ZERO-VALENT IRON AND ACTIVATED CARBON FOR ARSENIC REMOVAL

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Abstract

This research has focused on removing arsenic from groundwater by coupling iron-tailored activated carbon with iron solubilization. This was achieved by solubilizing iron grains that were interspersed within the tailored activated carbon. When the activated carbon was iron loaded by an evaporation method, this media processed 25,000 bed volumes (BV) of water before 10 ppb arsenic breakthrough when processing natural groundwater that contained 40-60 ppb As. In contrast, when iron-loaded GAC was interspersed with up to 30% zero-valent iron grains, arsenic breakthrough above 10 ppb occurred at 45,000 bed volumes. This event corresponded to when most of the zero-valent iron source had visibly become corroded and converted to an iron hydroxide floc. Although some solubilized iron escaped through the GAC media, this iron could be captured in a subsequent sand or activated carbon filter, so as to yield water that would meet both primary and secondary drinking water standards.
Keywords: activated carbon, iron oxide, zero-valent iron

Introduction

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). Arsenic contamination is especially serious in Bangladesh, Taiwan, India and Chile. The USEPA had lowered the arsenic standard from 50 ppb to 10 ppb in 2001 and all public water systems must comply with the new standard as of January 1st 2006 or plead on exception. So there is an urgent need for simple and cost effective technologies for arsenic removal.

Thus far, research had been focused on developing new arsenic adsorbents because adsorption systems have proved to be able to lower the arsenic to less than 10 ppb. Studies have shown that iron oxides, such as granular ferric hydroxide (GFH) (Driehaus eth al. 1995, 1998) and hydrous ferric oxide (HFO) (Dixit and Hering 2003) can be effective to remove both As (V) and As (III) from aqueous solutions. GFH is reported to have a high treatment capacity of 30,000-40,000 bed volumes to a 10 μg/L breakthrough when the influent contained 50 ppb arsenic (Driehaus et al. 1998). Dixit and Hering reported maximum sorption of about 0.24 mol As (V)/mol Fe (322 mg As/g Fe) in HFO at pH 4.0 in isotherm tests with an initial As(V) concentration 100 μM (7.5 mg/L) and this corresponded to an iron efficiency of 3 g Fe/g As (Dixit and Hering 2003). But HFO is not know for exhibiting structural integrity and GFH or HFO granules might crumble and disintegrate when they experience prolonged use. For example, it was reported that GFH with a media particle size at 0.8-2.0 mm would need a backwashing every 5000 bed volumes to remove GFH fines (Selvin et al. 2000). Also, after backwashing, there could be a significant amount of head loss built up in the system (Westerhoff et al. 2005).

Studies have revealed that iron (III) has a high affinity toward inorganic arsenic species and are very selective in the sorption process. Infrared spectroscopic evidence supports the formation of inner-sphere complexes of As(V) and As(III) on ferrihydrite (Sun and Doner 1998). Analysis of As(III) and As(V) adsorption complexes in the Fe^0 corrosion products and synthetic iron oxide (goethite, hematitie, lepidocrocit, maghemite and magnetite) by extended X-ray adsorption fine structure (EXAFS) spectroscopy indicate that both As species form inner-sphere bidentate complexes (Manning et al. 2002). Another EXAFS study further demonstrated that As(V) forms predominantly bidentate corner-sharing complex on the iron oxides (ferrihydrite, goethite, hematite and maghemite (Sherman and Randal 2003).

