ :As molar ratio					
Initial As	20X		5X		0X	
50	7.8	84.4%	6.1	87.8%	12.5	75.0%
Initial As	20X		5X		0X	
50	1.8	96.4%	2.2	95.6%	4.2	91.6%
	20X	5X	0X			
15 min	90	95.6	96.8			
30 min	87.6	76.4	84.2			
1 hour	98	89.2	75.4			
2 hour	87.6	95.2	79.4			
6 hour	84.4	87.8	75			
24 hour	96.4	95.6	91.6			
	20X	5X	0X			
15 min	5	2.2	1.6			
30 min	6.2	11.8	7.9			
1 hour	0.9	5.4	12.3			
2 hour	6.2	2.4	10.3			
6 hour	7.8	6.1	12.5			
24 hour	1.8	2.2	4.2			

APPENDIX C

BATCH TESTS: Effect of Sulfate

Table C-1: Sulfate Interference Raw Data

(used sulfuric acid to adjust pH instead of HCl)

(contact time of 24 hours)

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
500	50	final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	10	7	5.2	9.3	5.3	5.7	5.3
10	25	3.6	5.0	7.1	5.1	4.7	5.0
25	50	13.7	5.2	7.1	5.1	5.1	5.0
50	100	5.1	5.1	13.1	5.1	3.6	4.9
100	200	31	5.1	30.3	5.1	19.3	5.1
200	500	18.1	4.7	12.2	5.0	5.1	5.0
500		91.4	5.0	43.9	4.9	24.8	4.9
controls							
500		1110.1	-	1174	-	887.3	-
50		92.4	-	85.5	-	59.4	-
5		-	-	-	-	-	-
DI blank		-	-	-	-	-	-
system blank		6.6	5.0	7.5	5.0	4.3	5.0

Table C-2: Sulfate Interference Removal Efficiencies

(used sulfuric acid to adjust pH instead of HCl)

(contact time of 24 hours)

pH ≅ 5

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20x		5x		ox	
uncorrected	corrected	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.	removal efficiency
5	7.9	7	11.5%	9.3	0.0%	5.7	27.9%
10	15.8	3.6	77.2%	7.1	55.1%	4.7	70.3%
25	39.6	13.7	65.4%	7.1	82.0%	5.1	67.1%
50	79.1	5.1	93.6%	13.1	83.4%	3.6	95.4%
100	211.4	31	85.3%	30.3	85.7%	19.3	90.9%
200	422.9	18.1	95.7%	12.2	97.1%	5.1	98.8%
500	1057.1	91.4	91.4%	43.9	95.8%	24.8	97.7%

controls							
target value	actual	average					
500		1057.1	1110.1		1174	887.3	-
50		79.1	92.4	•	85.5	59.4	•
5							
DI blank							
system blank			6.6	5.0	7.5	5.0	4.3

APPENDMD

BATCH TESTS: Effect of Using **Arsenite** Instead of Arsenate

Table D-1: Arsenite Removal Study Raw Data

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	5.5	2.5	4.4	2.5	8.4	2.4	
50	11.2	2.4	7.8	2.4	13.2	2.4	
500	86.2	2.4	119	2.4	138	2.4	

Initial As Concentration (ppb) or µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	0.9	5.8	2.7	4.8	0.5	5.0	
50	2.7	5.0	2.4	4.7	5.4	4.8	
500	1.6	4.7	8.3	4.6	104.6	4.7	

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20x		-5x		ox	
		final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	2.1	6.0	1.5	6.2	0.4	6.1	
50	1.5	6.0	5.5	6.2	15.1	6.3	
500	0.8	5.8	48.8	6.2	291.3	6.2	

Initial As Concentration (ppb) or (µg/L)		Initial FeCl ₂ :As molar ratio					
		20X		5x		ox	
		final As conc.	final pH	final As conc.	final pH	final As conc.	final pH
5	9.3	10.6	10	10.6	15.5	10.7	
50	38.6	10.6	43	10.7	49.1	10.6	
500	344.7	10.6	520.5	10.6	503.6	10.6	

Controls

Initial As Concentration (ppb) or (µg/L)	final As conc.
500	523.4
500	526.4
500	527

Table D-2: Arsenite Removal Study Removal Efficiencies

Initial As Concentration (ppb) or ($\mu\text{g/L}$)	Initial FeCl_2 :As molar ratio					
	20X		5x		ox	
	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.	removal efficiency
5	5.5	0%	4.4	12%	8.4	0%
50	11.2	78%	7.8	64%	13.2	74%
500	86.2	83%	119	76%	136	72%

Initial As Concentration (ppb) or ($\mu\text{g/L}$)	Initial FeCl_2 :As molar ratio					
	20X		-5x		bx	
	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.	removal efficiency
5	0.9	82%	2.7	46%	0.5	90%
50	2.7	95%	2.4	95%	5.4	89%
500	1.6	100%	8.3	98%	104.6	79%

Initial As Concentration (ppb) or ($\mu\text{g/L}$)	Initial FeCl_2 :As molar ratio					
	20X		5x		ox	
	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.	removal efficiency
5	2.1	56%	1.5	70%	0.4	92%
50	1.5	97%	5.5	89%	15.1	70%
500	0.8	100%	48.6	90%	291.3	42%

Initial As Concentration (ppb) or ($\mu\text{g/L}$)	Initial FeCl_2 :As molar ratio					
	20X					
	final As conc.	removal efficiency	final As conc.	removal efficiency	final As conc.	removal efficiency
5	9.3	0%	10	0%	15.5	0%
50	36.6	23%	43	14%	49.1	2%
500	344.7	31%	520.5	0%	503.6	0%

APPENDIX E

Freundlich Isotherms for Varied pH

Table E-1: Freundlich Isotherms For Varied pHs

pH=3 Freundlich Isotherm									
	Co (µg/L)	corrected Co (µg/L)	Ce (µg/L)	M (gram)	X=(Co-Ce)V (µg)	exper. X/M (µg/g)	log (X/M)	log (Ce)	linearized X/M (µg/g)
20X	5	5.15	2.9	1	0.0225	0.0225	-1.648	0.462	0.171
	10	10.3	2.5	1	0.078	0.078	-1.108	0.398	0.131
	25	25.75	3.6	1	0.2215	0.2215	-0.655	0.556	0.253
	50	51.5	3.4	1	0.481	0.481	-0.318	0.531	0.228
	100	102.88	6.8	1	0.9608	0.9608	-0.017	0.833	0.802
	200	205.76	7.6	1	1.9816	1.9816	0.297	0.881	0.982
10X	5	5.7	2.2	1	0.035	0.035	-1.456	0.342	0.104
	10	11.4	2.2	1	0.092	0.092	-1.036	0.342	0.104
	25	28.5	3.2	1	0.253	0.253	-0.597	0.505	0.205
	50	57	3.7	1	0.533	0.533	-0.273	0.568	0.266
	100	119.7	5.9	1	1.138	1.138	0.056	0.771	0.620
	200	239.4	8.4	1	2.31	2.31	0.364	0.924	1.177
5X	5	4.81	2.2	1	0.0261	0.0261	-1.583	0.342	0.104
	10	9.62	2.2	1	0.0742	0.0742	-1.130	0.342	0.104
	25	24.05	2.3	1	0.2175	0.2175	-0.663	0.362	0.112
	50	48.1	2.9	1	0.452	0.452	-0.345	0.462	0.171
	100	96.8	4.2	1	0.926	0.926	-0.033	0.623	0.335
	200	193.6	9.3	1	1.843	1.843	0.266	0.968	1.416
2X	5	4.81	2.2	1	0.0261	0.0261	-1.583	0.342	0.104
	10	9.62	2.2	1	0.0742	0.0742	-1.130	0.342	0.104
	25	24.05	2.3	1	0.2175	0.2175	-0.663	0.362	0.112
	50	48.1	2.9	1	0.452	0.452	-0.345	0.462	0.171
	100	96.8	4.2	1	0.926	0.926	-0.033	0.623	0.335
	200	193.6	9.3	1	1.843	1.843	0.266	0.968	1.416
1X	5	5.34	2.2	1	0.0314	0.0314	-1.503	0.342	0.104
	10	10.68	3	1	0.0768	0.0768	-1.115	0.342	0.182
	25	26.7	2.5	1	0.242	0.242	-0.616	0.477	0.131
	50	53.4	3.6	1	0.498	0.498	-0.303	0.398	0.253
	100	106.8	5.6	1	0.9296	0.9296	-0.032	0.556	0.564
	200	213.6	9.9	1	1.8722	1.8722	0.272	0.748	1.586
0X	5	5.89	5.7	1	0.0019	0.0019	-2.721	0.756	0.583
	10	11.78	3.6	1	0.0818	0.0818	-1.087	0.756	0.253
	25	29.45	4.8	1	0.2465	0.2465	-0.608	0.556	0.427
	50	58.9	3.5	1	0.554	0.554	-0.250	0.681	0.241
	100	117.8	7.9	1	1.1198	1.1198	0.049	0.544	1.053
	200	235.6	18.5	1	2.2396	2.2396	0.345	0.696	4.927
500	589.4	30.3	1	5.691	5.691	0.755	1.267	12.054	

constant = -1.605 K = 10^constant = 0.0248 µg/g
slope = 1/n = 1.813 n = 0.5515
linearized X/M = K * Ce^(1/n) r^2 = 0.346616

