



**Arsenic Water Technology Partnership**

# Arsenic Removal by Tailored Activated Carbon at Ambient pH



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# Arsenic Removal by Tailored Activated Carbon at Ambient pH

Prepared by:

**Weifang Chen, Jiying Zou, Min Jang,  
Fred S. Cannon, and Brian A. Dempsey**

The Pennsylvania State University  
Department of Civil and Environmental Engineering  
212 Sackett Engineering Building  
University Park, PA 16802

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## FOREWORD

The Water Research Foundation is a nonprofit corporation that is dedicated to the implementation of a research effort to help utilities respond to regulatory requirements and traditional high-priority concerns of the drinking water community.

The Arsenic Water Technology Partnership (AWTP) program is a partnership between Water Research Foundation, Sandia National Laboratories (SNL) and WERC, a Consortium for Environmental Education and Technology Development at New Mexico State University that is funded by DOE and the Water Research Foundation. The goal of the program is to provide drinking water utilities, particularly those serving small and rural communities, with cost-effective solutions for complying with the new 10 ppb arsenic MCL. This goal is being met by accomplishing three tasks: 1) bench-scale research to minimize operating, energy and waste disposal costs; 2) demonstration of technologies in a range of water chemistries, geographic locales, and system sizes; and 3) cost effectiveness evaluations of these technologies and education, training, and technology transfer.

The AWTP program is designed to bring new and innovative technologies developed at the laboratory and bench-scale to full-scale implementation and to provide performance and economic information under actual operating conditions. Technology transfer of research and demonstration results will provide stakeholders with the information necessary to make sound decisions on cost-effective arsenic treatment.

The Foundation participates in the overall management of the program, helps to facilitate the program's oversight committees, and administer the laboratory/bench-scale studies. SNL conducts the pilot-scale demonstrations and WERC oversees the education, training, economic analysis, and outreach activities associated with this program.

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## **EXECUTIVE SUMMARY**

A new arsenic limit of 10 ppb became effective in 2006 for United States drinking water systems. This new regulation would make small public water facilities face heavy financial burdens, unless less costly methods of arsenic removal are developed. There is an urgent demand for an economical, effective, and reliable technique that is capable of removing arsenic species to this new level. Arsenic in drinking water is of environmental concern because it is a carcinogen. At 50 ppb arsenic level, 13 people out of 1000 could die from cancer to the liver, lung, kidney, or bladder (Smith et al. 1992). The arsenic dilemma is especially serious in Bangladesh and West Bengal India, where arsenic levels as high as 1 mg/L contaminate groundwater.

Our research herein has focused on developing an arsenic removal system that couples the high pore volume, structural cohesiveness, and low costs of granular activated carbon (GAC) with the arsenic-adsorbing propensity and low costs of iron. Our overall approach has been to preload iron into the GAC pores in such a manner as to achieve (a) the highest internal loading of iron, while also maintaining (b) the highest efficiency of iron use; i.e. the most milligrams of arsenic adsorbed per gram of iron. When this underlying objective is met, we anticipated, we would achieve the longest bed life for removing arsenic in an easy-to-operate adsorption column, while maintaining low costs and structural stability.

## **RESEARCH OBJECTIVES**

The Objectives of this research were to:

1. Devise a technically viable and economically reasonable approach for removing arsenic from drinking water down to 10 ppb or less. Provide a durable approach suitable for very small systems that incurs low capital, operational, and energy costs, while requiring only simple operations, and minimal monitoring.
2. Tailor activated carbon with iron in such manner as to extend its bed life for removing arsenic.
3. Enhance the iron solubilization and tailoring processes so as to render a robustness that is adaptable to a wide array of water compositions.

## **APPROACH**

The authors have explored several means of pre-tailoring GAC so as to extend its bed life for removing arsenic from water. These tests have mostly employed rapid small scale column tests (RSSCTs), which have used #200×400 mesh GAC in a 5.0 mm diameter by 13.5 cm long column with a 1 minute empty bed contact time. In the RSSCT experiments, we monitored the bed volumes of water that could be treated before the initial breakthrough of arsenic to above 10 ppb. For some of the tests herein, the authors conducted batch isotherm tests and kinetic test; and these generally used Rutland groundwater that had been spiked with a relatively higher level of arsenic.

## **CONCLUSIONS**

Thus far, we have developed an iron-preloaded media that can remove arsenic to below 10 ppb for 26,000–33,000 bed volumes (BVs). When this iron tailoring has been coupled with

solubilizing zero-valent iron within the same bed, arsenic was removed to below 10 ppb for 43,000 BVs. In prior work, we observed that when the zero-valent iron preceded the iron-tailored GAC, bed life could extend to 150,000 bed volumes. These tests employed Rutland, MA water, which contained 50–55 ppb As. As an integral part of this success, we have recently devised a means of forming hydrous ferric oxide (HFO) within the GAC pores; and this hydrous ferric oxide has a high affinity for arsenic. Our manufacturing contacts, as part of their marketing studies, indicate that these are cost-effective means of removing arsenic.

## **RECOMMENDATIONS**

Cost data provided by our industrial in-kind partner, Siemens Water Technologies, indicates that the cost of this iron-tailored GAC is quite cost-competitive with the conventional granular iron, titanium, and resin media that are now being sold. The unit price of the iron-tailored GAC is projected to be at the low end of the cost spectrum relative to these others; and the bed life is about comparable (see Chapter 5). The experience is that these other media have projected bed lives of 28,000–50,000 when removing arsenic in the 11–50 ppb range down to below 10 ppb; and the beds are not operated for longer than that because either they break through with >10 ppb arsenic, or because particulates build up and cause excessive pressure loss. At least a portion of these particulates can originate from fragile granular iron media.

In comparison, the iron tailored media herein, can match this 28,000–50,000 bed volumes for the same or less cost. Moreover, with the granular carbon sheath around the hydrous ferric oxides, this media has a more favorable skeletal strength.

## **FUTURE AND ONGOING RESEARCH**

In future and ongoing research, we aim to discern yet more favorable means of loading higher amounts of iron into the GAC pores, and render the iron surface to be yet more active in adsorbing arsenic. Also, we aim to discern the proper balance between zero-valent iron and iron-tailored GAC, such that the zero-valent iron does not corrode so quickly as to release iron hydroxide into the effluent media, yet it corrodes quickly enough to capture all the arsenic.

# CHAPTER 1

## INTRODUCTION

### BACKGROUND

#### Arsenic Contamination

Arsenic exceeds 10 ppb in at least 4000 community and non-community wells that appear in more than 45 U.S. states (Frey et al. 1998). Half of all the states in America have more than ten community wells that exceed this new limit; and they are (from roughly west to east): Alaska, California, Oregon, Washington, Nevada, Idaho, Montana, Utah, Arizona, New Mexico, Colorado, Texas, Oklahoma, Nebraska, South Dakota, North Dakota, Minnesota, Wisconsin, Michigan, Indiana, West Virginia, New Jersey, Massachusetts, Vermont, Maine, and Florida (Welch et al. 2000). Many of these wells service small and very small community water systems; and for the majority of these, an arsenic removal facility will represent the first treatment system that the small providers have had to install, beyond chlorination.

#### Health Impacts of Arsenic in Drinking Water

Arsenic in drinking water can cause chronic arsenic intoxication (arsenicosis), which may lead to harm of respiratory, digestive, renal circulatory, neural systems and internal organs (ATSDR 2000; IPCS, WHO, 2001). There are reported clinical effects and symptoms including Raynaud's syndrome, hypertension, cerebral infarction (Chen 1995), encephalopathy (Poklis et al. 1990), damage of the peripheral nerve bodies (Bansal, 1991), diabetes mellitus (Lai et al. 1994), and circulatory disorders. In large regions of Bangladesh and West Bengal, India, the drinking water contains arsenic concentrations as high as 1 mg/L; and as many as 50–65 million people are being poisoned by this (Das et al. 1994). In this area, 170,000 people have exhibited symptoms of chronic arsenicosis (Das et al. 1995).

The most significant consequence of chronic arsenic intoxication is the induction of cancers in various organs. Therefore, arsenic has been recognized as Class I human carcinogen and is a public concern due to its widespread usage in both industry and agriculture. An area in Taiwan has had drinking water sources in which arsenic concentrations ranged from 170 to 800 ppb. On the basis of the cancer that was observed there, Smith et al. (1992) surmised that a 50 ppb arsenic level would translate to a lifetime risk that 13 people per 1000 could die from cancer to the liver, lung, kidney, or bladder. Arsenic also causes skin cancer at low concentrations (Ratnam et al. 1992), and it poisons the heart and gastrointestinal tract at high concentrations (Rates et al. 1992).

Inorganic arsenic in low and micro molar doses can cause great genotoxicity. Researchers have reported that Sodium arsenite can induce chromosome aberrations, sister chromatic exchanges, and DNA-protein crosslinks (Dong et al 1993).

#### Regulatory Perspective

In early 2001, the USEPA published a revised arsenic standard of 10 ppb in drinking water. This is considerably lower than the previous 50 ppb standard, which was established in 1942. All public water systems must comply with this 10 ppb standard within 5 years after this

rule was published (i.e. by 2006). The USEPA estimates that 3,000 community water systems and 1,100 non-community water systems will need to take measures to lower their arsenic levels. On the basis of technology that was available in the late 1990's, the USEPA anticipated that throughout the nation, it will cost these communities a cumulative \$195–\$675 million to comply; with a 10 ppb arsenic standard, this would translate to \$58-327 per household per year. Other individuals have projected yet higher compliance costs. The cost burden for removing arsenic will be greatest on very small community systems, which have traditionally employed no treatment beyond simple chlorination. Thus, there is great need to devise new and innovative technologies that are inexpensive to use, easy to operate, and durable through long-term use.

## LITERATURE REVIEW

### Arsenic Chemistry

In natural environment, arsenic is rarely encountered as a free element. It can occur in four oxidation states (-3, 0, +3, +5). The most prevalent species of arsenic in drinking water are arsenate (+V valence) and arsenite (+III valence). The occurrence, distribution, mobility and speciation of arsenic rely on numerous factors including pH, redox level, distribution of other ionic species, aquatic chemistry and microbial activity (Shih, M.C., 2005). Oxidation-reduction potential (Eh) and pH are the most important ones controlling arsenic speciation. The arsenate prevails in oxidized waters, while the arsenite prevails in reduced waters that also contain hydrogen sulfide. Clifford and Ghurye (2000) compiled data indicating that arsenate represented more than 80% of the arsenic species in the wells that were tested in California, New Mexico, Arizona, Taiwan, and Chile; while arsenite predominated in Bangladesh, West Bengal, and Alaska wells. The acid/base species of arsenate (V) are  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HAsO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$  with corresponding pKa's of 2.35, 6.75, and 11.6. This means that when the water pH is between 2.35 and 6.75, the  $\text{H}_2\text{AsO}_4^-$  species will prevail; and when the water pH is between 6.75 and 11.6, the  $\text{HAsO}_4^{2-}$  species will prevail. Since both of these species that predominate in the near-neutral pH region are charged, charge-based processes will remove arsenate. Moreover, when the pH is above neutral, the arsenate exchange bonding will be greater (with the double negative charge) than below neutral (with the single negative charge).

Similarly, the acid/base species of arsenite (III) are  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HAsO}_3^{2-}$ , and  $\text{AsO}_3^{3-}$ , with pKa's of 9.23, 12.11, and 13.41. This means that below pH 9.23, the non-charged  $\text{H}_3\text{AsO}_3$  species will predominate, and charge-based processes will not remove arsenite.

Ghurye and Clifford (2000) observed that arsenite will be oxidized to arsenate when it is exposed to chlorine for one minute; while dosing with just three times the stoichiometrically required level of chlorine. This means that in typical groundwaters, a chlorine dose of <0.1 mg/L would convert all arsenite to arsenate. Most groundwater-based municipalities already have adopted chlorination; and thus oxidation of As (III) to As (V) will not be an additional issue.

Studies have shown that ionic competition with arsenic for the adsorption sites should mainly arise from oxyanions (Silicate, phosphate etc.) because arsenic itself appears as an oxyanion in water (Su and Puls 2001, Gu et al. 2005).

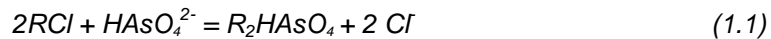
## **Arsenic Removal Technologies**

### ***Modified conventional treatment methods***

Modified conventional treatment methods include coagulation with Alum or iron, Fe-Mn oxidation and lime softening. A large fraction of the larger utilities affected by the new MCL standards have already installed these methods. For them, Chen et al. (1999) proposed the lowest-cost As removal method is to remove arsenic and reduce hardness with these conventional methods. But for very small water systems, it is not cost effective to install a new coagulation or softening process for removing arsenic alone.

### ***Ion exchange***

Among Ion exchange media, the strong-base anion exchange (SBA) is the most favorable for arsenic removal. Equation 1.1 illustrates the mechanism for this exchange.



After exhaustion, the resins can be regenerated with a NaCl solution, which could be illustrated as Equation 1.2:



High sulfate concentrations or high total dissolved solids in the influent tend to hinder ion exchange treatment due to competition (Ghurye et al, 1999). For example, when sulfate concentration increases from 50 ppm to 220 ppm, the run length of a SBA resin (Ionac ASB-2, type 2) was decreased by 70% (from 900 to 250 bed volumes (BVs)) (Ghurye et al. 1999). The run lengths of ion exchange are very short compared with activated alumina or granular ferric hydroxide processes, but with ion exchange, the empty bed contact times can be shorter, and the bed can be regenerated. Clifford et al. (2003) observed that after regeneration with sodium chloride, ion exchange resins could be reused up to 20 times with no effect on As leakage and minimal effect on run length (Clifford, et al, 2003).

A significant disadvantage of ion exchange is the potential for arsenic peaking or dumping, especially when sulfate is present. Edwards et al observed a spike of nearly 400% of the influent arsenic elute is from an ion exchange column when the threshold  $15 \times 10^{-5}$  M  $SO_4^{2-}$  passed.

### ***Reverse osmosis***

Reverse Osmosis are generally highly effective for arsenic removal, but because of the high operating costs, Reverse Osmosis is not recommended for very small systems (Chen et al 1999)

Reverse Osmosis is more effective in removing arsenate than arsenite. The arsenite removal efficiency is 20–85% (Ning et al. 2002, Kang et al. 2000). Waypa et al. (1997) has been able to obtain an arsenate removal rate of above 97% with Reverse Osmosis. Thus to achieve a better result, an oxidizing agent needs to be added to the water to convert all the arsenite to arsenate. But oxidizing agents are generally harmful to reverse osmosis membranes (Koch

Membrane Systems, 2001). Moreover, researchers reported the brine stream from the reverse osmosis accounts for 15–30% of the feed water (Ramachandran, 2005). This is an unacceptable level in most applications. The brine would have to be disposed of in a special manner, or it would have to be treated by some other means.

### ***Adsorption***

Several adsorption technologies have successfully been applied for the removal of arsenic; and the research herein has built on this prior research. In general, adsorption processes require only simple operations, low costs, and little maintenance. They are adaptable to various kinds of well sites. Low dosing of chemicals is required (if any) and also the amount of residuals is low when adsorbents with high adsorption capacities are used.

***Adsorption by iron hydroxide:*** Hydrous ferric oxide (HFO) has been extensively studied as a promising adsorptive material for removing both arsenate and arsenite from aqueous phase due to its high iso-electric points (8.1) (Dixit and Hering, 2003) and selectivity for arsenic species. However, the hydrous ferric oxide made by those authors was a suspension that was not suitable for use in column applications due to low hydraulic conductivity (Zeng 2003). To overcome this disadvantage, granulation techniques have been developed.