This paper has focused on an innovative technique of coupling iron-preloaded activated carbon with zero-valent iron (ZVI) as a soluble iron source. The iron-preloaded carbons were created by preloading GAC with organic acid-iron complexes, by oxidizing the activated carbon surface with nitric acid etc. and then pre-loading iron, or by iron-impregnation via evaporation. The solubilization makes use of corrosion products such as iron (oxyhydr)oxide to adsorb arsenic. 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 and Puls 2001a, b). Possible arsenic removal processes in zero-valent iron system include: (a) surface adsorption onto corrosion products, e.g. iron (oxyhydr)oxides (Dixit and Hering 1998, Manning et al. 2002), (b) precipitation such as formation of symplesite ($Fe_3(AsO_4)_2 \cdot 8H_2O$) (Nikolaidis et al. 2003), (c) co-precipitation (e.g. arsenic co-precipitation with carbonate green rust) (Lien and Wilkin 2005), (d) redox reaction such as As (III) oxidized to As(V) by corrosion products or impurities such as MnO_2 (Melitas et al. 2002). Lien and Wilkin (2005)

used zero-valent iron as a permeable reactive barrier (PRB) for a simulated groundwater with 50 mg/L arsenic. The arsenic removal capacity was determined to be approximately 7.5 mg/g Fe or 0.1 mmol As/g Fe which would correspond to an iron efficiency of 130 g Fe/g As (Lien and Wilkin 2005). Melitas et al. (2005) observed that rates of arsenate removal by ZVI were highly dependent on the continuous generation of iron oxide adsorption sites as iron corroded.

When zero-valent iron systems have been used alone, they have exhibited profound clogging; so the intent herein has been to couple iron-preloaded GAC with ZVI so as to avoid this plugging issue. In this scenario, iron-loaded GAC would function as the main arsenate removal sink until the corrosion of iron reaches a steady state. After that, iron oxide products from corrosion and the remaining capacity of the GAC will work together as the adsorption sites for arsenic. GAC also would provide adsorption sites for corrosion products due to its high surface area and large pore volume, rendering it possible to retain most of the corrosion products.

The objectives of this research have been to:

1. Preload iron onto granular activated carbon in a manner that maximizes both the extent of iron loading and the availability of a unit amount of iron to sorb arsenic,

2. Determine a favorable surface area of zero-valent iron so as to achieve a useful corrosion rate of the iron that furnishes a continuous source of corroded iron from sorbing arsenic,

3. Couple the iron-preloaded GAC with zero-valent iron into a single media vessel for removing arsenic.

Materials and Methods

Materials

All chemicals were reagent grade. Citric acid was from J. T. Baker company. Ferric chloride ($FeCl_3 \cdot 6H_2O$) was from Fisher Scientific Company. As (V) solution was made from $Na_2HAsO_4 \cdot 7H_2O$. Zero-valent iron filings obtained from Edmund Scientific Co. were of particle size US mesh #50 (300 μm, specific surface area 2.7 m^2/g) and those obtained from Sigma Aldrich had a particle size of #10-20 mesh (2000-850 μm, surface area 0.06 m^2/g). The activated carbon employed herein was UltraCarb (Bituminous coal carbon) from Siemens Water Technologies. The non-tailored carbon was designated as virgin UltraCarb. Unless otherwise specifically identified, the UltraCarb was #200×400 mesh which was crushed, wet-sieved then dried prior to use or tailoring. Quartz sand was from EMD Chemical Inc.with a particle size of US mesh #50 (300 μm).

The groundwater 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 1.

Table 1. Characteristics of Rutland Groundwater (unit: mg/L unless specified).

pH	As* (μg/L)	Fe (μg/L)	Hardness (as $CaCO_3$)	TOC	Na	Mg	Chloride	Sulfate	Silica as 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

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

Methods

1. Iron loading

Iron loading by iron-impregnation of GAC was a method adopted from the method proposed by Vaishya and Gupta (2003a, b) for iron-impregnated sand. To achieve an iron oxide impregnation on activated carbon, 2 g of UltraCarb was added to 200 mL solution with 2 g of $Fe(NO)_3 \cdot 9H_2O$. The mixture was heated at 100ºC 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*.