Table E-1 (cont.): Freundlich Isotherms For Varied pHs

		pH=5 Freundlich Isotherm								
		Co (µg/L)	corrected Co (µg/L)	Ce (µg/L)	M (gram)	X=(Co-Ce)V (µg)	exper. X/M (µg/g)	log (X/M)	log (Ce)	linearized X/M (µg/g)
2 0 X		5	5.78	1.1	1	0.0468	0.0468	-1.330	0.041	0.082
		10	11.56	1.7	1	0.0986	0.0986	-1.006	0.230	0.172
		25	28.9	1.8	1	0.271	0.271	-0.567	0.255	0.189
		50	57.8	1.8	1	0.56	0.56	-0.252	0.255	0.189
		100	115.6	4.5	1	1.111	1.111	0.046	0.653	0.889
		200	231.2	4.2	1	2.27	2.27	0.356	0.623	0.791
		500	578	9	1	5.69	5.69	0.755	0.954	2.867
1 0 X		5	3.4	1.3	1	0.037	0.037	-1.432	0.230	0.172
		10	10.6	1.3	1	0.095	0.095	-1.022	0.114	0.109
		25	27	2.4	1	0.246	0.246	-0.609	0.380	0.307
		50	54	3.6	1	0.504	0.504	-0.298	0.556	0.609
		100	108	5.5	1	1.025	1.025	0.011	0.740	1.247
		200	216	11.7	1	2.043	2.043	0.310	1.068	4.466
		500	540	15.3	1	5.247	5.247	0.720	1.185	7.028
5 0 X		5	3.2	1.3	1	0.039	0.039	-1.409	0.114	0.109
		10	10.4	1.4	1	0.09	0.09	-1.046	0.146	0.124
		25	26	1.9	1	0.241	0.241	-0.618	0.279	0.207
		50	52	2.2	1	0.498	0.498	-0.303	0.342	0.265
		100	109.58	4.9	1	1.0468	1.0468	0.020	0.690	1.026
		200	219.16	12.7	1	2.0646	2.0646	0.315	1.104	5.130
		500	547.9	28.8	1	5.191	5.191	0.715	1.459	20.464
2 5 X		5	4.5	1.5	1	0.03	0.03	-1.523	0.176	0.139
		10	9	1	1	0.08	0.08	-1.097	0.000	0.070
		25	22.5	0.9	1	0.216	0.216	-0.666	-0.046	0.059
		50	45	2.3	1	0.427	0.427	-0.370	0.362	0.286
		100	13.66	3.6	1	1.1026	1.1026	0.042	0.556	0.609
		200	27.76	7.6	1	2.2016	2.2016	0.343	0.881	2.154
		500	569.4	13.4	1	5.56	5.56	0.745	1.127	5.617
5 5 X		5	4.05	1.3	1	0.0365	0.0365	-1.436	0.114	0.109
		10	9.9	3.2	1	0.067	0.067	-1.174	0.114	0.499
		25	24.75	1.5	1	0.0915	0.0915	-0.635	0.505	0.155
		50	49.5	2.9	1	0.466	0.466	-0.332	0.204	0.423
		100	99	5.2	1	0.938	0.938	-0.026	0.462	1.135
		200	198	7.5	1	1.905	1.905	0.260	0.716	2.107
		500	495	12.7	1	4.823	4.823	0.663	0.875	5.130
2 5 X		5	4.61	1.4	1	0.0341	0.0341	-1.467	0.146	0.124
		10	9.62	1.0	1	0.0772	0.0772	-1.112	0.146	0.207
		25	24.05	2.2	1	0.2185	0.2185	-0.661	0.279	0.265
		50	48.1	4.0	1	0.439	0.439	-0.358	0.342	0.791
		100	119.68	5.7	1	1.1398	1.1398	0.057	0.623	1.325
		200	239.36	3.4	1	2.3596	2.3596	0.373	0.756	0.553
		500	598.4	28.6	1	5.698	5.698	0.756	0.531	20.225

constant = -1.155 K = 10^{constant} = 0.0700 µg/g
slope = 1/n = 1.690 n = 0.5918
linearized X/M = K * Ce^(1/n) r² = 0.748006

Table E-1 (cont.): Freundlich Isotherms For Varied pHs

		pH=6 Freundlich Isotherm								
		Co (µg/L)	corrected Co (µg/L)	Ce (µg/L)	M (gram)	X=(Co-Ce)V (µg)	exper. X/M (µg/g)	log (X/M)	log (Ce)	linearized X/M (µg/g)
2 0 X		10	12.68	5.8	1	0.0688	0.0688	-1.162	0.763	0.164
		25	31.7	10.7	1	0.21	0.21	-0.678	1.029	0.291
		50	63.4	13.9	1	0.495	0.495	-0.305	1.143	0.372
		100	127.4	19.1	1	1.083	1.083	0.035	1.281	0.500
		200	254.8	3.4	1	2.514	2.514	0.400	0.531	0.100
	500	637	24.9	1	6.121	6.121	0.787	1.396	0.641	
1 0 X		10	10.56	6	1	0.0456	0.0456	-1.341	0.778	0.170
		25	26.4	5.9	1	0.205	0.205	-0.688	0.771	0.167
		50	52.8	20.6	1	0.322	0.322	-0.492	1.314	0.537
		100	119.3	19.8	1	0.995	0.995	-0.002	1.297	0.517
		200	238.6	31.9	1	2.067	2.067	0.315	1.504	0.808
	500	596.5	104.1	1	4.924	4.924	0.692	2.017	2.437	
5 X		5	7.21	7	1	0.0021	0.0021	-2.678	0.845	0.196
		10	14.42	6.4	1	0.0802	0.0802	-1.096	0.806	0.180
		25	36.05	4.1	1	0.3195	0.3195	-0.496	0.613	0.119
		50	72.1	19.6	1	0.525	0.525	-0.280	1.292	0.512
		100	219.28	11.1	1	2.0818	2.0818	0.318	1.045	0.301
		200	438.56	105.9	1	3.3266	3.3266	0.522	2.025	2.476
	500	1096.4	250.3	1	8.461	8.461	0.927	2.398	5.529	
2 X		25	24.8	6.9	1	0.179	0.179	-0.747	0.839	0.193
		50	49.6	21.9	1	0.277	0.277	-0.558	1.340	0.568
		100	96.76	37.4	1	0.5936	0.5936	-0.227	1.573	0.937
		500	483.8	9.7	1	4.741	4.741	0.676	0.987	0.266
1 X		5	5.33	4.2	1	0.0113	0.0113	-1.947	0.623	0.122
		10	10.66	9.6	1	0.0106	0.0106	-1.975	0.623	0.263
		50	53.3	7.9	1	0.454	0.454	-0.343	0.982	0.219
		100	125.06	29.8	1	0.9526	0.9526	-0.021	0.898	0.758
		200	250.12	43.6	1	2.0652	2.0652	0.315	1.474	1.081
	500	625.3	107.6	1	5.177	5.177	0.714	1.639	2.513	
0 X		25	25	17.8	1	0.072	0.072	-1.143	2.032	0.468
		50	50	15	1	0.35	0.35	-0.456	1.250	0.399
		100	100	68.8	1	0.312	0.312	-0.506	1.176	1.655
		200	200	134	1	0.66	0.66	-0.180	1.838	3.085
	500	500	351	1	1.49	1.49	0.173	2.127	7.582	

constant =	-1.497	K = 10 ^{constant} =	0.0313 µg/g
slope = 1/n =	0.934	n =	1.0709
linearized X/M = K * Ce ^(1/n)		r ² =	0.294909

Table E-1 (cont.): Freundlich Isotherms For Varied pHs

pH=7 Freundlich Isotherm									
	C_0 ($\mu\text{g/L}$)	corrected C_0 ($\mu\text{g/L}$)	C_e ($\mu\text{g/L}$)	M (gram)	$X=(C_0-C_e)V$ (μg)	exper. X/M ($\mu\text{g/g}$)	$\log(X/M)$	$\log(C_e)$	linearized X/M ($\mu\text{g/g}$)
2	25	25.55	15	1	0.1055	0.1055	-0.977	1.176	0.042
0	50	51.1	27.5	1	0.236	0.236	-0.627	1.439	0.125
X	100	102.88	41.5	1	0.6138	0.6138	-0.212	1.618	0.261
	200	205.76	29.8	1	1.7596	1.7596	0.245	1.474	0.144
	500	514.4	111.2	1	4.032	4.032	0.606	2.046	1.536
	5	5.61	5.6	1	0.0001	0.0001	-4.000	0.748	0.007
1	10	11.22	10.7	1	0.0052	0.0052	-2.284	1.029	0.023
0	25	28.05	17.6	1	0.1045	0.1045	-0.981	1.246	0.056
X	50	56.1	29.8	1	0.263	0.263	-0.580	1.474	0.144
	200	227.12	53.9	1	1.7322	1.7322	0.239	1.732	0.418
	500	567.8	72.1	1	4.957	4.957	0.695	1.858	0.705
5	200	443.76	202.2	1	2.4156	2.4156	0.383	2.306	4.499
X	500	1109.4	258.6	1	8.508	8.508	0.930	2.413	7.002
2X	200	240	118.3	1	1.217	1.217	0.085	2.073	1.717
1X	100	100	92.8	1	0.072	0.072	-1.143	1.968	1.110
0	25	22.5	12.1	1	0.104	0.104	-0.983	1.083	0.028
X	500	450	352.3	1	0.977	0.977	-0.010	2.547	12.207
constant =		-3.492		$K = 10^{\text{constant}} =$		0.0003 $\mu\text{g/g}$			
slope = $1/n =$		1.796		$n =$		0.5563			
linearized $X/M = K * C_e^{(1/n)}$ plotted on log-log scale						$r^2 = 0.58596$			