Granular ferric hydroxide (GFH) consists of a poorly crystallized  $\beta$ -FeOOH (250–300 m<sup>2</sup>/g surface area, 75%–80% porosity). It was synthesized from ferric chloride solution by neutralization and precipitation with sodium hydroxide, followed by centrifugation and granulation under high-pressure (Thirunavukkarasu et al. 2003, Gu et al. 2005). There are no drying procedures in the preparation, so GFH pores are filled with water, which renders it high amount of adsorption sites and thus high adsorption capacity.

At slightly above neutral pH values, GFH was discovered to have nearly equal adsorption capacity for both arsenate and arsenite (Driehaus, 2002). Driehaus et al. explored this process's arsenic removal capacity with an influent water which has pH 8.2 and arsenic content of 16 ug/L. With GFH grain sizes 0.2–0.4 mm and EBCT 32 second, this process is able to remove As for 34,000 bed volumes until the 10 ppb As occurs (Driehaus et al., 1998). Westerhoff et al. (2005) had conducted several lab columns with GFH. The results revealed that at pH 7.6, GFH could remove As from 50 ppb to 10 ppb MCL for 25,000 BVs when the EBCT is 2.5 minutes. But suppliers have commented that these iron oxide granules can crumble and disintegrate when they experience prolonged use, Selvin et al. (2000) reported that GFH with a media particle size at 0.8–2.0 mm will need a backwashing every 5000 Bed volumes. Also, after backwashing, a significant amount of head loss pressure will build up in the system (Gu et al., 2005).

***Removal by zero-valent iron:*** In this method, arsenic is adsorbed onto corrosion products of zero-valent iron (ZVI) as the ZVI converts so such species as iron (oxyhydr) oxide. Studies have shown that the performance of ZVI is limited by its initial removal capacity and any additional capacity that may come about after iron metal corrodes in water (Lackovic et al. 2000, Su et al. 2001a, and b). Possible arsenic removal processes in zero-valent iron system include surface adsorption onto corrosion products, e.g. iron (oxyhydr)oxides (Manning et al. 2002, Dixit and Hering 2003), precipitation such as formation of symplectite ( $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) (Nikolaidis et al 2003), co-precipitation ( e.g. arsenic co-precipitation with carbonate green rust) (Lien and Wilkin 2005) or redox reaction such as As (III) oxidized to As(V) by corrosion products or impurities such as  $\text{MnO}_2$  (Melitas et al. 2002, Manning et al. 2002). Both As (III) and As (V)

could be removed effectively from aqueous solution using zero-valent iron according to studies by Nikolaidis et al. (2003). The arsenic removal capacity was determined to be approximately 7.5 mg/g Fe or 0.1 mmol As/g Fe. Melitas et al. (2002) found that rates of arsenate removal by ZVI were highly dependent on the continuous generation of iron oxide adsorption sites by comparing arsenate removal by freely corroding and cathodically protected iron. Municipal service representatives comment that zero-valent iron systems have considerable problems with plugging and hydraulic pressure build up.

Karschunke and Jekel (2002) investigated arsenic removal with fine iron wool. The iron wool was corroded in oxygenated water, and the iron hydroxide formed by the corrosion adsorbed As (V). They also tested if galvanic corrosion could improve arsenic removal by enhancing iron release. The results revealed that when combined with a sand filtration process, the galvanic corrosion system could remove Arsenic from 500 ppb down to 50 ppb for 32,000 Bed Volumes. According to Karschunke and Jekel, there are two major concerns that prevent this process from implementing, they are the cathodic formation of hydrogen and the risk of copper release when the contact breaks down.

***Iron bearing media:*** Studies revealed that iron (III) has a high affinity toward inorganic arsenic species; and it is very selective to arsenic in the sorption process. Recent research has focused on creating cheap and stable iron bearing adsorbents. Some of these media are discussed below.

(1) Iron oxide coated sand. For this media, the sand only serves as an (inert) support, and it is the iron oxide coating that removes arsenic. Gupta et al. (2005) observed that the adsorption of As (III) onto iron oxide coated sand could reach 0.03 mg/g at pH 7.5.

(2) Iron oxide impregnated activated carbon. By precipitating iron salts onto activated carbon (presumably primarily external loading), these authors could achieve an iron loading of 7%. At pH 7, with 1 mg/L arsenic, and 0.2 g/L Fe oxide impregnated activated carbon, this adsorbent could get an As (III) adsorption of 4.7 mg/g or an As (V) adsorption of 4.5 mg/g (Vaughan et al. 2005, Vaughan et al. 2000). It is noted that the author herein have built on these results to achieve considerably higher arsenic loadings (see below).

(3) Fe (III)-loaded cellulose sponge. The sponge is claimed to contain free available ethyleneamine and iminodiacetate groups, which interact with Fe (III) by chelation and ion exchange. The Fe (III) loading capacity was 0.25 mmol Fe/g sponge, which corresponded to a 1.4% Fe content. The media had an As (V) adsorption capacity of 1.83 mmol As /g sponge; and an As (III) adsorption capacity of 0.24 mmol As/g sponge (Munoz, 2002).

(4) Granular activated carbon (GAC) based iron containing adsorbents. This media was made in 2 steps, first Fe (II) was adsorbed onto GAC, and then the Fe (II) was oxidized to Fe (III) by O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub> or NaClO. When lignite based carbon was employed, the iron loading could reach 7.9%, and they proposed that the impregnated iron was mostly in coordinated form with various functional groups on GAC, but not in polymeric iron hydroxide form. The adsorbent could remove arsenic to 7500 bed volumes before reaching 10 ppb breakthrough when influent contained 50–60 ppb of As (V) or As (III) (Gu et al. 2005). As shown below; the Penn State iron loaded GACs have 3–5 times longer bed life than this.

(5) Amorphous iron oxide preloaded media. Amorphous oxide had been loaded on sand (Vagliasindi et al, 1998), and in incinerator melted slag (Zhang et al. 2005), iron has also been embedded in a macroporous cation exchange bead (DeMarco et al. 2003) and the latter two had been tested for arsenic removal. The porous cation exchange resins could obtain an iron loading

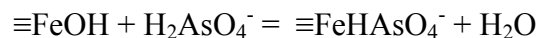
of 25% based on dry bead weight, and 50% of the iron loading is in the form of FeOOH. This product could remove arsenic from 50 ppb down to 10 ppb for 45,000 BVs. DeMarco et al. (2003) also pointed that the HFO agglomerates in the beads were very stable, turbulence and mechanical stirring did not result in any loss of HFO. The iron oxide loaded on melted slag was believed to be chemically bonded with the Si inside the slag, which prevented the crystallization of FeOOH, and Zhang (2005) claim this material had better arsenic removal (arsenate of 78.5 mg/g slag) capacity than FeOOH.

### Mechanisms of Arsenic Removal by Iron-Bearing Media

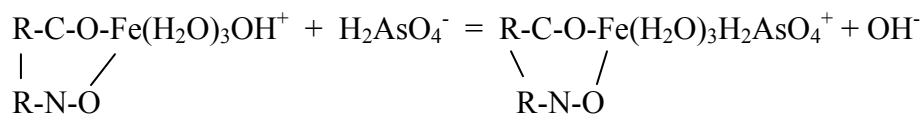
The adsorption of arsenate and other anions have been reported to be dependent on the characteristics of the anion and the adsorbent surface. Mechanisms of arsenic adsorption onto iron oxides, including the poorly crystalline iron oxides, e.g. ferrihydrite, is predominately by ligand exchange with surface structural OH<sub>2</sub> and/or OH<sup>-</sup> at the surface adsorption sites (Raven et al. 1998). The retention of both arsenite and arsenate is strongly pH dependent, but with opposite trends. At low to moderate arsenic adsorption levels, the adsorption envelopes of arsenite and arsenate usually cross within the pH range of 6–7.5. Ferrihydrite exhibits a relatively greater retention of arsenate at low pH values, whereas arsenite is more strongly retained at higher pH values (Raven et al. 1998). Several papers (Vaishya and Gupta 2003, Raven et al. 1998, Zeng 2003) have indicated that As(V) adsorption decreases with increasing pH, while As(III) sorption increases with increasing pH up to pH 10.

The reaction of arsenate and arsenite with iron oxide has been studied by X-ray absorption fine structure (EXAFS) (Waychunas et al. 1993, Manceau et al. 1995) and infrared (IR) spectroscopy (Lumsdon et al. 2001). These studies have provided strong evidence that arsenate is adsorbed onto iron oxide surfaces predominately by forming bidentate binuclear complexes (Figure 1.1), while arsenite is adsorbed on goethite surface in the same way (Sun and Doner, 1998).

Several authors have offered characterizations of the iron-arsenic binding. Dixit and Hering (2003) invoked the following mechanism for iron-hydroxide granules:

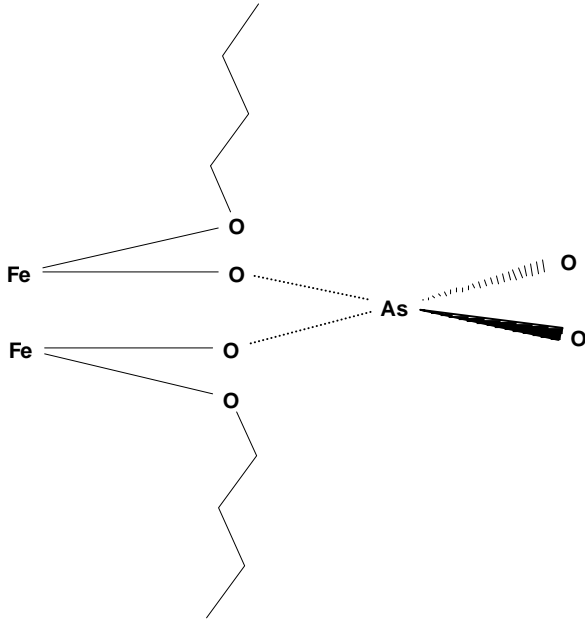


These authors also observed more favorable As(V) sorption at pH below 5–6, in contrast; As(III) is favored at pH above 7–8. Pattanayak et al. (2000) noted that a fly ash carbon (28% ash) adsorbed As(III) better (up to 75–90 mg/g carbon) than did a low ash carbon (0.2% ash). Haron et al. (1999), when employing resin-iron composites, invoked the model:



It is noted for both of these mechanisms that stoichiometrically, there can be no greater than a 1:1 molar relationship between As : Fe. For example, Haron et al. (1999) observed only as much as 0.25 M As / M Fe ( 0.33 g As / g Fe) when adsorbing As from a 500 mg/L (i.e. 500,000

ppb) As solution, onto a resin composite that contained 19% Fe (i.e., even at 500 mg/L As, the moles As : moles Fe was lower than 1:1).



**Figure 1.1 Schematic illustrations of the bidentate binuclear adsorption mechanisms of arsenate onto goethite (bidentate binuclear complexes)**

Adsorption capacity of materials depends on many factors, such as the nature of the adsorbate, the presence of other substances in water which act competitively towards the substance under study, the experimental conditions of the adsorption process like pH, temperature, contact time etc. (Diamadopoulos et al. 1992).

When the aqueous solution contains nearly equi-molar concentrations of As and Fe, chemically complexed iron could have the highest arsenic removal capacity of 0.94 mol As /mol Fe (Fukushi et al. 2003). HFO has a maximum arsenic removal capacity of 0.2–0.3 mol As /mol Fe.  $\beta$ - FeOOH could only reach 0.015 mol As/mol Fe.  $\alpha$ -FeOOH and hematite have even lower capacities (Dixit et al. 2003). But GFH has not reached that capacity in column tests, on the contrary, the ratio is pretty low. That is because GFH is very unstable under the conventional water treatment environment. According to Selvin et al. (2000), the adsorption capacity for As is reduced by 50% when larger sized media (1.0–2.0 mm) are employed.

Pierce and Moore (1982) reported that arsenate reacts with amorphous iron oxide much faster than arsenite. Kim et al. (2004) reported that mesoporous alumina adsorbed arsenate two times faster than arsenite and attributed it to the smallness of the radius of an arsenate ion (4.0–4.2Å) compared with that of an arsenite ion (4.8Å).

## **Metal Immobilization onto Porous Media (Activated Carbon)**

### ***Activated carbon***

This research focused on activated carbon as the porous media for iron loading. Activated carbon is comprised of graphene planes that are packed together and then bonded together. Each graphene plane consists of a benzene ring lattice. The pi-electrons in this lattice can exhibit pi-bonding energy with other graphene layers, and also with adsorbents. Hydrophobic organic compounds prefer to adsorb onto these non-polar regions of the activated carbon, rather than staying in polar water. The edges of the graphene planes can host a number of oxidized sites, including the oxygenated substituents: carboxyls, phenolics, carbonyls, and lactones. In contrast, the interiors of the graphene planes can pose a localized low-redox potential; since N can be substituted for C in the lattice structure, creating an electron-rich region (Leon y Leon and Radovic, 1994).

Activated carbon is created by thermally treating carbon-based solids, such as bituminous coal, lignite coal, or wood. The pyrolysis step in thermal treatment creates narrow fissures between graphene planes; and the oxidation step facilitates the gasification of some graphene layers so as to create slightly wider spaces between the layers. Following activation, the edge sites can be left with incomplete electron configurations; and are therefore reactive. Oxygen can chemisorb to such reactive sites, and form oxygenated groups (Nowack et al. 2002). The edge sites can also thermally react with ammonia to form a positively charged and low-redox edge (Chen et al. 2005a, 2005b); but this formation capacity is limited by the number of reactive edge sites available.

The spaces between graphene planes are generally planar, or slit-shaped. In conventional bituminous granular activated carbons (GAC's), the large majority of pores have widths of 4–30 Å; and organic molecules can just barely fit into these pores. Iron-citrate complexes (with tag-along waters of hydration) have dimensions of 5–20 Å. Perhaps the most useful pore widths for adsorbing molecules are 1 to 13 times their dimension, i.e. 5–250 Å (Nowack et al. 2002, Krupa and Cannon 1996, Rangel-Mendez et al. 1996). Based on a mass/volume basis; a single continuous flat graphene plane would exhibit a surface area (top and bottom) of 2,000 m<sup>2</sup>/g; and commercial activated carbons generally have N<sub>2</sub>BET surface areas of 900–1,200 m<sup>2</sup>/g. If rigorously accurate, this indicates that about half of all the graphene planes have two surfaces exposed. These surface areas are 2–3 times higher than for granular iron media.

The large surface area, high pore volume, and rigid structure of GAC render it an ideal backbone for hosting iron species or iron complexes.

### ***Impregnation***

Pore volume impregnation, and specifically incipient wetness, is one of the most prevalent methods used in the area of catalyst production. The impregnation procedure comprises two steps. First, saturate the pores of the porous support with aqueous metal salt solution; then dry and calcine the impregnated support in order to convert the metal salt to metal oxide. It had been reported that 10–12 % Cu impregnation could be achieved via this method (Montanari et al. 1997, Marchi et al, 2003). This impregnation procedure affords relatively large metal crystallites concentrated at the surface of the support particle (Vaishya and Gupta, 2003).

As we had discussed in section 1.2.3, crystallized iron oxides are far less effective compared to amorphous iron oxides.

