Environ. Sci. Technol. **2005**, *39,* 3833−3843

Preparation and Evaluation of GAC-Based Iron-Containing Adsorbents for Arsenic Removal

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Granular activated carbon-based, iron-containing adsorbents (As-GAC) were developed for effective removal of arsenic from drinking water. Granular activated carbon (GAC) was used primarily as a supporting medium for ferric iron that was impregnated by ferrous chloride ($FeCl_2$) treatment, followed by chemical oxidation. Sodium hypochlorite (NaClO) was the most effective oxidant, and carbons produced from steam activation of lignite were most suitable for iron impregnation and arsenic removal. Two As-GAC materials prepared by $FeCl_2$ treatment (0.025−0.40 M) of Dacro 20 × 50 and Dacro 20 × 40LI resulted in a maximum impregnated iron of 7.89% for Dacro 20 × 50 and 7.65% for Dacro 20 × 40LI. Nitrogen adsorption−desorption analyses showed the BET specific surface area, total pore volume, porosity, and average mesoporous diameter all decreased with iron impregnation, indicating that some micropores were blocked. SEM studies with associated EDS indicated that the distribution of iron in the adsorbents was mainly on the edge of As-GAC in the low iron content (∼1% Fe) sample but extended to the center at the higher iron content (∼6% Fe). When the iron content was > ∼7%, an iron ring formed at the edge of the GAC particles. No difference in X-ray diffraction patterns was observed between untreated GAC and the one with 4.12% iron, suggesting that the impregnated iron was predominantly in amorphous form. As-GAC could remove arsenic most efficiently when the iron content was approximately 6%; further increases of iron decreased arsenic adsorption. The removal of arsenate occurred in a wide range of pH as examined from 4.4 to 11, but efficiency was decreased when pH was higher than 9.0. The presence of phosphate and silicate could significantly decrease arsenate removal at pH > 8.5, while the effects of sulfate, chloride, and fluoride were minimal. Column studies showed that both As(V) and As(III) could be removed to below 10 μg/L within 6000 empty bed volume when the groundwater containing approximately 50 μg/L of arsenic was treated.

Introduction

Arsenic is of serious concern because of its marked negative impacts to human health that range from acute lethality to chronic and carcinogenic effects (*1*). One of the major sources of arsenic exposure by the general population is drinking water (*2*−*5*). To limit such exposure, the U.S. Environmental Protection Agency has recently revised the maximum contaminant level (MCL) of arsenic in drinking water from 50 μg/L to 10 μg/L (*6*).

Common arsenic species in the environment include arsenate (As(V)), arsenite (As(III)), dimethylarsinic acid (DMA), and monomethylarsenic acid (MMA) (*7*). Inorganic forms of arsenic (As(V) and As(III)) are more toxic than the organic forms. As(V) is dominant in surface waters, consisting primarily of $H_2AsO_4^-$ and $HAsO_4^{2-}$ species (*8*). It could still be the major form of arsenic in groundwater systems. For example, >90% of arsenic in the groundwater from Socorro, New Mexico, is As(V) (*9*). A variety of treatment processes have been examined for arsenic removal (*10*−*12*). Major technologies include coagulation/precipitation (*13*), membrane separation (*14*−*16*), ion exchange (*17*), and adsorption (*18*−*21*). While these approaches can remove arsenic to below 10 μg/L under optimal conditions, most of the systems are expensive, not suitable for small water systems with limited resources.

Much work has been done on arsenic removal through adsorption because the system can be simple to operate and cost-effective. Effectiveness of adsorption-based methods depends primarily on the adsorbent used. Several iron(III) oxides, such as amorphous hydrous ferric oxide (*22*), poorly crystalline hydrous ferric oxide (ferrihydrite) (*23*, *24*), and goethite (α-FeOOH) (*25*, *26*), are well-known for their ability to remove both As(V) and As(III) from aqueous solutions. During the coagulation/flocculation process with ferric chloride or sulfate, for example, the iron salts hydrolyze to form amorphous ferric hydroxides, resulting in arsenic removal to below 10 ppb at an appropriate dosage (*27*, *28*). Mechanisms for arsenic removal include adsorption onto the hydroxide surfaces, entrapment of adsorbed arsenic in the flocs, and formation of ferric arsenate ($FeAsO_{4(s)}$). When alum is used as coagulant, arsenic is similarly removed; the efficiency is, however, somewhat lower than that with $FeCl_3$ (*13*, *29*). The amount removed is a function of arsenic oxidation states and concentration, iron dosage, pH, and other competing water constituents. Arsenate is more effectively removed by ferric (hydr)oxides than arsenite (*14*). The presence of other anions such as sulfate, chloride, and in particular, silicates, phosphate, and natural organic matters, may significantly decrease arsenic adsorption (*30*−*32*). Using iron (hydr)oxides in fine powdered or amorphous forms, however, requires follow-on solid/water separation, such as by sedimentation and granular medium filtration, with substantially added cost. For packed-bed adsorption system, high-efficient granular forms of adsorbent have to be used.

Granular media used for arsenic adsorption include granular activated alumina (*33*) and granular activated carbon (*34*). These materials are intrinsically less effective than iron (hydr)oxides for arsenic adsorption. Recently, several iron-based granular materials or processes have been developed and applied for arsenic removal. (1) Greensand filtration: A strong correlation between influent Fe(II) concentration and arsenic percentage removal was observed (*35*, *36*). The removal efficiency increased from 41% to >80% as the Fe/As ratio was increased from 0 to 20, as demonstrated by tests with tap water containing 200 mg/L of spiked arsenic; (2) iron oxide coated sand (IOCS) (*37*−*39*): The sand particle itself does not adsorb much arsenic but primarily serves as a support for iron oxides. Breakthrough empty-bed volume is approximately 150 when the influent arsenic concentration

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10.1021/es048179r CCC: $30.25

is 1.0 mg/L; (3) sulfur-modified iron (SMI) (*40*): The material was prepared by mixing powdered iron, powdered sulfur, and an oxidizing agent (H_2O_2) and then was added to the water to be treated; and (4) granular ferric hydroxide (GFH): It was prepared by a high-pressure process for granulation, aiming to take advantage of the high affinity of iron (hydr)-oxides to arsenic and granular form of the material suitable for packed-bed applications (*41*). GFH had a high treatment capacity of 30 000−40 000 bed volumes before the breakthrough concentration reached 10 μg/L (*42*). Among over 50 media tested for As removal at a laboratory scale, GFH was most effective (*43*), and with a media particle size at 0.8−2.0 mm, it treated approximately 5000 bed volumes of water prior to a need for backwashing. Some shortcomings with GFH, however, exist (*43*): (i) Robustness and mechanical strength of the granular iron oxides are not very good and need improvement. (ii) A headloss pressure is produced quickly with time (ca. 2 days) and becomes more significant after backwashing, probably because of the weakening of the material that produces fine particles. (iii) When larger sized media (1.0−2.0 mm) is used, the adsorption capacity for As is reduced by 50%. In addition, the cost of GFH is high, currently at approximately $4000 per ton (*30*). While regeneration of GHF seems feasible, it generates an alkaline solution with high levels of arsenate, which requires further treatment and disposal.

The objective of this study is to develop and characterize an iron-impregnated granular activated carbon (As-GAC) that can be used for effective drinking water treatment. A key attribute for activated carbon is its high specific surface area ranging from several hundred to around two thousand m^2/g, resulting from its porous structure. Activated carbon, either granular or powdered (GAC or PAC), is widely used as an adsorbent for water and advanced wastewater treatment. It is capable of adsorbing a wide variety of organic contaminants and heavy metals (*44*) and is designated as the best available technology (BAT) by the U.S. EPA for the removal of synthetic organic contaminants. The surfaces responsible for contaminant adsorption are primarily internal pores with various dimensions. Use of activated carbon for water treatment is a mature technology for removal of synthetic and natural organic compounds, odor and taste, and trace metals, with numerous treatment systems in operation and a good track record. Fixed-bed adsorption using GAC is most common, because of its suitable mechanical properties for water/solid separation (*45*).

Arsenic adsorption onto virgin activated carbon is minimal, so it cannot be directly applied for arsenic treatment (*46*). Literature has, however, shown that the adsorption on activated carbon can be significantly increased by treatment with various iron compounds (*47*, *48*). It is likely that some iron compounds produced by the treatment are cross-linked to activated carbon, resulting in an enhanced As sorption (*47*). Enhanced arsenic adsorption was similarly observed with copper-treated activated carbon (*49*).

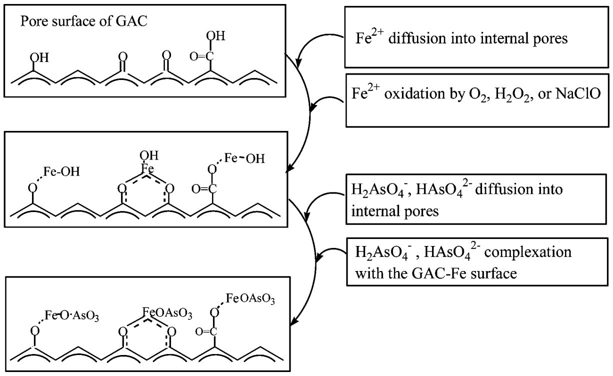

FIGURE 1. An illustrative model for preparation of As-GAC and arsenic adsorption.