Table E-2: Freundlich Isotherms For Best Results at pH of 5

20X,pH=5 Freundlich Isotherm							
S e t	Co	Ce	M	X=(Co-Ce)V	exper.	log (Ce)	linearized
	(µg/L)	(µg/L)	(gram)	(µg)	X/M , log (X/M)		X/M
1	5.9	1.1	1	0.048	0.048	-1.319	0.124
	11.7	1.7	1	0.1	0.1	-1.000	0.188
	29.3	1.8	1	0.275	0.275	-0.561	0.199
	58.7	1.8	1	0.569	0.569	-0.245	0.199
	114.4	4.5	1	1.099	1.099	0.041	0.481
	228.8	4.2	1	2.246	2.246	0.351	0.450
	571.9	9	1	5.629	5.629	0.750	0.937
	7.5	4.4	1	0.031	0.031	-1.509	0.471
	15	4.9	1	0.101	0.101	-0.996	0.522
	37.5	3	1	0.345	0.345	-0.462	0.325
2	75	4.1	1	0.709	0.709	-0.149	0.440
	109.8	1	1	1.088	1.088	0.037	0.113
	219.6	8.1	1	2.115	2.115	0.325	0.847
	549	24	1	5.25	5.25	0.720	2.411
	7.2	3.8	1	0.034	0.034	-1.469	0.409
	14.3	2.6	1	0.117	0.117	-0.932	0.284
	35.8	1.2	1	0.216	0.216	-0.666	1.454
	71.6	10.9	1	0.607	0.607	-0.217	1.127
	138.1	12.6	1	1.255	1.255	0.099	1.206
	276.3	23.7	1	2.526	2.526	0.402	2.382
3	690.7	11.8	1	6.789	6.789	0.832	1.217

constant =	-0.947	K = 10 ^{constant} =	0.1130 µg/g
slope = 1/n =	0.963	n =	1.0384
linearized X/M = K * Ce ^(1/n)		r ² =	0.29218

Table E-2(cont.): Freundlich Isotherms For Best Results at pH of 5

5X,pH=5 Freundlich Isotherm								
	Co (µg/L)	Ce (µg/L)	M (gram)	X=(Co-Ce)V (µg)	exper. X/M (µg/g)	log (X/M)	log (Ce)	linearized X/M (µg/g)
S e t 1	5.9	1.3	1	0.046	0.046	-1.397	0.114	0.069
	11.7	1.4	1	0.103	0.103	-0.987	0.146	0.074
	29.3	1.9	1	0.274	0.274	-0.562	0.279	0.100
	58.7	2.2	1	0.565	0.565	-0.249	0.342	0.116
	114.4	4.9	1	1.095	1.095	0.039	0.690	0.255
	226.6	12.7	1	2.161	2.161	-0.335	1.104	0.651
	571.9	26.0	1	5.431	5.431	0.735	1.459	1.460
S e t 2	7.5	6.2	1	0.013	0.013	-1.886	0.792	0.321
	15	1.5	1	0.135	0.135	-0.870	0.176	0.079
	37.5	3	1	0.345	0.345	-0.462	0.477	0.157
	75	12.4	1	0.626	0.626	-0.203	1.093	0.636
	109.8	22.0	1	0.868	0.868	-0.061	1.362	1.170
	219.6	57.9	1	1.718	1.718	0.235	1.679	2.405
S e t 3	549	5.4	1	4.92	4.92	0.692	1.756	2.861
	7.2		1	0.016	0.016	-1.745	0.732	0.280
	14.3	6.7	1	0.076	0.076	-1.119	0.826	0.347
	35.6	10.6	1	0.252	0.252	-0.599	1.025	0.545
	71.6	12.7	1	0.589	0.589	-0.230	1.104	0.651
	136.1	29.2	1	1.089	1.089	0.037	1.465	1.480
	276.3	38.8	1	2.375	2.375	0.376	1.589	1.958
690.7	58.8	1	6.319	6.319	0.801	1.769	2.950	
constant = -1.274 k=10^constant= 0.0532 µg/g slope = 1/n = 0.986 n= 1.0147 linearized X/m = 0.0853 Ce^(1.320) r ² = 0.498796								

Table E-2(cont.): Freundlich Isotherms For Best Results at pH of 5

0X,pH=5 Freundlich Isotherm								
	Co (µg/L)	Ce (µg/L)	M (gram)	X=(Co-Ce)V (µg)	exper. X/M (µg/g)	log (X/M)	log (Ce)	linearized W M (µg/g)
s e t 1	5.9	1.4	1	0.045	0.045	-1.347	0.146	0.126
	11.7	1.9	1	0.098	0.098	-1.009	0.279	0.160
	29.3	2.2	1	0.271	0.271	-0.567	0.342	0.180
	58.7	4.2	1	0.545	0.545	-0.264	0.623	0.298
	114.4	5.7	1	1.087	1.087	0.036	0.756	0.379
	228.8	3.4	1	2.254	2.254	0.353	0.531	0.253
	671.9	28.6	1	5.493	5.493	0.735	1.456	1.344
s e t 2	15	2	1	0.13	0.13	-0.886	0.301	0.167
	37.5	11.4	1	0.261	0.261	-0.589	1.057	0.653
	75	16.3	1	0.587	0.587	-0.231	1.212	0.865
	109.8	27.7	1	0.821	0.821	-0.086	1.442	1.311
	219.6	22.9	1	1.967	1.967	0.294	1.360	1.129
	549	112.7	1	4.363	4.363	0.640	2.052	3.943
	7.2	6.3	1	0.009	0.009	2.046	0.799	0.410
s e t 3	-14.3	6.3	1	0.08	0.08	-1.097	0.799	0.410
	35.8	4.8	1	0.31	0.31	-0.509	0.681	0.331
	71.6	10	1	0.616	0.616	-0.210	1.000	0.589
	138.1	29.5	1	1.086	1.086	0.036	1.470	1.377
	276.3	2.5	1	2.738	2.738	0.437	0.398	0.199
	690.7	119.9	1	5.708	5.708	0.756	2.079	4.139
constant = -1.01436 k=10^constant= 0.097 µg/g slope = 1/n = 0.785 n= 1.2744 linearized x/m = 0.0692 Ce^(1.465) r ² = 0.360184								

APPENDIX F

Langmuir Isotherms for Varied pH

Table F-1: Langmuir Isotherms for Varied pHs

		pH=3 Langmuir Isotherm							
		Co ($\mu\text{g/L}$)	corrected Co ($\mu\text{g/L}$)	Ce ($\mu\text{g/L}$)	M (gram)	X=(Co-Ce)V (μg)	exper. M/X (gram/ μg)	1/Ce (L/ μg)	linearized M/X
2 0 X	5	5.15	2.9	1	0.0225	44.444	0.345	11.804	
	10	10.3	2.5	1	0.079	12.821	0.400	14.654	
	25	25.75	3.6	1	0.2215	4.515	0.278	8.340	
	50	51.5	3.4	1	0.421	2.079	0.294	9.184	
	100	102.88	6.8	1	0.9608	1.041	0.147	1.588	
	200	205.76	7.6	1	1.0816	0.505	0.132	0.788	
	500	514.4	14.8	1	4.996	0.200	0.068	-2.519	
1 0 X	5	5.7	2.2	1	0.035	28.571	0.455	17.472	
	10	11.4	2.2	1	0.092	10.870	0.455	17.472	
	25	28.5	3.2	1	0.253	3.953	0.313	10.134	
	50	57	3.7	1	0.533	1.876	0.270	7.953	
	100	119.7	5.9	1	1.138	0.879	0.189	2.747	
	200	239.4	8.4	1	2.31	0.433	0.119	0.141	
5 X	5	4.81	2.2	1	0.0261	38.314	0.455	17.472	
	10	9.62	2.2	1	0.0742	13.477	0.455	17.472	
	25	24.05	2.3	1	0.2175	4.598	0.435	16.451	
	50	48.1	2.3	1	0.435	2.299	0.345	11.804	
	100	96.0	4.2	1	0.926	1.080	0.238	6.290	
	200	193.6	9.3	1	1.843	0.543	0.108	-0.454	
	500	484	3.3	1	4.807	0.208	0.303	9.645	
2 X	25	25.75	3.8	1	0.2195	4.556	0.263	7.585	
	50	51.5	4.5	1	0.47	2.128	0.222	5.470	
	100	104.32	7	1	0.9732	1.028	0.143	1.371	
	200	208.64	7.5	1	2.0114	0.497	0.133	0.879	
	500	521.6	15.9	1	5.057	0.198	0.063	-2.760	
1 X	5	5.34	2.2	1	0.0314	31.847	0.455	17.472	
	10	10.68	3	1	0.0768	13.021	0.333	11.210	
	25	26.7	2.5	1	0.242	4.132	0.400	14.654	
	50	53.4	3.6	1	0.498	2.008	0.278	8.340	
	100	98.56	5.6	1	0.9296	1.076	0.179	3.216	
	200	197.12	9.9	1	1.8722	0.534	0.101	-0.791	
0 X	500	492.8	21.3	1	4.715	0.212	0.047	-3.584	
	10	11.78	3.6	1	0.0818	12.225	0.278	8.340	
	25	29.45	4.8	1	0.2465	4.057	0.208	4.753	
	50	58.9	3.5	1	0.554	1.805	0.286	8.750	
	100	119.88	7.9	1	1.1198	0.893	0.127	0.530	
	200	239.76	18.5	1	2.2126	0.452	0.054	-3.217	
500	599.4	30.3	1	5.891	0.176	0.033	-4.304		
intercept =					-6.009		Xm=1/intercept=		-0.166 g/ μg
slope =					51.658		k=1/(Xm*slope)=		-0.116
linearized M/X=intercept+1/(Xm*k)*1/Ce							r ² =		0.405902

