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Iron Oxide-Coated on Glass Fibers for Arsenic Removal

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A highly efficient adsorbent for arsenic removal from water has been prepared by impregnating high surface area iron oxides on glass fibers. Arsenic in water can easily and efficiently be removed by this adsorbent, without the need to pre-oxidize As(III) to As(V). The iron oxides coated on glass fibers (IOCGFs) can remove both arsenic species well below EPA MCL (10 ppb). IOCGFs should have the following four additional advantages: greatly improved contact efficiency; higher adsorption capacity because of high surface area; low cost and easily available adsorbent since the starting reagents ($FeCl_3$ and $NH_3 \cdot H_2O$) and glass fiber are cheap and readily available; and high adsorption efficiency of As(III) and As(V).

Keywords Arsenic removal; iron oxide; glass fibers; groundwater

INTRODUCTION

Arsenic is well known for its acute toxicity. Because of this, arsenic contamination of water has become a major concern in many parts of the world including Bangladesh and many regions in the USA. Traditional technologies for arsenic removal include precipitation, membrane processes (reverse osmosis and electrodialysis), ion exchange, and adsorption. Precipitation may not be viable due to low arsenic removal efficiency and the need to dispose of toxic waste sludge. The membrane and ion exchange processes are expensive. While adsorption technique is becoming more and more popular because of its simplicity, potential of regeneration and sludge free operation (1,2).

In recent years, much research has been conducted to identify low-cost and low-tech systems for arsenic removal in small, rural communities. Many of these systems involved iron compounds, which have a very strong affinity for arsenic. Iron oxides are promising effective adsorbents for both As(III) and As(V) removal from water. Because of the ready availability of iron oxides, their use for arsenic remediation would be relatively inexpensive. However, most iron oxides are only available as fine powders and are difficult to recover from aqueous solution after adsorption. Because of this, the USEPA has proposed Iron Oxide-Coated Sand (IOCS) filtration as an emerging technology for arsenic removal from small water treatment facilities (3,4). The BET surface area of IOCS is only about 3–4 m^2/g, which limits the system efficiency and the empty-bed contact time. Therefore, researchers have impregnated iron oxides on other substrates including slag (5) and ion exchange beads (6), and fibers (7). Previous work has shown that coating adsorbents on low-cost glass fibers can remove many contaminants well below 1 ppb (8,9). Thus, coating high surface area iron oxide on glass fibers for arsenic removal was designed. In this paper the efficiency of such an approach was shown.

EXPERIMENTAL

Reagents

Iron(III) chloride hexahydrate (>98%) and ammonium hydroxide (28–30%) was received from Sigma-Aldrich. The substrate fiber was a non-woven fiberglass mat, Craneglas 230, (0.015 nominal, fiber diameter of 6.5 μm), made by CRANE & CO.

Equipment

Brunauer-Emmett-Teller (BET) surface area and micro- and mesoporous volumes were carried out on an Autosorb-1 apparatus (Quantachrome). All samples were degassed at 100°C until the outgas pressure rise was below 5 micro Hg/min prior to analysis. N_2 isotherm results at 77 K in the appropriate relative pressure ranges were used for subsequent calculations. The BET equation was used to determine the surface area. The Dubinin-Radushkevich (DR) equation was used to deduce micropore (<2 nm) volumes. The total pore volume was estimated from the amount of nitrogen adsorbed at $P/Po = 0.95$. The volume of mesopores (2–50 nm) was calculated by subtracting the volume of micropores from the total pore volume at a relative pressure of 0.95.

Transmission electron microscopy (TEM) was carried out on a JEOL 2100 cryo and 2010F microscope.

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Wide angle X-ray diffraction (WAXD) experiments were carried out on a Rigaku D/Max-b diffractometer with a copper X-ray source controlled by MDI's DataScan. 45 kV and 20 mA were the parameters used. The scanning angle range (2θ) was 15–80 degree, while the scanning rate was 0.6 degree/min, with a step increment of 0.05. Iron oxide powder was distributed on a double side tape on a glass slide.