### ***Precipitation***

The precipitation method, also called precipitation-deposition, comprises inducing precipitation of a dissolved metal species which then deposits upon a finely powdered solid support. Conventionally, the most widely studied chemical method to prepare iron oxides has been the precipitation of iron ions from aqueous solutions of their nitrate, chloride, perchlorate, or sulfate salts (Lee et al. 1996). The precipitation of ferric ions is usually driven by thermolysis or by the addition of base to the aqueous solution. The characteristics of the final product, i.e. oxide phase, particle size and surface area, depend highly on the precipitation conditions, especially the concentration of the iron ions, the nature of the counter-ions present, and the pH of the solutions. Goethite ( $\alpha$ -FeOOH), ferrihydrite ( $\text{Fe}_5\text{HO}_8\cdot\text{H}_2\text{O}$ ) or akagenite ( $\beta$ -FeOOH) are usually the initial precipitates, which are converted to low surface area  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> under moderate heat treatment (Jolivet et al. 2000, Schwertmann and Cornell 1991).

High metal loading can be achieved via precipitation (e.g., 50% or more). But aggregation might accompany this, such that the metal is not uniformly distributed on the support. Khaleel (2004) had discovered that the metal crystallites size produced by this method can be as large as 30 nm.

### ***With chelating agent***

Surface modification of activated carbon by immobilizing organic compounds is recognized as an effective approach for enhancement of heavy metal removal. Surface modification of GAC by citric acid had been reported to enhance copper adsorption by 140% (Chen et al. 2003). The presence of ethylenediamine tetra-acetic acid (EDTA) was reported to improve the cadmium adsorption by 2–3 times (Preston et al, 1995). It is noted that iron, citric acid, EDTA and fatty acids are non-toxic and commonplace in water and foods. No primary drinking water standards exist for any of these species.

Citric acid is found to serve as a redox species, and it also facilitates considerably greater internal sorption of iron than could be achieved with mere salts such as FeCl<sub>3</sub> (Chen et al. 2003). Liu and Huang (2003) observed that citrate presence also inhibited the formation of iron-based crystals, even after 135 days of precipitation. Rather, the citrate promoted short-range ordered materials. The authors herein note that the short-range order would induce higher surface areas and greater porosity for As to adsorb, and this is favorable for what we want to accomplish.

### **Summary**

In light of all this previous research, iron loaded GAC shows promises for arsenic removal in the following aspects:

Iron is highly selective for both As (III) and As (V). With iron dispersed finely in GAC pores, we could predict that the iron loaded GAC will have high arsenic removal efficiency;

Activated carbon structure is rigid and robust. It provides an ideal backbone for iron, so the iron loaded GAC columns could run stably until they are exhausted;

Activated carbon has high pore volume and large surface area; which renders it useful for preloading high amount of uniformly dispersed iron.

## **PREVIOUS WORK**

Before working on this project, the authors have been conducting bench-scale work under an AwwaRF (now Water Research Foundation) research grant titled, “Innovative Arsenic Removal onto Activated Carbon that is Preloaded with Surfactant-Iron Complexes (RFP 3013). Our results under that AwwaRF contract indicated that iron-citrate preloaded carbon, when coupled with a soluble iron source – galvanized steel fittings, could remove arsenic to below 10 ppb As for 150,000 BVs when the influent was 50 ppb.

### **Arsenic Removal by Tailored GAC Coupled with Soluble Iron Source — Galvanized Steel Fittings**

For these tests, the GAC was preloaded with citrate-Fe preloaded GAC to an iron content of 1.07%, and this preloaded GAC were inserted into the RSSCT chamber. Next, galvanized steel fittings were placed before and after this mini-column; and the groundwater pH was adjusted to pH 6.0. The GAC was sandwiched between two glass wool plugs. As shown in Figure 1.2, the effluent As rose from 4 ppb up to 8–9 ppb during the first 10,000–20,000 BVs, but did not exceed 10 ppb. Then, the system was stopped for 6 days at 26,000 BVs. Then after treatment operation was resumed (with fresh Rutland water) the effluent arsenic concentration dropped to below 4 ppb. It reached 10 ppb at 150,000 BVs and showed no signs of full exhaustion above 25 ppb, even at 250,000 BVs. A nearly repeat experiment was conducted with Citrate-Fe-Mg (0.81) carbon. This Citrate-Fe-Mg column also had to be stopped at 22,000 BVs for 6 days (due to running out of water) before resuming. This column offered similar results, although the Mg yielded higher As levels (up to 20 ppb) during the first 22,000 BVs. These runs indicated that the iron solubilization significantly improved performance, but the proper rate and extent to which the iron corroded was an important factor (See below).

### **Arsenic Distribution**

To discern how the arsenic was removed in the columns that operated with galvanized steel fittings, we conducted digestion of all the possible arsenic adsorbents.

The authors conducted sequential leaching for a representative 0.75 grams of the activated carbon that had been used in the Citrate-Fe (1.07) column for 250,000 BVs (i.e. the activated carbon from Figure 1.2). These results were combined with results from the digestion of the tubing and glass wool for the column. The total As accounted for, per Table 1.1, summed to 19.3 mg of As. Yet further iron and arsenic had accumulated on the first two plugs of glass wool, which had been changed out twice. In comparison, the total As removed, as calculated from the difference between the influent and effluent was 29.1 mg. When comparing the values, one surmises that 8.3 mg (29%) of all removed arsenic was adsorbed by the carbon bed, 3% by the effluent tubing, and 5% by the fittings. The glass wool that was analyzed had removed 29% of the arsenic. This left about a third of the removed arsenic that would have been adsorbed with the iron deposits that had accumulated on the first two plugs of influent glass wool — the influent glass wool had been changed-out twice during the 250,000 BVs of operation.

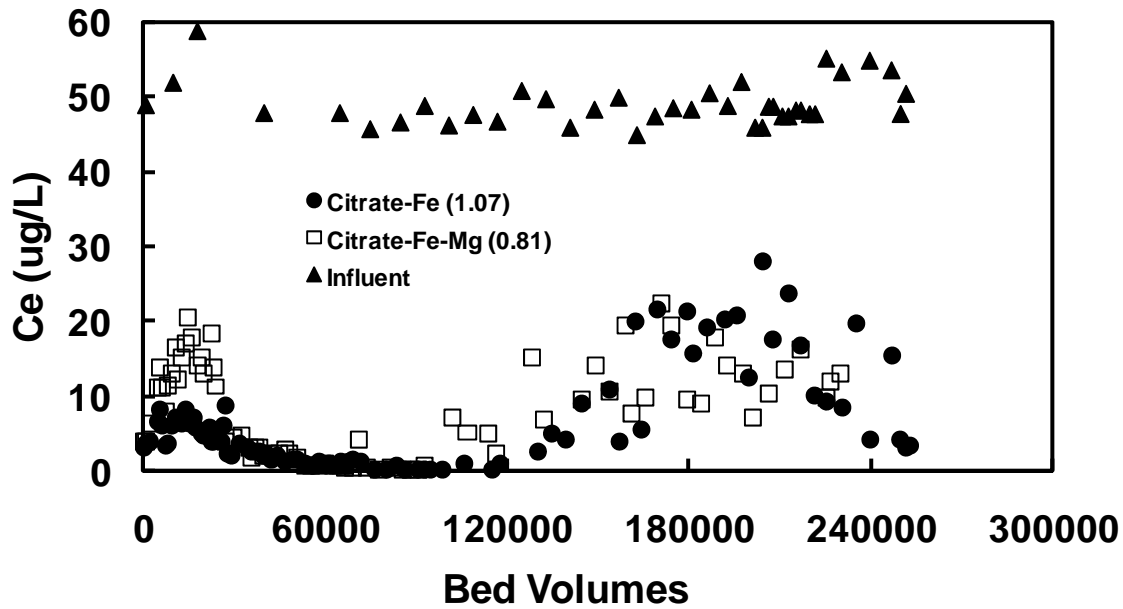


Figure 1.2 RSSCT results for citrate-Fe preloaded GAC augmented with soluble iron

Table 1.1

Arsenic distribution in *citrate-Fe (1.07)* after 250,000 BVs

Adsorbents	Fe ( $\mu\text{g}$ )	As ( $\mu\text{g}$ )	As/Fe (mg/g)	As/Fe (mole/mole)
Effluent tubing	26,200	760	29	0.022
Bottom (Entry) Glass wool (third plug)	82,400	8,380	100	0.076
Top (Exit) Glass wool (third plug)	1,480	230	159	0.12
HCl washed rust from Galvanized steel fittings	--	1,600	--	--
0.75 g carbon*	40,730	3,724	91	0.068
normalized to 1.67 g carbon	90,692	8292	91	0.068
Total (with 1.67 g carbon)	200,772	19,262	96	0.072

\*A representative 0.75 g activated carbon was evaluated, out of 1.67 g loaded activated carbon present at the start of this RSSCT run.

For the research herein, the authors have conducted considerable experimentation so as to better understand this proper rate. The concepts of this fittings / tailored GAC have offered integral impetus to our subsequent experiments with zero-valent iron that is coupled with iron-tailored activated carbon.

## RESEARCH OBJECTIVES

Our goal has been to develop innovative arsenic removal technologies that are suitable for very small water systems; and these must be able to reduce energy costs, minimize operating costs, and cut down quantities of waste. We propose that these goals can be achieved by tailoring activated carbon with iron through activated carbon surface modification. Indeed, we anticipate that the operation of this tailored GAC system will cost no more than it costs to pump water out of the ground.

The specific objectives have included:

1. Devise a new, cost-effective, and innovative treatment technology for removing arsenic from drinking water down to 10 ppb or less. Provide a durable approach suitable for very small systems that incur low capital, operational, and energy costs; while requiring only simple operations, and minimal monitoring.
2. Tailor the bed to maximally operate at neutral (unaltered) pH while processing primarily As(V) (i.e. oxidized) water.
3. Develop the most favorable means of preloading GAC with iron, so as to greatly extend their arsenic adsorption capacity and bed life.
4. Avoid the abrasion losses and non-durability of conventional granular iron or coated activated alumina processes by adsorbing iron within an activated carbon structure that is rigid and robust.
5. Enhance the iron solubilization so as to render a robustness that is adaptable to a wide array of water compositions.

## CHAPTER 2 MATERIALS AND METHODS

### MATERIALS

All chemicals were reagent grade. Iron chemicals were from Fisher Scientific Company. Arsenic solutions were made from  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  for arsenate and  $\text{As}_2\text{O}_3$  for arsenite. Both are from Alfa Aesar. Citric acid, palmitic acid, oxalic acid and EDTA were from J.T.Baker Company.

Zero-valent iron (ZVI) was from Edmund Scientific Co. (New York) with particle size US mesh #50 (300  $\mu\text{m}$ ) and those with US mesh #10–20 (2,000–850  $\mu\text{m}$ ) were from Sigma-Aldrich. Quartz sand was from EMD Chemical Inc. with particle size US mesh #50 (300  $\mu\text{m}$ ).

Carbons used included Ultracarb from Siemens Water Technologies (formerly US Filter) (Bituminous coal carbon), SAI carbon (bituminous) was from Superior Adsorbents Inc., SuperDarco carbon (lignite) from NORIT Americas and three wood-based carbons: NORIT C-Grain (from NORIT), Nuchar (from Westvaco) and PICASOL carbon (from PICA). Superdarco is a mesoporous carbon developed at Penn State (Nowack et al. 2004, Rangel-Mendez et al. 2005) with surface area 797  $\text{m}^2/\text{g}$ , micropore (<20 Å) volume about 0.2 mL/g carbon and mesopore volume (20–500 Å) about 0.3 mL/g carbon while Ultracarb has a surface area 723  $\text{m}^2/\text{g}$ , micropore volume 0.3 mL/g and mesopore volume 0.1 mL/g. The PICA carbon had a surface area of 1462  $\text{m}^2/\text{g}$  and micropore volume 0.4 mL/g. These virgin granular activated carbons were crushed and sieved to the US mesh #200  $\times$  400 size before they were loaded with iron.

The ground water tested originated from the well of the Cool Sandy Beach Community Water System of Rutland, MA (named Rutland water hereafter). The total Arsenic in this groundwater varied from 40 to 60 ppb. Characteristics of the groundwater have been presented in table 2.1.

**Table 2.1**  
**Characteristics of Rutland groundwater (unit: mg/L unless specified)**

pH	As* ( $\mu\text{g}/\text{L}$ )	Fe ( $\mu\text{g}/\text{L}$ )	Hardness (as $\text{CaCO}_3$ )	TOC	Na	Mg	Chloride	Sulfate	Silica as $\text{SiO}_2$	Ca	Turbidity (NTU)
7.6–8.0	40–60	3	70.3	0.85	27.5	11.3	9.32	26.4	12.5	59.0	0.08

\* 70–75% As(V) and 25–30% As(III) per molybdate blue method of Murphy and Riley (1962)

### METHODS

#### Iron Loading by Organic Carboxylic Acid

Palmitic acid, citric acid, oxalic acid, and ethylenediamine tetra-acetic acid (EDTA) were employed as chelating agents to load iron onto GAC. In these tests, 2 g of carbon was added to 1 L of organic acid-iron solution (molar ratio 1:1). Organic acid concentration ranged from  $10^{-4}$  to

$10^{-1}$  M. The mixture was then shaken on a horizontal shaker table at 150 rpm for 24 hours to make sure equilibrium was reached. The adsorbent was filtered out and washed thoroughly with distilled water. The tailored carbon was dried in a drying oven (utility oven model 1305 U from VWR Scientific) at  $105^{\circ}\text{C}$  overnight and stored in a desiccator for use. The organic acid-iron loaded carbons have been designated as organic acid-Fe combination that was used.

### **Carbon Oxidation Plus Iron Loading.**

Three oxidation protocols were tested:

*Protocol 1: Oxidation by nitric acid:* 2 g of carbon (US mesh 200  $\times$ 400) was mixed (by a magnetic stirrer at speed 30 rpm) with 100 mL of 70% nitric acid for 1 h at room temperature. All the following mixings were conducted the same way.

*Protocol 2: Oxidation by nitric acid/sulfuric acid mixture:* 2 g of carbon (US mesh 200  $\times$ 400) was mixed with 100 mL of acid mixture (50 mL of each concentrated acid) for 1 hour at room temperature.

*Protocol 3: Oxidation by nitric acid, acetic anhydride and potassium permanganate:* 3 g of carbon (US mesh 200 $\times$ 400) was first mixed with 2.1 g of potassium permanganate and then added to a solution of 15 mL of 70% nitric acid and 20 mL of concentrated acetic anhydride. The whole mixture was then stirred for an hour at room temperature.

Oxidized carbons were thoroughly washed by distilled water to remove acid adsorbed before iron loading in 1 L of  $10^{-2}$  M iron solution made from ferric or ferrous chloride. The pH under this iron loading condition remained at 2.0–3.2. The carbon was then filtered, washed with distilled-deionized water and dried in a drying oven at  $105^{\circ}\text{C}$  for further use. Thus obtained carbon was designated as *oxidized carbon-Fe*.

Boehm titrations (Boehm 1964) were carried out to monitor the acidic surface functional groups of the oxidized carbons. Details of Boehm titrations as adapted for these carbons could be found in Chen et al. (2005).