Table F-1 (cont.): Langmuir Isotherms for Varied pHs

pH=5 Langmuir Isotherm								
	Co ug/L	corrected Co (µg/L)	Ce ug/L	M gram	X=(Co-Ce)V ug	exper. M/X gram/ug	1/Ce L/ug	linearized M/X
2 0 X	5	5.78	1.1	1	0.0468	21.368	0.909	17.821
	10	11.56	1.7	1	0.0986	10.142	0.588	10.804
	25	28.9	1.8	1	0.271	3.690	0.556	10.089
	50	57.8	1.8	1	0.56	1.786	0.556	10.089
	100	115.6	4.5	1	1.111	0.900	0.222	2.799
	200	231.2	4.2	1	2.27	0.441	0.238	3.146
1 0 X	5	5.4	1.7	1	0.037	27.027	0.588	10.804
	10	10.8	1.3	1	0.095	10.526	0.769	14.762
	25	27	2.4	1	0.246	4.065	0.417	7.052
	50	54	3.6	1	0.504	1.984	0.278	4.014
	100	108	5.5	1	1.025	0.976	0.182	1.915
	200	216	11.7	1	2.043	0.489	0.085	-0.192
5 X	5	5.2	1.3	1	0.039	25.641	0.769	14.762
	10	10.4	1.4	1	0.09	11.111	0.714	13.561
	25	26	1.9	1	0.241	4.149	0.526	9.450
	50	52	2.2	1	0.498	2.008	0.455	7.880
	100	109.58	4.9	1	1.0468	0.955	0.204	2.402
	200	219.16	12.7	1	2.0646	0.484	0.079	-0.339
2 X	5	4.5	1.5	1	0.03	33.333	0.667	12.519
	10	9	1	1	0.08	12.500	1.000	19.809
	25	22.5	0.9	1	0.216	4.630	1.111	22.239
	50	45	2.3	1	0.427	2.342	0.435	7.448
	100	113.88	3.6	1	1.1028	0.907	0.278	4.014
	200	227.76	7.6	1	2.2016	0.454	0.132	0.817
1 X	5	4.95	1.3	1	0.0365	27.397	0.769	14.762
	10	9.9	3.2	1	0.067	14.925	0.313	4.773
	25	24.75	1.6	1	0.2315	4.320	0.625	11.608
	50	49.5	2.9	1	0.466	2.146	0.345	5.480
	100	99	5.2	1	0.938	1.066	0.192	2.145
	200	198	7.5	1	1.905	0.525	0.133	0.855
0 X	5	4.81	1.4	1	0.0341	29.326	0.714	13.561
	10	9.62	1.9	1	0.0772	12.953	0.526	9.450
	25	24.05	2.2	1	0.2185	4.577	0.455	7.880
	50	48.1	4.2	1	0.439	2.278	0.238	3.146
	100	119.00	3.7	1	1.1390	0.877	0.175	1.770
	200	239.36	3.4	1	2.3596	0.424	0.294	4.371
500	596.4	20.0	1	5.964	0.176	0.035	-1.296	
intercept =		-2.051		Xm=1/intercept=		-0.435 g/ug		
slope =		21.971		k=1/(Xm*slope)=		-0.094		
linearized M/X=intercept+1/(Xm*k)*1/Ce						r ² = 0.435293		

Table F-1 (cont.): Langmuir Isotherms for Varied pHs

pH=6 Langmuir Isotherm								
	Co ug/L	corrected Co (ug/L)	Ce ug/L	M gram	X=(Co-Ce)V ug	exper. M/X gram/ug	1/Ce L/ug	linearized M/X
2 0 X	10	10.56	6.4	1	0.0688	14.535	0.172	6.236
	25	31.7	10.7	1	0.21	4.762	0.093	3.989
	50	63.4	13.9	1	0.495	2.020	0.072	3.377
	100	127.4	19.1	1	1.083	0.923	0.052	2.820
	200	254.6	3.4	1	2.514	0.398	0.294	9.699
	500	637	24.9	1	6.121	0.163	0.040	2.473
1 0 X	10	10.56	6	1	0.0456	21.930	0.167	6.073
	25	26.4	5.9	1	0.205	4.878	0.169	6.153
	50	52.8	20.6	1	0.322	3.106	0.049	2.711
	100	119.3	19.8	1	0.995	1.005	0.051	2.767
	200	238.6	31.9	1	2.067	0.484	0.031	2.222
	500	596.5	104.1	1	4.924	0.203	0.010	1.603
5 X	10	14.2	6.4	1	0.0802	12.469	0.156	5.776
	25	36.05	4.1	1	0.3195	3.130	0.244	8.270
	50	72.1	19.6	1	0.525	1.905	0.051	2.782
	100	219.28	11.1	1	2.0818	0.460	0.090	3.893
	200	438.56	105.9	1	3.3266	0.301	0.009	1.599
	500	1090.4	200.0	1	8.401	0.110	0.004	1.444
2 X	25	24.8	6.9	1	0.179	5.587	0.145	5.454
	50	49.6	21.9	1	0.277	3.610	0.046	2.629
	100	96.76	37.4	1	0.5936	1.685	0.027	2.091
	500	483.8	9.7	1	4.741	0.211	0.103	4.263
1 X	50	53.3	7.9	1	0.454	2.203	0.127	4.932
	100	125.06	29.8	1	0.9526	1.050	0.034	2.285
	200	250.12	43.6	1	2.0652	0.484	0.023	1.983
	500	625.3	107.6	1	5.177	0.193	0.009	1.594
0 X	25	25	17.8	1	0.072	13.889	0.056	2.928
	50	50	15	1	0.35	2.857	0.067	3.227
	100	100	68.8	1	0.312	3.205	0.015	1.743
	200	200	134	1	0.66	1.515	0.007	1.542
	500		351	1	1.49	0.671	0.003	1.411
intercept =		1.330		Km=1/intercept=		0.752 g/ug		
slope =		26.456		k=1/(Xm*slope)=		0.047		
linearized M/X=intercept+1/(Xm*k)*1/Ce					r ² = 0.09984			

Table F-1 (cont.): Langmuir Isotherms for Varied pHs

pH=7 Langmuir Isotherm								
	Co ug/L	corrected CO (ug/L)	Ce ug/L	M gram	X=(Co-Ce)V ug	exper. M/X gram/ug	1/Ce L/ug	linearized M/X
2 0 X	25	25.55	15	1	0.1055	9.479	0.067	8.240
	50	51.1	27.5	1	0.236	4.237	0.036	4.801
	100	102.88	41.5	1	0.6138	1.629	0.024	3.409
	200	205.76	29.8	1	1.7596	0.568	0.034	4.483
	500	514.4	111.2	1	4.032	0.248	0.009	1.695
1 0 X	25	28.05	17.6	1	0.1045	9.569	0.057	7.123
	50	56.1	29.8	1	0.263	3.802	0.034	4.483
	200	227.12	53.9	1	1.7322	0.577	0.019	2.780
	500	567.8	72.1	1	4.957	0.202	0.014	2.249
5 X	200	443.76	202.2	1	2.4156	0.414	0.005	1.236
	500	1109.4	258.6	1	8.508	0.118	0.004	1.113
2X	200	240	118.3	1	1.217	0.822	0.008	1.634
1X	100	100	92.8	1	0.072	13.889	0.011	1.897
0 X	25	22.5	12.1	1	0.104	9.615	0.083	10.054
	500	450	352.3	1	0.977	1.024	0.003	0.997
intercept =		1		Xm=1/intercept=		1.483 g/ug		
slope =		113		k=1/(Xm*slope)=		0.006		
linearized		M/X=intercept+1/(Xm*k)*1/Ce		r ² =		0.373317		

