

Method of grafting hydrous ferric oxide within granular activated carbon

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Introduction

Both arsenic and perchlorate contaminations in ground and surface water are creating serious environmental problems for human beings and other living organisms. Arsenic is a highly toxic metalloid that is now regulated at 10 parts per billions (ppb) by the World Health Organization (WHO) and the US Environmental Protection Agency (USEPA). About 40–60% of the population (125 million people) in Bangladesh, and many in West Bengal, India are estimated to be adversely affected by arsenic-contaminated drinking water (Goldberg and Johnston 2001).

Our ultimate goal is to develop materials that could selectively remove arsenic species. The authors herein offer adsorption onto iron-tailored GAC as one of the more promising technologies that could be cost-effective. The research has aimed to take advantage of the skeletal structure of the GAC that could preclude the crumbling phenomenon that mere iron oxides may face. A synthesis method was adopted to implant amorphous hydrous ferric oxide (HFO) to create a sorptive material that had high selectivity for arsenic (arsenate and arsenite). HFO was grafted within GAC pores via an incipient wetness impregnation (IWI) method. Incipient wetness impregnation is a commonly used technique for the synthesis of heterogeneous catalysts. Typically, the active metal precursor is dissolved in an aqueous or organic solution. Then the metal-containing solution is added to a catalyst support containing the same pore volume as the volume of solution that was added. Capillary action draws the solution into the pores (Giessen 1966).

The **objectives** of this study were to: (1) incorporate homogeneously active HFO into the pores of GAC through an incipient wetness impregnation technique; (2) evaluate the arsenic adsorption capacities of the media produced by examining the adsorption edges, and rapid small-scale column tests (RSSCTs) using synthetic solutions; and (3) understand the adsorption behavior of the media through physicochemical characterization techniques.

Materials and Methods

Water Source

Synthetic arsenic-containing water was prepared for small-scale column tests with DI water. This water contained 0.3 mM NaHCO₃, 0.01 M NaCl and 300–2,000 µg/L arsenic as arsenate. The pH of the synthetic water was kept at 6.5±0.2 using 0.1 M of NaOH or HCl.

Media preparations

Iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O) was employed as a precursor for iron oxide incorporation into the pores of granular-size porous GAC. The GAC used was SuperDarco, a thermally-tailored lignite developed at Penn State (Nowack et al. 2004, Rangel-Mendez et al. 2005) with grain sizes US mesh #80×140 (178–105 µm; median 141 µm) or 100×140 (148–105 µm; median 126 µm). The following tailoring procedure was developed to achieve homogeneous impregnation: (1) 1.0–1.5 mL of ferric nitrate solution at concentrations 0.5–1 g/mL was dispersed over the 1 g of dried GAC and mixed thoroughly, (2) GAC was then dried at room temperature for 24 hours before it was placed in a rotary evaporator for Fe oxide/hydroxide precipitation at temperatures of either 60°C, 80°C, or 90°C for 12 hours, (3) after Fe oxide/hydroxide precipitation, the GAC was cooled to room temperature then washed thoroughly with deionized water. The washed solids were dried again for 24 h prior to use. Parenthetically, the washing prevented subsequent nitrate leaching. Carbon samples prepared are identified by their iron contents (in percent), and preparing temperature. For example, Fe(11)-GAC-@80 was GAC SuperDarco iron-loaded at 80 °C under conditions that achieved an iron content of 11% by mass.

Characterization of materials

XRD. X-ray diffraction (XRD) patterns were obtained using Philips X'Pert MPD system, which was equipped with CuK α radiation (40 kV, 30 mA) with a 0.02° step size and 2.5 second step time over the range 10° <2 θ < 70°. Diffuse reflectance infra-red fourier transform (DRIFT) spectra for several prepared samples were recorded between 4000 and 700 cm⁻¹ using a Bruker IFS 66/S FT-IR Spectrometer. 5 mg of sample was homogeneously mixed with 330 mg of KBr.

Rapid small-scale column tests (RSSCTs)

Mini-columns employed a 1 mL syringe (diameter: 6 mm, length: 10 cm) with empty bed contact times (EBCTs) 0.8–2 min. An EBCT of 1 min was mainly used for the media with US mesh #100×140 and US mesh #80×140. In accordance with the proportional diffusivity similitude (Crittenden et al. 1986), the mini-column tests with 1 min EBCT (100×140 mesh) simulated an EBCT of 8.4 minutes for US mesh #12×40 (1700–425 μm; median 1060 μm), or 3.5 minutes for US mesh #20×50 (850–300 μm; median 440 μm) at full scale. By using this 1-mL syringe mini-column, we could find accurate bulk densities of different media and exclude spent solids from contact with oxygen before future spectroscopic observations.