2. Rapid small-scale column tests (RSSCT's)

Rapid small-scale column tests (RSSCT's) were conducted to evaluate GAC's arsenic adsorption capacity. The RSSCT design employed the proportional diffusivity model (Crittenden et al. 1986). The RSSCT's in this paper were designed to simulate a full scale carbon bed with empty bed contact time (EBCT) of 10 minutes and carbon particle size US mesh #12×40 (1700-425 μm) or EBCT of 5.4 min with US mesh #20×50 (850-300 μm). The column tests used carbon

particle size US mesh #200×400 (75-38 μm). The columns used were 13.5 cm long and 0.5 cm in diameter. Each test held about 1.67 g of carbon with actual EBCT of 0.53 min. Detailed configuration of the columns has been discussed in parallel work of our Penn State team (Chen et al. 2005). All RSSCT's were carried out at a room temperature of 20-23°C and at native groundwater pH of 7.6-8.0 unless specified. The RSSCT systems were set up to run in an upflow configuration.

For activated carbon (*evaporation UltraCarb)* and zero-valent iron column tests, 10-35% by volume of ZVI (0.75-2.8 g, US mesh #10×20) was thoroughly mixed with about 0.6-1.4 g (65-90% by volume) activated carbon before installing these together into an RSSCT.

3. Analytical methods

Arsenic analyses have been conducted via Shimadzu atomic absorption spectrophotometer-hydride vapor generation system (AAS-HVG)[6], in accordance with water and wastewater standard method 206.3.

To test the iron loading on tailored GAC, a portion of the loaded GAC was ashed in a muffle furnace at 600°C for 24 hours. The ashed GAC was dissolved in 25 mL of concentrated hydrochloric acid (HCl). After a minimum contact time of 24 hours, the solution was filtered and the filtrate was then diluted to 250 mL. Solutions were analyzed for iron by the ICP-MS and later via Shimadzu Atomic Absorption spectrophotometer (AA-6601F) unit with flame atomization. The As(V) was distinguished from the As(III) by the molybdate blue method (Murphy and Riley, 1962).

When operating column tests that employed zero-valent iron, the collected 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.

The specific surface area of ZVI was determined by adsorption of argon vapor onto GAC samples by means of isotherms with progressively increasing relative pressures from 10^{-6} to 0.993 atm/atm by ASAP 2010 units[7].

Results and discussions

In parallel research at Penn State, experiments were conducted using galvanized iron fittings in concert with rapid small scale column tests. It was observed that the continuous corrosion of iron from this fitting could greatly extend the bed life to 150,000 bed volumes before 10 ppb arsenic breakthrough (Zou et al. AWWA final report 2005). Zero-valent iron has also been found to be very effective in arsenic removal by itself, although others in the industry have observed that ZVI alone can cause considerable plugging issues.

For the RSSCTs herein, the authors wanted to build on this favorable earlier result by devising a bed that combined a mixture of both iron-tailored carbon plus the ZVI as a soluble iron source. Several iron-tailored carbons were employed to test the ZVI/GAC combination idea. The most favorable combination of tailored GAC and ZVI that the authors have developed thus far included 30% ZVI (mesh # 10×20) plus 70% iron-tailored GAC (*evaporation UltraCarb*) which treated 45,000 bed volumes prior to 10 ppb arsenic breakthrough. Without the ZVI, this GAC offered 25,000 bed volumes to breakthrough based on parallel studies at Penn State (Chen et al. 2006). These *evaporation UltraCarb* columns were coupled with ZVI in proportion of 10%, 20%, 30% and 35% by volume.

In the column with 30% and 35% ZVI, the ZVI was mixed with the first two-thirds of the carbon and then the rest of the carbon was installed at the downstream of the column. Thus, the ZVI represented the percent of the entire bed volume, but all of the ZVI was evenly distributed within the bottom (inlet) two-thirds of the bed. For the case of the 10% and 20% ZVI mixtures, the ZVI was evenly distributed throughout the bed.