Our approach was based on hypotheses that dissolved ferrous iron could diffuse deep into the internal pores of granular activated carbon, and followed by in-situ oxidation of ferrous to ferric iron, the ferric species could cross-link with various functional groups in a dispersive way on the carbon, maximizing subsequent adsorption for arsenic (Figure 1). The granular nature of activated carbon is maintained during and after the iron impregnation, so the materials would be suitable for packed-bed applications. The investigation focused on optimizing the preparation conditions, which included initial Fe concentration, oxidant type and dosage, and GAC types. The adsorbents were characterized by scanning electron microscope (SEM) with energy-dispersive spectroscopy (EDS), X-ray diffraction (XRD), and nitrogen adsorption analyses for Brunauer−Emmett−Teller (BET) specific surface area and mesoporous size distribution. The ability of adsorbents for arsenic removal was evaluated through both batch and column studies. Effects of ionic strength, pH, and other competing constituents on the arsenic removal were also studied in batch systems.

Experimental Section

Materials. All chemicals were of regent grade and solutions were prepared by Milli-Q water (Q-H_2O, Millipore Corp. with resistivity of 18.2 MΩ-cm). Sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$,

TABLE 1. GAC Properties and the Amounts of Iron Impregnated by 0.10 or 0.20 M of Ferrous Chloride Treatment

						$[Fe]_{ads}$ (%)[c]	
sample[a]	surface area, m^2/g[b]	total pore volume, mL/g[b]	density, g/L[b]	particle diameter, mm[b]	pH, water extract[c]	$[Fe]_{ini}$, 0.10 M	$[Fe]_{ini}$, 0.20 M
NUSORB[1]	1000	0.90	400∼600	0.85∼2.0 0	8.6	1.37	1.77
GC8 30[2]	1000	n.a.	430∼480	0.50∼2.0 0	8.2	1.05	1.37
F-200[3]	650	0.90	400∼700	0.85∼1.7 0	8.5	1.33	1.84
F-300[3]	650	0.90	400∼700	0.85∼1.7 0	8.5	1.69	1.98
F-400[3]	650	0.90	400∼700	0.85∼1.7 0	8.4	2.09	2.34
OVC 4×6[3]	600	0.90	350∼500	2.00∼4.0 0	9.4	0.58	0.72
Dacro 20×50[4]	650	0.95	400	0.30∼0.8 5	3.8	4.60	6.53
Dacro 12×20[4]	650	0.92	400	0.85∼2.0 0	4.6	3.32	4.36
GAC 1240+[4]	1000	0.90	510	0.42∼2.0 0	5.8	1.67	2.00
Dacro12×20 LI[4]	650	0.95	390	0.85∼1.7 0	3.8	3.71	5.09
Dacro20×40LI[4]	650	0.95	400	0.42∼1.0 0	4.9	4.51	6.36
HD3000[4]	600	0.93	400	0.60∼2.3 6	4.8	3.82	5.23
HD4000[4]	625	0.93	400	0.60∼2.0 0	4.9	3.38	4.73

[a] Sample sources: 1-NII: Nucon International Inc.; 2-GCC: General Carbon Co.; 3-CCC: Calgon Carbon Co.; 4-ANCI: American Norit Co. Inc. [b] Reported by the manufacturers. [c] This study.

99%), sodium arsenite ($NaAsO_2$, 99%), and hydrogen peroxide (H_2O_2, 31.3%) were obtained from Sigma; ferrous chloride ($FeCl_2\cdot4H_2O$, ACS reagent) was from Fisher; and sodium hypochlorite (NaClO, 10−13%) was from Aldrich. The stock solutions of 100.0 mg/L As(V) and As(III) were prepared by dissolving $Na_2HAsO_4\cdot7H_2O$ and $NaAsO_2$ in water, respectively, and filtering through a 0.22-μm membrane.

A total of 13 commercially available granular activated carbons were tested for their ability for iron impregnation and arsenic removal. The main characteristics of these carbons are listed in Table 1, including the BET specific surface area, total pore volume, density, particle diameter, and pH of the water extract. Specific surface areas ranged from 600 to 1000 m^2/g and particle sizes from 0.3 to 4.00 mm diameter.

Adsorbent Preparation. Preliminary tests indicated that the ability of Darco 12 × 20 carbon for arsenate removal was enhanced upon ferrous chloride treatment, so this material was used to select an appropriate oxidant for ferrous iron oxidation. The preparation began by adding 10.0 g of the GAC sample into a series of Erlenmeyer flasks, each containing 150.0 mL solution of increasing $FeCl_2$ concentration (0.0020, 0.0050, 0.010, 0.020, 0.050, 0.10 M). Each series was then treated under different oxidation conditions for a total of 24 h at 25 ± 1 °C, followed by washing with 200 mL Q-H_2O three times and drying of GAC at 80 °C for 4 h. The treatments resulted in the following iron-impregnated samples. (i) GAC−Fe−degas: Ferrous chloride was dissolved into the degassed water containing GAC and the pH was adjusted to 4.2−4.5. The bottle was tightly closed and shaken for 24 h, followed by washing and drying. (ii) GAC−Fe: The same as i but without degassing for oxygen removal. (iii) GAC−Fe−O_2: During the mixing process, air was constantly bubbled through the system. The pH was adjusted to 5.0 with NaOH solution for the first 8 h and to 6.5 for the next 16 h, prior to washing and drying. (iv) GAC−Fe−H_2O_2: Hydrogen peroxide was added four times during the mixing, with a 6-h interval, according to the ratio of $FeCl_2\cdot4H_2O/H_2O_2$ = 10 g/20 mL each time. pH was controlled at 4.5−5.0. (v) GAC−Fe−NaClO: Sodium hypochlorite was added four times during the mixing, with a 6-h interval, according to a ratio of $FeCl_2\cdot4H_2O$/NaClO = 10 g/20 mL. pH was controlled at 4.5−5.0.

As shown in the next section, NaClO was the most effective oxidant for iron impregnation and arsenate removal. Thus, subsequent treatment involving all 13 GAC samples used NaClO. Two GAC (Dacro 20 × 50 and Dacro 20 × 40LI) were studied in more detail to identify the most appropriate initial Fe(II) concentration for GAC treatment that would maximize arsenic removal as well as the effects of pH and various anions for arsenate treatment. The iron-impregnated Dacro20 × 40LI was selected in the column studies for the removal of both arsenate and arsenite.

Sample Characterizations and Chemical Analyses. The prepared As-GAC samples were examined by scanning electron microscope (SEM) (AMRAY 1600) for the surface morphology. A working distance of 5−10 mm, spot size of 2−3, secondary electron (SE) mode, and accelerating voltage of 20 keV were used to view the samples. SEM images and energy-dispersive spectroscopy (EDS) at various parts of a granular activated carbon were collected using a digital data acquisition system. X-ray diffraction (XRD) analysis was conducted with the MiniFlex automated, microprocessor-controlled X-ray powder diffractometer, with Cu Kα X-ray source and semiconductor detector, operated at 15 mA and 30 kV. The BET surface area and mesoporous size distribution were measured by nitrogen adsorption using PMI Automated Brunauer−Emmett−Teller (BET) Sorptometer (Porous Materials, Inc.).

The performance of As-GAC materials was assessed on the basis of both the amount of iron impregnated and the arsenic adsorption isotherm and pH edge. Iron in As-GAC was extracted following the established acid extraction procedure (*50*): 0.100 g of sample was mixed with 30 mL of 1:1 HCl, followed by shaking (150 rpm) at 25 ± 1 °C for 2 h and then heating in a water bath at 90 °C for 20 min. The supernant was collected by filtration and analyzed by ferrozine spectrophotometric method (*51*, *52*).

The ability of various As-GAC samples for arsenic removal was assessed in batch systems using arsenate. In each test, 90.0 mg of the adsorbent was weighed into 50-mL glass bottle, followed by addition of 30.00 mL arsenic solution, resulting in a solid loading of 3.00 g/L. Ionic strength was controlled at 0.10 M by $NaNO_3$, and pH was controlled at 4.70 by acetic acid buffer (0.010 M $[Ac^-]_T$). Constant ionic strength and pH were maintained to better compare the performance of adsorbents prepared under various conditions, even though preliminary tests showed acetate buffer could slightly decrease arsenate adsorption. After mixing on a shaker (150 rpm) for 24 h at 25 ± 1 °C, the sample was filtered through a 0.45-μm membrane and the filtrate was analyzed for arsenic. The quantity of adsorbed arsenic was calculated by the difference between the initial and residual amounts of arsenic in solution divided by the weight of the adsorbent. An adsorption isotherm was obtained by changing initial arsenic concentration from 0.10 to 30.0 mg/L at constant pH of 4.70 (acetate buffer). The adsorption edge was measured at 0.05−5.0 mg/L of total arsenic and the pH was adjusted by NaOH or HNO_3. The maximum amount of NaOH or HNO_3 added was 0.20 mmol, so the ionic strength of the system was from 0.100 to 0.107.

The As-GAC material prepared from Dacro 20 × 40LI (American Norit Co) was further studied through column experiments to evaluate its potential for arsenic removal from drinking water. Groundwater from the University of Missouri-Columbia (UMC) campus was used as the source water. The main chemical components in the water were (mg/L) Ca = 57.4, Mg = 28.0, Na = 52.0, K = 6.4, Cu = 0.064, Fe = 0.029, S = 11.7, and B = 0.5, determined by inductively coupled plasma spectroscopy (ICP). Natural organic matter in the source water was low, with less than 1.5 mg/L of total organic carbon (TOC). Three columns were set up and fed by influents spiked with (i) 57.2 μg/L As(V), (ii) 56.1 μg/L As(III), and (iii) 113 μg/L total As (57.2 μg/L As(V) + 56.1 μg/L As(III)), respectively. The column size was 250 × ϕ6 mm, so the column had a length-to-diameter ratio of about 40:1. A total of 3.60 g of As-GAC adsorbent was used to fill each column. Empty bed contact time (EBCT) was controlled at 5 min. The selected EBCT was significantly longer than those of typical point-of-use (POU) devices but comparable to those of conventional water treatment plant GAC absorbers, which had EBCTs in the range of 5−20 min (*53*). Since large As-GAC particles (0.42−0.84 mm) were used in the testing, the results should represent the lower limit of the adsorption capacity of the porous material. The corresponding flow rate of arsenic solution was about 1.50 mL/min.

