

Development of an Anionic Exchange Glass Fiber Substrate POU Device to Remove Arsenic

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Final Report
Midwest Technology Assistance Center

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Project Significance

Arsenic poisoning is one of the most widespread water-related problems in the world (Cullen and Reimer, 1989). Arsenic in drinking water causes bladder, lung, and skin cancer. Even very low doses of arsenic may damage the central and peripheral nervous systems, heart, and blood vessels, and may also lead to serious skin problems. The U.S. Environmental Protection Agency (USEPA) has set a maximum contaminant level (MCL) for arsenic in drinking water at 10 micrograms per liter ($\mu\text{g/L}$). A National Academy of Sciences report (2001) has indicated that, even at levels as low as 3 $\mu\text{g/L}$, the risk of cancer is still ten times that of EPA's acceptable value (0.1 per 1000 people). Thus the acceptable levels for arsenic may be further lowered in the future. Based on the best available data, it is conservatively estimated that more than 34 million Americans drink tap water from water supplies containing average levels of arsenic greater than 3 $\mu\text{g/L}$ (Kartinen and Martin, 1995; National Academy of Sciences, 2001; Johnston and Heijnen, 2001; Wilson et al., 2004; Newcombe and Möller, 2006). Many millions more are at risk worldwide, most notably in Bangladesh and eastern India. In the Midwestern United States, numerous wells contain arsenic concentrations higher than 10 $\mu\text{g/L}$. A map showing public water supply wells in Illinois with arsenic concentrations $> 10 \mu\text{g/L}$ is shown in Figure 1 (Wilson et al., 2004). The development of improved or new treatment technologies for removal of the two major arsenic ions, arsenate [As(V)] and arsenite [As(III)], is needed to help mitigate worldwide problems of arsenic-contaminated water and protect public health.

In this project, an iron oxide (Fe_2O_3) system supported on a glass fiber substrate developed at the Department of Materials Science at the University of Illinois at Urbana-Champaign was evaluated for removal of arsenic from water. Laboratory tests were performed to evaluate the effectiveness of these filters in removing arsenic to concentrations below the MCL and determine how long the filters remained effective. Both deionized (DI) water and natural groundwater spiked with arsenic were used in the laboratory tests to evaluate the rate of fouling and determine the significance of solute (i.e., anions such as bicarbonate, silicate, and phosphate) interference. Finally, a prototype of a point-of-use (POU) device was developed and tested in the homes of volunteers who had elevated arsenic concentrations in their well water.

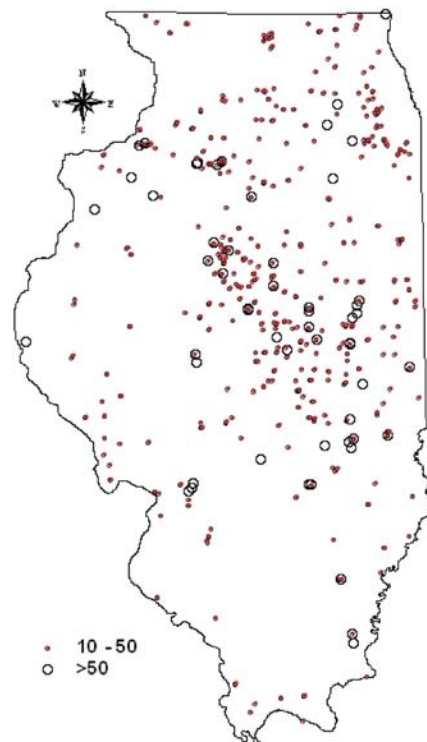


Figure 1. Locations of municipal wells in Illinois with at least one raw water sample having an arsenic concentration $> 10 \mu\text{g/L}$ (Wilson et al., 2004). Data from Illinois EPA.

Materials Synthesis

In order to prepare the iron oxide coating on the glass fiber (IOCGF) substrate, a nonwoven glass fiber mat with 7 wt % PVA binder (Craneglass 230, Crane & Co. Inc.) was dipped into an aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.05 moles per liter [mol/L]) for 3 minutes. After drying at 90°C for 5 minutes, the sample was immersed into an aqueous solution of NH_4OH (0.15 mol/L). It was then heated at 90°C for 10 minutes. The resulting iron hydroxide was dried at 190°C for 4 hours (Lin et al., 2005). After this, it was washed several times with distilled water until the water became clean (Figure 2). Six sets of batch tests were done with DI water spiked with various concentrations of As(V) (<1 to $17,000 \mu\text{g/L}$) and As(III) (144 – $17,500 \mu\text{g/L}$).