### **Iron-impregnation by Precipitation**

Carbon used for iron impregnation included Ultracarb, Superdarco and SAI carbon. Impregnation by precipitation into activated carbon was conducted in a similar manner to that employed by Thirunavukkarasu et al. (2003) for precipitating iron on silica sand. Two grams of carbon was added to 8 mL of 2 M  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  solution, and 0.1 mL 10 M sodium hydroxide was added to increase the pH to 4–5 and create an iron precipitate. The mixture was heated at  $105^{\circ}\text{C}$  overnight. Upon cooling, the activated carbon was observed to be covered with a thick layer of orange-colored iron oxide. The GAC had to be separated mechanically with a glass rod to separate the grains, and it was then sieved through a US mesh #400 sieve. To remove the external iron fines and carbon fines, the coated activated carbon was then washed thoroughly with deionized-distilled water till the orange-colored solids were washed away. The sample was designated as *Precipitation Ultracarb* or *Precipitation Superdarco*. The *Precipitation SAI* was used only with sieving without washing and was name *Coating SAI* herein.

## Iron-impregnation by Iron-salt Evaporation

This method is adopted from the method proposed by Vaishya and Gupta (2003) for iron-impregnated sand. To achieve an iron oxide impregnation on activated carbon, 2 g of carbon was added to 200 mL solution with 2 g of  $\text{Fe}(\text{NO})_3 \cdot 9\text{H}_2\text{O}$ . The mixture was heated at  $100^\circ\text{C}$  until dry, cooled at room temperature and washed with distilled water, dried and sieved. This protocol excluded the NaOH pH adjustment and thus the authors observed no iron precipitation at the resultant pH of 1.8–2.5 before the drying step. Thus obtained carbon was designated as *evaporation Ultracarb* or *Evaporation Superdarco*.

## Rapid Small Scale Column Tests (RSSCTs)

RSSCTs were conducted to evaluate the GAC's arsenic adsorption capacity in the lab and these were designed to simulate the adsorption conditions that would occur in a full-scale bed. The tests were conducted with GACs of grain size US mesh #200×400 (75–38  $\mu\text{m}$ ) and empty bed contact time (EBCT) of 0.53 min which with proportional diffusivity (Crittenden et al. 1986) would simulate full-scale operation that employs a grain size US mesh #12×40 (1,700–425  $\mu\text{m}$ ) with EBCT of 10 min or EBCT of 5.4 min with US mesh #20×50 (850–300  $\mu\text{m}$ ). The columns used were 15 cm long and 0.5 cm in diameter. Each column test held about 1.67 g carbon.

For activated carbon and zero-valent iron column tests, three iron-preloaded GACs were tested in couple with ZVI. For *citric acid-Fe* and *oxidized Ultracarb-Fe* columns, 10–20% by volume of ZVI (corresponding to 0.8–1.6g, US mesh #50) was thoroughly mixed with 1.0–1.35 g (80–90% by volume) activated carbon thoroughly before installing these together into a RSSCT column. For *evaporation Ultracarb*, 10–35% by volume of ZVI (0.8–2.8 g, US mesh #10–20) was thoroughly mixed with about 0.6–1.4 g (65–90% by volume) iron tailored activated carbon before installing these together into an RSSCT. When installing the mixture, attention was paid to make sure that ZVI particles were evenly distributed throughout the GAC column. Sand filter used the same column as RSSCT (15 cm long and 0.5 cm in diameter) each holding 4 g of quartz sand (US mesh #50).

Per the nomenclature herein, the RSSCT breakthrough bed volume has been identified as the bed volumes of water that have passed through the column when the effluent As concentration reached 10 ppb. All RSSCTs were carried out at room temperature  $20\text{--}23^\circ\text{C}$  and at native groundwater pH 7.6–8.0 unless specified. And RSSCT systems were set up to run in an upflow stream.

## Adsorption Kinetics

In kinetics tests, 0.1 g of iron-loaded carbon was added to 8 syringes that each contained 100 mL of Rutland water that had been spiked to 1 mg/L of arsenic As(V) or As(III). The syringes were put on an end-over-end shaker at room temperature. One syringe was taken off the shaker and water filtered through 0.45- $\mu\text{m}$  filter paper at 0.5, 1, 2, 4, 6, 12 and 24 hours. Filtrate was analyzed for arsenic.

## Adsorption Isotherm

Adsorption isotherm tests were conducted using the bottle-point method. 100 mL of deionized-distilled water that was spiked to 20–22 mg/L of arsenate ( $\text{Na}_2\text{HAsO}_4$ ) or arsenite ( $\text{As}_2\text{O}_3$ ) as As was added to glass bottles containing 0.01–2 g of *evaporation Ultracarb*. The bottles were sealed and put on a shaker for 24 h at 20°C. After that, the mixture was filtered through 0.45  $\mu\text{m}$  glass fiber filters to separate the carbon particles, and the filtrate was analyzed for arsenic. Adsorption tests were carried out at pH 6 and 8. Only *evaporation Ultracarb* was evaluated for adsorption isotherm since it had the best performance in RSSCT for arsenic removal.

The most common equations for single-solution adsorption are the Freundlich and Langmuir equations.

The Freundlich has the form:

$$q_e = KC_e^{1/n} \quad (2-1)$$

It can be linearized to:

$$\log q_e = \log K + 1/n \log C_e \quad (2-2)$$

where  $q_e$ : mass adsorbate/mass adsorbent

$C_e$ : mass /volume

K, 1/n: constants

K in Freundlich equation is the capacity of the adsorbent for the adsorbate, and 1/n is a function of the strength of adsorption. The larger the value of K, the larger is the capacity when  $C_e=1$ . The smaller the value of 1/n, the stronger is the adsorption bond when  $C_e$  and K are fixed, i.e. less variable with  $C_e$ .

The Langmuir equation has the form:

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2-3)$$

where b and  $q_{\max}$  are constant and  $q_e$  and  $C_e$  are the same as in Freundlich equation. The  $q_{\max}$  corresponds to the surface concentration at monolayer coverage and is the maximum value of  $q_e$  that can be achieved as  $C_e$  increases. b is related to the energy of adsorption and increases as the strength of the adsorption bond increases. The Langmuir equation assumes that: (1) only monolayer adsorption can occur; (2) adsorption is localized, with no adsorbate-adsorbate interactions, (3) the heat of adsorption is independent of surface coverage and (4) the adsorbent has a homogeneous surface. Characteristics that affect isotherms include adsorbent surface area, pore size distribution, and surface chemistry.

## Chemical Analysis

Arsenic analysis was conducted via a Shimadzu atomic absorption spectrophotometer-hydride vapor generation system (AAS-HVG), in accordance with water and wastewater standard method 206.3 or via inductively coupled plasma–mass spectrophotometry (ICP–MS) per EPA method 6020. To test the iron loading amount on tailored GAC, about 0.5 g of GAC

was ashed at 600°C and then acid digested with 25 mL of concentrated HCl. The digestion solutions were analyzed for iron by a Shimadzu Atomic Absorption spectrophotometer (AA-6601F) unit with flame atomization.

When operating column tests that employed zero-valent iron, the water samples were acidified (2 mL of concentrated HCl to 16 mL of sample) overnight before analysis for iron or arsenic. Thus, the observed iron and arsenic concentrations represented both the dissolved plus particulate fractions.

TOC was monitored by a Shimadzu TOC 5000A unit equipped with an ASI 5000A autosampler. The furnace temperature was set at 679°C and high selectivity TC catalyst was used in the combustion tube. Silica was analyzed using a molybdosilicate method according to water and wastewater standard methods 4500. pH was monitored by an Accumet model 10 pH meter from Fisher Scientific.



## CHAPTER 3 RESULTS AND DISCUSSION

### ARSENIC REMOVAL BY ORGANIC ACID-FE TAILORED GAC

Iron was preloaded with four carboxylic acids onto Ultracarb GAC, and the protocol yielded iron loadings of 0.5–1.33% as listed in Table 3.1. Arsenic breakthrough behaviors for virgin carbon and tailored carbons were explored with RSSCT, and results are illustrated in Figures 3.1 (at pH 7.6–8.0) and 3.2 (at pH 6.0). The bed volumes to 10 ppb breakthrough are also listed in Table 3.1.

**Table 3.1**  
**Iron loading by organic acid**

Tailored carbon	Iron content (%)	Bed volume to 10 ppb breakthrough (at pH6.0)	Bed volume to 10 ppb breakthrough (at pH 7.6–8.0)	mg As/g Fe at 10 ppb breakthrough (at pH 7.6–8.0)
Citric acid-Fe	1.26	7,440	6,250	61
Oxalic acid-Fe	0.58	-	5,650	81
Palmitic acid-Fe	0.59	-	5,700	110
EDTA-Fe	1.33	8,250	7,030	58

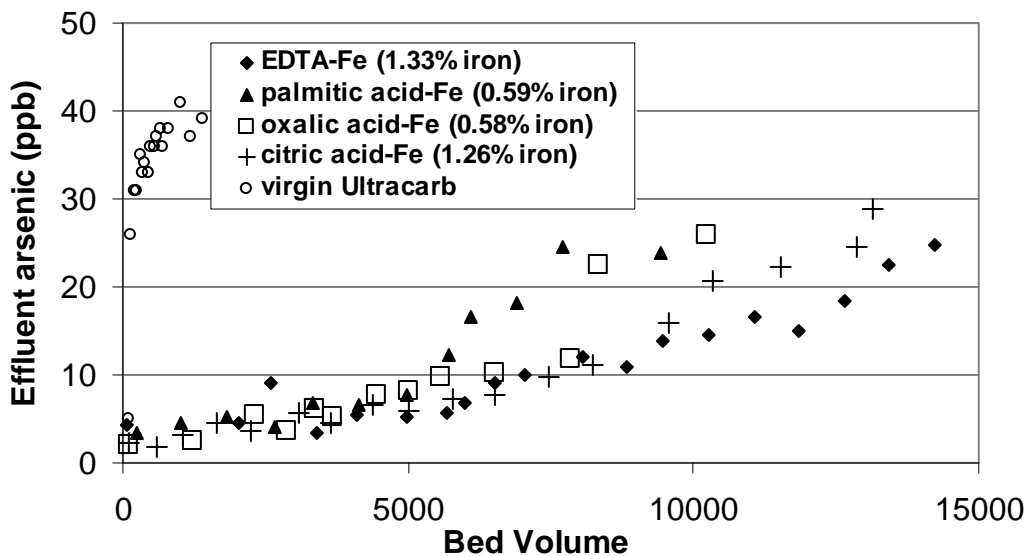
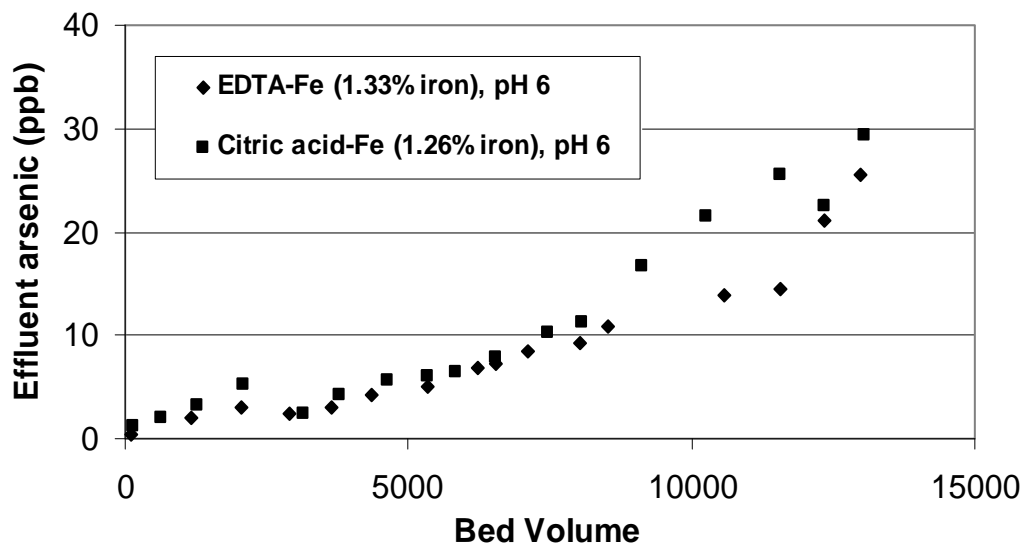


Figure 3.1 RSSCT results for organic acid-Fe preloaded GAC at pH 7.6–8.0. Percentages depict the % iron pre-loading.



**Figure 3.2 RSSCT results for EDTA–Fe and citric acid–Fe preloaded GAC at pH 6**

The RSSCT breakthrough curves revealed that organic acid-Fe preloaded carbons could be fairly effective for arsenic removal. In general, arsenic breakthrough to 10 ppb occurred at 5,000–8,200 BVs for these organic acid-Fe variants at pH 6.0 or pH 7.6–8.0. The EDTA-Fe loaded GAC performed slightly better than the others. The iron in the palmitic acid-Fe GAC performed the most efficiently with the highest amount of As (0.11g ) adsorbed on 1 gram of iron thus one out of every 12.2 iron atoms adsorbed an arsenic atom, and this represents a high fraction. In contrast, when a virgin Ultracarb (iron content 0.15%) was employed without iron preloading, arsenic breakthrough occurred almost immediately as shown in Figure 3.1.

As pH decreased from the native 7.6–8.0 down to 6.0, there was an increase of about 10–20% on the bed volumes to 10 ppb breakthrough for citric acid-Fe loaded carbon and EDTA-Fe carbon (see Figure 3.2 and Table 3.1). This is attributed to the arsenic speciation at various pH values and surface chemistry of activated carbon. At the pHs tested by the column tests, As(III) species will mostly exist as  $\text{H}_3\text{AsO}_3^0$  ( $\text{pK}_{\text{a}1}=9.23$ ). For arsenate, the dominant species is  $\text{H}_2\text{AsO}_4^-$  at pH 6 and  $\text{HAsO}_4^{2-}$  at pH around 8. With increasing pH, the net surface charge of the iron-loaded activated carbon becomes less positive. The more negative surface at high pH produces a higher repulsive electrostatic force between  $\text{H}_2\text{AsO}_4^-$  or  $\text{HAsO}_4^{2-}$  and the adsorbent.

TOC monitoring indicated that there was no apparent leaching out of organic acid during operation. TOC in the effluent stayed at lower than 0.5 mg/L during all the column tests.

### **CARBON OXIDATION FOLLOWED BY IRON LOADING**

Carbons were oxidized chemically and then loaded with iron. These iron-loaded carbons then were appraised for arsenic removal via RSSCT's that employed Rutland groundwater. Table 3.2 shows the results of iron loading for these oxidized carbons and their bed volumes to breakthrough in RSSCT. Carbon oxidation was generally quite effective for iron loading. Nitric acid/sulfuric acid oxidation achieved more iron loading than did oxidation by nitric acid alone. Moreover, oxidized wood-based carbons showed better iron loading than oxidized bituminous Ultracarb. This is explained by noting that the wood-based carbons had higher micropore volume,

higher surface area. The wood-based GAC contained more edge sites that were vulnerable to oxidation, as discussed below.

The highest iron loading following oxidation occurred after the wood-based NORIT C-Gran carbon had been exposed to nitric acid/sulfuric acid and this loading reached 15.40%. The authors noted that when the wood-based carbons experienced oxidation, they suffered too high a mass loss after this intense acid oxidation, and they also collapsed under the pressure of RSSCT experiments. With this in mind, the authors focused subsequent oxidation trials on the bituminous-based Ultracarb. However, Ultracarb after the nitric acid/sulfuric acid oxidation only accrued 2.2% iron loading. In contrast, the Ultracarb could withstand yet greater oxidation intensity, incurred by combining nitric acid, acetic anhydride and potassium permanganate and this protocol (3) yielded 7.6–8.0% iron loading, regardless of whether iron(II) or iron(III) was used. The authors surmise that when protocol 3 oxidation was performed on the Ultracarb, either iron(III) or iron(II) in dissolved form could “walk” (some may call this surface diffusion) along the abundant functional groups so as to enter the recessed GAC pores. This was also true for the wood-based carbons that received any oxidation. However, for the Ultracarb GAC that received oxidation by protocol 1 or 2, less functionality caused a higher fraction of the iron to precipitate before it entered the pores (see RSSCT discussion below).