X-ray Photoelectron Spectroscopy (XPS) data were obtained from IOCGF using a Physical Electronics PHI Model 5400 surface analysis system. Before analysis all samples were washed with D.I. water and then fully dried. XPS spectra were obtained using an achromatic Mg K_α (1253.6 eV) X-ray source operated at 300 W. Survey scans were collected from 0–1100 eV with a pass energy equal to 178.95 eV. High-resolution scans were performed with the pass energy adjusted to 35.75 eV. The pressure inside the vacuum system was maintained at approximately 10^{-9} Torr during all XPS experiments. A non-linear least squares curve fitting program (XPSPEAK4.1 software) with a symmetric Gaussian-Lorentzian sum function and Shirley background subtraction was used to deconvolve the XPS peaks. The carbon 1s electron binding energy corresponding to graphitic carbon was referenced at 284.5 eV for calibration (10).

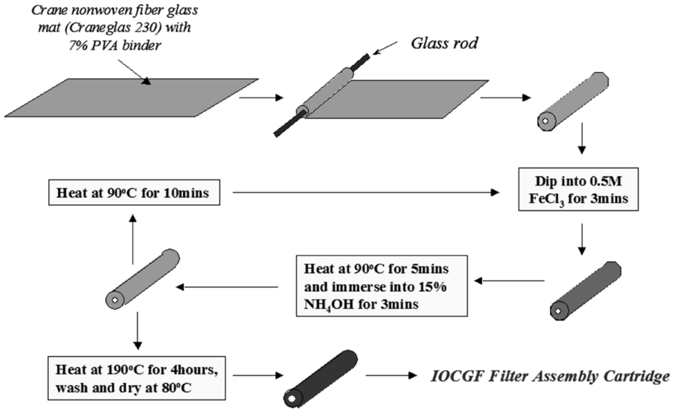


FIG. 1. Preparation of IOCGF filters.

Measurement of Arsenic Concentration

There are several methods to measure arsenic concentration (11).

I. Paper test: Arsenic test kit Quantofix® from Aldrich was used to monitor arsenic qualitatively.

II. Johnson and Pilson's molybdate-based method using UV–vis spectrophotometer: This method was modified to measure the arsenic concentration in the breakthrough experiment where DI water spiked with arsenic was used as the influent. The minimum detect limit of this method is around 2 ppb. Stock solutions of 30 mg L^{-1} As(V) and As(III) were prepared freshly by dissolving analytical grade (Sigma) sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and sodium arsenite ($NaAsO_2$) in deionized water. Secondary As standards (2, 5, 10, 25, 50, 100, 300, 600, 1000 ppb) were prepared by diluting the stock solutions. DI water and trace-metal grade acids were used for all reagents, standards, and blank solutions. The general procedure is described in references (12–14).