To test the IOCGF filter in a flow-through system, it was assembled into a cartridge, which included a glass tube with the two ends sealed and wrapped with one layer of PTFE threaded 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 Figure 3. The setup contained a cartridge pump and a pre-prepared stock arsenic solution with DI water or groundwater spiked with $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ or NaAsO_2 to a final concentration of $300 \mu\text{g/L}$ As(III) or As(V). The flow rate was controlled by the pump. Effluent was collected in HDPE

bottles, and the arsenic concentration was measured using an arsenic test kit (Quantofix[®] from Aldrich).

Regeneration of this system is being examined for potential use in facilities that are required to process large quantities of contaminated water. For domestic systems, it was anticipated that the filter would be disposed of as household waste once past its useful lifetime.

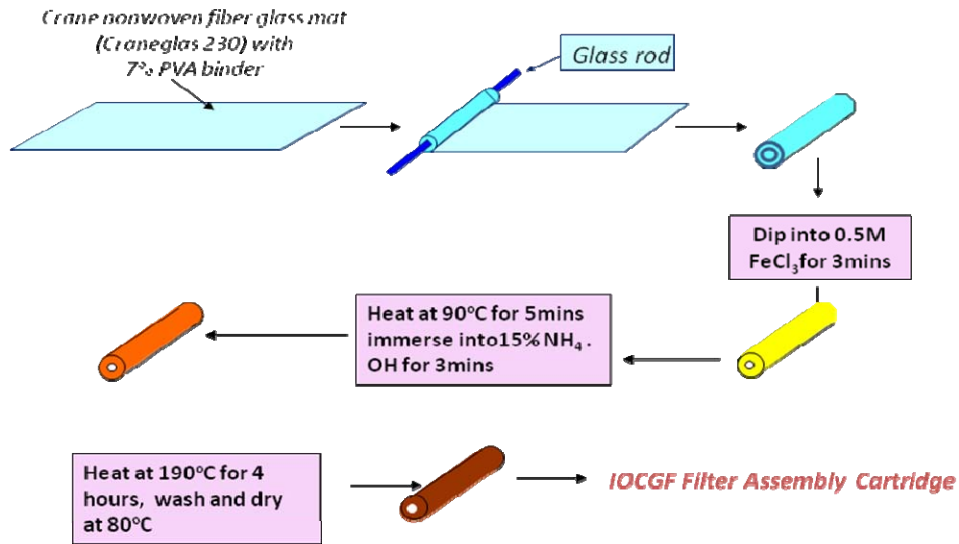


Figure 2. Preparation of Iron Oxide Coating on Glass Fibers (IOCGF)