**Table 3.2**  
**Iron loading by oxidized carbons**

Carbon	Carbon type	Preparation protocol*	Iron loading via FeCl <sub>3</sub> or FeCl <sub>2</sub> ** (%)	Bed volume to 10 ppb breakthrough at pH 7.6–8.0	mg As/g Fe
Ultracarb	bituminous	1-oxidation	2.28	-	-
Ultracarb	bituminous	2-oxidation	2.23	-	-
Ultracarb	bituminous	2-oxidation	4.51**	-	-
Ultracarb	bituminous	3-oxidation	7.99**	12,090	33
Ultracarbon	bituminous	3-oxidation	7.60	11,700	24
NORITC-Gran	wood	1-oxidation	6.52	-	-
NORITC-Gran	wood	2-oxidation	15.40	5600	16
Nuchar	wood	1-oxidation	3.78	-	-
Nuchar	wood	2-oxidation	7.40	6800	19
PICA	wood	1-oxidation	5.63	-	-
PICA	wood	2-oxidation	9.13	10300	21
PICA	wood	2-oxidation	9.21**	-	-

\* 1-oxidation: with concentrated nitric acid

2-oxidation: with 1:1 concentration nitric acid and sulfuric acid

3-oxidation: with nitric acid, acetic anhydride and potassium permanganate

\*\* iron loading by ferrous chloride

Acidic surface functional group contents as discerned by Boehm titrations (Boehm 1964) have been shown in Table 3.3. The oxidation process greatly increased the oxygen-containing groups on the carbon surfaces. The stronger the oxidation, the higher the oxygen-containing groups and the higher the iron loading for the same carbon. Overall, wood-based carbon was more readily oxidized than did bituminous carbon for a given oxidation protocol. Oxidation by nitric acid, acetic anhydride and potassium permanganate created the highest number of oxygen-

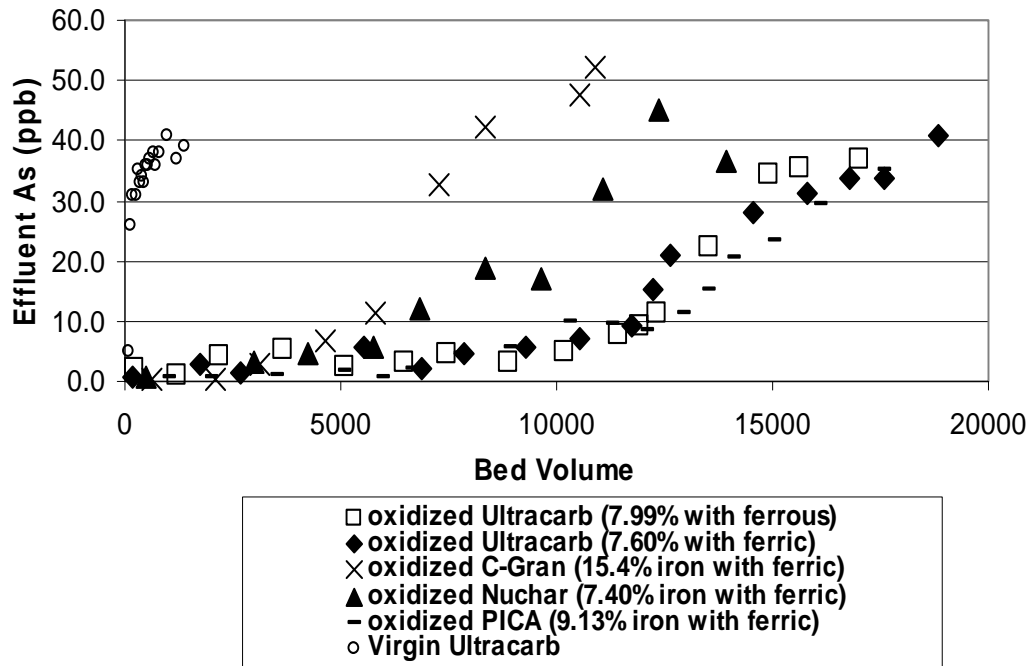
containing surface groups (1.95 mmol/g) and the highest iron loading (7.60%) for bituminous Ultracarb. Intriguingly, for the bituminous carbons, the millimoles of iron loading from Fe(II) corresponded to the millimoles of carboxylic groups, and the millimoles of Fe(II) loading on oxidized PICA carbon corresponded to the millimoles of all functional groups (Table 3.3); this indicated that the Fe(II) complexed to the functional groups on the carbon surface.

**Table 3.3**  
**Oxygen-containing surface functional groups by Boehm titration**

Carbon	Preparation protocol	Carboxylic (mmol/g)	Phenolic (mmol/g)	Lactone (mmol/g)	Total (mmol/g)	Fe(II) loading (mmol/g)
Ultracarb (bituminous)	none	0.35±0.04	0.15±0.05	0.20±0.04	0.71±0.13	-
Ultracarb	1-oxidation	0.60±0.03	0.20±0.01	0.17±0.03	0.97±0.07	-
Ultracarb	2-oxidation	0.78±0.06	0.29±0.03	0.18±0.05	1.25±0.14	0.81
Ultracarb	3-oxidation	1.39±0.08	0.31±0.03	0.25±0.05	1.95±0.16	1.43
PICA (wood-based)	none	0.58±0.05	0.25±0.04	0.26±0.04	1.09±0.13	-
PICA	2-oxidation	1.02±0.10	0.42±0.04	0.25±0.02	1.69±0.16	1.64

Based on the iron loading results alone, either wood-based carbon oxidation or Ultracarb oxidized by protocol 3 was promising for arsenic removal. Rapid small-scale column tests were carried out with oxidized and then iron-loaded NORIT C-Gran, Nuchar, PICA (all by protocol 2) and Ultracarb (by protocol 3) carbons since those carbon had relatively high iron loading (7.4–15%). Figure 3.3 is the RSSCT results for arsenic removal by those carbons. Figure 3.3 shows that oxidized PICA (by nitric acid/sulfuric acid, or protocol 2) and two Ultracarb (by nitric acid, acetic anhydride and potassium permanganate, or protocol 3) carbons showed the highest capacity for arsenic removal. The number of bed volumes to 10 ppb breakthrough was around 12,000–13,000 for oxidized Ultracarb (protocol 3) and PICA (protocol 2).

The relatively poor performance by NORIT C-Gran or Nuchar carbons (about 6,000 BVs) was attributed to the compression of the oxidation-weakened carbon during column tests by the high pressure build-up. Both intra-granular and extra-granular porosity was lost as the column depth compressed by about 30%, and the compression also caused short-circuiting of water. Carbon with higher attrition resistance, such as Ultracarb and possibly PICA carbons would be recommended for practical applications of this oxidation protocol.



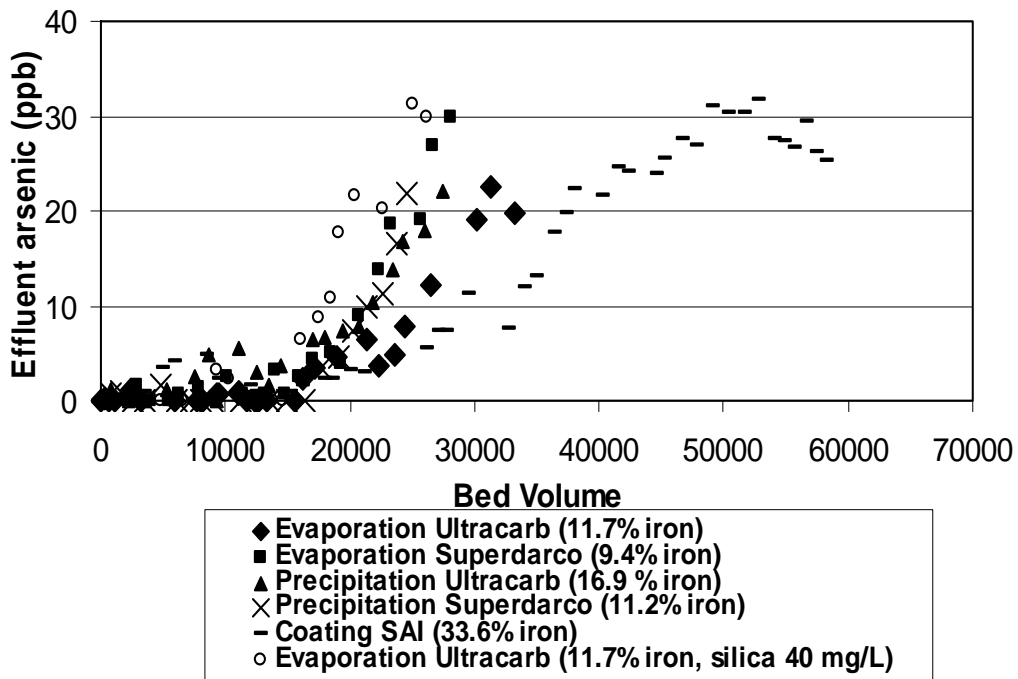
**Figure 3.3 RSSCT results for oxidized and iron-loaded carbons at original Rutland water (40–60 ppb of As) with pH 7.6–8.0**

### IRON-IMPREGNATED CARBON

Iron content and bed volumes to breakthrough for carbons impregnated with iron via precipitation and evaporation are shown in Table 3.4. Iron-content results indicate that iron oxide impregnation via either evaporation or precipitation greatly increased the iron content of activated carbon to 9.4–16.9%. The iron oxide impregnated GAC exhibited very good RSSCT performance (Figure 3.4) with 10 ppb breakthrough occurring at 20,000–25,000 BVs. *Coating SAI* obtained the highest amount of iron and bed volume to breakthrough. Although the iron content of *coating SAI* was almost 3 times higher than the *evaporation Ultracarb*, the bed volume to breakthrough was 36% more. The problem with *coating SAI* was that the external iron was mainly deposited onto the surface by precipitation and it was easily peeled off during use thus making its iron content unstable.

**Table 3.4**  
**Iron loading by impregnation**

Tailored carbon	Iron content (%)	Bed volume to 10 ppb breakthrough	mg As/g Fe at breakthrough
Evaporation Ultracarb	11.7	25,000	24
Precipitation Ultracarb	16.9	22,000	22
Evaporation Superdarco	9.4	20,500	20
Precipitation Superdarco	11.2	21,000	18
Coating SAI	33.6	34,000	11



**Figure 3.4** RSSCT results for iron-impregnated carbons at original Rutland water at pH 7.6–8.0 (silica: 12 mg/L as SiO<sub>2</sub> unless specified)

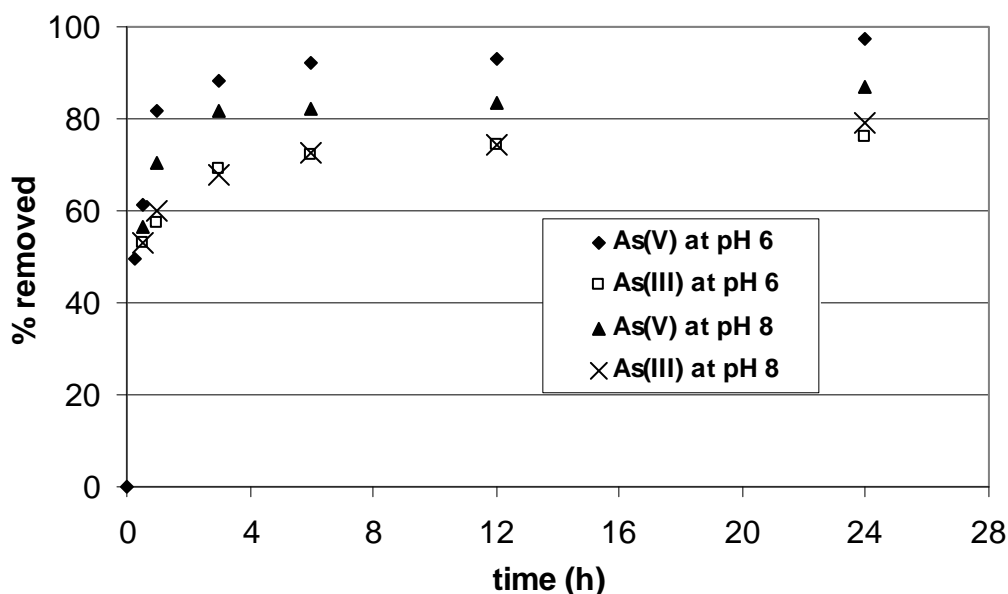
RSSCT results of the oxidized carbons and iron-impregnated carbons showed that bed volume to breakthrough was not always proportional to the iron-content of carbons, and the iron efficiency for removing arsenic ranged from 11 mg As/g Fe for *coating SAI* to 33 mg As/g Fe for oxidized Ultracarb. This highlights that the accessibility of the preloaded iron was also important for arsenic removal. For carbons with higher iron content such as iron-impregnated carbon, some of the iron may have been located within micropores of carbon that could be out of reach for arsenic. It appears that a higher portion of the iron on *coating SAI* was not available for arsenic. It is important to optimize the distribution of iron during the iron-tailoring process.

The Rutland water contained moderate concentration of silica (about 12 mg/L). To study the effect of anion competition with arsenic, an iron-impregnated carbon, *evaporation Ultracarb*, was tested with Rutland water that had been spiked to a silica concentration of about 40 mg/L at native pH 7.6–8.0. The RSSCT breakthrough with arsenic has also been shown for this spiked water in Figure 3.4. The bed volume to 10 ppb breakthrough dropped to about 17,000 bed volume with the increased silica concentration compared to 25,000 bed volume with native silica.

The effluent silica concentration changed only slightly during column tests with native Rutland silica level and spiked silica level. In general, silica in effluent was 1 to 2 mg/L lower than the influent. The comparisons between native and spiked silica levels indicate that the adsorbed silica occupied sorption sites that would otherwise be available to arsenic.

## **KINETICS TESTS**

Figure 3.5 is the result of kinetic tests with arsenate and arsenite at an initial concentration 1 mg As/L. These tests employed 0.1 g of the *evaporation Ultracarb* (11.7% iron) in 100 mL of As-spiked Rutland water. More than 80% of As(V) was removed after 3 hours of contact at both pH 6 and 8 for As(V). At the concentration tested, more As(V) was adsorbed at pH 6 than at pH 8 after 24 hours, and As(V) shows more removal than As(III). Only 80% of As(III) was removed even after 24 hours of contact. For As(III), there is no significant difference in percentage of removal at pH 6 and 8.



**Figure 3.5 Kinetics of aeseinite and arsenate adsorption on *evaporation Ultracarb* at initial arsenic concentration of 1 mg/L**

Kinetic data from this study were fit to first-order, second-order and parabolic diffusion equations. The parabolic diffusion equation could best describe the kinetic results with  $R^2$  greater than 0.92 for both As(V) and As(III), and this infers that the reactions between arsenic and activated carbon were diffusion-controlled as shown in Table 3.5. For the parabolic diffusion equation, the effective diffusivity ( $D_{eff}$ ) was in the range of  $4.5-7.2 \times 10^{-9}$ . Our results are in general agreement with those of Raven et al. (1998) with arsenic adsorption onto ferrihydrite.