XANES

Arsenic K-edge XANES spectra were collected at beamline X10C at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. Fluorescence spectra from air-dried samples were detected using a solid-state passivated implanted planar silicon (PIPS) detector. Cut-off mirrors at beamline X10C eliminated the need for detuning. The monochromator energy was calibrated with the gold L_{III}-edge (11,919 eV), which lies close to the arsenic K-edge (11,867 eV). The XANES spectra were collected with a 0.2 eV step size between –20 eV and 50 eV relative to the elemental arsenic K-edge energy. XANES spectra were normalized using MacXAFS version 4.1 (Bouldin et al. 1995), after averaging several scans of each samples.

Chemical analysis

Arsenic concentrations were determined with a Shimadzu Atomic Absorption spectrophotometer (AA-6601F) unit with flame atomization that was connected to a hydride vapor generating system (HVG-1, Shimadzu®). A colorimetric method adapted from Johnson (1971) was employed to monitor arsenic concentrations for samples with arsenic concentrations >300 μg/L. And the same method was also used to distinguish As redox species (arsenite and arsenate).

To test the iron loading amount on tailored GAC, about 0.1–0.2 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.

Results and discussion

X-ray Diffraction

To evaluate whether the iron-loading process achieved an HFO-type loading, iron-preloaded GACs were analyzed by X-ray diffraction analyses and compared to virgin GAC. Virgin GAC exhibited many crystallized peaks (quartz, Figure 1), indicating that this GAC contained some SiO₂, as is consistent with coal-based activated carbons that have been acid washed. For the iron-impregnated GACs, broad diffraction peaks were shown at 35.9° with relatively smaller peaks at 62.4°. It has been reported that two-line ferrihydrite (or HFO) shows two broad diffraction peaks at 35.9° and 61.4°, corresponding to d spacings of 0.250 and 0.148 nm, respectively (10,11). Peaks observed for the media were smaller than would be observed in pure iron oxide/hydroxide media, since the iron was sorbed inside the GAC pore structure, where the carbon and its ash would possibly mask the signal. Nonetheless, a broad shape of peak and position (at 35.9°) indicates that the dominant phase of iron oxide in the media was HFO. The distinctions in the peak shapes for the various media indicate that these iron oxides exhibited various degrees of crystallinities. Specifically, sample Fe(13.2)-GAC-@90 exhibited a sharper peak at 35.0° than did the other media. This indicated that the media corresponded to a dominant phase of akaganéite. For the case of Fe(11)-GAC-@80, the broad peak of HFO at 35.9° was submerged; and the quartz peaks became relatively diminished, indicating the dominant phase of iron oxide might not be HFO. Presumably, another phase of iron mineral such as Fe₂SiO₄ was manifesting itself.

Arsenic Adsorption as a Function of pH.

Figure 2 is the adsorption characterized As(V) and As(III) as a function of pH. The y-axis of figure at top is arsenic adsorption capacity per gram of the media while the y-axis of the figure at the bottom is adsorption capacity per gram of loaded iron. These experiments appraised the behavior of two media: Fe(7.5)-GAC-@60 and Fe(11)-GAC-@80. For Fe(7.5)-GAC-@60, the arsenate sorption was the same as the arsenite sorption at a pH of 7.5. In contrast, media Fe(11)-GAC-@80 was more efficient in removing arsenate than arsenite. It was reported that HFO can remove arsenite with the same efficiency as arsenate at the crossover pH of 7.5–8.5 (Dixit and Hering 2003), while at pH's below this cross-over point, HFO removes more As(V), and above this pH, HFO removes more As(III). In contrast, more crystalline iron oxides remove more As(V) than As(III) across the pH range. Thus, this result corroborated the x-ray diffraction data, and inferred that the iron oxide that formed in the 60°C media was amorphous HFO, whereas the iron oxide formed in the 80°C media was more crystallized. Moreover, the media prepared at 60 °C with 7.5% Fe showed higher adsorption capacities of both