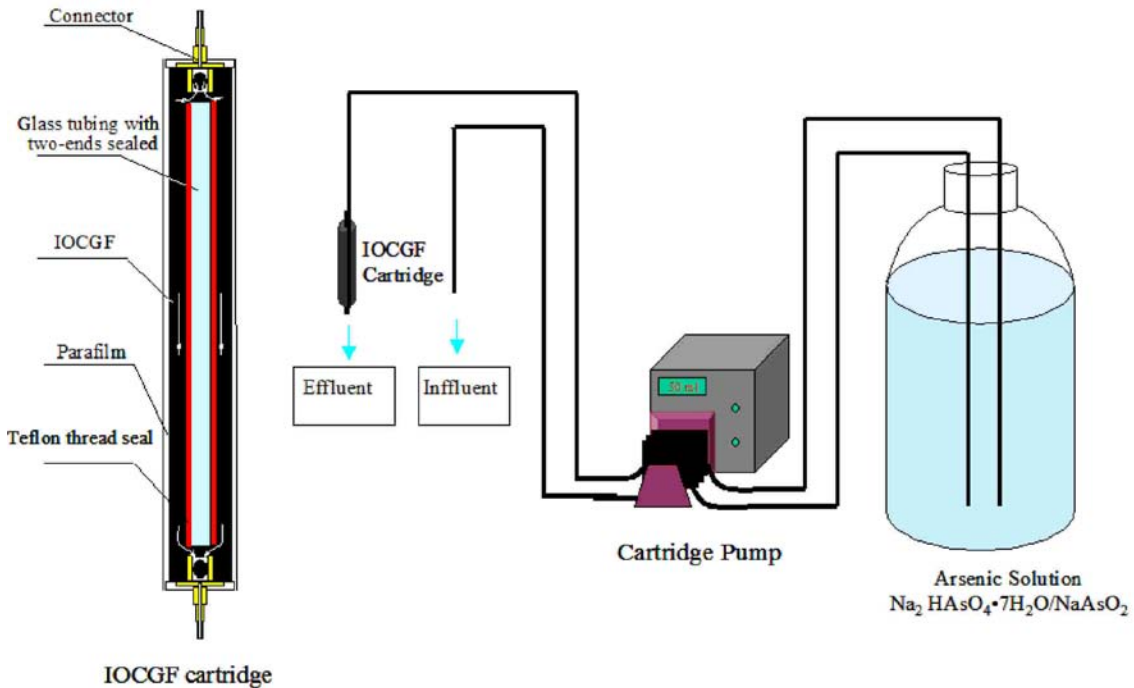


Figure 3. Schematic diagrams of IOCGF cartridge and breakthrough setup

Characterizations of Iron Oxide Coating on Glass Fibers

A scanning electron microscope (SEM) image of IOCGF (Figure 4) shows iron oxide nanoparticles were well attached to the glass fiber substrate. A transmission electron microscope (TEM) image of iron oxide nanoparticles (Figure 5) indicates that nanoparticles were spherical with diameters between 2 to 20 nanometers (nm). The X-ray diffraction pattern of the iron oxide nanoparticles (Figure 6) showed that they were hematite with no other phases present. The isoelectrical point (IEP) of the IOCGF was characterized by the zeta potential versus pH of the iron oxide nanoparticle solution, determined to be 8.14. The results of these characterizations indicated that iron oxide nanoparticles should be positively charged ($\text{pH} \leq 8.14$) and efficiently absorb the negatively charged arsenate and arsenite (Figure 7). The BET surface area of the IOCGF was about $80 \text{ m}^2/\text{g}$.

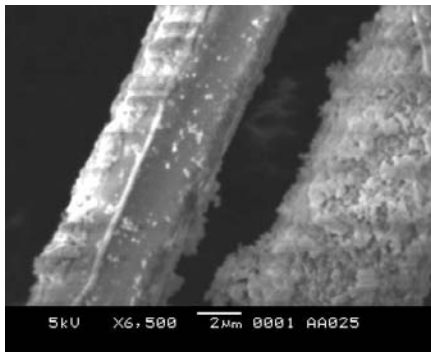


Figure 4. SEM of IOCGF

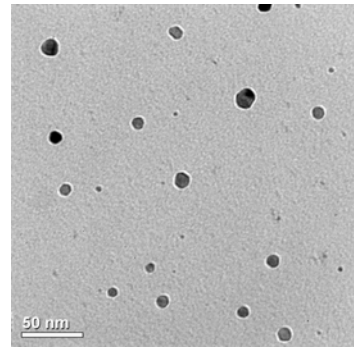


Figure 5. TEM of Fe_2O_3

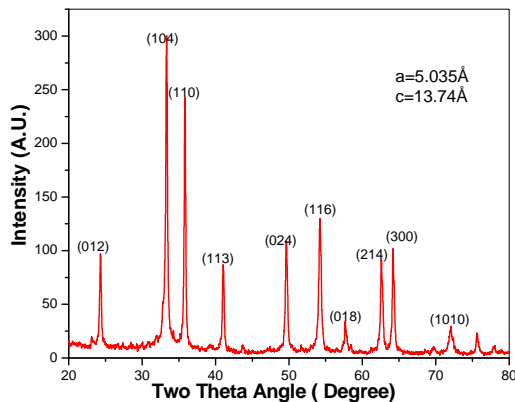


Figure 6. XRD of Fe_2O_3

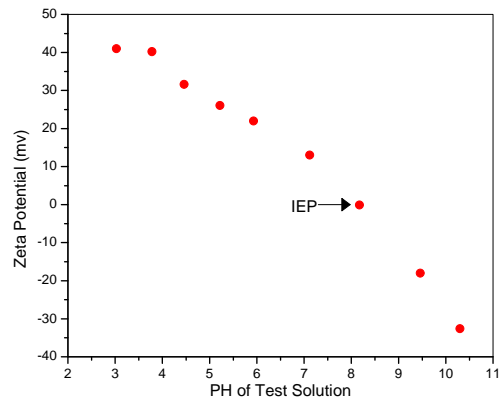


Figure 7. Zeta Potentials of Fe_2O_3

Batch Tests

The adsorption capacity of the IOCGF was about 13 mg/g when the initial concentration of As (III/V ratio = 1/1) was 33 mg/L and the adsorbent concentration was 1.86 g/L. As shown in Table 1, the IOCGF removed both As (III) and As(V) efficiently.