Figure 1 is the RSSCT results for the arsenic breakthrough of these *evaporation UltraCarb*-ZVI and *evaporation UltraCarb* columns. The results indicate that with these #10×20 US mesh ZVI particles, the authors did not encounter a problem with hydraulic clogging and the column was able to run over 45,000 BVs before 10 ppb breakthrough with 30% of ZVI. Moreover, with the 30% ZVI mixture, the effluent arsenic remained below 2 ppb for all but three data points, indicating that this % ZVI and its distribution at the influent side achieved good polishing. In addition, arsenic speciation analysis of the effluent samples showed that the effluent contained the same ratio of As(III) to As(V) (1:3) as the original Rutland water, this means that the system not selective for As(III) and As(V) adsorption.
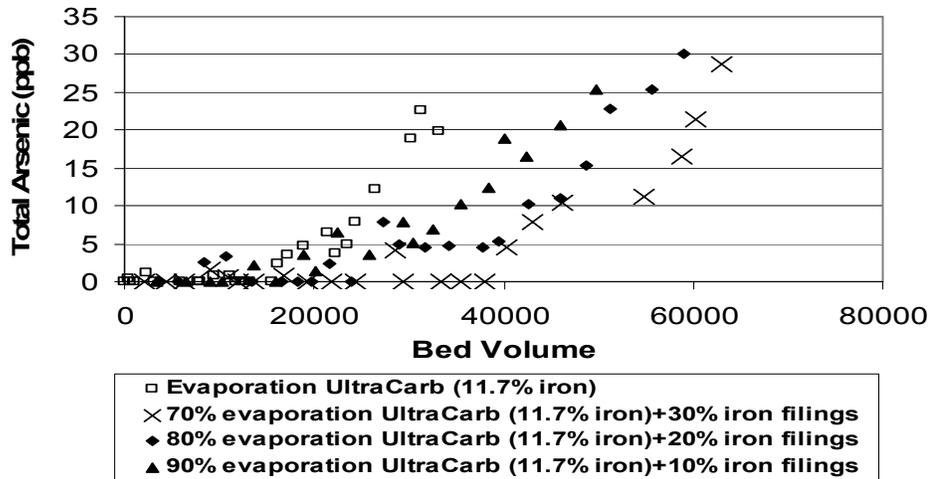
Figure 1. RSSCT of 10-30% ZVI (US mesh #10×20) mixed with evaporation UltraCarb (11.7% iron) at native pH of 7.6-8.0 (influent 40-60 ppb As)

In comparison, with a 20% ZVI/80% tailored GAC combination, the bed life was 42,000 and with 10% ZVI/90% tailored GAC combination, the bed life was 35,000. When 35% of ZVI was blended with *evaporation UltraCarb*, the combo exhibited clogging after only 5,000 bed volume of operation (data not shown here). The right combination of GAC and ZVI could further extend the bed volume.

When the 30% ZVI was placed in the first 2/3 of the bed, nearly all of the corroded iron was captured within the media and the media yielded less than 0.3 mg/L iron bleed into the effluent as shown in Figure 2a. This worked better than the configurations where the 10% or 20% ZVI was blended throughout the bed. In those cases, there was considerable iron that exited the GAC-ZVI column as shown in Figure 2b. The effluent iron concentration with 20% ZVI was regularly higher than that from the column with 10% ZVI. This indicates that by strategically arranging the installation of the column, the system was not only able to achieve long bed life for arsenic removal but also maintain control of iron leaching.
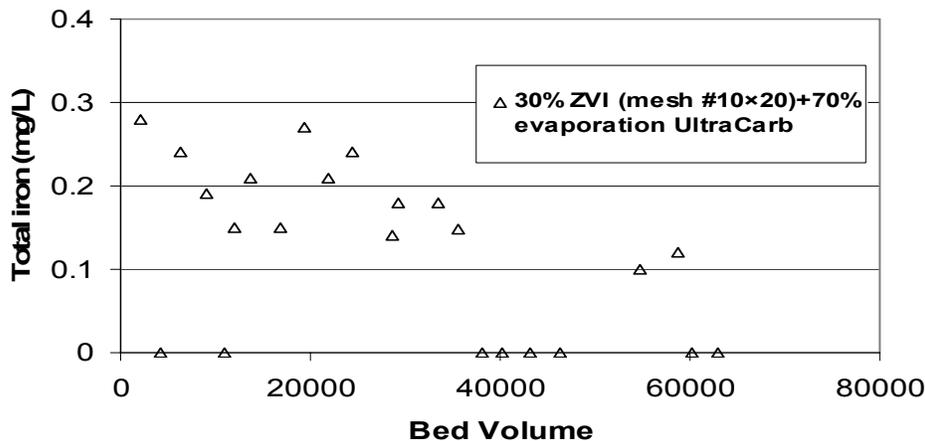