**Table 3.5**  
**Correlation coefficients ( $R^2$ ) determination for the kinetic study of**  
**arsenate and arsenite on iron-preloaded GAC**

Kinetic equation	Linear plot*	arsenate		arsenite	
		pH=6	pH=8	pH=6	pH=8
First order	$\ln[1-(As_t/As_\infty)]$ vs t	0.45	0.42	0.21	0.32
Second order	$1/[1-(As_t/As_\infty)]$ vs t	0.54	0.36	0.32	0.29
Parabolic diffusion	$(As_t/As_\infty)/t$ vs $t^{-0.5}$	0.92	0.94	0.95	0.92

\*  $As_t$ : As adsorbed at time t

$As_\infty$ : As adsorbed at equilibrium

t: reaction time

The higher removal rate of As(V) versus As(III) may be due to the easy formation of ferric arsenate with As(V) as compared to As(III), which is undissociated at near neutral pH, may be the reason (Joshi and Charudhuri, 1996).

## ADSORPTION ISOTHERM

Adsorption isotherm tests were carried out with the native Rutland water (pH 7.6–8.0) for the *evaporation Ultracarb* with 11.7% iron content (see Figure 3.6). This iron-preloaded carbon had performed the best in mini-column test. These isotherm tests employed Rutland water that had been spiked with 20–22 mg/L of arsenic. Based on kinetic tests, there was not much arsenic removal after 12 hours of contact time; and the authors herein used a 24-hour pseudo-equilibrium time, which was a sufficient time for the comparisons herein. The 24-hour sorption data have been correlated using both Langmuir and Freundlich models with adsorption constants as listed in Table 3.6. Based on correlation coefficients, the data fitted Langmuir model ( $R^2=0.94-0.96$ ) better than Freundlich ( $R^2=0.90-0.93$ ). As determined from the Langmuir equation, the maximum adsorption capacities ( $q_{\max}$ ) for arsenite and arsenate are 51.3 and 38.8 mg/g GAC respectively at pH 6 and this corresponds to an iron efficiency of 33–40 mg As/g Fe. This is similar to the iron efficiency that Dixit and Herring (2003) observed for freshly-made hydrous ferric oxide (33 mg As/g Fe) that was suspended in solution. Thus this evaporation protocol loaded iron into GAC in a manner that rendered it as efficient as HFO in removing arsenate.

The obtained iron efficiencies for iron-impregnated Ultracarb from this study compares favorably with that for iron oxide materials or iron-impregnated carbon or activated alumina (Huang and Fu 1984, Matis et al. 1999a, b). Moreover, an advantage of this iron-loaded GAC material described is that it could be used directly in a fixed-bed system.

For arsenate,  $q_{\max}$  at pH 8 is about 15% less than that at pH 6. In contrast, for arsenite there is no significant sorption difference between these two pHs (Figure 3.6 and Table 3.6). These distributions are attributed to the difference in speciation of arsenate and arsenite. Arsenite exists mostly as undissociated species at these two pHs while arsenate mostly exists as mono-ionic  $\text{H}_2\text{AsO}_4^-$  at pH 6 and as  $\text{HAsO}_4^{2-}$  at pH 8. According to Langmuir theory,  $q_{\max}$  is a direct measurement of uptake for As monolayer coverage of the available Fe.

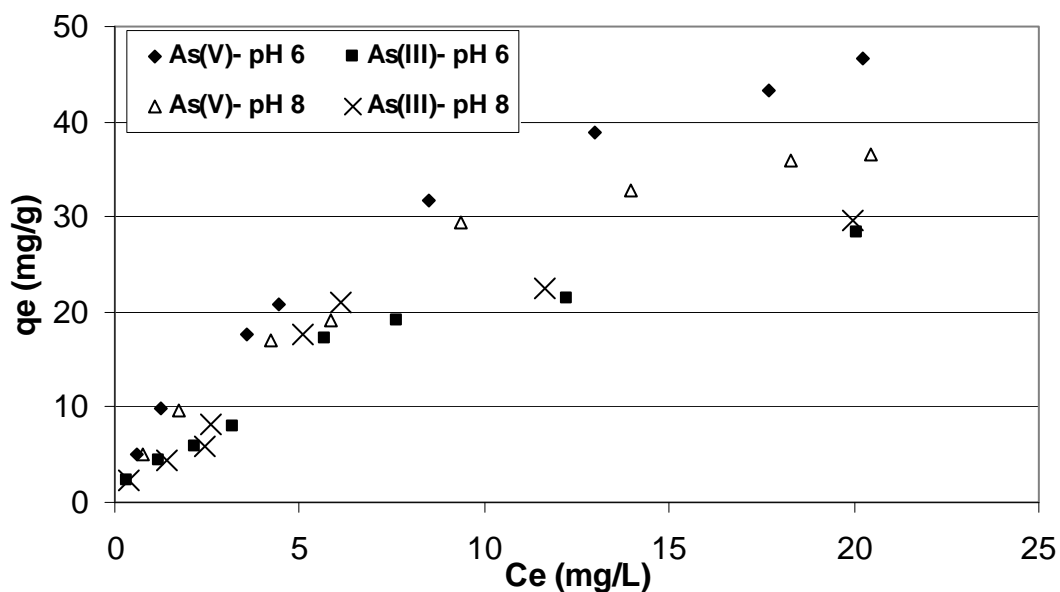


Figure 3.6 Adsorption isotherms for arsenite and arsenate by *evaporation Ultracarb* ( $C_0 = 20\text{--}22$  mg/L)

Table 3.6  
Adsorption constants of *evaporation Ultracarb* for arsenate and arsenite  
(As  $C_0=20\text{--}22$  mg/L)

pH	Species	Freundlich ( $q_e=kC_e^{1/n}$ )*		Langmuir ( $C_e/q_e=1/(Kq_{max})+C_e$ ( $1/q_{max}$ )*		Iron efficiency at $q_{max}$ (g Fe/g As) **
		$k$ ( $\frac{mg}{g}/(\frac{mg}{L})^{1/n}$ )	$1/n$	$b$	$q_{max}$ (mg/g)	
6.0	Arsenate	8.8	0.57	0.18	51.3	0.36
	Arsenite	3.8	0.71	0.27	38.8	0.33
8.0	Arsenate	7.5	0.55	0.15	43.6	0.40
	Arsenite	3.8	0.76	0.31	39.2	0.33

\* $q_e$  (mg/g): arsenic adsorption at equilibrium concentration  $C_e$

$C_e$  (mg/L): equilibrium arsenic concentration

$k$ ,  $1/n$ ,  $b$ ,  $q_{max}$ : adsorption constants

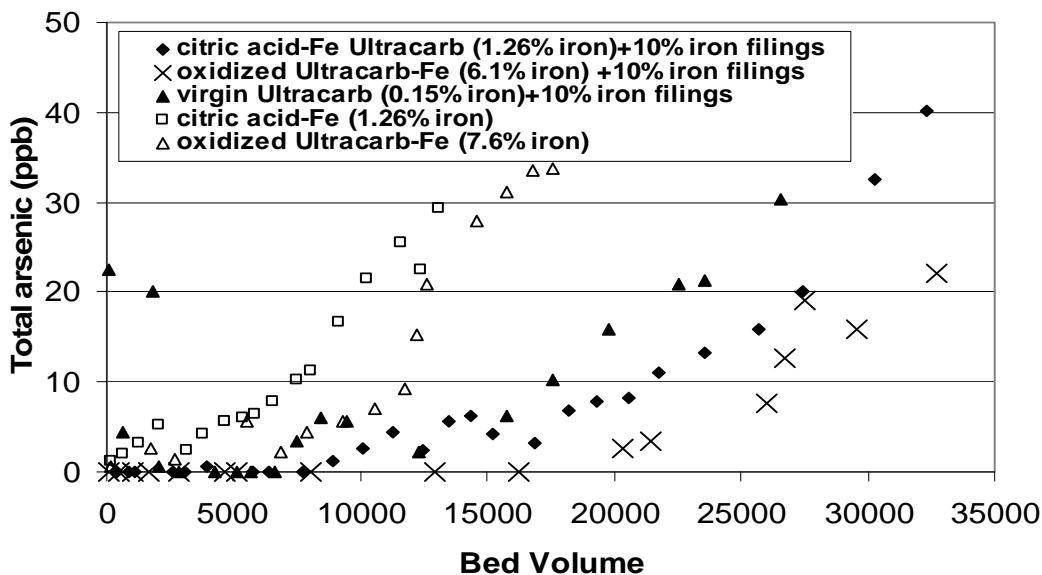
\*\*iron efficiency at  $q_{max}$  as determined at  $C_0=20\text{--}22$  mg/L

## ARSENIC REMOVAL BY TAILORED GAC MIXED WITH SOLUBLE IRON SOURCE

In previous research (Chapter 2) at Penn State, we have observed that when using galvanized iron fittings in concert with rapid small scale tests (RSSCT's), the continuous corrosion of iron from this fitting could greatly extend the bed volume to 10 ppb arsenic breakthrough of activated carbon to 150,000 bed volumes. Zero-valent iron has also been found to be very effective in arsenic removal by itself although ZVI corrosion alone can cause considerable plugging issues.

For the research herein, RSSCTs were carried out that mixed iron-tailored carbon with ZVI as a soluble iron source. ZVI was mixed with iron pre-loaded carbon and *virgin Ultracarb* for comparison. Iron pre-loaded carbons include *citric acid-Fe Ultracarb* (1.26% iron), an *oxidized Ultracarb-Fe* (6.1% iron) and evaporation Ultracarb (11.7% iron). Figure 3.7 is the RSSCT total arsenic breakthrough. Column tests showed that when the oxidized Ultracarb was preloaded to 6.1% iron, and then coupled with 10% (volume) ZVI, the combination could operate as long as 26,000 bed volumes before 10 ppb arsenic breakthrough occurred. As a further comparison, when 7.6% Fe had been preloaded onto GAC (Figure 3.3), and iron filings were excluded, 10 ppb As occurred at 12,000 BVs.

In contrast, when *virgin Ultracarb* was mixed with ZVI, there was arsenic breakthrough to 20 ppb during the first 2,000 BVs of operation after which arsenic concentration decreased to less than 10 ppb till final breakthrough at about 17,000 bed volume. This is attributed to the fact that *virgin Ultracarb* had very little adsorption capacity for arsenic, and it took about 2000 bed volumes for ZVI corrosion products to take effect in arsenic removal. These results highlight the importance of having an iron-preloaded carbon which can polish the water and remove the arsenic that the ZVI corrosion products do not remove. In addition, the 17,000 BVs for *virgin Ultracarb*/ZVI combo was mainly attributed to the effect of 10% ZVI due to the very limited adsorption capacity of the *virgin Ultracarb* itself. When considering the 12,000 BVs for a full bed of *oxidized Ultracarb-Fe* (6.1% iron), adjusted to 11,000 BVs when using 90% of this volume, and adding to the 17,000 BVs by the 10% ZVI, one might expect that this combination should be able to treat arsenic to below 10 ppb for 28,000 BVs, and indeed, this was about equal to the 26,000 BVs that were obtained. Similarly, *citric acid-Fe* (1.26% iron) preloaded GAC coupled with 10% iron filings removed As to less than 10 ppb for 21,000 BVs (Figure 3.7). With just *citric acid-Fe* (1.26% iron), As was removed to below 10 ppb for 6,200 BVs (or 5,600 BVs when filling 90% of the volume with GAC). If the 17,000 BVs for 10% iron filings with *virgin Ultracarb* was added to this, the sum would be 22,600 BVs and this was close to the 21,000 BVs that was in fact achieved. Thus, the performance of the mixed beds was nearly equal to the sums of the performances of the independent beds.



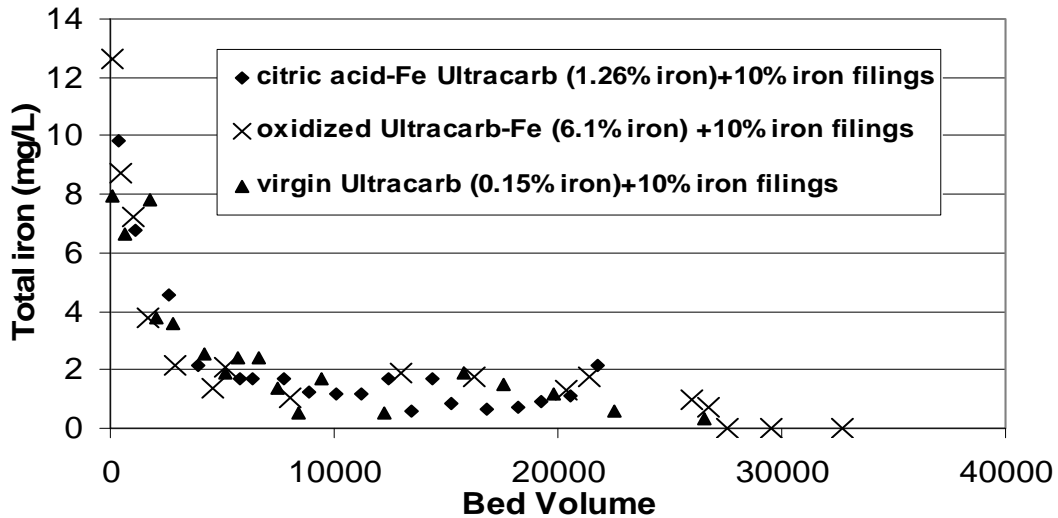
**Figure 3.7** RSSCT results for various activated carbons mixed with 10% zero-valen iron, operated at native pH of 7.6–8.0 (50–55 ppb of As in influent)

At the completion of the RSSCT, the 1.35 g of oxidized Ultracarb-Fe carbon plus 10% (volume) iron filings contained a total of 0.88 g of iron, and these together removed 3.6 mg of As by the time that 10 ppb As had broken through at 26,000 BVs. Thus the iron efficiency in this mixed bed was 4 mg As/g Fe. This is a considerably less favorable iron efficiency than with iron-tailored GAC media (58–100 mg As/g Fe as shown in Table 3.1). Nonetheless, the ZVI amendment improved the overall bed life for arsenic removal.

Figure 3.8 is the total iron (dissolved and particulate) concentration in the effluent. As a product of corrosion, ferric hydroxides are formed which build up layers on the iron and activated carbon surface. A portion of these hydroxides left the reactor as particles and produced a light yellow color in the effluent. In contrast, when employing iron-preloaded GAC's, the authors never visibly observed any iron exiting the RSSCT columns and the total iron concentration in the effluent remained at less than 0.1 mg/L. Total iron in the effluent for ZVI columns showed the same trend regardless of the nature of activated carbon. Iron concentration in the effluent dropped from 8–13 mg/L to less than 2 mg/L in about 7,000 bed volumes. After 20,000 bed volumes, a gradual decrease in rust production occurred, and effluent iron concentration dropped below 0.6 mg/L. For the virgin GAC–ZVI run, the drop in rust production corresponded to an increasing arsenic concentrations, as shown in Figure 3.7. Based on the data shown in Figure 3.8, about 0.4–0.6 g out of the initial 0.8 g iron leached out of the GAC bed by 30,000 bed volume. Moreover, by about 30,000 BVs, most of the metallic color and impervious texture of the ZVI had been transformed to a yellow or orange color and amorphous texture, indicative of rust.