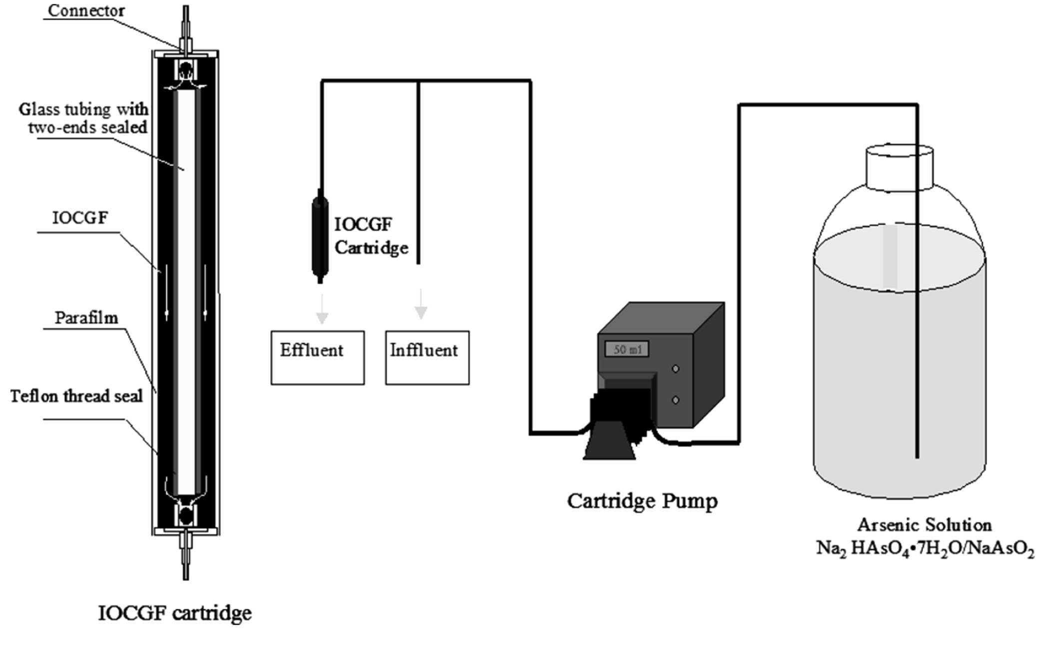


FIG. 2. Schematic drawings of IOCGF cartridge and breakthrough setup.

TABLE 1
Newmark well chemistry at University of Illinois

Solute (mg/L)	Carbonate	Bicarbonate	Carbonic acid	Chloride	Sulfate	Sulfite	Sulfide	pH	Nitrate
	0.51	206	8.74	1	1.1	<0.5	<0.1	8.21	0.14
	Potassium	Magnesium	Ammonia (as N)	Calcium	Phosphate	Sodium	Silica	DOC	Total dissolved iron
	1.59	27.39	2	38.56	0.062	35	15.08	2.88	0.2

TABLE 2
Arsenic adsorption of IOCGF

Initial concentration (ppb)	As(III)	144	360	374	839	1825	17500
	As(V)	1.0	<1	344	573	1774	17100
Residual concentration (ppb)	As(III)	0.3	1.1	1.9	2.1	7.0	1570
	As(V)	0.4	1.1	1.7	1.7	4.5	10800
Total arsenic capacity (mg/g)	As(III+V)	0.07	0.18	0.36	0.70	1.8	11

III. ICP-MS: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using niobium as an internal standard. A Dionex Ion-Exchange column coupled to the front end (sample introduction) of a Thermo-Elemental ExCell ICP-MS instrument was used to speciate arsenic. (Measured by Illinois Waste Management and Research Center, USA.) This method was used to measure the arsenic concentration in batch experiments and the breakthrough experiments with an influent of ground water spiked with arsenic. The minimum detection limit is 0.2 ppb.

Preparation of IOCGF

Iron oxide was prepared by precipitation method based on the procedure described by Lin et al. with a modification for the deposition on glass fibers (15). In a typical procedure, a nonwoven glass fiber mat with 7 wt% PVA binder (Craneglas 230 from Crane & Co. Inc.) was dipped into an aqueous solution of $FeCl_3$ (0.05 mol in 100 ml H_2O) for 3 mins. After drying at 90°C for 5 mins, it was immersed into an aqueous solution of NH_4OH (15%). It was then heated at 90°C for 10 mins. This process was repeated two more times. The resulting iron hydroxide was dried at 190°C for 4 hours. After this, it was washed several times with distilled water until the water became colorless. The general process for the IOCGF filter is illustrated in Fig. 1.

Batch Experiments

Stock solutions of 30 mg L^{-1} As(V) and As(III) were prepared freshly by dissolving analytical grade (Sigma) sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) and sodium arsenite ($NaAsO_2$) in deionized water. Specifically, a series of 100 ml capped polyethylene bottles were employed. Arsenic concentrations as shown in Table 2 were prepared from the stock solutions. 50 ml of the arsenic solution and 0.1 g IOCGF were put into the bottles. All samples were shaken for 24 h. The arsenic concentration was determined by ICP-MS.