Table F-2: Langmuir Isotherms For Best Results at pH of 5

		20X, pH=5 Langmuir Isotherm							
		co	corrected	Ce	M	X=(Co-Ce)V	exper.	1/Ce	linearized
		ug/L	co (ug/L)	ug/L	gram	ug	M/X gram/ug	L/ug	M/X
s e t 1	5	5.9	1.1	1	0.048	20.833	0.909	10.908	
	10	11.7	1.7	1	0.1	10.000	0.588	8.444	
	25	29.3	1.0	1	0.275	3.636	0.556	8.193	
	50	56.7	1.6	1	0.569	1.757	0.556	8.193	
	100	114.4	4.5	1	1.099	0.910	0.222	5.634	
	200	226.6	4.2	1	2.246	0.445	0.238	5.756	
	300	371.9	9	1	5.629	0.178	0.111	4.781	
s e t 2	5	7.5	4.4	1	0.031	32.258	0.227	5.673	
	10	15	4.9	1	0.101	9.901	0.204	5.495	
	25	37.5	3	1	0.345	2.899	0.333	6.487	
	50	75	4.1	1	0.709	1.410	0.244	5.800	
	100	109.8	1	1	1.066	0.919	1.000	11.606	
	200	219.6	8.1	1	2.115	0.473	0.123	4.875	
	500	549	24	1	5.25	0.190	0.042	4.247	
s e t 3	5	7.2	3.8	1	0.034	29.412	0.263	5.948	
	10	14.3	2.6	1	0.117	8.547	0.385	6.881	
	25	35.8	14.2	1	0.216	4.630	0.070	4.468	
	50	71.6	10.9	1	0.607	1.647	0.092	4.632	
	100	138.1	12.6	1	1.255	0.797	0.079	4.537	
	200	276.3	23.7	1	2.526	0.396	0.042	4.252	
	500	690.7	11.6	1	6.789	0.147	0.085	4.578	
intercept =		3.928			Xm=1/intercept=		0.255 g/ug		
slope =		7.676			k=1/(Xm*slope)=		0.512		
linearized		M/X=intercept+1/(Xm*k)*1/Ce					r ² = 0.048079		

Table F-2(cont.): Langmuir Isotherms For Best Results at pH of 5

10X,pH=5 Langmuir Isotherm								
		Co ug/L	Ce ug/L	M gram	X=(Co-Ce)V ug	exper. M/X gram/ug	1/Ce L/ug	linearized M/X
s e t 1	5	5.9	1.3	1	0.046	21.739	0.769	11.907
	10	11.7	1.4	1	0.103	9.709	0.714	11.085
	25	29.3	1.9	1	0.274	3.650	0.526	8.273
	50	58.7	2.2	1	0.565	1.770	0.455	7.200
	100	114.4	4.9	1	1.095	0.913	0.204	3.453
	200	228.8	12.7	1	2.161	0.463	0.079	1.579
s e t 2	500	571.9	28.8	1	5.431	0.184	0.035	0.920
	10	15	1.5	1	0.135	7.407	0.667	10.372
	25	37.5	3	1	0.345	2.899	0.333	5.387
	50	75	12.4	1	0.626	1.597	0.081	1.607
	100	109.8	23	1	0.868	1.152	0.043	1.051
	200	219.6	47.8	1	1.718	0.582	0.021	0.714
s e t 3	500	549	57	1	4.92	0.203	0.018	0.663
	10	14.3	6.7	1	0.076	13.158	0.149	2.633
	25	35.8	10.6	1	0.252	3.968	0.094	1.812
	50	71.6	12.7	1	0.589	1.698	0.079	1.579
	100	138.1	29.2	1	1.089	0.918	0.034	0.913
	200	276.3	38.8	1	2.375	0.421	0.026	0.786
	500	690.7	58.8	1	6.319	0.158	0.017	0.655
intercept =		0.401		Xm=1/intercept=		2.494 g/ug		
slope =		14.957		k=1/(Xm*slope)=		0.027		
linearized M/X=intercept+1/(Xm*k)*1/Ce						r² = 0.49117		

Table F-2(cont.): Langmuir Isotherms For Best Results at pH of 5

OX,pH=5 Langmuir Isotherm								
		Co ug/L	Ce ug/L	M gram	X=(Co-Ce)V ug	exper. M/X gram/ug	1/Ce L/ug	linearized M/X
s e t 1	5	5.9	1.4	1	0.045	22.222	0.714	13.415
	10	11.7	1.9	1	0.098	10.204	0.526	9.821
	25	29.3	2.2	1	0.271	3.690	0.455	8.448
	50	58.7	4.2	1	0.545	1.835	0.238	4.310
	100	114.4	5.7	1	1.087	0.920	0.175	3.112
	200	228.8	3.4	1	2.254	0.444	0.294	5.381
	500	571.9	28.6	1	5.433	0.184	0.035	0.426
s e t 2	10	15	2	1	0.13	7.692	0.500	9.318
	25	37.5	11.4	1	0.261	3.831	0.088	1.435
	50	75	16.3	1	0.587	1.704	0.061	0.930
	100	109.8	27.7	1	0.821	1.218	0.036	0.448
	200	219.6	22.9	1	1.967	0.508	0.044	0.592
	500	549	112.7	1	4.363	0.229	0.009	-0.073
s e t 3	10	14.3	6.3	1	0.08	12.500	0.159	2.792
	25	35.8	4.8	1	0.31	3.226	0.208	3.741
	50	71.6	10	1	0.616	1.623	0.100	1.669
	100	138.1	29.5	1	1.086	0.921	0.034	0.406
	200	276.3	2.5	1	2.738	0.365	0.400	7.405
	500	690.7	119.9	1	5.708	0.175	0.008	-0.083
intercept =		-0.243		Xm=1/intercept=		-4.122 g/ug		
slope =		19.120		k=1/(Xm*slope)=		-0.013		
linearized M/X=intercept+1/(Xm*k)*1/Ce						r ² = 0.500845		

APPENDMG

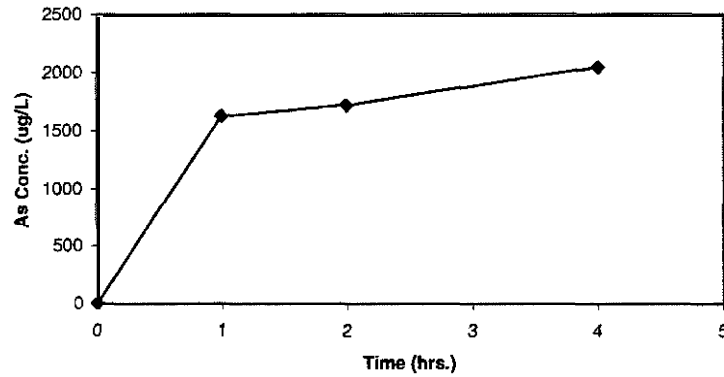
COLUMN TESTS

Chart 1

column 1

influent conc = 2091.4 µg/L

run time of column (hours)	arsenic concentration (µg/L)
0	0.8
1	1626.3
1 7 2.1	9
4	2048.2



area ft2	0.016695
Q gal/min	0.004139
FR	0.247929

column 2

influent conc = 109.3 µg/L

run time of column (hours)	arsenic concentration (µg/L)
0	5
1	40
2	39.1
4	57.6
19	122.6
24	61.9
43	74.9
51	89.2
67	50.8
71	67
75	67
91	83.2

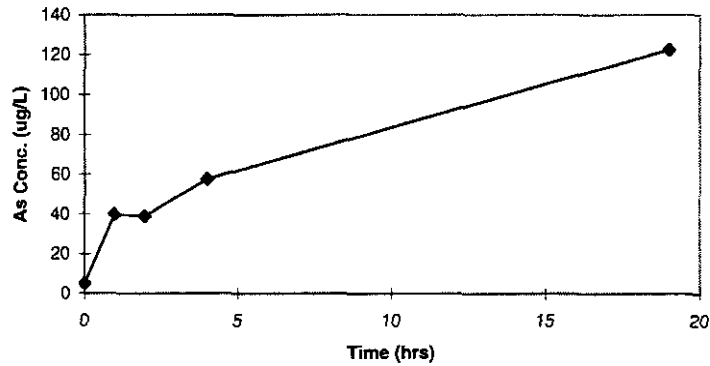
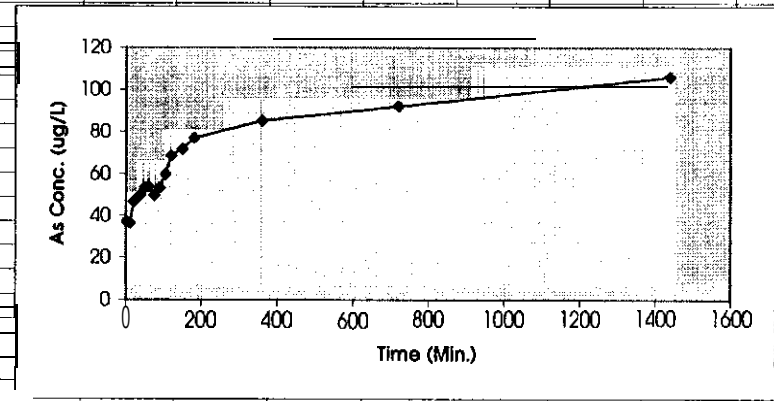