Table 1. Arsenic adsorption of IOCGF in batch tests

Initial Concentration (µg/L)	As (III)	144	360	374	839	1825	17500
	As (V)	1.0	<1	344	573	1774	17100
Residual Concentration (µg/L)	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

Note: Adsorbent concentration is 2 g/L.

Column Tests

The effects of different parameters such as arsenic species, flow rate, and influent concentration on the performance of IOCGF were studied in column breakthrough experiments. Results using DI water spiked with arsenic are shown in Figure 8. The IOCGF system was able to remove arsenic to well below the maximum contaminant level (10 µg/L). Both As(V) and As(III) concentrations were below 1 µg/L before breakthrough, which occurred after about 350 bed volumes for As(V) and 450 bed volumes for As(III). Effluent arsenic concentrations were less than 10 µg/L for approximately 5000 bed volumes for As(V) and 2000 bed volumes for As(III). After that point, effluent arsenic concentrations increased significantly, indicating the IOCGF was no longer efficiently removing arsenic. These breakthrough bed volumes were at least two times better than those for a system using iron oxide coated on sand (IOCS) reported by Joshi and Chaudhuri (1996), while the flow rate was five times larger. The IOCGF is expected to have several advantages over IOCS: (1) improved contact efficiency due to the glass fiber substrate; (2) higher adsorption capacity due to high surface area; (3) low cost and easily available adsorbent since the starting reagents (FeCl₃ and NH₃·H₂O) are inexpensive; (4) easy preparation and suitable for column use; and (5) high adsorption efficiency of As (III) and As (V).

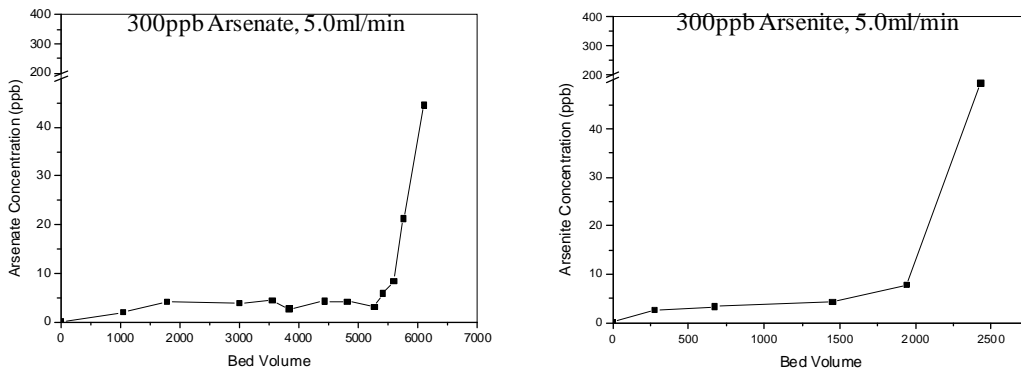


Figure 8. Breakthrough curves for DI water spiked with different arsenic species

Natural groundwater spiked with arsenic was also tested in column experiments. The source of the water was a well located in the Newmark Engineering building at the University of Illinois. The groundwater contained many competing ions including phosphate, silicate, and bicarbonate (Table 2). The results of the experiments are shown in Figure 9. Effluent arsenic concentrations were determined by 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. Although the breakthrough bed volume was reduced due to the competition effects from other anions, arsenic was still removed to concentrations well below 3 $\mu\text{g/L}$.