Column Test

The IOCGF filter was then assembled as part of the cartridge, which included a glass tube with two-ends sealed and wrapped with one layer of PTFE thread seal tape (to reduce the shortcut path between the IOCGF and the glass tube), two plastic connectors, and parafilm wrapped around the IOCGF filter. The schematic drawing of the IOCGF cartridge and the experimental apparatus for breakthrough tests is shown in Fig. 2. The setup contained a cartridge pump and a pre-prepared stock arsenic solution with DI water or groundwater spiked with $Na_2HAsO_4 \cdot 7H_2O$ or $NaAsO_2$. The groundwater was from Newmark Well at University of Illinois at Urbana-Champaign with the contents listed in Table 1. The flow rate of the arsenic solution was controlled by the pump. The arsenic concentration in the effluent was monitored by the arsenic test kit Quantofix® from Aldrich and collected in a HDPE bottle.

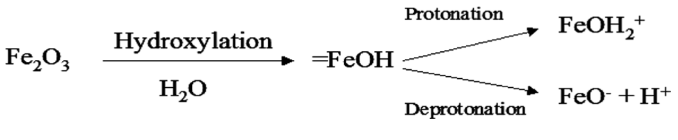
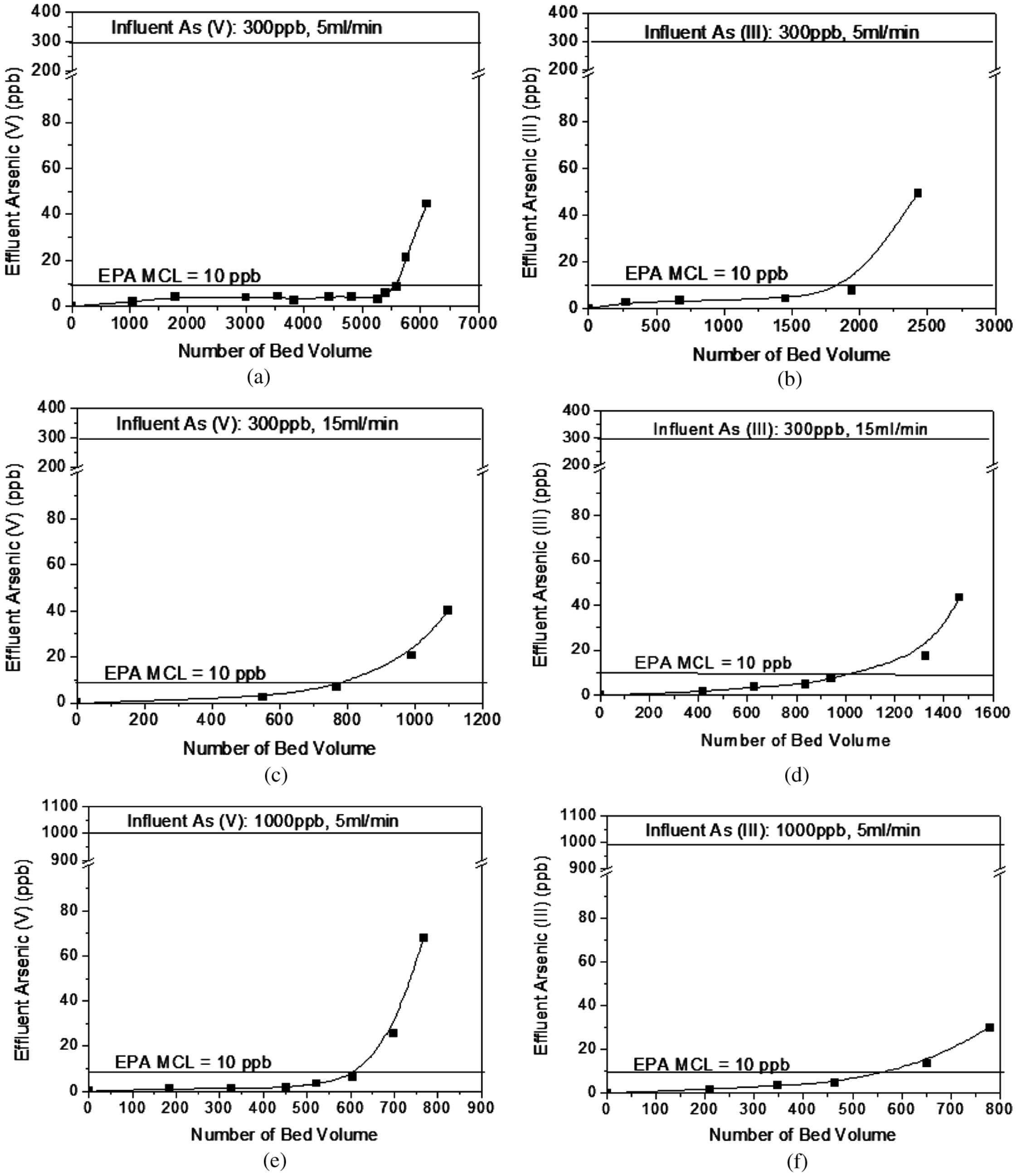