Chart 2: column 3						
Arsenic Standards (µg/L)	Absorbance Readings			Average Absorbance	Arsenic Concentration (µg/L)	Influent pH was 5.1 to 5.4 Effluent pH ranged from 6.42 to 6.57
	#1	#2	#3			
10	0.008	0.005	0.007	0.0065	7	
25	0.022	0.018	0.020	0.02	24	
50	0.051	0.043	0.045	0.047	58	vol (ml) 30280 moles/L moles/mole
100	0.075	0.077	0.078	0.076	95	conc As(mg/L) 0.1 0.000814 32.34813 As:Fe conc Fe(mg/L) 0.005 2.51E-05
arsenic conc. =				1268.0 x	absorbanc	-1.1402
Run Time of column (minutes)	Absorbance Readings			Average Absorbance	Arsenic Concentration (µg/L)	
	#1	#2	#3			
0	0.031	0.029	0.029	0.03	37	
10	0.03	0.029	0.029	0.0295	36	
20	0.04	0.035	0.037	0.0375	46	
30	0.041	0.037	0.039	0.039	48	
40	0.041	0.04	0.041	0.0405	50	
50	0.044	0.042	0.043	0.043	53	
60	0.045	0.042	0.041	0.0435	54	
75	0.04	0.04	0.041	0.04	50	
90	0.046	0.04	0.043	0.043	53	
105	0.047	0.049	0.049	0.048	60	
120	0.056	0.054	0.055	0.055	69	
150	0.059	0.056	0.058	0.0575	72	
180	0.061	0.062	0.06	0.0615	77	
360	0.069	0.067	0.067	0.068	85	
720	0.071	0.076	0.074	0.0735	92	
1440	0.084	0.085	0.106	0.0845	106	



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Column 4			pH Influent	5.23-5.46
			pH effluent	7-Jun
Time (min)	Concentration ug/L As	(hours)		
0	4.8	0		
10	6.4			
20	6.4			
30	7.2	0.5		
40	7.9			
50	8.5			
60	9.2	1		
75	10.2			
90	11.1	1.5		
150	11.9			
180	13.5	3		
240	17.2	4		
380	22.4	6		
720	31.7	12		
1440	39.5	24		

vol (ml)	37850	moles/L	moles/mole
conc As(mg/L)	0.1	0.000814	As:Fe
conc Fe(mg/L)	none		

Column 5			Influent pH was	5-5.2
			Effluent pH ranged from	5.1-5.3
Time (min)	Concentration ug/L As	(hours)		
0	19.8	0		
10	13.5			
20	11.2			
30	10.1	0.5		
40	9.6			
50	9.5			
60	9	1		
75	8.8			
90	8.4	1.5		
105	8.2			
120	7.9	2		
150	7.6			
180	7.9	3		
360	7.1	6		
720	7.5	12		

vol (ml)	37850	moles/L	moles/mole
conc As(mg/L)	0.1	0.000814	32.34813 As:Fe
conc Fe(mg/L)	0.005	2.51E-05	

Column 7			Influent pH was	5.5
			Effluent pH was	6
Time (min)	Concentration ug/L As	(hours)		
0	3.8	0		
30	2.6	0.5		
60	2.6	1		
90	2.5	1.5		
120	2.5	2		
150	2.5			
180	2.4	3		
360	2.7	6		
610	6.3	13.5		
1380	7.8	23		
1830	9.9	30.5		

vol (ml)	26495	moles/L	moles/mole
conc As(mg/L)	0.1	0.000814	32.46454 As:Fe
conc Fe(mg/L)	0.004982	2.51E-05	

2 gpm/ft2

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APPENDIXH

ARSENIC REMOVAL TECHNOLOGIES PAPER

Bates, J., A. Hanson, F. Cadena, B. Thomson, A. Bristol, Technologies
for the Removal of Arsenic From Drinking Water in New Mexico,
New Mexico Science Journal, 1998

Technologies for the Removal of Arsenic From Drinking Water in New Mexico

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Abstract

The U.S. EPA is proposing changes to the Safe Drinking Water Act (SDWA) which will drastically reduce the level of arsenic allowed in public water supplies. This regulatory change may have a dramatic impact on the arid southwestern states. Unfortunately, there are very few low tech, inexpensive ways to remove this contaminant. The traditional treatment technologies are reverse osmosis, and coagulation/flocculation. Both of these are expensive, one because of the technology, the other because of the large volume of tankage involved. Ion exchange is a fully developed alternative technology which is well understood. Unfortunately, the high sulfate waters in New Mexico reduce the usefulness of ion exchange. Innovative technologies which are being considered include membrane processes and specialty filters. Membrane processes, including; nanofiltration, ultrafiltration, and microfiltration with a coagulant. Activated alumina filters and oxidizing filters are both being proposed as appropriate technologies for smaller communities, but neither technology is fully developed.

Problem Identification:

How wide spread is the problem? Arsenic (As) concentrations in groundwater and surface waters can vary widely, with the most elevated concentrations on the order of tens of mg/L, while average concentrations are in the range of 2 to 5 g/L (Herring and Chiu, 1998). Based on a number of recent surveys EPA (Reid, 1994) estimates the following relationship between Maximum Contaminant Level (MCL) set and the number of systems affected in the United States:

MCL Adopted (g/L)	Number of systems impacted nationally (69,491 total)	% of systems impacted
20	745	1%
5	4,921	1%
2	12,440	18%

New Mexico is likely to be disproportionately impacted by a new arsenic standard for two reasons: 1) over 90% of the states potable water sources are groundwater, and 2) the state has

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experienced extensive volcanic activity which is often associated with high concentrations of As in the

surrounding groundwater formations it. The Environment Department provides the following statistics for the State of New Mexico.

MCL Adopted ($\mu\text{g/L}$)	Number of systems
20	4.4 %
10	15.3 %
2	50.8 %

It is apparent that New Mexico, and most certainly the other arid southwestern states, bear a disproportionate burden in attempting to comply with the proposed arsenic regulation.

Arsenic has been recognized as a poison for nearly 4,000 years. The lethal effects are well documented, but the toxicity of As to humans at very low dosages is still not well understood. Some issues to be resolved include: micro nutrient value of arsenic & threshold effect, and the human body's ability to metabolize arsenic. EPA has concluded that arsenic is carcinogenic, and therefore the desirable maximum contaminant level (MCL) is zero. However, the analytical means to measure arsenic at low levels is not available. Under this scenario EPA sets the limit MCL at the practical quantitative limit (PQL), and then has the option of lowering the MCL as quantitative methods improve. This lowering arsenic limits is not a local phenomenon, the Canadian government recently decreased the maximum acceptable concentration (MAC) in Canada to 25 $\mu\text{g/L}$. EPA is currently considering MCLs in the range of 2 to 20 $\mu\text{g/L}$ arsenic. EPA has recently initiated a major study of the toxicology of As that is scheduled to be completed in 2002. This information is to be used in developing the new MCL. Again, in addition to the toxicity study, the MCL will be based on the PQL criteria. As quantitative methods improve the MCL will probably become more restrictive. EPA sets limits based on a health risk criteria, and these risk based limits are then modified by other considerations, such as ability to measure (PQL) and ability to treat (BAT). In the case of arsenic, the contaminant level associated with an acceptable risk level is lower than the proposed MCL, thus as the PQL becomes more sensitive we can expect to see the MCL become more restrictive.

Another concern is the high cost of and uncertain performance of As treatment technologies. A large fraction of the communities which would be affected by a new, more stringent MCL, are very small systems. Furthermore, many of these systems rely upon groundwater and therefore do not provide any water treatment at present. Implementation of a more stringent MCL would require these water utilities to implement treatment, which would likely be quite costly. Accordingly, the financial impact of the new standard will be greatest on a per capita basis in small communities. The individual households in smaller communities will bear a much higher cost per household than the households in larger communities. The City of Albuquerque, NM

has estimated that a MCL of 5 $\mu\text{g/L}$ will cost \$200 million in capital investment and \$10 million/year in operating costs. The State NMED estimated the State wide cost of compliance to be \$187 million. Regardless of which estimate is more accurate, it is clear that there will be a large cost associated with regulatory compliance. The citizens in the small communities are also the citizens who can least afford the cost of protection.

Summary of the Solution Chemistry of Arsenic

The chemistry of As is complicated because it may occur in four stable oxidation states depending on the environmental conditions, each of which may participate in acid-base reactions. Examples of species associated with different environmental conditions are summarized in Table 1.

Table 1. Summary of the principal arsenic species found in the environment, and the general environmental conditions under which they are stable.

Environmental Conditions	Name	Principal As Species
Oxidizing Conditions	Arsenates	$\text{H}_3\text{AsO}_4, \text{H}_2\text{AsO}_4^-, \text{HAsO}_4^{2-}, \text{AsO}_4^{3-}$
	Arsenites	$\text{H}_3\text{AsO}_3, \text{H}_2\text{AsO}_3^-$
Reducing Conditions	Elemental Arsenic	As(s)
	Common Arsenic Minerals	$\text{As}_2\text{O}_3(\text{s})$ - Arsenolite $\text{AsS}(\text{s})$ - Realgar $\text{As}_2\text{S}_3(\text{s})$ - Orpiment $\text{FeAsS}(\text{s})$ - Arsenopyrite
Methanogenic Conditions	Methylated As Compounds	$\text{CH}_3\text{AsO}(\text{OH})_2$ - Methylarsonic Acid $(\text{CH}_3)_2\text{AsO}(\text{OH})$ - Dimethylarsinic Acid
	Arsines	$\text{H}_3\text{As}, \text{H}_2\text{As}(\text{CH}_3), \text{HAs}(\text{CH}_3)_2, \text{As}(\text{CH}_3)_3$

In water, As is almost always present in either the arsenate form (As(V)) or the arsenite form (As(III)) (NOTE: The Roman Numeral in parentheses indicates the oxidation state of the compound). Both classes of compounds are very soluble. It is frequently assumed that As(III) predominates in ground water as subsurface environments are generally more reducing, however,

surveys by Edwards et al. (1997) and results of Clifford et al. (1998) show that As(V) often is the dominant species in ground water supplies.