Table 2. Newmark Well Chemistry at University of Illinois

Solute	Carbonate	Bicarbonate	Carbonic acid	Chloride	Sulfate	Sulfite	Sulfide	Phosphate	NO ₃ ⁻
(mg/L)	0.51	206	8.74	1	1.1	<0.5	<0.1	0.062	0.14

Solute	DOC	pH	Ammonia (as N)	Calcium	Magnesium	Sodium	Silica	Potassium	Total Dissolved Iron
(mg/L)	2.88	8.21	2	38.56	27.39	35	15.08	1.59	0.2

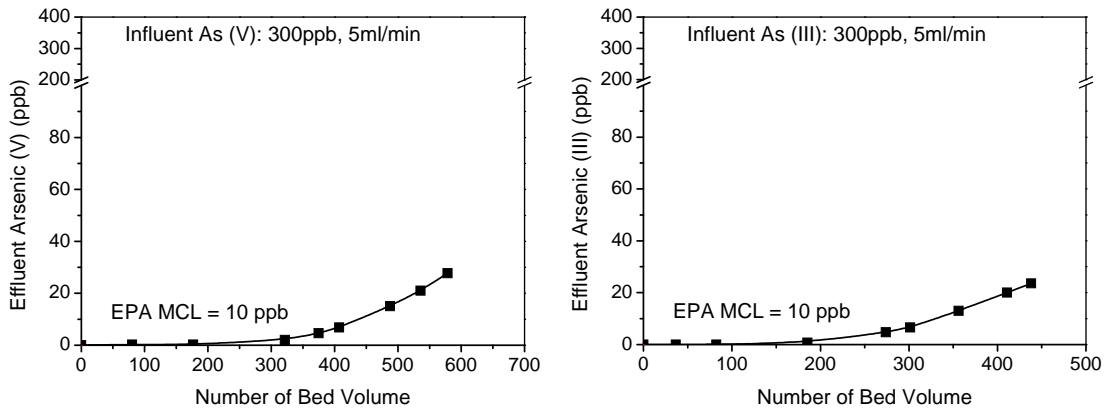


Figure 9. Breakthrough curves for groundwater spiked with arsenic

Field Tests

A POU prototype was designed and constructed for field tests. Off-the-shelf water pitchers with activated carbon filters were purchased and modified. The activated carbon filters were removed and replaced with IOCGF. The top section of the pitcher was filled with approximately one liter of water which then percolated through the IOCGF into the bottom storage section of the pitcher (Figure 10).



Figure 10. Schematic design for IOCGF pitchers used in field tests

Five of these POU pitchers were prepared and given to volunteers who had domestic wells that had been determined to have elevated levels of arsenic. Four of the wells were located in Tazewell County and the fifth in DeWitt County. The volunteers were instructed to fill the pitcher once a day and collect samples from the tap and the pitcher once a week. Test results are shown in Table 3.

Table 3. Results of POU Field Tests. Each day represents one volume of water (i.e., filling of the pitcher ~1 L).

Volunteer ID	Date	Day	Tap As (µg/L)	Pitcher As (µg/L)	As removal (µg/L)	Fraction removed
A	6/26/2008	1	33.0	22.7	10.3	0.31
	7/6/2008	7	34.2	27.6	6.6	0.19
	7/13/2008	14	34.2	27.0	7.2	0.21
	7/20/2008	21	29.4	29.1	0.2	0.01
	7/29/2008	27	34.5	34.9	-0.4	-0.01
	8/2/2008	30	34.8	20.1	14.7	0.42
	8/9/2008	36	27.5	23.8	3.6	0.13
B	7/2/2008	7	63.2	38.0	25.3	0.40
	7/9/2008	13	65.8	43.9	21.9	0.33
	7/16/2008	20	62.4	40.3	22.1	0.35
	7/23/2008	27	76.6	44.7	31.9	0.42
	8/1/2008	34	68.0	46.9	21.1	0.31
	8/7/2008	38	74.7	40.3	34.4	0.46
	8/14/2008	44	74.9	56.1	18.8	0.25
C	6/27/2008	2	91.7	68.9	22.7	0.25
	7/4/2008	9	94.5	72.9	21.6	0.23
	7/11/2008	16	92.8	82.3	10.5	0.11
	7/18/2008	22	92.4	93.4	-1.0	-0.01
	7/24/2008	27	92.1	98.8	-6.8	-0.07
	8/7/2008	32	97.1	97.1	0.0	0.00
	8/14/2008	39	92.4	90.1	2.3	0.02
D	7/7/2008	1	90.7	69.3	21.4	0.24
	7/14/2008	6	91.0	84.6	6.4	0.07
	7/21/2008	13	84.7	85.2	-0.5	-0.01
	7/28/2008	20	96.7	92.3	4.3	0.04
	8/4/2008	27	90.5	86.2	4.3	0.05
	8/11/2008	34	93.0	86.3	6.7	0.07
E	5/19/2008	1	13.2	16.8	-3.6	-0.28
	6/21/2008	9	21.1	18.6	2.5	0.12
	6/30/2008	12	20.0	18.9	1.1	0.05
	7/7/2008	15	17.8	20.4	-2.7	-0.15