Even with a relatively high total iron concentration in the effluent before 7,000 BVs, total arsenic concentration in the effluent for the acidified samples stayed below 10 ppb before final breakthrough for the *citric acid-Fe Ultracarb* and *oxidized Ultracarb-Fe GAC*. This means that As adsorbed mainly onto the iron-preloaded GAC and onto the ZVI corrosion products that was caught by activated carbon. Moreover, the high level of iron exiting the GAC bed indicated that

the ZVI was corroding at an unnecessary excessive rate, and the iron hydroxides that escaped the GAC had little further role in arsenic removal. Even so, with this configuration, iron hydroxides had to be removed for aesthetic reasons.



**Figure 3.8 Total iron concentration from zero-valent iron columns during RSSCTs**

To capture the iron corrosion products that escaped the activated carbon column, the authors placed sand filter (quartz sand, particle size US mesh #50) downstream of the GAC column. Figures 3.9 and 3.10 are the arsenic and iron concentrations, respectively, before and after the sand filter when the preceding mixed RSSCT column contained *oxidized Ultracarb-Fe* (6.1% iron) GAC and 10% zero-valent iron. Most of the dissolved and particulate iron from the zero-valent iron column's effluent was removed completely through the sand column. The iron concentration stayed below 0.3 mg/L throughout the operation as shown in Figure 3.10. No primary drinking water standards exist for iron while the secondary standard is 0.3 mg/L. The sand filter offered only scant arsenic removal as shown in Figure 3.9, and the As removal that did occur was attributed to the iron hydroxides that built up in the sand column.

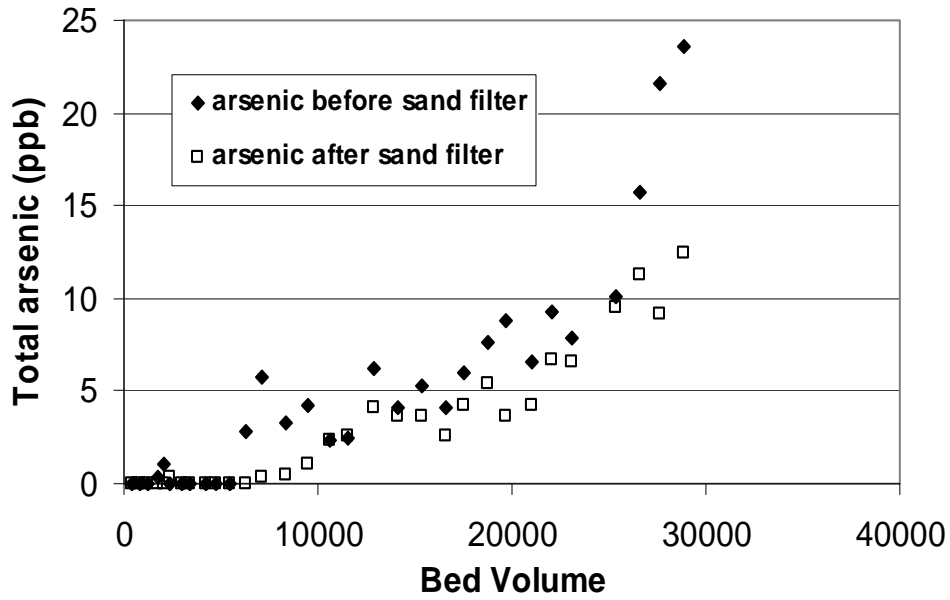


Figure 3.9 Total arsenic concentration before and after a sand filter that followed a bed of *oxidized Ultracarb-Fe* carbon (6.1% iron) mixed with 10% zero-valent iron at native pH of 7.6–8.0

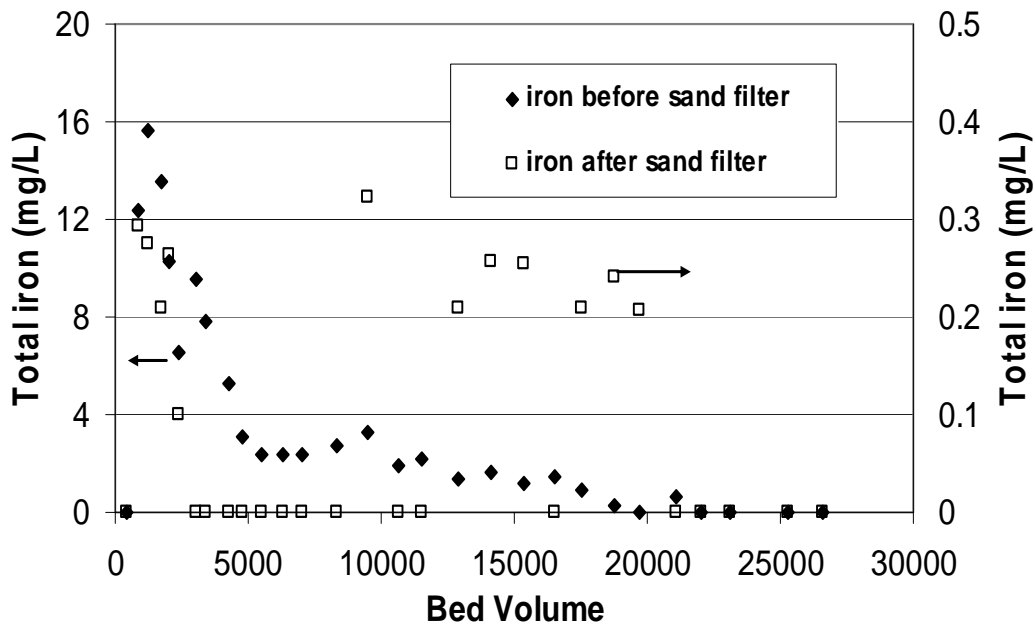
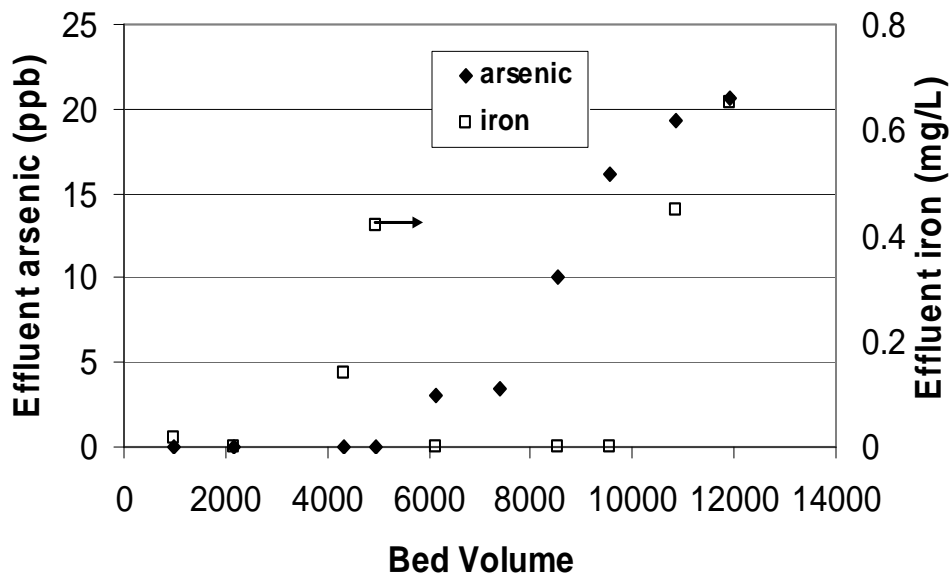


Figure 3.10 Total iron before and after a sand filter that followed a bed of *oxidized Ultracarb-Fe* carbon (6.1% iron) mixed with 10% zero-valent iron at native pH 7.6–8.0

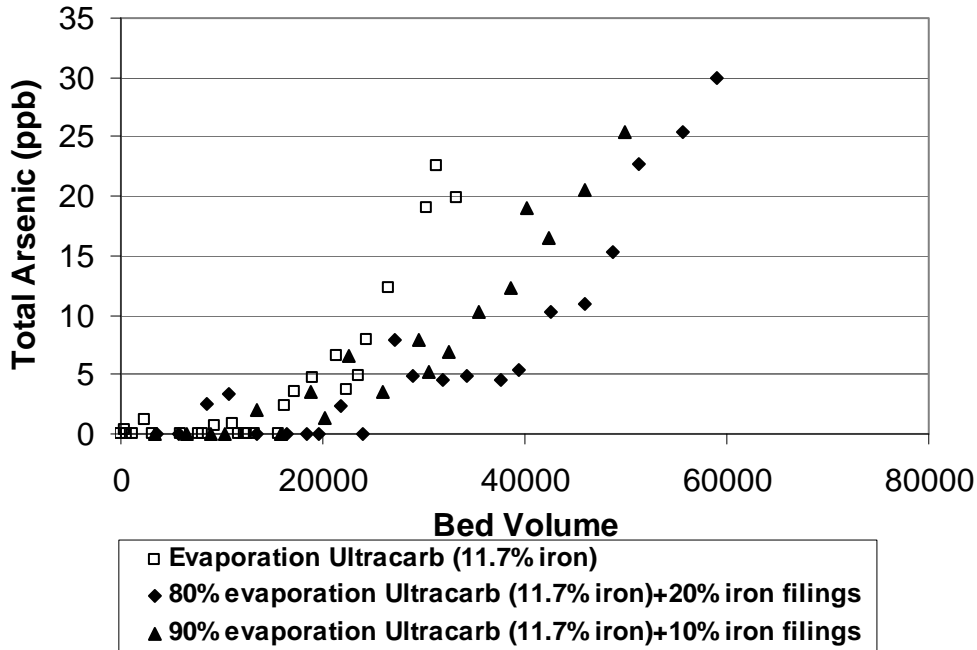
In order to appraise the value of activated carbon when coupling with ZVI, this couple was compared to a column packed with the same volume ratio of sand and ZVI (90% sand, 10% iron) in Figure 3.11. The arsenic breakthrough for the sand-ZVI couple occurred significantly faster than for the activated carbon/ZVI couple. The iron efficiency for arsenic removal in the sand-ZVI couple was 4 mg As/g Fe whereas the virgin GAC-ZVI couple achieved an iron efficiency of 12 mg As/g Fe. A batch study of this sand (data not shown herein) revealed that the quartz sand offered no sorption of arsenic. Thus, the arsenic removal with the sand-ZVI couple was completely due to the iron and its corrosion products that collected on the sand. Compared with the activated carbon-ZVI column (Figure 3.7), the sand column exhibited a very low iron level in its effluent. Iron was constantly less than 0.7 mg/L in effluent although there was clearly corrosion happening in the column.



**Figure 3.11 Effluent arsenic and iron concentrations of a column with sand and zero-valent iron layers only**

Based on the results achieved thus far from iron-preloaded GAC and solubilizable ZVI, it appeared that the bed life of GAC-ZVI column was highly dependent on the ZVI volume and the capacity of GAC. However, the volume of ZVI was limited by hydraulic plugging when authors coupled 20% of #50 mesh ZVI with GAC. The column with 20% ZVI was blocked by corrosion products after only 5000 bed volume of operation. This plugging issue disappeared when larger grained ZVI (US mesh #10–20, or 2,000–850  $\mu\text{m}$ ) was used. To test this, yet another iron-impregnated GAC was coupled with ZVI. This iron-impregnated GAC was *evaporation Ultracarb* (11.7% iron) and without the ZVI, this GAC offered 25,000 bed volumes. The columns were set up with 10%, 20% and 35% by volume of ZVI respectively. Figure 3.12 is the RSSCT results for the arsenic breakthrough of this *evaporation Ultracarb*-ZVI and *evaporation Ultracarb* columns. The results indicate that larger ZVI particle size could alleviate the problem of clogging and the column was able to run over 42,000 BVs before 10 ppb breakthrough with

20% of ZVI. In comparison, with a 10% ZVI and 90% GAC combination the bed life was 35,000 while 35% of ZVI had clogging after only 5,000 bed volume of operation (data not shown here). The result indicates that the right combination of GAC and zero-valent iron could further extend the bed volume. The authors do not know yet whether the RSSCTs offer a good prediction of what percentage ZVI can be included in full-scale GAC media without pressure loss. This is an issue yet to be addressed with forthcoming pilot studies.



**Figure 3.12** RSSCT results for 10% or 20% ZVI (US mesh #10–20) mixed with *evaporation Ultracarb* (11.7% iron) at native pH of 7.6–8.0 (40–60 ppb As in influent)

The iron concentrations in the effluent that exited the GAC-ZVI column have been shown in Figure 3.13. Iron concentration in the effluent with 20% ZVI was regularly higher than that from the column with 10% by volume of ZVI. Figure 3.14 is the corrosion rate of ZVI with US mesh # 50 and US mesh #10–20 calculated from the change of iron concentration in the effluent (Figure 3.13). The corrosion rate of ZVI with US mesh #50 was 0.005–0.0065 mg Fe/min which was more than 2 times higher than that of the larger size (#10–20) at 8,000 bed volume and this was because the smaller particle size had higher specific surface area and more corrosion sites. The corrosion rate dropped to around 0.001–0.002 mg Fe/min for #50 ZVI between 10,000 and 25,000 bed volume and finally no leaching out was observed after 30, 000 bed volume. For #10–20 ZVI, the corrosion rate stayed around 0.001–0.002 mg Fe/min till 40,000 bed volume of operation.

Overall, about 1.2 g of the original 1.6 g of iron was leached out after 60,000 bed volume of operation for the column that employed 20% US mesh #50 ZVI and 80% *evaporation Ultracarb*.