Total arsenic was analyzed by a PSA millennium analytical system (P.S. Analytical Ltd) on the basis of hydride generation−atomic fluorescence spectroscopy (HG−AFS) (*54*, *55*). A calibration curve, with a concentration series of 0, 1, 2, 5, 10, 20, and 50 μg/L, was prepared using arsenic reference solution (1000 ppm ± 1%, Fisher certified) and had a correlation coefficient (R^2) always higher than 99.9%. The method had a detection limit of approximately 50 ng/L. The RSD% of repeatability for 2, 5, 10, 20, and 50 μg/L samples ($n = 10$ at each concentration level) were 4.66, 4.00, 2.33, 3.14, and 2.19%, respectively. Speciation analysis for As(V) and As(III) was conducted in selected systems by high-performance liquid chromatography (HPLC) separation

TABLE 2. Arsenic Removal Efficiency (%) by Adsorbents Treated by Various Concentrations of Ferric Iron and Oxidants

		percentage arsenate removal (%)			
$[As]_{initial}$ (μg/L)	$[Fe(II)]_0$ used for carbon treatment (mol/L)	GAC−Fe	GAC−Fe−O_2	GAC−Fe−H_2O_2	GAC−Fe−NaClO
105	0	14.0	14.0	14.0	14.0
	0.002	50.6	59.1	91.5	95.7
	0.005	98.1	95.0	90.7	95.9
	0.010	98.0	95.3	95.0	99.5
	0.020	98.8	93.1	98.4	98.1
	0.050	94.6	94.9	84.5	97.9
	0.100	98.5	98.6	81.0	87.2
1031	0	6.76	6.76	6.76	6.76
	0.002	15.8	29.8	80.1	84.2
	0.005	94.5	79.7	90.5	92.3
	0.010	94.2	94.6	94.0	92.9
	0.020	95.0	95.4	97.8	97.9
	0.050	93.4	96.8	98.4	97.9
	0.100	95.0	97.9	98.0	92.1

(Shimadzu LC-10A) followed by HG−AFS detection. A Hamilton PRP-X100 (250 × 4.1 mm I/D, 10-μm particle size) HPLC column was suitable for the separation. No transformation between As(V) and As(III) was detected in any tests reported in this study. TCLP (toxicity characteristic leaching procedure) experiments were conducted for As-GAC samples used for arsenate treatment following the established procedure (U.S. EPA method 1311).

Results and Discussion

Selection of an Oxidant for in-situ Fe(II) Oxidation and Iron Impregnation. As illustrated in Figure 2, the amount of iron impregnated onto GAC (Dacro 12 × 20) increased with increasing initial concentrations of Fe(II), tested with up to 0.10 M of $FeCl_2$. The test conducted in an anaerobic nitrogen environment (a) represented the amount of ferrous iron that could be impregnated into the GAC, since significant ferrous iron oxidation was not expected. Other sets involved oxidation of ferrous iron by oxygen present in the ambient air (b), supplied by active aeration (c), by addition of H_2O_2 (d), or NaClO (e), during the impregnation process. Results showed that the amount of iron impregnated was the lowest when no oxidant was present. Slightly more, but similar, amounts of iron were impregnated when oxygen was present in the ambient air or provided by active aeration: 14.5 and 12.8 mg/g of iron were impregnated, respectively, when an initial Fe^{2+} concentration was 0.10 M. Addition of H_2O_2 at very low Fe^{2+} concentration did not enhance iron impregnation, but at higher concentrations (0.05 and 0.10 M) it doubled the amount impregnated when compared to oxygenation alone. Sodium hypochlorite (NaClO) was most effective, with the impregnated amount reaching 40 mg/g of GAC at an initial iron concentration of 0.10 mol/L.

GAC contains several surface functional groups, and its structure can be described as a combination of carbon particles connected with a random distribution of carboxyl, hydroxyl, phenol, and quinone groups on the surfaces of the porous material (*56*). Surface chemical differences and conditions influence the sorption capacity toward iron (*57*). Since Fe(III) in general has stronger complexation with ligands such as carboxyl and phenol groups than Fe(II), iron impregnation should be more effective when iron is present in trivalent oxidation state. Treatment of GAC directly with Fe(III) salts such as $FeCl_3$, however, is not effective, because Fe(III) easily hydrolyzes to form (hydr)oxides when pH is higher than ~3.0 (at 0.10 M) (*57*). Solid forms of iron (hydr)oxides cannot diffuse easily into the internal pores of GAC but are more likely to precipitate in the macropores and coat the outer surfaces of the particles. Use of a strong acidic solution (pH < 1.0) of $FeCl_3$ could not be effective either, because strong competition of protons for the surface sites would diminish Fe(III) adsorption on the GAC (*57*).

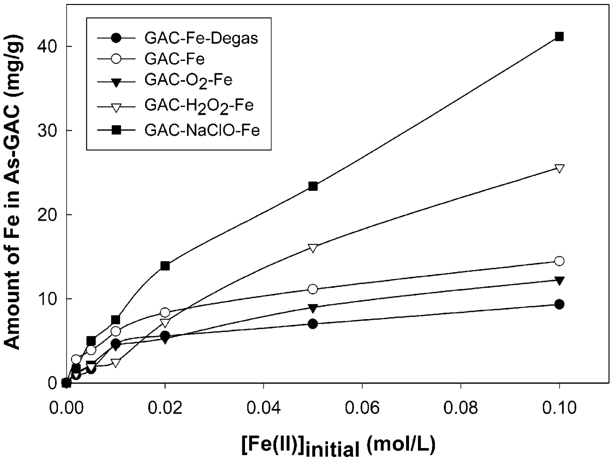

FIGURE 2. Iron impregnated into GAC with increasing initial ferrous chloride concentrations in the presence of different oxidants.

In the procedure developed in this study, Fe(II) is soluble at pH 4.5−5.0 and should be able to diffuse into the internal pores of GAC, forming a weak complex with the surface ligands. Subsequent in-situ oxidation of Fe(II) to Fe(III) could result in formation of strong Fe(III) surface complexes when compared to Fe(II). Additionally, the oxidation process could modify the carbon surfaces and lead to enhanced equilibrium quantity of iron impregnated (*56*, *57*). On the basis of energetics, all oxidants could lead to complete Fe(II) oxidation (*58*, *59*), and Fe(III) produced can further hydrolyze to form hydr(oxides) or bind to various functional groups on the carbon (eqs 1−4):

reaction equation	$E_h°$ (eV)	
$Fe^{2+} + {}^{1}/_{4}O_{2(g)} + H^{+} = Fe^{3+} + {}^{1}/_{2}H_{2}O$	0.459	(1)
$Fe^{2+} + {}^{1}/_{2}H_{2}O_{2} + H^{+} = Fe^{3+} + H_{2}O$	1.006	(2)
$Fe^{2+} + {}^{1}/_{2}ClO^{-} + H^{+} = Fe^{3+} + {}^{1}/_{2}Cl^{-} + {}^{1}/_{2}H_{2}O$	0.284	(3)
$Fe^{3+} + 2H_{2}O = FeOOH_{(am)} + 3H^{+}$		(4)

Sodium hypochlorite is apparently most effective at enhancing iron impregnation. The reason is unclear; it is probable that NaClO modifies the carbon surface more significantly or has faster oxidation kinetics with ferrous iron than with other oxidants.

Removal of Arsenic by Adsorbents Prepared with Various Oxidants. Batch tests on arsenate removal were conducted

TABLE 3. The Maximum Adsorption of Arsenic on As-GAC (with 0.050 M Iron Chloride Treatment) and the Ratio of Iron in GAC and the Maximum Arsenic Adsorption

samples	$q_{\max}$ (μg As/g adsorbent)	b	R^2 (%)	$[Fe]_{ads}$ (mg/g GAC)	Fe:As (mol/mol)
untreated GAC	3.78×10^1	536	94.1	0	
GAC−Fe (0.05 M)	2.96×10^3	655	97.6	11.1	5.05
GAC−Fe−O_2 (0.05 M)	1.92×10^3	376	95.6	8.07	5.63
GAC−Fe−H_2O_2 (0.05 M)	3.94×10^3	517	98.3	16.1	5.49
GAC−Fe−NaClO (0.05 M)	6.57×10^3	893	96.8	23.4	4.64

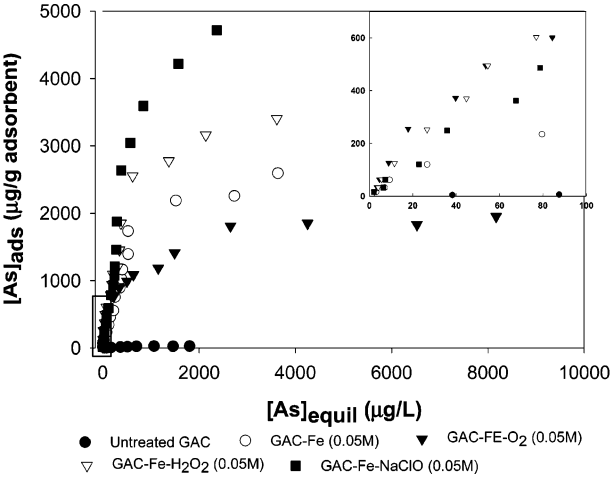

FIGURE 3. Arsenate adsorption isotherms on various As-GAC samples. The inset is for low concentration data points (pH = 4.70 controlled by 0.010 M acetate buffer; 3.0 g/L solid loading; temperature = 25 °C).

at two initial arsenic concentrations (105 and 1031 μg/L) for all treated GAC samples under various initial concentrations of iron coupled with different oxidants. Because of the high adsorption capacity of the adsorbents, relatively high concentrations of arsenate had to be used to compare the relative effectiveness of different materials. Solid/solution ratio in the tests was 90.0 mg solid/30.0 mL solution. Solution pH was at 4.70, controlled by 0.010 M acetate buffer, and temperature was 25.0 ± 1 °C. The equilibration time was 24 h. Results (Table 2) indicated that arsenic removal reached 99.5% at $[As(V)]_0 = 105$ μg/L and 98.4% at $[As(V)]_0 = 1031$ μg/L.