It is important to understand the difference in solution chemistry of As(V) and As(III) species as this greatly affects water and wastewater treatment options. In near neutral pH solution, As(V) is present as H_2AsO_4^- and HAsO_4^{2-} , whereas As(III) is present as uncharged H_3AsO_3 . This difference has enormous significance as many treatment processes are able to achieve selective removal of ionic constituents, while removal of non-ionized compounds is almost always difficult. Treatment processes which are effective for As(V) but not As(III) include ion exchange, adsorption onto activated alumina or ferric hydroxide, precipitation processes, and membrane filtration.

In considering the behavior of As in solution it is also important to recognize that the As(V) molecule is similar to that of sulfate (SO_4^{2-}) in that both are anionic molecules dominated by the presence of four O atoms. This similarity carries over to their solution chemistry where both are very soluble anions. Thus, many treatment processes which remove As(V) are affected by high sulfate concentrations. The situation is further complicated by the fact that treatment processes are expected to treat As(V) at concentrations of 10^{-6} moles/L (75 $\mu\text{g/L}$) or lower in a solution containing sulfate at 10^{-3} moles/L (96 mg/L) or greater. Therefore, the treatment process must either be very selective for As(V), or it must be expected to remove large mass of sulfate in order to remove a small mass of As.

Potential Solutions

The following paragraphs will discuss the current status of the treatment technologies available for the removal of arsenic from drinking water. Particular emphasis will be placed on issues of importance in New Mexico.

Membrane technologies

Membrane technologies represent a variety of options for treating water including: microfiltration (MF), ultrafiltration(UF), nanofiltrations(NF), and hyperfiltration or reverse osmosis (RO). These processes represent four overlapping categories of increasing selectivity related to decreasing membrane pore size. Brandhuber and Amy (1998) report on a large number of studies which indicate that membrane processes are suitable for the removal of arsenic from water. Membranes can selectively exclude As from passing through them by two mechanisms: 1) exclusion based on size, and 2) exclusion based on electrostatic repulsion of the As ion. Brandhuber and Amy (1998) note that this is most fortuitous since most UF and NF membranes are negatively charged, and arsenic in natural waters tends to be in the anionic arsenate form.

Brandhuber and Amy (1998) showed, at a laboratory scale, RO and NF would remove 95 to 99 percent of all As(V) present in the water. Unfortunately, only 20 to 90 percent of the As(III) was removed depending on the pore size of the membrane. Energy costs can be reduced and production can be increased if an NF membrane is selected and pre-oxidation is performed to insure that As(V) is being treated. One danger associated with pre-oxidation, is that many of the membranes are sensitive to strong oxidants. It is important to either tightly control oxidant

dosage, or select an oxidant tolerant membrane. The UF membranes tested were unable to achieve necessary arsenic removal.

Ghurye, Clifford, and Tong (1998) are involved in a study evaluating the use of iron coagulation coupled with MF for the removal of arsenic from Albuquerque, NM groundwater. The City of Albuquerque has 92 drinking water wells, with arsenic concentrations ranging from 0.3 to 45.9 $\mu\text{g/L}$. The MCL eventually selected by EPA will have a large impact on treatment costs; if a MCL of 25 $\mu\text{g/L}$ is selected, 13 wells will be in violation; if a MCL of 2 $\mu\text{g/L}$ is selected, 72 wells will be in violation. Because of the geographically dispersed nature of the water system in Albuquerque, iron coagulation in conjunction with a Memcor Self Cleaning Continuous Microfiltration system appeared potentially attractive, since the system is compact and fully automated. The field scale testing demonstrated a number of things:

- 1) the system is not sensitive to sulfate concentrations (71 and 177 mg/L)
- 2) elevated silica levels are detrimental to the process
- 3) with the ferric salt a minimum mixing contact time of 17 seconds is required prior to filtration or the filter fouled 2-3 minutes into the filtration cycle
- 4) As adsorption is nearly completed within 10 seconds and is complete by 50 seconds.
- 5) a mixing intensity (G) of 144 sec^{-1} is adequate
- 6) membrane pore opening is important; 0.22 μm pore opening works well
- 7) increasing backwash interval from 18-29 minutes and flux from 1.0 to 1.4 gpm/ft^2 produces no adverse impacts on either arsenic removal or on transmembrane pressure.
- 5) The system is pH sensitive; to achieve a treatment goal of 2 $\mu\text{g/L}$, a ferric dose of 2.5 mg/L is sufficient at a pH of 6.4, but a dose of 8 mg/L is required without pH adjustment.

The coagulation/microfiltration system proved very robust and performed well. This result was confirmed by Brandhuber and Amy (1998b), who noted that they also had excellent results with a coagulation/microfiltration system.

Ion Exchange

Anion exchange has been suggested as the “method of choice” for the removal of arsenic from drinking water (Clifford, 1995). If As is to be removed effectively by anion exchange, it must be in the +5 valence state. This will frequently require pre-oxidation. In New Mexico the main concerns regarding the use of ion exchange are: the large amounts of salt brine associated with regeneration of the resin, sulfate competition, TDS interference, and disposal of the arsenic containing brine regenerant. Clifford, et. al.(1998), addresses each of these issues in a paper evaluating ion exchange with brine reuse. The paper is based on work done in evaluating treatment alternatives for Albuquerque, NM. This work showed that a conventional sulfate selective type 2 modified porosity polystyrene resin (ASB-2) gave the longest run lengths to arsenic breakthrough. The functional group on this resin is a quaternary amine. The work by Clifford, et. al.(1998) further demonstrated that, if there is significant carbonate in the water, pH

could be used as an indicator of bed exhaustion. When the effluent pH matches the influent pH, the media is exhausted. This characteristic provides a field parameter which is easily monitored for operational control and prevents arsenic peaking from being a major concern. Clifford et. al., (1998) used the University of Houston/EPA Mobil Drinking Water Treatment Facility to treat waters with arsenic in the range of 20 to 40 $\mu\text{g/L}$ and sulfates in the range of 70 to 100 mg/L .

The water was successfully treated to less than 2 $\mu\text{g/L}$. The system had:

empty bed contact time (ebct) of 1.5 min.
30-40 inch deep resin bed
run lengths of 400 to 450 bed volumes (BV)
superficial regenerate velocity of 2 cm/min

Because the water consumption and waste generation associated with regenerating the resin are a serious concern, Clifford et. al., (1998) investigated the reuse of regenerate. The brine was reused 26 times in this study with no loss of effectiveness. The chloride consumption was reduced by 50% and the volume of brine discharged was reduced by 90%. It was also possible, through ferric hydroxide coagulation/filtration, to remove the arsenic from the brine and further increase the useful life of the brine. Ion exchange with brine recycle shows great promise; there are, however, concerns. Based on mathematical modeling, Clifford (1998) showed that arsenic removal run length is very sensitive to sulfate concentration. The modelling produced the following raw water sulfate concentration (mg/L) to Bed Volumes(BV) of water produced ratios: 50 mg/L :1200 BV, 100 mg/L :500 BV, 200 mg/L :400 BV, 300 mg/L :200 BV. He recommended that ion exchange not be seriously considered if sulfate concentrations exceeded 250 mg/L , and one would prefer concentrations less than 120 mg/L sulfate. Clifford (1998) also states, if anion exchange is to be used for arsenic removal, the TDS concentration should be less than 500 mg/L . Unfortunately many waters in New Mexico have high sulfates and high TDS, thus this very simple in-expensive alternative has limited application for many of the small communities in New Mexico.

Activated Alumina

Activated alumina can be viewed as a specialty filter media which would replace sand in a rapid sand filter. It exchanges arsenic out of water in much the same way that anion exchange does, but the As is removed by a complexation mechanism. Because of the difference in mechanisms, the activated alumina is not sensitive to sulfate concentration or TDS. Activated alumina is a pH sensitive process. Recent work has shown that As could be removed for 100,000 BV at pH of 6.0, but at a pH of 8 only 10,000 BV could be treated. There appears to be a loss of initial capacity when the activated alumina is regenerated. This phenomena is not well understood.

There are a number of things about this technology which are attractive. Activated alumina looks very promising for arsenic removal, and it will do simultaneous fluoride removal which is attractive in New Mexico where the two often appear together. The on-off operation which is typical of small systems, appears to extend the life of this media.