Figure 2a. Total iron from tailored GAC-ZVI (US mesh #10×20) columns during RSSCTs when employing 30% ZVI (US mesh #10×20) that is dispersed in first two-thirds of the bed
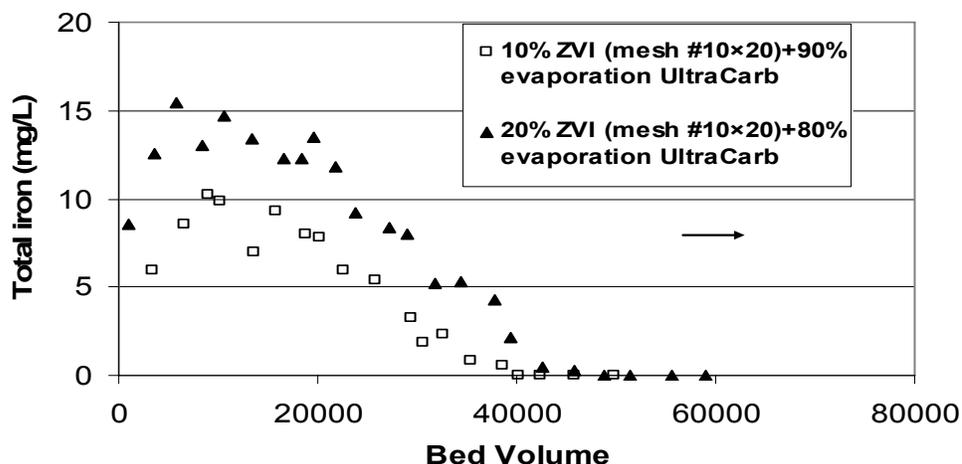
Figure 2b. Total iron from tailored GAC-ZVI (US mesh #10×20) columns during RSSCTs when employing 10% and 20% ZVI (US mesh #10×20) that is equally dispersed throughout the bed

The corrosion rate of ZVI with US mesh #10×20 averaged 6.5-9.4 mg Fe/day for the first 30,000 BV and the rate dropped to near zero after 50,000 BV (Figure 3). As comparison, in a related research, the corrosion rate with US mesh #50 was 19-25 mg Fe/day which was more than 2 times higher than that of the larger #10×20 size at 8,000 bed volumes (Chen et al. 2007). This is because the smaller particle sizes had higher specific surface area, thus more corrosion sites. The corrosion rate dropped to around 8.9 mg Fe/day for #50 ZVI between 10, 000 and 25,000 bed volume and finally no leaching out was observed after 30, 000 bed volume.