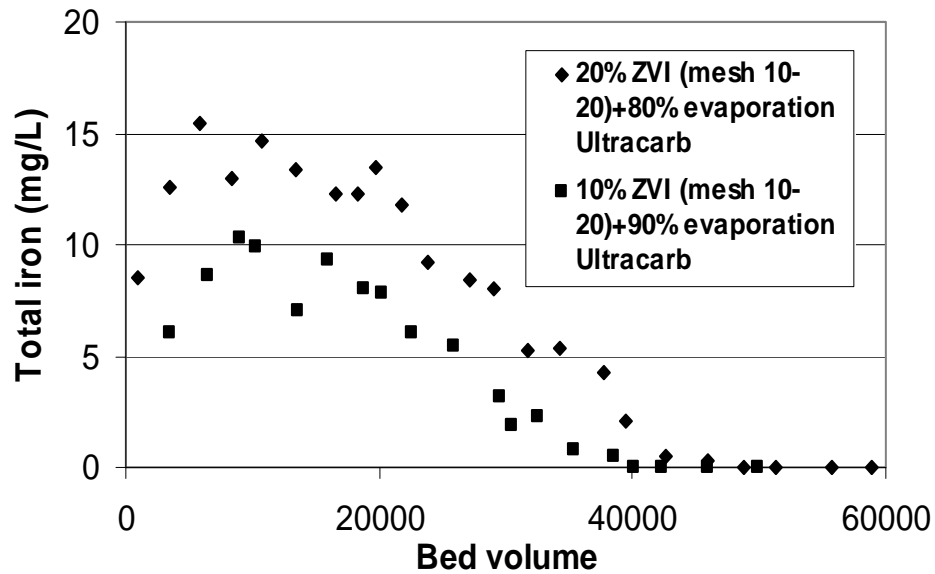


Figure 3.13 Total iron from zero-valent iron columns (US mesh #10–20) during RSSCTs

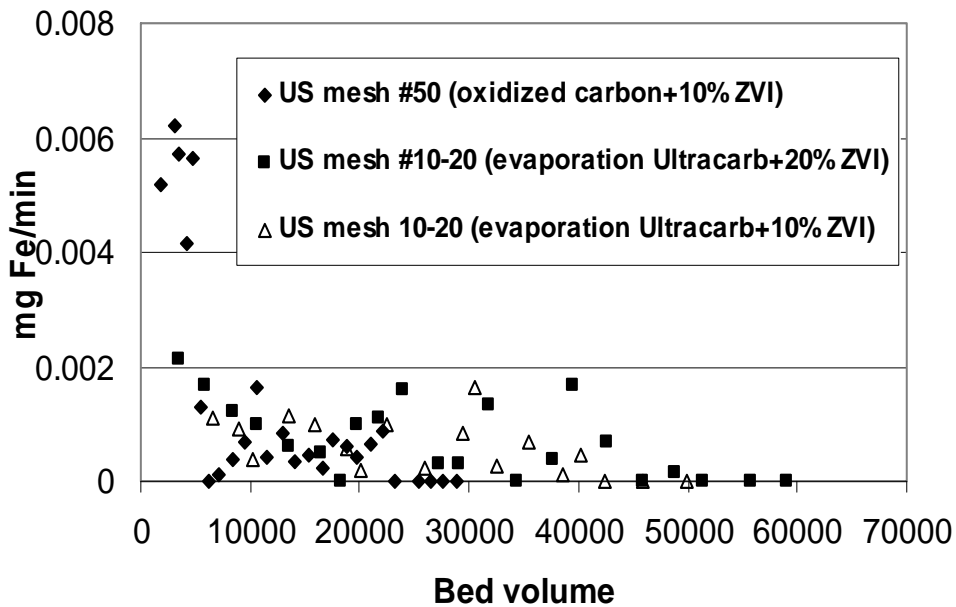


Figure 3.14 Corrosion rate of ZVI with US mesh #50 and #10–20 during RSSCTs



## CHAPTER 4 CONCLUSIONS

The organic acid-Fe that preloaded onto GAC had greatly improved its arsenic adsorption capacity. Comparing RSSCT results, organic acid-Fe carbon could get over 200 times longer bed life than virgin carbon.

Iron content is an important parameter to look at when choosing the arsenic removal adsorbents. But it is also important that the iron avails itself to arsenic sorption. When processing Rutland water through RSSCTs with 40–60 ppb arsenic, the iron-loaded oxidized carbons and iron-impregnated carbons had an iron efficiency of 11–33 mg As/g Fe which compares favorably to literature values of 2–29 mg As/g Fe for an array of iron-containing media (Jekel and Seith 2000, DeMarco et al. 2003, Daus et al. 2004). Thus, when employing iron preloading methods from this research, the iron apparently loaded in such a manner that much of it was available to adsorb arsenic. Kinetic and isotherms tests for iron-impregnated carbon reveal that this carbon is quite favorable when compared with other materials both in its maximum adsorption capacity and removal rate.

The soluble iron plus tailored GAC bed could remove arsenic to 10 ppb level for around 43,000 bed volumes with the appropriate combination of ZVI volume and particle size. An iron-preloaded carbon could serve as a sink for arsenic before the corrosion products take effect. Granular activated carbon systems are inherently simple to operate, and the solubilizable iron and tailored GAC beds will pose few if any complicated water treatment operation requirements above those for non-tailored GAC. Iron is non-toxic and commonplace in water and foods, and the secondary standard for Fe is 0.3 mg/L. GAC media are durable and will not decompose under abrasion, and this distinguishes GAC from the alternate granular iron oxide or iron hydroxide media which can abrade, decompose and plug up.

The bottom line will be that when this technology becomes commercially available, arsenic-tainted water sources can be treated to below arsenic standards with less cost, labor, and residuals management than even for conventionally treating surface waters that do not contain arsenic. This will provide water purveyors with the impetus to process arsenic-tainted waters, rather than abandoning them.

The soluble ZVI does incur iron leaching that exits the GAC media, but this can be captured by simple sand filter or a GAC filter; and our subsequent research will be addressing the use of this GAC filter.



## CHAPTER 5

### SIGNIFICANCE TO UTILITIES

As significance to utilities, a new arsenic limit of 10  $\mu\text{g/L}$  became effective in 2006 for the United States drinking water systems. This new regulation would make small public water facilities face heavy financial burdens, unless less costly methods of arsenic removal are developed. There is an urgent demand for an economical, effective, and reliable technique that is capable of removing arsenic species to this new level.

Adsorption onto iron-tailored GAC is considered to be one of the more promising technologies because it is economical and easy to set up, and because the skeletal structure of the GAC is strong, whereas granular iron media are fragile. For the research herein, we focused on devising a synthesis method that would pre-load amorphous hydrous ferric oxide (HFO) into the pores of GAC, so that this active sorptive material could complex both arsenite and arsenate with high sorption capacities. Our aim was to develop a media preparation method that is environmentally acceptable, cost-effective, and simple.

Yet further, our research herein has focused on developing an arsenic removal system that couples the high pore volume, structural cohesiveness, and low costs of granular activated carbon (GAC) with the arsenic-sorbing propensity and low costs of iron. Our overall approach has been to preload iron into the GAC pores in such a manner as to achieve (a) the highest internal loading of iron, while also maintaining (b) the highest efficiency of iron use; i.e. the most mg of arsenic adsorbed per gram of iron. When this underlying objective is met, we anticipated, we would achieve the longest bed life for removing arsenic in an easy-to-operate adsorption column, while maintaining low costs. Thus far, through the coupled research activity of Contract 3158 and 3163, we have developed an iron-preloaded media that can remove arsenic to below 10  $\mu\text{g/L}$  for 26,000–33,000 BVs; and when this iron tailoring has been coupled with solubilization of zero-valent iron in the same vessel, arsenic was removed to below 10  $\mu\text{g/L}$  for 43,000. In prior work, we had observed that when iron solubilization preceded the GAC vessel, we could achieve 150,000 BV. These tests employed Rutland, MA water, which contained 50–55  $\mu\text{g/L}$  As.

Our industrial in-kind partner, Siemens Water Technologies, has provided information regarding costs of this iron-tailored GAC, when coupled with zero-valent iron. Their data show the capital equipment costs for the equipment and media installation costs for small arsenic systems (Figure 5.1). Option A1 is for two media vessels in parallel with a 5 minute empty bed contact time through each bed. Option B1 is for four media vessels: two beds in series in two parallel trains; and 5 minutes empty bed contact time through each bed. This data is from 92 installations of arsenic-removing systems, with media costs of a similar nature (or higher) than for the iron-tailored GAC. For example, for a very small system rated for 50 gpm, the equipment and initial media cost for a tailored GAC system could be \$25,000–\$53,000.

Siemens Water Technologies has also provided data on water production costs as a function of bed volume throughput (Figure 5.2). These represent the sales costs for media installation, media replacement after exhaustion, and disposal of the spent media as a non-hazardous waste in a land fill. These exclude the on-site operating costs or water pumping costs. Siemens has provided four curves: two for commercially competitive metal-based media, one for a commercially competitive resin, and the fourth for iron-tailored GAC. The first three curves reflect data of actual sales prices, whereas the fourth curve projects the approximate costs of iron-tailored GAC based on the unit costs for (a) granular activated carbon, (b) iron salts and (c)

the labor for preloading the iron onto the GAC. The fourth curve is preliminary and therefore approximate; and actual sales values could be plus or minus 20%.

As shown in Figure 5.2, the iron-tailored GAC media is as inexpensive (or far less expensive) than any of the commercially available media that are currently being sold. This is the case when comparing media that achieve the same number of bed volumes before the spent media must be wasted and replaced. Most of the recent market experience of Siemens is with groundwaters that contain 10–50  $\mu\text{g/L}$  arsenic; these are the waters that must now be treated with the new 10- $\mu\text{g/L}$  standard, whereas waters with  $>50$   $\mu\text{g/L}$  already have had arsenic removal systems in order to comply with the previous 50  $\mu\text{g/L}$  standard. The Siemens experience is that with 10–50  $\mu\text{g/L}$  influent arsenic, the commercial media will remain in operation for 28,000 to 50,000 bed volumes before they should be replaced—either because the effluent arsenic approaches the 10  $\mu\text{g/L}$  limit, or because particulate buildup and excessive hydraulic pressure causes the media to bind. A portion of this particulate buildup can be because the granular iron media is fragile.

The authors note that with our current results in the 3163 project, we have observed iron-tailored GAC media alone (i.e. without ZVI) to last 26,000 bed volumes before 10  $\mu\text{g/L}$  arsenic breakthrough. When iron-tailored GAC is coupled with 20 % zero-valent iron, we have reached 43,000 BVs before 10  $\mu\text{g/L}$  arsenic breakthrough; and when preceding the iron-tailored GAC bed with ZVI, we have achieved up to 150,000 BVs before 10  $\mu\text{g/L}$  As breakthrough. From the Figure 5.2 curve for iron-tailored GAC, a 50,000 bed volume life would correspond to \$0.8/1000 gallons, which equals \$260/acre foot. A 150,000 bed volume life with more ZVI required (although off the Figure 5.2 chart, since conventional media are not operated that long) would correspond to \$0.40/1000 gallons, which equals \$130/acre foot.

Thus, the costs for the iron tailored GAC (with or without ZVI) are already in the ballpark of being competitive. In follow-up research, the authors intend to make the iron-tailored GAC yet more competitive.

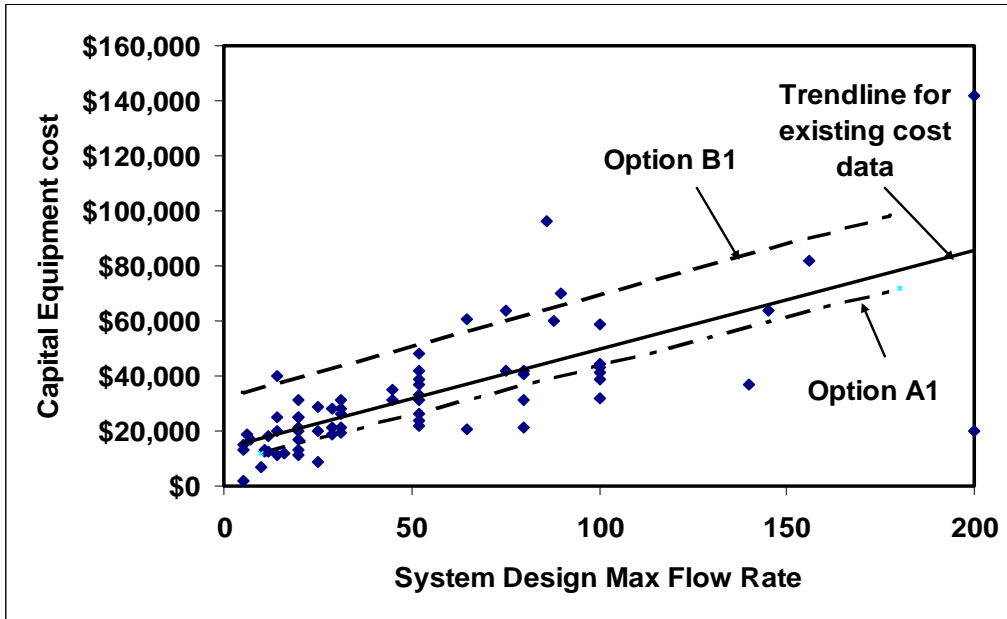


Figure 5.1: Equipment and media installation cost for small arsenic systems versus system design maximum flow rate (gpm). Option A1: two beds in parallel, each with 5-minute empty bed contact time. Option B1: four beds — two in series in each of two parallel trains.

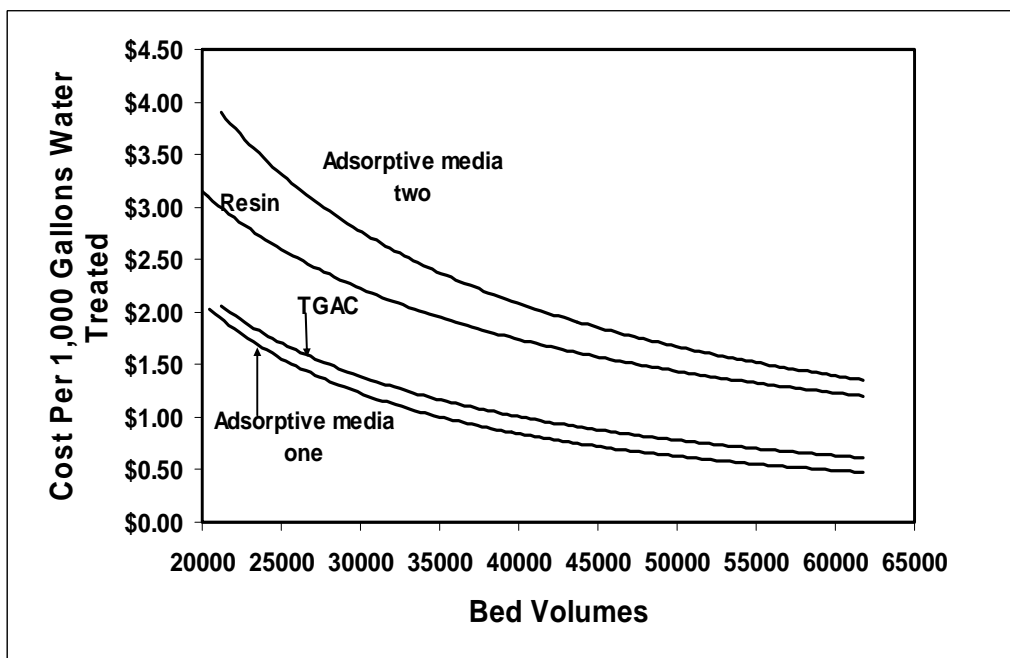


Figure 5.2: Water production cost versus bed volumes of operation before media change-out. Costs include media materials cost, labor for installation and removal, and wasting to non-hazardous land fill. Costs exclude power for pumping through the media or operating the systems.



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## ABBREVIATIONS

AAS	atomic absorption spectrometry
As(III)	arsenite
As(V)	arsenate
BV	bed volume
C	the concentration of arsenic in the solution
C <sub>0</sub>	the initial arsenic concentration
CA-Fe-SD	citrate ions added iron incorporated super darco
CPC	cetylpyridinium chloride monohydrate
CS-Fe-SD	cationic surfactant and iron incorporated super darco
CTAC	cetyltrimethylammonium chloride
D <sub>app</sub>	the apparent diffusivity of arsenic
δ	the liquid film thickness
EBCT	empty bed contact time
Fe(II)-Fe-SD	ferrous ions sequential impregnated iron incorporated surper darco
Fe-GAC	iron incorporated granular activated carbon
Fe-SD	iron incorporated super darco
Fe-UC	iron incorporated ultra carb
GAC	granular activated carbon
HFO	hydrous ferric oxide
HFO-GAC	hydrous ferric oxide incorporated granular activated carbon
HVG	hydride vapor generator
IWI	incipient wetness impregnation
mg/g	milligram per gram
mg/L	milligram per liter
mm	millimeter
µg/L	microgram per liter
POE/POU	point of use/point of entry
ppb	part per billion

R	the average radius of adsorbent particles
RSSCTs	rapid small-scale column tests
SD	super darco
t	time
TDS	total dissolved solid
UC	ultra carb
WHO	world health organization
X	the fraction of the arsenic adsorbed to adsorbent
XRD	X-ray diffraction