There are also some concerns. The manufacturer that traditionally supplied activated alumina to the drinking water industry no longer has activated alumina available. The current availability of large quantities of high quality activated alumina has yet to be demonstrated. It does appear that the currently marketed activated alumina works well. There are some unanswered questions regarding the physical handling of activated alumina in a municipal system, Placing the media in

the filter appears to be critical. A freshly placed bed must be extensively backwashed the first time it is wetted, or it sets up like cement. The backwashing operation, which may take hours, removes the rockflour from the media, and hydrates the media. As more is known about this technology, it may become the clear technology of choice.

Coagulation with iron and aluminum salts

Coagulation with iron and aluminum salts has been proposed by a number of investigators, and it appears to work well (Edwards, 1994, Cheng et. al., 1994, McNeill and Edwards, 1995, Scott et. al., 1995). However, it also requires a treatment plant having a large number of treatment units (coagulation/flocculation/settling/filtration) with a treatment plant detention time of approximately 9 to 10 hours. Co-removal of arsenic during oxidation of Fe-Mn has also been suggested for the removal of As from drinking water (Edwards, 1994, McNeill and Edwards, 1995). Again, this technology appears to be very successful, but requires a number of treatment units. A minimum plant would include: aerator, curing tank, filters. It may require settling and possibly coagulation/flocculation.

Batch experiments on As removal by ferric hydroxide coagulation indicate a high potential for success (Edwards, 1994). It is well known that the Fe-hydroxyl functional group which is present on the surface of $\text{Fe}(\text{OH})_3$ solids has a high affinity for oxyanions, including arsenate. The adsorption of arsenate results from the formation of a surface complex on $\text{Fe}(\text{OH})_3$ as represented by the following reaction:



where the symbol =Fe represents an iron atom on a particle surface.

Edwards (1994) reported that approximately 5 times more As was sorbed by ferric hydroxide precipitation when $\text{Fe}(\text{Cl})_3$ and arsenate were added simultaneously as compared to adding arsenate to “pre-formed” or existing $\text{Fe}(\text{OH})_3$ colloid particles. The increased removal of As was attributed to co-precipitation of Fe and As, with co-precipitation defined as the incorporation of As into a growing hydroxide phase. These observations are consistent with the result that the measured As removals were approximately 5 times greater than the amount of arsenate adsorption predicted by a diffuse-layer surface complexation model. Arsenate removal was greatest at pH of 7.0, and decreased as pH was increased to 9.0. The amount of arsenate removed was found to depend on the amount of Fe added, or the ferric coagulant dosage, and the lowest final arsenate concentrations were obtained when the ratio of Fe to As in the solid phase was 20: 1 to 50: 1. Greater than 95% removal of arsenate was achieved by ferric hydroxide coagulation in some cases.

Although ferric hydroxide coagulation was effective in removing arsenate, it was emphasized that the $\text{Fe}(\text{OH})_3$ flocs that were formed were very stable in suspension, and filtration was required to separate the co-precipitated Fe-As solid phase.

Oxidizing filters

Oxidizing filters are used mainly for the removal of iron, manganese, and hydrogen sulfide. The term oxidizing filter is a broad one and refers to processes which oxidize soluble forms of metal species to insoluble forms either prior to or directly in the filter.

Some of the oxidants commonly used are:

- oxygen (air),
- chlorine (Cl_2),
- potassium permanganate (KMnO_4),
- ozone (O_3), or
- chlorine dioxide (ClO_2).

In most cases in oxidation filters, the oxidation is carried out at adsorption sites on the media with net result of considerable savings in the amount of retention time (i.e. tank volume) required.

Some materials can be used as oxidizing media by treating them with solutions of Mn(II) and permanganate. The treated material develops a coating of manganese dioxide which has a large adsorption capacity for both Fe(II) and Mn(II) . Some common base materials are:

- natural zeolite (glaucinite/manganese greensand)
- some forms of silica gel zeolite
- some forms of cation polystyrene resin
- pumicite
- and other materials, such as anthracite

Filter systems using any of these media types are commonly referred to as oxidizing catalyst filters.

Although the oxidation of As(III) by oxygen is slow, As(III) is readily oxidized by manganese oxide surfaces (Herring and Chiu, 1998). Similar oxidation of As(III) by amorphous ferric oxyhydroxides has been proposed, but does not occur in a time frame of a few hours (Herring and Chiu, 1998). As(III) is also not oxidized by crystalline iron oxides (Scott and Morgan, 1995). The effectiveness of arsenate removal during the oxidation of Fe(II) to Fe(III) should be similar to that observed for removal by ferric hydroxide coagulation via addition of Fe(III) , since in both cases the Fe(OH)_3 sorbent is produced. For example, the formation of 2 mg/L Fe solid precipitate should decrease soluble As concentration from 10 ppb to 0.75 ppb, based on predictions from adsorption modeling (Edwards, 1994). If co-precipitation is operative as well, even greater As removal should be obtained. The ferric hydroxide precipitate was also predicted to be much more effective than Mn oxide precipitate in the removal of arsenate.

Thus an iron oxide coated filter is appropriate for removal of As(V) , and a manganese dioxide coated filter media is appropriate for oxidation of As(III) to As(V) and removal of the As(V) . McMullin et. al. (1998) report on a pressure filter using an iron oxide based media which is

capable of treating water spiked with 200 $\mu\text{g/L}$ to 2 $\mu\text{g/L}$ for 4500 bed volumes, This media works well over a pH range. of 6 to 8, but it is actually optimized at a pH of 5.5. Since this media is insensitive to either sulfate concentration up to 250 mg/L or chloride concentration, it appears that the media is forming surface complexes with the As and not undergoing ion exchange. A laboratory created iron coated sand has been shown in bench scale tests to be effective in removing As(V) from low pH waters (Benjamin et. al., 1996). Unfortunately, there have been difficulties regenerating the media. A manganese dioxide coated media is capable of arsenic and iron adsorption with subsequent oxidation on the surface of manganese dioxide media. There is anecdotal evidence that this process may also be successful for the co-removal of As. A manganese greensand filter run in continuous regeneration mode removed 86% of the As in the water (Fonte, M, 1982). Edwards (1994) reports on a study in which 89 percent of the As present was removed using a greensand filter. The water treated had 59 $\mu\text{g/L}$ As (V), 2.9 mg/L Fe (II), and 0.47 mg/L Mn (II). No pH data was reported and no attempt was made to manipulate Fe-As ratios. Given the success of Fe-Mn oxidation in a conventional plant it is reasonable that the Manganese dioxide filters could be optimized for removal of arsenic if Fe(II) is being removed.

In some cases the filter media is simply “aged”. Aging refers to the practice of exposing the filter media to the raw water for a period of time, which allows a thin coating of oxide to accumulate on the media. The thin coating of oxide provides active adsorption sites. Aged media is most often used to remove Fe(H) and Mn(II). In these cases, ferric oxide and manganese dioxide are the respective precipitates, and it is noted that these materials have high sorption capacities for the reduced species Fe(II) and Mn(II), respectively.

Point of Use

Reverse Osmosis is commonly used to remove arsenic from water in point of entry/point of use (POE/POU) applications, This technology requires some sophistication of the operator and the membranes have a limited life.

The Village of San Ysidro, NM, provides a good case study of the problems facing rural community water systems. The Village, located 70 miles northwest of Albuquerque along the southern flank of the Jemez Mountains, has a community water system that relies upon shallow ground water resources which are plagued with problems of very poor quality due to high concentrations of As (average concentration about 170 $\mu\text{g/L}$) and F (average concentration about 2.5 mg/L). The Village is very poor and cannot afford a conventional water treatment system. The water system was upgraded in 1987 at which time individual on-site water treatment devices were installed in each of the residences and commercial establishments. These under-the-sink point-of-use (POU) treatment systems provide filtration, activated carbon adsorption, and reverse osmosis treatment: of up to 10 gallons/day of water which is used for direct human consumption. A monthly charge of \$7 was added to each residential water bill to cover the costs of maintaining these systems by Village staff.

A study was conducted to evaluate the performance of the POU treatment systems in San Ysidro (Thomson and O’Grady, 1998). It was found that POU systems can provide a very high degree of treatment, including producing water with an As concentration of less than 10 $\mu\text{g/L}$, provided they are properly maintained. However, it was also found that the overall performance of these systems has degraded due principally to inadequate maintenance. The POU system operation

and maintenance programs were found to be strongly dependent upon the organization, technical abilities, and diligence of the water utility staff. The following recommendations were presented: 1) establish an adequate funding mechanism specifically dedicated to operation and maintenance of POU treatment units in the community; 2) develop a reliable system for tracking operation and maintenance activities for all POU treatment units in the community; 3) provide operator training and equipment for measuring the performance of POU systems; and 4) provide appropriate operator training and equipment for maintaining POU treatment systems. This study concluded that POU systems are an effective alternative to conventional centralized water treatment systems, but that a high degree of regular attention to each customer's POU system is required by water utility personnel.

Conclusion

Clearly, the new drinking water standards for arsenic being set by the USEPA pose a potential financial problem for many communities. There are a number of technologies which may be appropriate for use in rural New Mexico, but most appear to require a very sophisticated operator. An operator with a reasonable level of sophistication, will be an expensive employee, if one can be found to hire. There are no easy answers to this problem. The technologies exist to solve the problem of treating our waters to acceptable levels, but do the funds exist to pay for the treatment?

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