FIG. 3. Development of charge at the iron oxide/solution interface.

TABLE 3
Surface areas and pore volumes of IOCGF

Sample	BET surface area (m^2g^{-1})	Total pore volume ($P/P_0 = 0.95$) (10^{-2} cm^3 g^{-1})	Micropore volume (10^{-2} cm^3 g^{-1})	Mesopore volume (10^{-2} cm^3 g^{-1})
IOCGF	80.75	8.35	2.85 (34.1%)	5.50 (65.9%)



(a) (b) (c) (d) (e) (f)

FIG. 4. Breakthrough curves for DI water spiked with arsenic with different arsenic species, flow rates and influent concentration.

RESULTS AND DISCUSSION

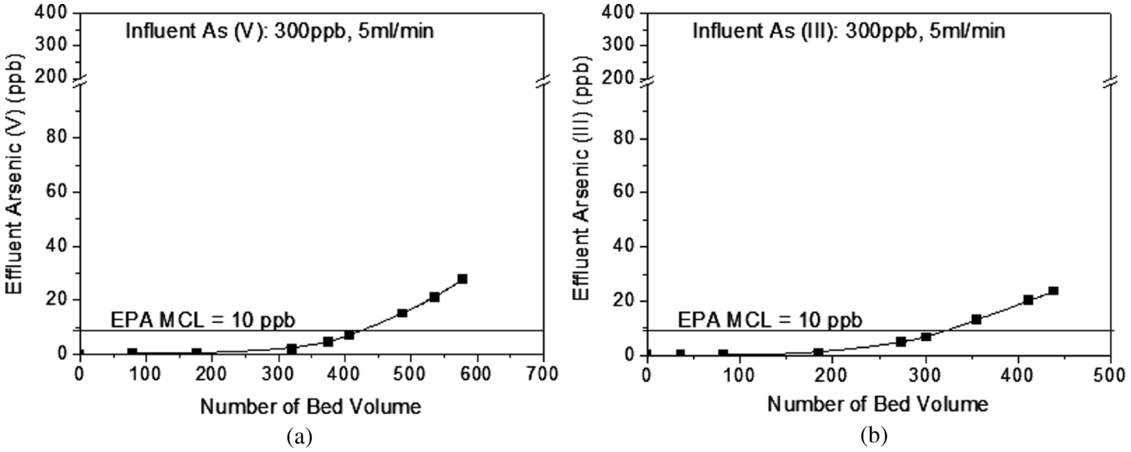
Batch Adsorption

Charge on the iron(III) oxide surface results from the dissociation of the surface hydroxyl groups. The adsorption or desorption of protons depends on the pH of the solution. The situation can be treated as acid/base equilibrium, represented by reactions shown in Fig. 3. Besides the interaction between the surface hydroxyl group and protons, the underlying metal ion acts as a Lewis acid and exchanges the OH group for other ligands to form surface complexes. The latter is also termed chemisorption, inner sphere adsorption, or ligand exchange. This kind of adsorption is very strong and not easily broken. As a result, adsorption may take place on a neutral surface or even with the same charge as the adsorbing species. Both of the above interactions provide iron oxides with a high sorption affinity toward both As(V) and As(III), which are Lewis bases (i.e., electron pair donors). Ions such as nitrate and perchlorate do not exhibit Lewis acid–base characteristics, and are adsorbed only through outer sphere complexes, or electrostatic interaction (16).