Arsenate adsorption isotherms were determined for untreated activated carbons and treated GAC samples by 0.50 M Fe(II) (Figure 3). Arsenic adsorption onto untreated GAC was minimal; in comparison, all As-GAC samples had much higher adsorption and the amount adsorbed was the highest for the one treated with NaClO. As expected, the adsorbed amount of arsenic increased with increasing equilibrium concentration of aqueous arsenic. The adsorption followed Langmuir equation (eq 5):

$$q_e = \frac{q_{\max} C}{b + C} \tag{5}$$

where q_e (μg As/g adsorbent) was the amount of arsenic adsorbed and C was the equilibrium concentration of arsenic (μg/L) in the solution. $q_{\max}$ and b are fitting parameters representing the maximum adsorption of arsenic and the adsorption constant, respectively. The parameters, obtained through nonlinear fit of the experimental data, are listed in Table 3. The maximum adsorption of arsenic was the highest for the sample prepared by NaClO oxidation, reaching 6572 μg As/g of adsorbent with 2.34% of iron. Data analysis also showed that Freundlich adsorption model could not represent the adsorption data adequately.

TABLE 4. The Amounts of Iron Impregnated by Treatment with Different Initial Concentrations of Fe(II)

	$[Fe]_{ads}$ (%)	
$[Fe(II)]_{ini}$ (M)	Dacro 20×50	Dacro 20×40LI
original	0	0
0.025	1.47	1.27
0.050	2.75	2.44
0.075	3.96	3.67
0.100	4.60	4.51
0.125	5.31	5.31
0.150	5.64	5.73
0.175	6.92	6.13
0.200	6.53	6.36
0.250	7.04	6.95
0.300	7.37	7.16
0.400	7.89	7.65

The molar ratio of iron to arsenic in iron-containing adsorbents is an important parameter because it indicates the intrinsic efficiency of iron for arsenic removal. The lower the ratio, the higher the efficiency for arsenic removal. When the SMI process was used to treat several types of water, approximately 20 mg As/g of iron was removed at pH 8, and 50 mg As/g of iron was removed at pH 7, indicating an Fe/As molar ratio of about 67 at pH 8 and 25 at pH 7 (*30*). In a packed-bed column test, the highest adsorption of arsenic for that material was 11 mg As/g of iron. For an iron-impregnated activated carbon with about 7% of iron, the ratio of iron and arsenic was reported to be around 6−13 (*48*). Driehaus et al. (*42*) used GFH for arsenic removal and found that the maximum ratio was about 7−18. Sorg (*60*) reported that the iron and manganese removal process had an Fe/As ratio of greater than 20:1, and such a process was considered to be very effective and was listed by the U.S. EPA as the best available technology. For the samples tested in this study, the molar ratio of iron and arsenic is as low as 4.64−5.63 (Table 3), which is the lowest for iron-containing adsorbents to our knowledge.

Effects of GAC Types on Iron Impregnation and Arsenic Removal. To select an efficient carrier medium, a total of 13 types of GAC samples from four different activated carbon companies were investigated for iron impregnation and arsenic removal. The amounts of iron impregnated following the treatment varied from 0.58 to 4.60% with 0.10 M Fe(II) treatment and from 0.72 to 6.53% with 0.20 M Fe(II) treatment (Table 1). Using the data with 0.20 M Fe(II) treatment, we found Dacro 20 × 50 and Dacro 20 × 40LI had the highest amounts of iron impregnated, 6.53% and 6.36%, respectively, and four other samples (Dacro 12 × 20, Dacro12 × 20 LI, HD3000, and HD4000) had relatively high iron contents ranging from 4.36 to 5.23%. These Dacro and HD samples were produced by steam activation of lignite, which may have generated structures and reactive moieties with high abilities for Fe impregnation. The pH of water extracts for these samples ranges from 3.8 to 5.8, suggesting the presence of acidic functional groups on the surfaces. Other carbons had a higher pH of 8.2−9.4 in their water extracts and showed much lower amounts of impregnated iron, ranging from

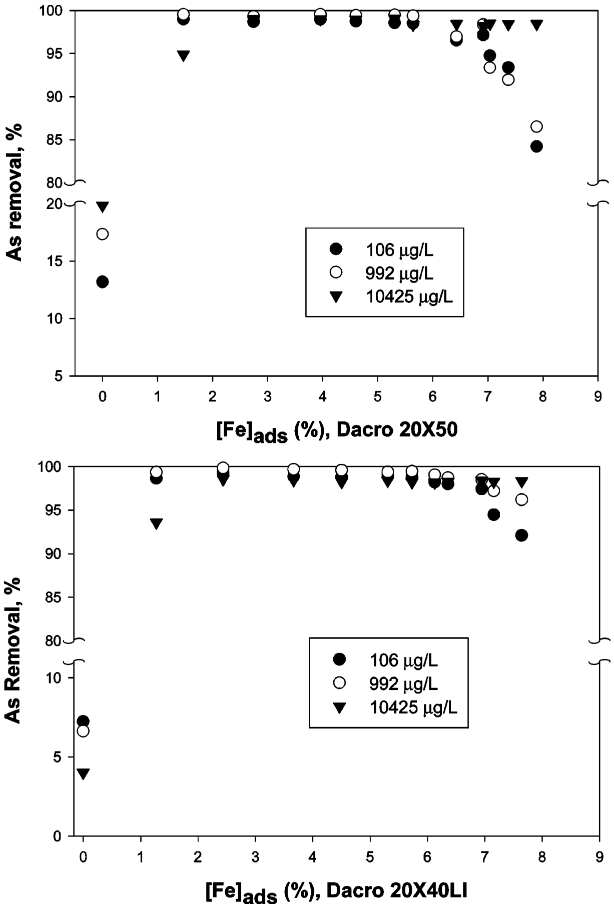

FIGURE 4. Percentage arsenate adsorption on two As-GAC samples with different amounts of impregnated iron (pH = 4.70 controlled by 0.010 M acetate buffer; 3.0 g/L solid loading; T = 25 °C).

0.72 to 2.34%. The carbons with low iron impregnation are originated from different sources: GAC 1240+ is produced by steam activation of select grades of coal; GC 8 × 30, F-200, F-300, and F-400 are virgin-activated carbons from bituminous coal; and OVC 4 × 6 and NUSORB are coconut-based. Arsenate adsorption on all these iron-treated materials was conducted at three levels of arsenate concentrations (100, 1000, 10000 ppb) at pH 4.70. The results indicated that the iron-treated Darco20 × 50 and Darco20 × 40LI had the highest arsenate adsorption (data not shown).

To optimize the initial concentration of Fe(II) that would result in maximum arsenic removal, further studies were conducted using Dacro 20 × 50 and Dacro 20 × 40LI as carrier media. Initial Fe(II) concentration ranged from 0.025 to 0.40 M. The result, as tabulated in Table 4, indicated that the iron could be increasingly impregnated, reaching 7.89% for Dacro20 × 50 and 7.65% for Dacro20 × 40LI, at an initial Fe(II) concentration of 0.40 M.

Figure 4 shows the percentage arsenate adsorption onto untreated and iron-treated Dacro20 × 50 and Dacro20 × 40LI with various iron contents. The untreated activated carbons have very low arsenic removal capability: under three initial arsenic concentrations of 106, 992, and 10425 ppb, untreated Dacro 20 × 50 had a percentage arsenic removal of 13.2, 17.3, and 19.8%, and untreated Dacro 20 × 40LI, 7.2, 6.6, and 4.0%, respectively. Both iron-treated samples removed more than 98% of arsenate when the iron content was less than 6%. To our surprise, when the iron content was higher than 6%, arsenic adsorption decreased with further increases of iron content. This is likely due to the decrease in total surface area and blocking of pores by iron hydr(oxides), as indicated by the specific surface area analysis discussed later.

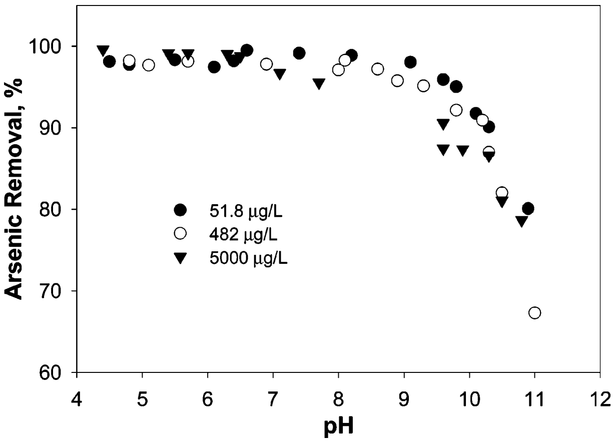

FIGURE 5. Effects of pH on arsenic adsorption at three initial arsenate concentrations (ionic strength controlled by the 0.10 M $NaNO_3$; 3.0 g/L of Dacro 20 × 40LI with 5.86% iron).