arsenite and arsenate than did the media prepared at 80°C, even though this 80°C media had 11% Fe. At the crossover pH of 7.5 for the media Fe(7.5)-GAC-@60 both the As(V) and As(III) sorption densities were 130 mg of As/g Fe; and this is as high a sorption density as has been reported for HFO flocs that are stirred in water (Raven et al. 1998). Thus, both the sorption-versus-pH tests and the column results showed obvious differences between the media prepared at 60°C versus 80–90°C. The main reason for the high adsorption capacity of HFO is that the specific surface area (350–600 m²/g) of HFO that is reported in the literature is much greater than those of other crystallized iron oxides such as goethite or magnetite (<150 m²/g).

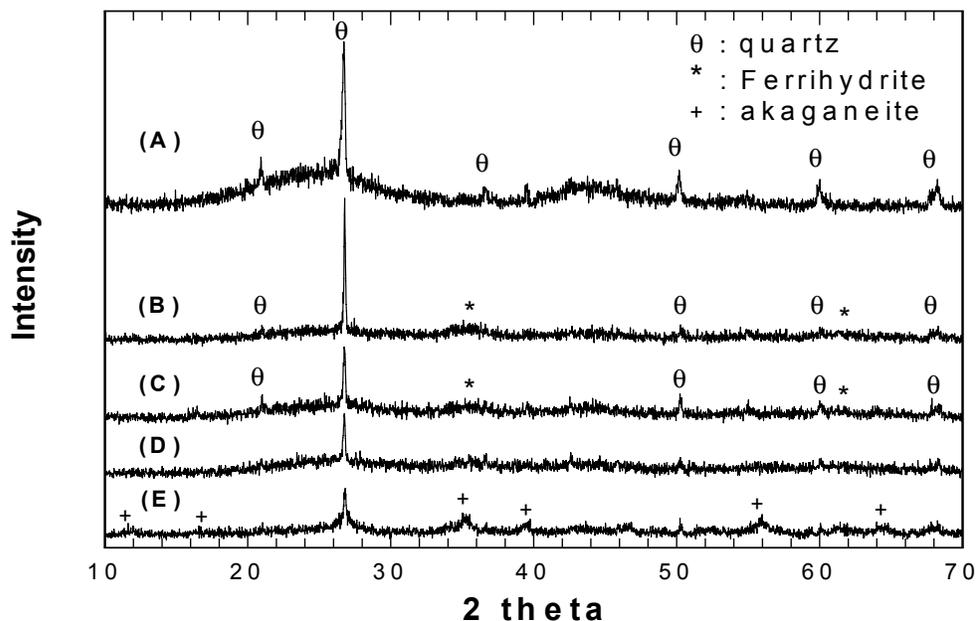


Figure 1. XRD results for (A) pure super darco (GAC), (B) Fe (7.5)-GAC-@60, (C) Fe(11.7)-GAC-@ 60, (D) Fe (11)-GAC-@ 80, (E) Fe(13.2)-GAC-@ 90. θ , +, and * indicate quartz, akaganéite, and 2-line ferrihydrite (or HFO) peaks, respectively.