Table 2 showed the results of batch experiments. Adsorbent concentration during the 72-hour batch experiments was 2 g/L. IOCGFs removed both As(III) and As(V) very efficiently. After treatment by IOCGF, the arsenic was removed well below 3 ppb when the initial concentrations were below 360 ppb and well below 10 ppb when the initial concentrations were below 1412 ppb, i.e., As(III) = 839 ppb and As(V) = 573 ppb. The total adsorption capacity was about 11 mg/g when the initial concentration of As(III) and As(V) was 17500 ppb and 17100 ppb, respectively. The high efficiency for As(III) and As(V) might be due to the high surface area of IOCGFs, which provides more adsorption sites for arsenic species. The surface properties of IOCGF was characterized by N_2 adsorption and listed in Table 3. Another possible factor might be the heat treatment at 190°C for four hours, which might result in special iron oxide structures. In most previous studies, researchers only heated their iron oxides around 100°C for arsenic removal application. Regeneration of the IOCGF was tried by using NaOH solution. Only about 65% capacity could be recovered. This result showed that disposable IOCGF filters might be preferable to regenerated filters. As suggested by EPA, for point of use in the household, used filters could be exempt from Federal regulations as hazardous waste under the Resource Conservation and Recovery Act (RCRA) as long as the filters pass its toxicity characteristic leaching procedure (17).

Column Studies Using DI Water Spiked with Arsenic

The effect of different parameters such as arsenic species, flow rate, and influent concentration on the performance of IOCGF were studied by breakthrough experiments. The results are illustrated in Fig. 4. The empty bed volume was about 4.3 ml. The weight of iron oxide is about 19% of the filter. The pH of the solution was 6–7. The new system was able to remove arsenic to well below the maximum contaminate level (MCL, 10 ppb) set by USEPA. The number of bed volume at breakthrough was about 5000 for arsenate in Fig. 4(a) and 2000 in Fig. 4(b) for arsenite when the influent concentration was 300 ppb. When the flow rate increased to 15 ml/min, the filter still functioned which meant fast adsorption kinetics and smaller empty-bed contact time. In contrast to the empty-bed contact time of several minutes in the literature (4,7), the value of our systems was about 17 seconds for the flow rate of 15 ml/min and 52 seconds for the flow rate of 5 ml/min. When the influent concentration was increased, the result was similar to what occurred when one increased the flow rate. Interestingly, in both cases, i.e., increasing the influent concentration and increasing the flow rate, the



(a) (b)

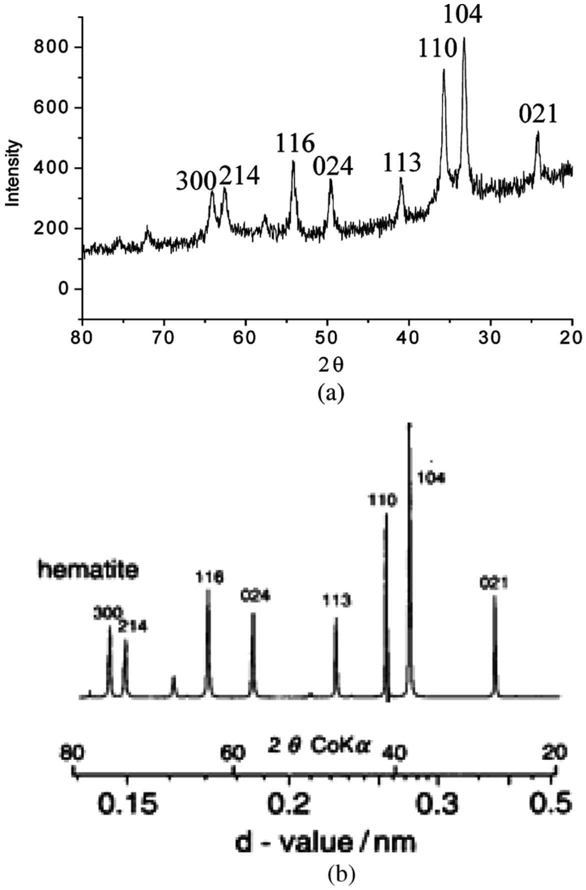
FIG. 5. Breakthrough curves for groundwater spiked with arsenic.