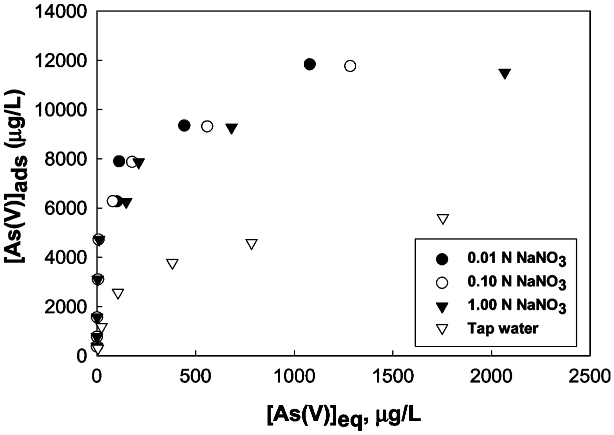

FIGURE 6. Effects of ionic strength and tap water constituents on As(V) adsorption (pH 4.70 controlled by 0.010 M acetate buffer, 3.0 g/L of Dacro 20 × 40LI with 5.86% iron).

Effects of pH on As(V) Removal. The effect of pH on As(V) removal was examined at three initial As(V) concentrations: 52, 482, and 5000 μg/L using iron-impregnated Dacro 20 × 40LI (Figure 5). pH was adjusted by HNO_3 and NaOH, and the ionic strength was controlled by 0.10 N $NaNO_3$. The adsorbed amounts of arsenic measured after 24 h of reaction indicated that pH had no obvious effect on As(V) removal from pH 4.4–9.0, with removal efficiency always higher than 95% under the experimental conditions. When pH was higher than 9.0, however, the As removal would decrease with increasing pH.

It has been well documented that increasing pH decreased arsenate adsorption on iron-containing adsorbents (*42*, *48*, *61*), typical of anionic adsorption. The adsorption edge of an anion depends on acid/base properties of the surfaces and the specific interactions of the adsorbate and the surface functional groups. For the As-GAC prepared in this study, significant decrease in arsenate adsorption was not observed until the pH was increased to >9.0 under the experimental conditions, suggesting that the material should be effective for the majority of water supplies, which normally have a pH range from 6.5 to 8.5. Further studies on the changes of the surface characteristics upon iron impregnation may provide additional insights into the mechanisms of arsenic adsorption at the interfaces.

Effects of Ionic Strength and Other Water Constituents on As(V) Removal. Figure 6 showed As(V) adsorption at three

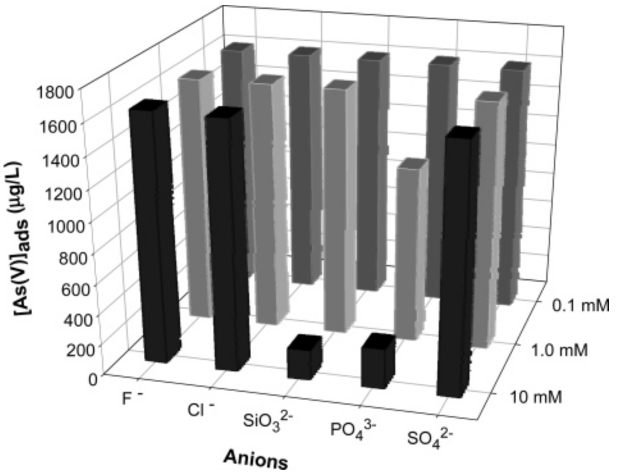

FIGURE 7. Effects of different anions on arsenate removal under fixed initial arsenate concentration (4906 μg/L) (pH 4.70 controlled by 0.010 M acetate buffer; 3.0 g/L of Dacro 20 × 40LI with 5.86% iron).

levels of ionic strength (0.010, 0.10, or 1.0 M $NaNO_3$) onto iron-impregnated Dacro 20 × 40LI at pH 4.7 (0.01 M acetate buffer). It was clear that increasing the ionic strength from 0.010 to 0.10 M did not have any effect on As(V) adsorption. This agrees with the fact that the dominant surface interaction between iron and arsenate is inner sphere in nature (*62*). When the ionic strength was increased to 1.0 M, a very small decrease in As(V) adsorption was observed. Arsenate adsorption from tap water at UMC campus was also presented in the figure. The main chemical components in the water were (mg/L) Ca = 57.4, Mg = 28.0, Na = 52.0, K = 6.4, and S = 11.7, with an estimated ionic strength of approximately 7×10^{-3} M. The water pH was 7.85 ± 0.10 after arsenate was spiked. Arsenic removal in the tap water was lower than that in the buffered solution with much higher ionic strength. This suggested that competitions of water constituents in the tap water and pH were more important than the ionic strength in controlling arsenate adsorption.

Competition of natural water constituents with arsenic for the surface sites should mainly arise from anions, such as oxyanions, because of the anionic nature of inorganic arsenic in water (*63*). Natural organic matters are ubiquitous in surface waters, but their concentration is normally low in groundwater where arsenic problem is the most serious. Three oxyanions (SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}) and two halide anions (Cl^-, F^-) were selected to assess the effects of co-anions on arsenate removal. At fixed pH of 4.70, the effects of different anions at three concentration levels (0.1, 1.0, and 10 mM) (Figure 7) showed that 10 mM of phosphate or silicate caused the greatest percentage decrease in arsenic adsorption among the anions. Under the concentration of 1.0 mM, phosphate resulted in a bigger decrease in arsenate removal than silicate. The effects of sulfate, chloride, and fluoride, even at 10 mM concentration, were minimal under the experimental conditions.

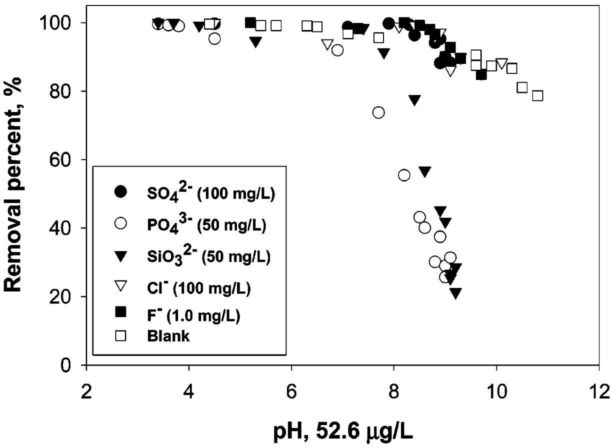

FIGURE 8. Effects of anions on arsenate removal under various pH conditions. Initial arsenate concentration is 52.6 μg/L (3.0 g/L of Dacro 20 × 40LI with 5.86% iron).

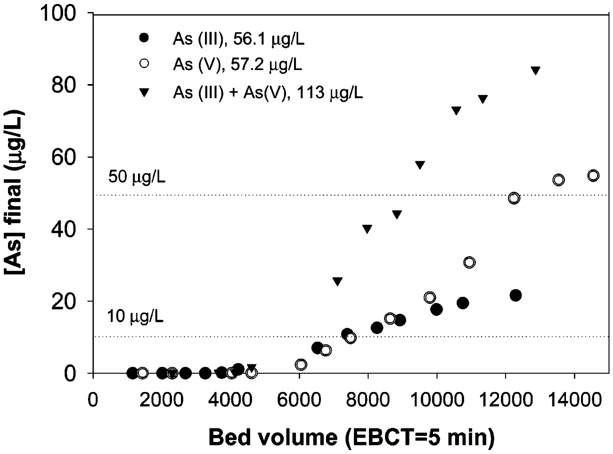

FIGURE 9. Arsenic concentration in the effluent as a function of empty bed volume (Dacro 20 × 40LI with 5.86% iron).

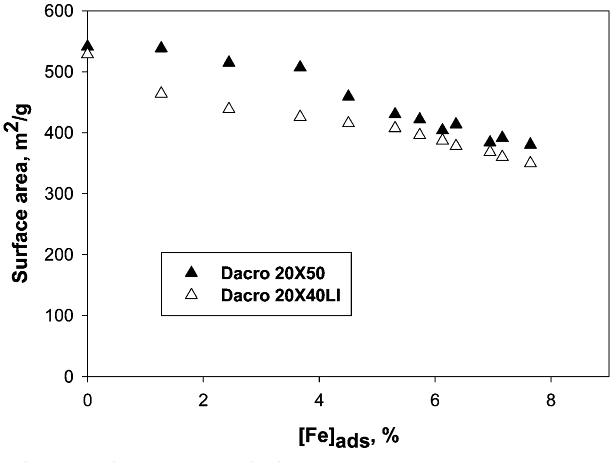

FIGURE 10. Surface area of GAC samples with different iron contents.

Effects of anions are coupled with pH, since anionic hydroxyl group is known to interact strongly with (hydr)oxide surfaces and also affects acid/base speciation of other anions. On the basis of the concentrations of anions in natural water (*44*), we selected different concentrations (1.0–100 mg/L) of anions (SO_4^{2-}, PO_4^{3-}, SiO_3^{2-}, Cl^-, F^-) and examined their effects on the removal of arsenic under various pHs. Arsenic concentration was set at 52.6 μg/L. As shown in Figure 8, SO_4^{2-}, Cl^-, and F^- did not significantly affect arsenate removal. A slight decrease in arsenic removal was observed at pH > 8.5, but the total removal was still over 80% and the results were comparable to the blank control. The presence of phosphate and silicate decreased arsenic removal slightly in the pH range from 3 to 6.5, but with further increases in pH, a significant effect on arsenic adsorption was observed. At pH ≥ 9.0, only 20% of arsenic could be adsorbed in the presence of phosphate and silicate. These indicate that phosphate and silicate outcompete hydroxyl group for the iron surface in the alkaline solution and subsequently decrease arsenate adsorption. The effect, however, appears to be minimal if As-GAC is used for water with pH ≤ 8.5, so the material should be suitable for the majority of groundwater sources.