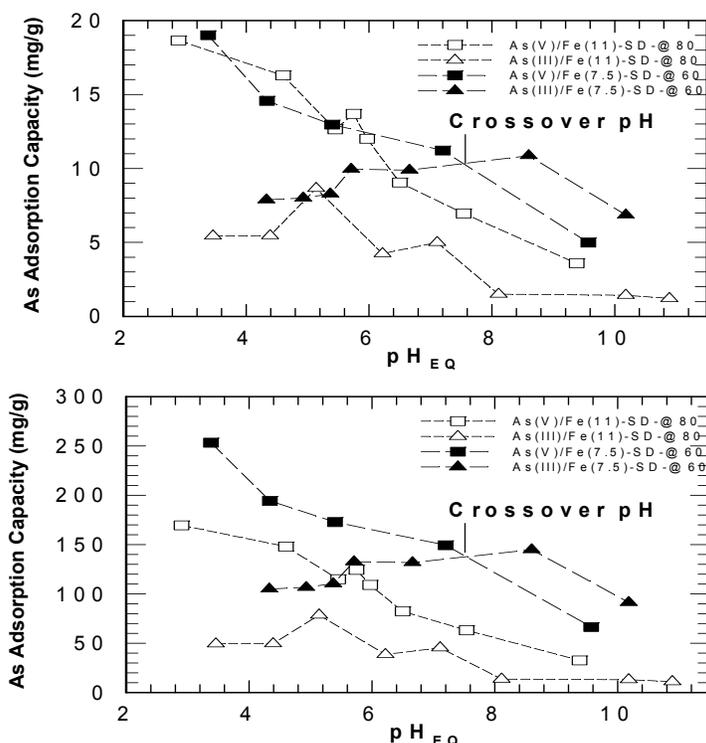


Figure 2. Adsorption as a function of pH arsenite and arsenate removal for Fe(11)-GAC-@80 (Δ/\square) and Fe(7.5)-GAC-@60 ($\blacktriangle/\blacksquare$), media concentration (0.1 g/L), arsenic concentrations (3 mg/L), stirring times (1 day). 2a: mg As / g iron; 2b: mg As / g GAC-iron hydroxide

RSSCTs results

Figure 3 shows RSSCT results for media that were prepared at an array of temperatures. These mini-column tests employed the synthetic water that contained 300 $\mu\text{g/L}$ As. The results clearly show that media Fe (7.5)-GAC@60 could remove arsenic for longer bed volumes than the 80°C-prepared media Fe (11)-GAC-@80. Fe (7.5)-GAC-@60 had about 3,400 BVs to breakthroughs of 50 $\mu\text{g/L}$, while Fe (11)-GAC-@80 broke through to 50 $\mu\text{g/L}$ at 1,500 BVs. Another media prepared at 60°C that gained 9.2% iron Fe(9.2)-GAC-@60 showed the same breakthrough BVs as Fe (7.5)-GAC@60, but arsenic concentrations were not detected in the initial period of column operation, as they had been for the Fe (7.5)-GAC@60 media. Thus, Fe(9.2)-GAC-@60 could give us more reliable arsenic removal. As an interesting aspect, media prepared at 60°C all showed flatter breakthrough curve than those prepared at 80 and 90°C. The steep slopes of breakthrough curve for Fe(11)-GAC-@80 and Fe(13.2)-GAC-@90 might be partly due to the formation of more crystallized iron oxide at 80°C or 90°C than at 60°C. With crystalline material, the surface is more approachable by As (i.e. less of the surface is recessed where accessible via slower diffusion modes); and thus all sites can be occupied at a concurrent time. This is in contrast with HFO-type iron, where some surface sites are remotely recessed in iron-sided pores and diffusion rate becomes important.

Media Fe(7.5)-GAC-@60, Fe(9.2)-GAC-@60, Fe(10.6)-GAC-@60 and Fe(11.7)-GAC-@60 were made from same carbon prepared at 60 °C for 12 hours by incipient wetness impregnation. The difference in the iron loaded was due to the fact that Fe(10.6)-GAC-@60 and Fe(11.7)-GAC-@60 were prepared with a higher initial ferric nitrate (around 1 g ferric nitrate/mL) concentration than Fe(7.5)-GAC-@60 or Fe(9.2)-GAC-@60. Further increase in the initial concentration did not lead to higher iron loading.