difference between the number of the breakthrough bed volume for As(III) and As(V) became smaller as shown in Figs. 4(e) and (f), sometimes even reversed as shown in Figs. 4(c) and (d), in contrast to the trend observed in Figs. 4(a) and (b). This observation suggested that the adsorption of As(III) on IOCGF had a faster kinetics. When the flow rate or influent concentration increased, the number of active sites occupied by As(III) exceeded that by As(V) due to the difference in the kinetics.

Column Studies Using Groundwater Spiked with Arsenic

Arsenic was spiked into the ground water from Newmark well. The results are demonstrated in Fig. 5. The ground water contains many competing ions including phosphate, silicate and bicarbonate, as shown in Table 1. Although the breakthrough bed volume was greatly reduced due to the combined effect from these ions (18), the arsenic can still be removed well below 3 ppb. Because of its fiber form and high surface area, IOCGF performed efficiently enough for real applications. IOCGFs are expected to have the following advantages:

1. Glass fibers which make it easy to separate iron oxide nanoparticles from aqueous system after adsorption;
2. Higher adsorption capacity and shorter equilibrium time because of high surface area and fiber form;
3. Low cost and easily available adsorbent since the starting reagents ($FeCl_3$ and NH_4OH) are inexpensive and available;
4. High adsorption efficiency of As(III), which is very difficult to be removed by other systems such as ion exchange or membranes.



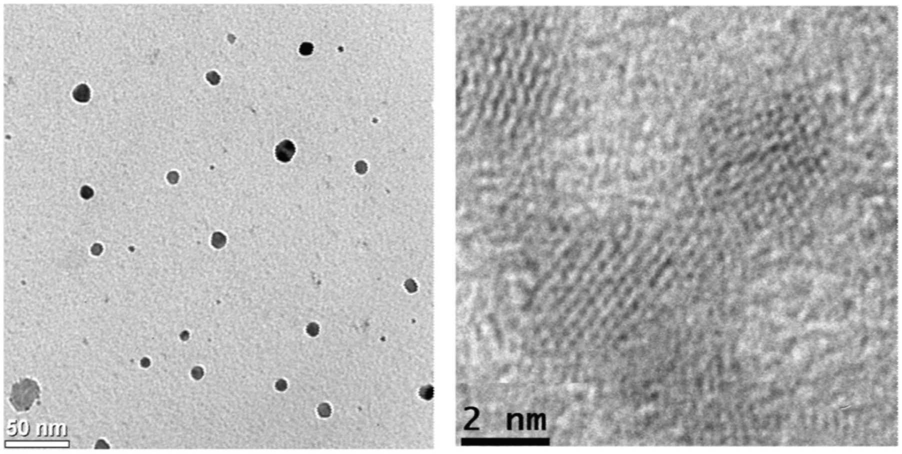
(a)

(b)

FIG. 6. X-ray powder diffractograms of Fe(III) oxides in the research and Hematite from Ref. (16).