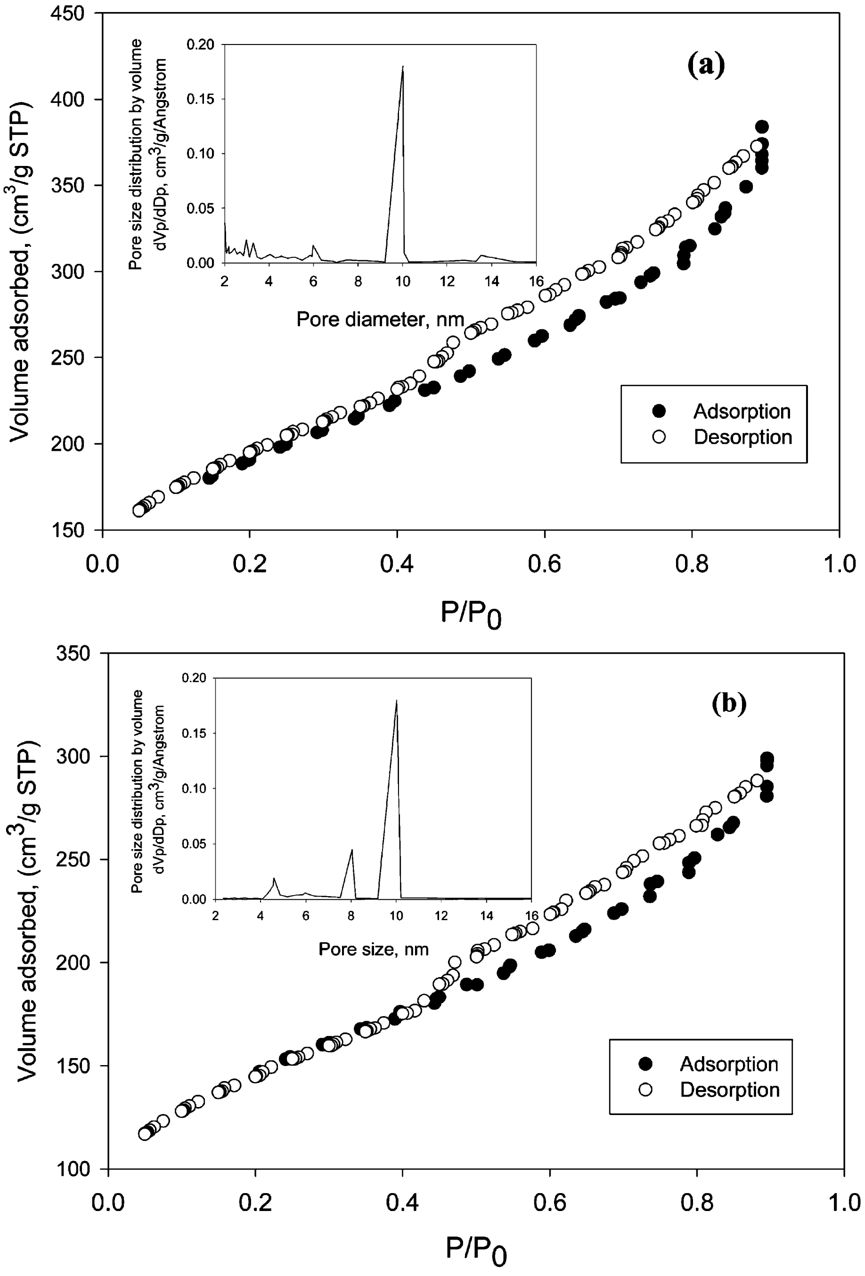

FIGURE 11. Nitrogen adsorption–desorption isotherms and corresponding mesopore size distribution by volume of (a) original Dacro 20 × 40LI and (b) As-GAC (5.86% Fe).

Column Tests. Arsenic breakthrough behaviors for an As-GAC sample prepared from Dacro 20 × 40 LI are illustrated in Figure 9. Influents were groundwaters at the UMC campus spiked with (i) 57.2 μg/L As(V), (ii) 56.1 μg/L As(III), or (iii) 113 μg/L total As (57.2 μg/L As(V) + 56.1 μg/L As(III)). The duration of column studies ranged from 45 days (ii) to 70 days (i), all with an empty bed contact time (EBCT) of 5 min. The results clearly demonstrated that the adsorbent could effectively remove both As(V) and As(III) from groundwater in the column setups. For the influent with 57.2 μg/L As(V), the breakthrough was not observed until approximately 6000 empty bed volume (EBV) and the effluent concentration reached 10 μg/L MCL at around 7500 EBV. The column was exhausted at approximately 13 000 EBV. In the systems with 56.1 μg/L As(III), the time for breakthrough (~6000 EBV) and 10 mg/L MCL (~7500 EBV) was essentially the same as for As(V), but it appeared that the column would last longer prior to exhaustion. When both As(V) and As(III) were in the system, the column could treat over 4500 EBV of water prior to breakthrough. The results suggest that some surface sites appear to be accessible to both As(V) and As(III). Compared with polymeric/inorganic hybrid sorbent (*19*) and other iron-containing sorbents (*23*, *38*, *64*), As-GAC has a good adsorption capacity.

In this brief study to assess the suitability of the As-GAC for arsenic removal, tap water with high alkalinity (260 mg/L as $CaCO_3$) and pH (7.85) was used. Arsenic adsorption in the tap water is lower than that in the acetate-buffered solution (Figure 6); thus, the results with the tap water should be more relevant to the practical treatment processes. In addition, the adsorbent, which had a particle diameter of 0.42–1.0 mm, was not ground to powder, different from the normal practice in assessing the adsorption capacity of activated carbon. This takes the diffusion kinetics into consideration, therefore, the results should represent the treatment efficiency when applied to packed-bed adsorption processes. Whether the material can be easily regenerated needs to be further investigated to assess the overall treatment cost. It is also conceivable that the material could be used in point-of-use (POU) devices. Since the contact times in

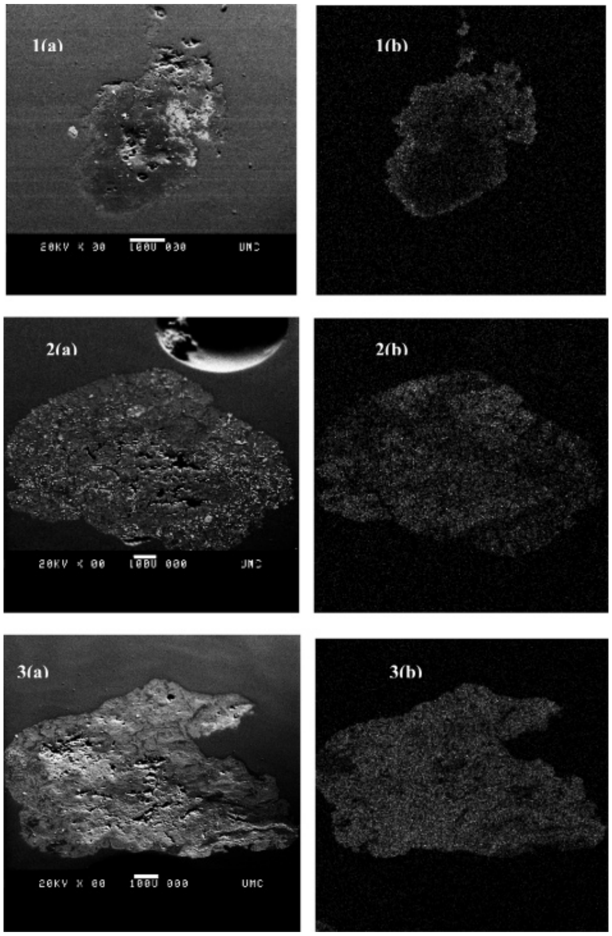

FIGURE 12. SEM micrographs and iron mapping of As-GAC samples treated with 0.025 M (1a, b), 0.15 M (2a, b), and 0.40 M (3a, b) of ferrous chloride (Dacro 20 × 40LI with 1.27, 5.73, and 7.65% Fe).

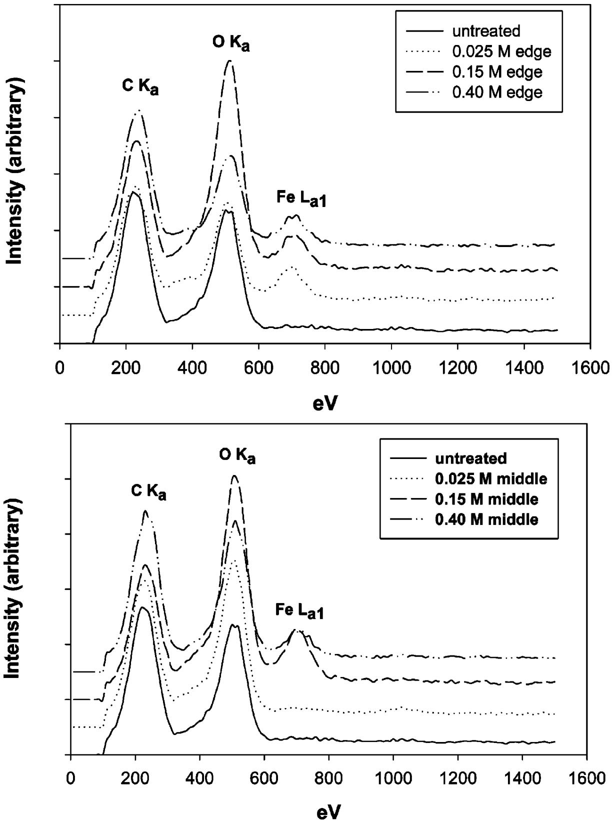

FIGURE 13. Energy-disperse spectra of untreated GAC and As-GAC adsorbents: (a) edge of As-GAC and (b) center of As-GAC.