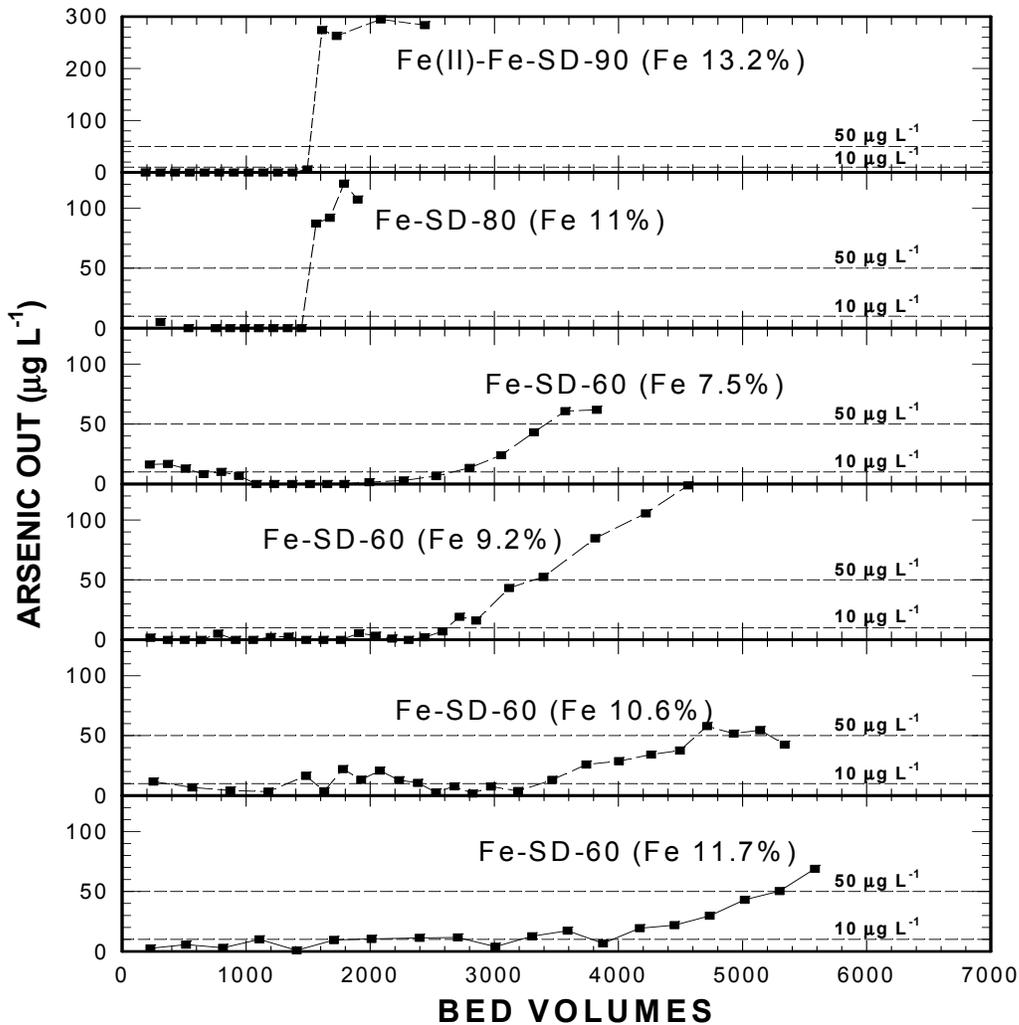


Figure 3. RSSCT for arsenic removal of iron loaded media: (media loading: 0.4g, EBCT: 1.07 ± 0.04 min, BV: 0.77 mL), Fe(7.5)-GAC-@60 (media loading: 0.26 g, EBCT: 1.09 ± 0.05 min, BV: 0.75 mL), Fe(9.2)-GAC-@60 (media loading: 0.3 g, EBCT: 1.09 ± 0.04 min, BV: 0.73 mL), Fe(10.6)-GAC-@60 (media loading: 0.336 g, EBCT: 1.04 ± 0.1 min, BV: 0.72 mL), (media loading: 0.375 g, EBCT: 1 min, BV: 0.73 mL). Influent As (V) $300 \mu\text{g/L}$, HCO_3^- 0.3 mM, and pH 6.5.

Conclusions

At similar Fe loadings (10–12%), the results of column tests showed obvious differences between media prepared at 60°C and 80–90°C: the media treated at 60°C offered about 3–4 times longer bed volumes to As breakthrough than did the media treated at 80–90°C. The arsenic adsorption tests as a function of pH also showed the media treated at 60°C had higher adsorption capacities for both arsenite and arsenate than media prepared at 80°C, even though the Fe content (7.5%) of media prepared at 60°C was much smaller than that (11%) of media prepared at 80°C. For the media prepared at 60°C, there was a pH crossover, at which adsorption capacities of arsenite and arsenate were same. This fact, along with others, indicated that the dominant phase of iron within the GAC was HFO. The main reason for a higher adsorption capacity of HFO is that the specific surface area ($350\text{--}600 \text{ m}^2/\text{g}$) of HFO is much greater than those of other crystallized iron oxide such as goethite or magnetite ($<150 \text{ m}^2/\text{g}$). The XRD results of the media treated at 60°C showed the two-line ferrihydrite (or HFO) while the media treated at higher temperatures exhibited a higher degree of crystallinities of iron oxides. The peaks for Fe(II)-Fe-SD (90°C, 4h) indicated dominant phase of akaganéite. At the Carbon conference, these results will be augmented with other HFO-loading data, and arsenic sorption results from other natural groundwaters.

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