Characterization of IOCGF

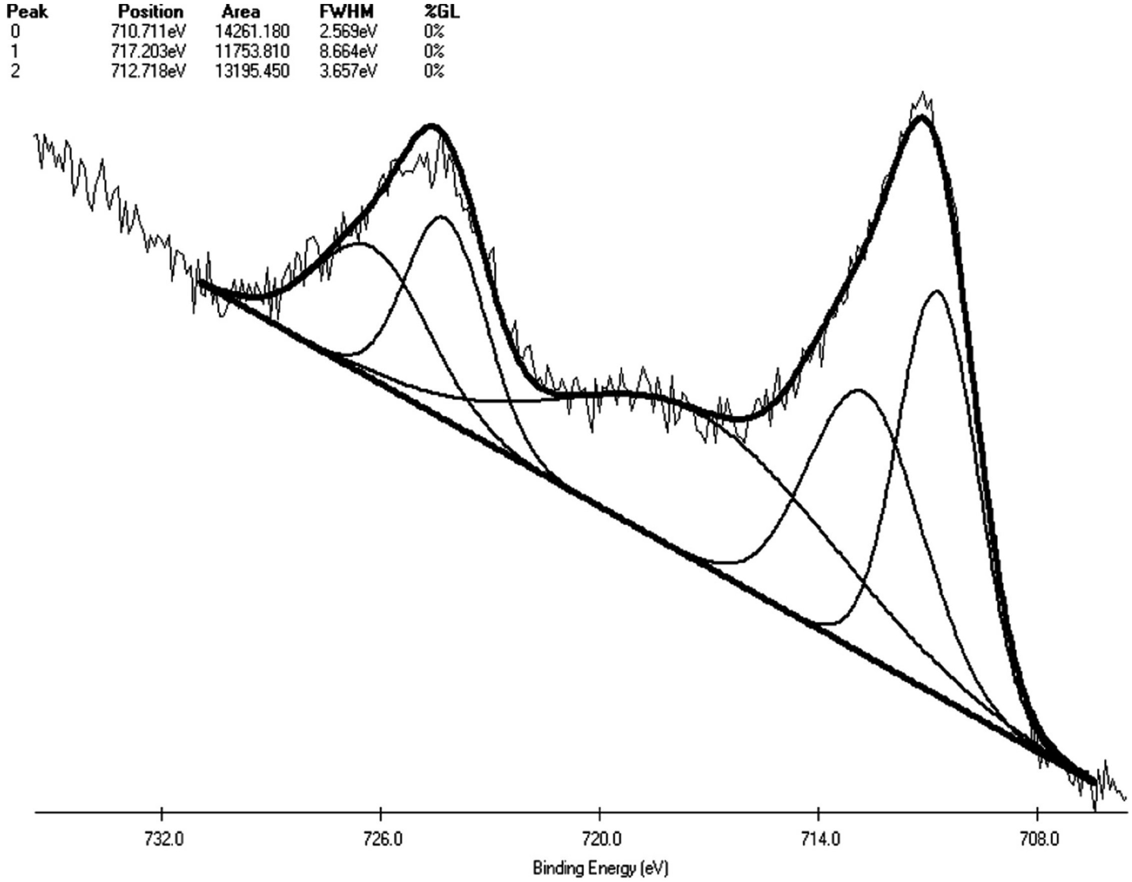
There are sixteen known iron oxides (16). XRD patterns in Fig. 6 showed that the iron oxide was the same as that of hematite. Through TEM in Fig. 7, it was found that the iron oxides were nanocrystals with diameters of several nanometers. XPS was employed to obtain information on



(a)

(b)

FIG. 7. (a) TEM and (b) HRTEM images.



Peak	Position	Area	FWHM	%GL
0	710.711eV	14261.180	2.569eV	0%
1	717.203eV	11753.810	8.664eV	0%
2	712.718eV	13195.450	3.657eV	0%

FIG. 8. XPS of our iron oxides.

the surface state of iron oxides. The spectrum in Fig. 8 was divided into three peaks at 710.7, 712.7, and 717.2 eV. Fe $2p^{3/2}$ appeared between 710.8 and 710.5 eV, which shows the presence of Fe_2O_3 and/or FeO(OH) species (15).

CONCLUSIONS

We have shown that by using the high surface area iron oxides coated on glass fibers arsenic in water can easily and efficiently be removed. Without the need to pre-oxidize As(III) to As(V), the IOCGF can remove both arsenic species well below EPA MCL (10 ppb). We also showed an easy way to measure arsenic concentration using a UV colorimetric method.

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