POUs are expected to be much shorter than the 5-min EBCT used in this study, the As-GAC needs to be ground to enhance the adsorption kinetics or to start the impregnation process with powdered activated carbon. Adsorbents in POU devices are likely disposed of without collection and regeneration, thus whether the material demonstrates hazardous characteristics after its application needs to be assessed. The TCLP results of As-GAC samples used for arsenic treatment in this study indicated that arsenic concentration in the leachate was 90 μg/L, significantly lower than the expected level of 1000 μg/L to be regulated by the U.S. EPA on the basis of the new 10 μg/L MCL for drinking water. Thus, the material is suitable for landfill disposal upon usage when needed.

Adsorbent Characterization. *BET Surface Area and Mesopore Size Distribution.* Solute adsorption depends on the surface area and other characteristics of the porous adsorbent. The BET surface areas of the iron-impregnated adsorbents are shown in Figure 10. The surface areas were significantly affected by the iron content: as the iron contents were increased to 7.89% for Dacro20 × 50 and 7.65% for Dacro20 × 40LI, the BET surface areas were decreased from 541 to 380 m^2/g and from 528 to 350 m^2/g, respectively. The drop at the low iron content was more dramatic for Dacro20 × 40LI than for Dacro20 × 50, but it becomes comparable at higher iron content. It appears that with more iron impregnated, an increasing fraction of pores in the GAC is blocked, leading to a lower specific surface area. The iron impregnation may have increased the density of the adsorbent and led to a decrease in the measured specific area, but the changes in density should not be more than several percent, and thus cannot fully explain the ~30% decrease in the BET specific surface areas observed.

The nitrogen adsorption−desorption isotherm and corresponding mesoporous size distribution (Figure 11) shows that the overall adsorption−desorption curves are comparable between untreated Dacro20 × 40LI (a) and the treated sample with 5.86% of iron (b); thus, the basic carbon structures must have been maintained during the treatment. Nevertheless, some differences exist. The hysteresis occurs at a higher relative nitrogen pressure for the iron-impregnated GAC, suggesting that a larger fraction of micropores is blocked in comparison to mesopores and macropores. The corresponding decreases in the total pore volume are from 0.59 cm^3/g to 0.46 cm^3/g, the porosity from 0.37 to 0.14, and the average mesoporous diameter from 9.80 nm to 9.05 nm. The mesoporous pore volume in the 2−4 nm range almost disappeared completely upon iron impregnation; these pores are likely blocked by iron, although we cannot rule out that they have become micropores (<2 nm).

Scanning Electron Microscopy (SEM). Representative micrographs and SEM comprehensive mapping of the As-GAC adsorbents are presented in Figure 12. Examination of granular adsorbents by SEM revealed the normal GAC structures with visible meso- and macropores as expected; the resolution was not high enough to visualize micropores. The SEM imaging and comprehensive mapping indicated that the distribution of iron in As-GAC was mainly on the outside edge at low iron content (~1% Fe) and was more uniformly distributed in high iron content (5−7% Fe) samples. For the sample with the highest iron content, the images indicated that there was an iron band on the outer edge of the GAC particles. The energy-dispersive X-ray spectrometer (EDS) detects X-rays from the sample excited by the highly focused, high-energy primary electron beam penetrating into the sample. Comparing EDS images of As-GAC adsorbents and untreated GAC (Figure 13) confirmed that when using low initial Fe(II) (0.025 M) to treat the GAC samples, the iron impregnated in GAC mainly on the edge of granular particle, and when higher initial Fe(II) (0.15 M) was used, the iron is distributed more evenly within the whole particle.

X-ray Diffraction. There was no difference observed between untreated GAC and those treated with Fe(II)/NaClO in terms of their XRD patterns (spectra not shown). The result suggests that the iron impregnated into As-GAC was predominantly amorphous. Amorphous iron (hydr)oxides are known to gradually transfer to crystalline iron(III) oxides (*65*), but it appeared that it did not take place for our samples, and even the preparation procedure involved drying at 80 °C for 4 h. It could be that the impregnated iron is mostly in a coordinated form with various functional groups on GAC, not in polymeric iron hydroxide form, so formation of crystalline iron(III) oxides was prohibited.

This study has demonstrated that granular activated carbon is an excellent carrier medium for iron impregnation and arsenic removal. To increase the adsorption capacity, the types of activated carbon, the conditions for iron impregnation, and the surface area have to be optimized. Advantages of using the iron-impregnated carbon include its high efficiency for arsenic treatment, easy commercial availability, low cost, and working experience of water treatment community on GAC. Among the known arsenic adsorbents, granular ferric hydroxide (GFH) has higher adsorption capacity than the As-GAC, but it has its own shortcomings including the high cost. We expect that the As-GAC is a useful adsorbent for arsenic and could be used both in conventional packed-bed filtration tower and POU systems. Further research is underway to see whether the As-GAC can still maintain its capability of organic contaminant removal such as pesticides and chlorinated solvents, resulting in simultaneous treatment of both arsenic and trace organic contaminants.

Acknowledgments

The analytical supports by Mr. Louis Ross, Jr. at the University of Missouri-Columbia (SEM), Mr. Edward J. Hinderberger at the University of Missouri-Columbia (ICP), and Dr. John Yang at Lincoln University (MO) (XRD) are greatly appreciated. Activated carbon samples were provided by American Norit Co. Inc., Calgon Carbon Co., Nucon International Inc., and General Carbon Co. Financial support for this research was provided by the U.S. National Science Foundation (No. BES- 0296109).

Literature Cited

(1) Borum, D. R.; Abernathy, C. O. In *Arsenic Exposure and Health Effects;* Chappel, W. R., Abernathy, C. O., Cothern, C. R., Eds.; Science and Technology Lett.; Northwood: U.K., 1994; pp 21−29.

(2) Saha, J. C.; Dikshit, A. K.; Bandyopadhyay, M.; Saha, K. C. A review of arsenic poisoning and its effects on human health. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 281−313.

(3) Pontius, F. W.; Brown, K. G.; Chen, C. J. Health implications of arsenic in drinking water. *J. Am. Water Works Assoc.* **1994**, *86* (9), 52−63.

(4) National Research Council. *Arsenic in Drinking Water*; National Academy Press: Washington, DC, 1999.

(5) National Research Council. *Arsenic in Drinking Water: 2001 Update*; National Academy Press: Washington, DC, 2001; http://www.nap.edu/ books/0309076293/html.

(6) *Fed. Regist.* **2002**, *67* (246), 78203−78209.

(7) Le, X. C.; Yalcin, S.; Ma, M. S. Speciation of submicrogram per liter levels of arsenic in water: on-site species separation integrated with sample collection. *Environ. Sci. Technol.* **2000**, *34*, 2342−2347.

(8) Cullen, W. R.; Reimer, K J. Arsenic speciation in the environment. *Chem. Rev.* **1989**, *89*, 713−764.

(9) Brandvold, L. A.; Frisch, P. L. Natural arsenic distribution in groundwater in the Socorro, NM area of the middle Rio Grande rift. *New Mexico Geol.* **2002**, *24* (2), 69.

(10) Bitner, M. J.; Chwirka, J. D. Arsenic removal treatment technologies for drinking water supplies. *Proceeding of 39th New Mexico Water Conference*, Albuquerque, NM, 1994; pp 251−255.

(11) Kartinen, E. O., Jr.; Martin, C. J. An overview of arsenic removal processes. *Desalination* **1995**, *103*, 78−88.

(12) Jekel, M. R. In *Arsenic in the Environment;* Nriagu, J. O., Ed.; Wiley: New York, 1994; Chapter 1, pp 1−58.

(13) McNeill, L. S.; Edwards, M. Predicting arsenate removal during metal hydroxide precipitation. *J. Am. Water Works Assoc.* **1997**, *89* (1), 75−86.

(14) Hering, J. G.; Elimelech, M. *Arsenic Removal by Enhanced Coagulation and Membrane Processes;* AWWA Research Foundation: Denver. 1996.

(15) Waypa, J. J.; Elimelech, M.; Hering, J. G. Removal of arsenic from water by membrane processes. *J. Am. Water Works Assoc.* **1997**, *89* (10), 102−114.

(16) Brandhuber, P. J.; Amy, G. Arsenic removal from drinking water via membrane technology. *Desalination.* **1998**, *117* (1−3), 1−10.

(17) Berdal, A.; Verrie, D.; Zaganiaris, E. Removal of arsenic from potable water by ion-exchange resins. *Proceedings of IEX 2000, 8th*, Cambridge, U.K., 2000; pp 101−108.

(18) O'Reilly, S. E.; Strawn, D. G.; Sparks, D. L. Residence time effects on arsenate adsorption/desorption mechanisms on goethite. *Soil Sci. Soc. Am. J.* **2001**, *65* (1), 67−77.

(19) Min, J. H.; Hering, J. G. Arsenate sorption by Fe(III)-doped alginate gels. *Water Res.* **1998**, *32*, 1544−1552.

(20) Dambies, L. Existing and prospective sorption technologies for the removal of arsenic in water. *Sep. Sci. Technol.* **2004**, *39*, 603−627.

(21) DeMarco, M. J.; SenGupta, A. K.; Greenleaf, J. E. Arsenic removal using a polymeric/inorganic hybrid sorbent. *Water Res.* **2003**, *37*, 164−176.