The POU devices did not perform adequately. They removed some arsenic from the water, but not enough for levels to fall below the MCL of 10 µg/L. The greatest removal was from site B, where the removal rate remained relatively consistent over six weeks. Two of the pitchers (at sites C and D) showed a definite decrease in removal efficiency with time. These two sites had the highest arsenic concentrations in their well water. At the site with the lowest arsenic concentration (E), there was little or no removal. Interference by other ions may have contributed to the poor removal efficiency. All the sites had much higher bicarbonate concentrations compared to the Newmark well, especially sites C, D, and E, which had the poorest removal rates (Table 4). Silicate concentrations were not significantly higher, except perhaps at site C.

Although it was not measured, dissolved organic carbon levels may also be high in these wells (> 1 mg/L), based on other sampling in the region.

Table 4. Tap Water Chemistry at Volunteer Sites

Site Name		A	B	C	D	E
Date	Units	6/26/2008	6/26/2008	6/26/2008	7/3/2008	9/19/2007
pH (lab)		7.74	7.76	7.57	7.81	7.90
Alkalinity (CaCO ₃)	mg/L	402	423	573	580	561
Bicarbonate	mg/L	490	516	699	707	684
Chloride	mg/L	14.3	44.1	2.9	30.2	20.3
Fluoride	mg/L	0.33	0.28	0.45	0.59	0.9
Sulfate	mg/L	< 0.31	< 0.31	0.31	< 0.31	< 0.31
Nitrate-N	mg/L	< 0.07	< 0.07	< 0.07	< 0.07	< 0.07
Calcium	mg/L	0.151	0.054	0.682	0.166	49.5
Potassium	mg/L	0.205	0.145	0.575	0.224	4.34
Magnesium	mg/L	0.065	0.05	0.259	0.049	36.4
Sodium	mg/L	203	220	291	312	144
Iron	mg/L	0.019	0.027	0.09	0.081	2.9
Silicate	mg/L	16.2	16.6	22.7	14.8	18.1
TDS	mg/L	467	543	642	694	585
Turbidity	NTU	0.3	< 0.1	1.4	0.2	6.7
Aluminum	µg/L	< 6.1	< 6.1	< 6.1	< 6.1	15
Arsenic	µg/L	34.4	64	95.1	85.7	18.5
Boron	µg/L	234	229	334	365	588
Barium	µg/L	< 0.85	< 0.85	1.9	1.6	130
Beryllium	µg/L	< 0.55	< 0.55	< 0.55	< 0.55	< 0.55
Chromium	µg/L	< 5.8	< 5.8	< 5.8	< 5.8	< 5.8
Copper	µg/L	< 0.79	18	< 0.79	< 0.79	1.4
Manganese	µg/L	< 1.5	< 1.5	< 1.5	< 1.5	15
Nickel	µg/L	< 14	< 14	18	< 14	< 14
Zinc	µg/L	< 7.3	< 7.3	< 7.3	16	155

Summary

The IOCGF system worked well in laboratory tests with both DI and natural groundwater spiked with arsenic. The number of bed volumes before IOCGF failure were large enough that the development of POU devices seemed promising. However, the POU devices failed to perform adequately in field tests. It seems likely that the interference of other ions, especially bicarbonate, may have compromised the ability of the filter to absorb arsenic. It is also possible that the POU design did not allow sufficient contact time with the water to efficiently remove arsenic.

Further research is being conducted at the Department of Materials Science, and a new filter system has been developed. This system depends on a chelating fiber that removes arsenic but is less vulnerable to competing ions and other contaminants than is IOCGF. Early laboratory results are promising, but further testing using natural groundwater needs to be done. Because of the simplicity and low cost of these systems, they still remain promising technologies for the removal of arsenic from drinking water.

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