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*.
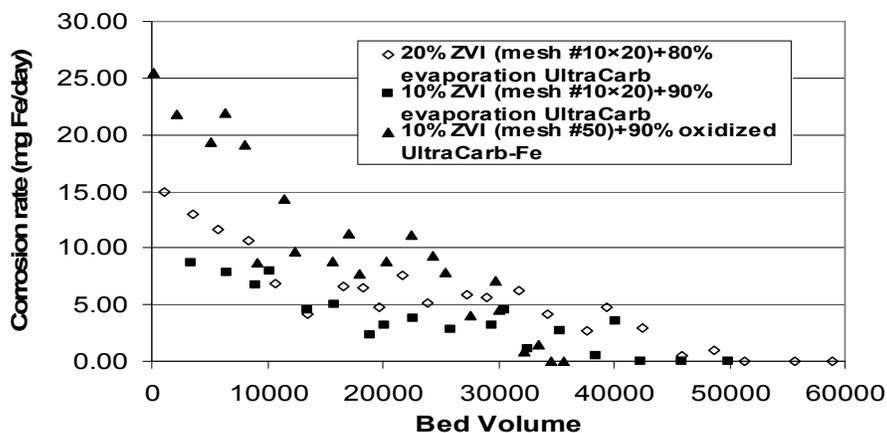

Figure 3. Corrosion rate of ZVI, comparing US mesh #50 and #10×20 during RSSCT operation

Table 2 summarizes the iron efficiency and corrosion rate for the GAC/ZVI combinations. As shown in Table 2, using a larger particle size made the iron corrode at a rate that is beneficial to arsenic removal and it improved the iron efficiency from 245 g Fe/g As to 165-198 g Fe/g As. Moreover, the corrosion rate of iron particles (mesh #10×20) was much higher per initial surface area than for the #50 mesh grains which further indicates that with larger particles, the iron was more effectively used.

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Table 2. Iron efficiency and corrosion rate for GAC/ZVI column.

	10% ZVI (mesh #50)+90% oxidized UltraCarb-Fe	10% ZVI (mesh #10×20)+90% evaporation UltraCarb	20% ZVI (mesh #10×20)+80% evaporation UltraCarb	30% ZVI (mesh #10×20)+70% evaporation UltraCarb
Iron efficiency (g Fe/g As)	245	198	165	178
Corrosion rate (mg Fe/day)	19-25	6.5	9.4	-
Corrosion rate/initial surface area (mg Fe/day)	7.0-9.3	108	156	-

Overall, by dispersing about 30% of ZVI into the iron-loaded GAC (*evaporation UltraCarb*), the bed life was extended to 45,000 BV from 25,000 BV (GAC alone) without causing clogging issues. Since ZVI is inexpensive, this ZVI/GAC combination has the potential to be a good solution to the arsenic contamination problem. The capacity of this ZVI/GAC combination for arsenic removal was highly related to both the presence of the ZVI, and the sorption capacity of the iron-tailored GAC. Moreover, the effectiveness of the ZVI was related to its particle size. When the RSSCT results are translated to full-scale grains, the RSSCT's simulation are not designed for predicting which specific ZVI grain size would most usefully provide the proper iron corrosion rate. Nor do the RSSCT's offer a prediction of the percent of ZVI that should be most appropriately included without excessive pressure loss. Rather, the RSSCT results offer the prediction that there is indeed a most appropriate ZVI grain size that can be found in forthcoming pilot studies.

Conclusions

The 30% ZVI plus 70% iron-tailored GAC bed could remove arsenic to 10 ppb level for around 45,000 bed volumes. An iron-preloaded carbon could serve as a sink for arsenic before the corrosion products take effect and as an arsenic polisher throughout the bed life. Moreover, when the ZVI is blended with GAC within the first two-thirds of the bed, the solubilizied iron will remain captured within the subsequent third of the tailored GAC media. Thus, the soluble ZVI does incur iron leaching that exits the GAC media when ZVI is blended throughout the bed, but this can be captured by the subsequent tailored activated carbon media that contains no interspersed ZVI.

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. No primary drinking water standards exist for iron while 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 may abrade, decompose and plug up.

The bottom line will be that when this technology becomes commercially available, arsenic-tainted groundwater 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.

Acknowledgements

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