(22) Pierce, M. L.; Moore, C. B. Adsorption of arsenite and arsenate on amorphous iron hydroxide. *Water Res.* **1982**, *16*, 1247−1253.

(23) Raven, K. P.; Jain, A.; Loeppert, R. H. Arsenite and arsenate adsorption on ferrihydrite: kinetics, equilibrium, and adsorption envelopes. *Environ. Sci. Technol.* **1998**, *32*, 344−349.

(24) Hsia, T. H.; Lo, S. L.; Lin, C. F. Characterization of arsenate adsorption on hydrous iron oxide using chemical and physical methods. *Colloids Surf., A* **1994**, *105*, 1−7.

(25) Matis, K. A.; Zouboulis, A. I.; Malamas, F. B.; Afonso, M. D. R.; Hudson, M. J. Flotation removal of As(V) onto goethite. *Environ. Pollut.* **1997**, *97*, 239−245.

(26) Sun, X.; Doner, H. E. Adsorption and oxidation of arsenite on goethite. *Soil Sci.* **1998**, *163*, 278−287.

(27) Shen, Y. S. Arsenic removal from drinking water. *J. Am. Water Works Assoc.* **1973**, *65* (8), 543−547.

(28) Edwards, M. A. Chemistry of arsenic removal during coagulation and Fe-Mn oxidation. *J. Am. Water Works Assoc.* **1994**, *86* (9), 64−78.

(29) Cheng, R. C.; Liang, S.; Wang, H. C.; Beuhler, M. D. Enhanced coagulation for arsenic removal. *J. Am. Water Works Assoc.* **1994**, *86* (9), 79−90.

(30) U.S. Environmental Protection Agency. *Technologies and Costs for Removal of Arsenic from Drinking Water;* Washington, DC, 2000.

(31) Meng, X.; Korfiatis, G. P.; Bang, S.; Bang, K. W. Combined effects of anions on arsenic removal by iron hydroxides. *Toxicol. Lett.* **2002**, *133* (1), 103−111.

(32) Redman, A. D.; Macalady, D. L.; Ahmann, D. Natural organic matter affects arsenic speciation and sorption onto hematite. *Environ. Sci. Technol.* **2002**, *36* (13), 2889−2896.

(33) Norton, M. V.; Chang, Y. J.; Galeziewski, T.; Kommineni, S.; Chowdhury, Z. Throw-away iron and aluminum sorbents versus conventional activated alumina for arsenic removal - pilot testing results. *Proceedings - Annual Conference, Am. Water Works Assoc.,* Washington, DC, 2001; pp 2073−2087.

(34) Pattanayak, J.; Mondal, K.; Mathew, S.; Lalvani, S. B. A parametric evaluation of the removal of As(V) and As(III) by carbon-based adsorbents. *Carbon* **2000**, *38*, 589−596.

(35) Subramanian, K. S.; Viraraghavan, T.; Phommavong, T.; Tanjore, S. Manganese greensand for removal of arsenic in drinking water. *Water Quality Res. J. Canada* **1997**, *32* (3), 551−561.

(36) Viraraghavan, T.; Subramanian, K. S.; Aruldoss, J. A. Arsenic in drinking water - problems and solutions. *Water Sci. Technol.* **1999**, *40*, 69−76.

(37) Santra, S.; Tapec, R.; Theodoropoulou, N.; Dobson, J.; Hebard, A.; Tan, W. Synthesis and characterization of silica-coated iron oxide nanoparticles in microemulsion: the effect of nonionic surfactant. *Langmuir* **2001**, *17*, 2900−2906.

(38) Benjamin, M. M.; Sletten, R. S.; Bailey, R. P.; Bennett, T. Sorption and filtration of metals using iron-oxide-coated sand. *Water Res.* **1996**, *30* (11), 2609−2620.

(39) Thirunavukkarasu, O. S.; Viraraghavan, T.; Subramanian, K. S. Arsenic removal from drinking water using iron oxide-coated sand. *Water, Air, Soil Pollut.* **2003**, *142* (1−4), 95−111.

(40) Schreier, C. G.; Santina, P. F. Sulfur-modified iron: a versatile media for *ex situ* water treatment. *Proceedings of the International Conference on Remediation of Chlorinated and Recalcitrant Compounds*, Monterey, CA, 2002; pp 2084−2091.

(41) Theis, T. L.; Iyer, R.; Ellis, S. K. Evaluating a new granular iron oxide for removing lead from drinking water. *J. Am. Water Works Assoc.* **1992**, *84* (7), 101−105.

(42) Driehaus, W.; Jekel, M.; Hildevrand, U. Granular ferric hydroxide-a new adsorbent for the removal of arsenic from natural water. *J. Water SRT—AQUA* **1998**, *47*, 30−35.

(43) Selvin, N.; Messham, G.; Simms, J.; Pearson, I.; Hall, J. The development of granular ferric media - arsenic removal and additional uses in water treatment. *Proceedings - Water Quality Technology Conference*, Salt Lake City, UT, 2000; pp 483−494.

(44) James, M. Montgomery Consulting Engineers, Inc. *Water Treatment Principles and Design*; Wiley & Sons: New York, 1985.

(45) Schroeder, E. D. *Water and Wastewater Treatment;*. McGraw-Hill: New York, 1976.

(46) Deng, B.; Caviness, M.; Gu, Z. Arsenic removal by activated carbon-based materials. In *Advances in Arsenic Research: Integration of Experimental and Observational Studies and Implications for Mitigation*, Vlassopoulos, D., Benning, L., Meng, X., O'Day, P., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2005.

(47) Huang, C. P.; Vane, L. M. Enhancing As^{5+} removal by a Fe^{2+}-treated activated carbon. *J.—Water Pollut. Control Fed.* **1989**, *61*, 1596−1603.

(48) Reed, B. E.; Vaughan, R.; Jiang, L. Q. As(III), As(V), Hg, and Pb removal by Fe-oxide impregnated activated carbon. *J. Environ. Eng. Div. (Am. Soc. Civ. Eng.)* **2000**, *126*, 869−873.

(49) Manju, G. N.; Raji, C.; Anirudhan, T. S. Evaluation of coconut husk carbon for the removal of arsenic from water. *Water Res.* **1998**, *32* (10), 3062−3070.

(50) Lu, J. Comparative study on determination of iron contents in activated carbon. *Linchan Huaxue Yu Gongye* **1995**, *15*, 57−61.

(51) Stookey, L. L. Ferrozine - a new spectrophotometric reagent for iron. *Anal. Chem.* **1970**, *42*, 779−781.

(52) Dawson, M. V.; Lyle, S. J. Spectrophotometric determination of iron and cobalt with ferrozine and dithizone. *Talanta* **1990**, *37*, 1189−1191.

(53) Dvorak, B. I.; Maher, M. K. GAC contactor design for NOM removal: implications of EBCT and blending. *J. Environ. Eng.* **1999**, *125* (2), 161−165.

(54) Le, X. C.; Ma, M. S.; Wong, N. A. Speciation of arsenic compounds using HPLC at elevated temperature and selective hydride-generation atomic fluorescence detection. *Anal. Chem.* **1996**, *68*, 4501−4506.

(55) Le, X. C.; Ma, M. S. Short-column liquid chromatography with hydride generation atomic fluorescence detection for the speciation of arsenic. *Anal. Chem.* **1998**, *70*, 1926−1933.

(56) Pakula, M.; Biniak, S.; Swiatkowski, A. Chemical and electrochemical studies of interactions between iron(III) ions and an activated carbon surface. *Langmuir* **1998**, *14*, 3082−3089.

(57) Onganer, Y.; Temur, C. Adsorption dynamics of Fe(III) from aqueous solutions onto activated carbon. *J. Colloid Interface Sci.* **1998**, *205*, 241−244.

(58) Hug, S. J.; Canonica, L.; Wegelin, M.; Gechter, D.; Von-Gunten, U. Solar oxidation and removal of arsenic at circumneutral pH in iron containing waters. *Environ. Sci. Technol.* **2001**, *35*, 2114−2121.

(59) Krishna, M. V. B.; Chandrasekaran, K.; Karunasagar, D.; Arunachalam, J. A combined treatment approach using Fenton's reagent and zerovalent iron for the removal of arsenic from drinking water. *Hazard. Mater.* **2001**, *B84*, 229−240.

(60) Sorg, T. J. Iron treatment for arsenic removal neglected. *Opflow* **2002**, *28* (11), 15.

(61) Wilkie, J. A.; Hering, J. G. Adsorption of arsenic onto hydrous ferric oxide: effects of adsorbates/adsorbent ratio and co-occurring solutes. *Colloids Surf., A* **1996**, *107*, 97−110.

(62) Zeng, L. A method for preparing silica-containing iron(III) oxide adsorbents for arsenic removal. *Water Res.* **2003**, *37* (18), 4351−4358.

(63) Su, C.; Puls, R. W. Arsenate and arsenite removal by zerovalent iron: effects of phosphate, silicate, carbonate, borate, sulfate, chromate, molybdate, and nitrate, relative to chloride. *Environ. Sci. Technol.* **2001**, *35* (22), 4562−4568.

(64) Dixit, S.; Hering, J. G. Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. *Environ. Sci. Technol.* **2003**, *37*, 4182−4189.

(65) Deng, Y.; Stumm, W. Reactivity of aquatic iron(III) oxyhydroxides--implications for redox cycling of iron in natural waters. *Appl. Geochem.* **1994**, *9* (1), 23−36.

Received for review November 19, 2004. Revised manuscript received March 1, 2005. Accepted March 10, 2005.

ES048179R