Removal of As(III) and As(V) in surface modified ceramic filters
Emily C. Robbins, Jing Guo and Craig D. Adams

ABSTRACT
A new point-of-use (POU) technology using porous ceramic filters with a ferric-iron coating was used to achieve simultaneous arsenic (III) and (V) removal along with filtrative disinfection. The surface modified ceramic filters (SMCF) were produced using standard ceramic filter methods with combustible materials to create a porous ceramic during firing, followed by coating with a ferric oxide surface coating. A majority of the testing was conducted using 2.0-cm thick, 1.3-cm diameter ceramic plugs to simulate full-scale filters in column studies. The SMCF was capable of filtering arsenic for long periods of time with essentially no As breakthrough. As in source water was reduced from 250 μg/L to less than the 10 μg/L WHO guideline for arsenic for 875 and 1,618 bed volumes (or 360 and 666 effective filter runs) with 0.51 and 2 M iron-coated filters, respectively. There was no significant difference in As(V) or As(III) removal performance over a pH range of 6 to 9. Filtration of lake water containing natural organic matter at 5 mg/L as C reduced performance of As(III) and As(V) removal approximately 34 to 38%, respectively. Other metals including cadmium, copper and chromate were also readily adsorbed by the SMCF while selenate was not.

INTRODUCTION
Millions of people worldwide drink water contaminated with naturally occurring arsenic at concentrations above the World Health Organization (WHO) drinking water guideline of 10 μg/L including in Bangladesh, West Bengal, India, China, and other East Asian countries causing arsenicosis (or hyperpigmentation), hyperkeratosis, cancers, and neurological and other disease (Hussam & Munir 2007; Chen et al. 2008).

Arsenic in natural waters may occur either as the reduced arsenite (As(III), e.g. AsO₂⁻) or as the oxidized arsenate (As(V), e.g. AsO₄³⁻). Adsorption of arsenic on amorphous Fe oxide is considered one of the most promising technologies because of both its efficiency and cost effectiveness (Gupta & Chen 1978; Dixit & Hering 2003; Jessen et al. 2005; Kundu & Gupta 2005; Jang et al. 2006; Liu et al. 2006; Ko et al. 2007; Maiti et al. 2010).

As(V) exists primarily as the anions H₂AsO₄⁻ from pH 2.3 to 6.8, HAsO₄²⁻ from pH 6.8 to 11.6, and as AsO₄³⁻ at pH above 11.6. As(III) is primarily in the neutral species, H₃AsO₃, up to pH 9.2, and in anionic forms above pH 9.2. Sorption of As(V) generally involves formation of inner-sphere complexes on the Fe oxide adsorbent, while the sorption of As(III) involves both inner- and outer-sphere complexes on the Fe oxide adsorbent (Manceau 1995; Goldberg & Johnston 2001; Bissen & Frimmel 2003; Sherman & Randall 2003). Water quality parameters including phosphate, natural organic matter, silicate, alkalinity, pH and oxidation reduction (redox) potential also have been shown to significantly impact sorption of arsenic species onto Fe oxides (Manju et al. 1998; Meng et al. 2002; Dixit & Hering 2003; Lee et al. 2003; Jessen et al. 2005). As a support for an amorphous Fe oxide adsorbent, researchers have studied and/or developed coating or impregnating materials including sand (Benjamin et al. 1996; Thirunavukkarasu et al. 2005; Jessen et al. 2005), porous diatomite (Jang et al. 2006), porous
catalytic (Li et al. 2010), and activated carbon (Lorenzen et al. 1995).

One of the most effective point-of-use (POU) water treatment devices is the ceramic filter, which consists of porous clay that allows passage of water and rejection of bacteria and larger pathogens (Clasen et al. 2007; Sobsey et al. 2008; Bielefeldt et al. 2009, 2010; Hunter 2009). Ceramic filters may be in the form of a porous vessel such as those promoted by Potters for Peace (2005), or as a filter element. The Potters for Peace type ceramic filter vessel is typically 20 to 24 cm high, with diameters on the order of 20 to 30 cm, with volumes ranging from 6 to 20 L.

The purpose of this research was to develop a POU water treatment technology using a monolithic porous ceramic filter to simultaneously treat biological and chemical contaminants including arsenic. Pathogens can often contaminate groundwater either in the ground (in shallow aquifers) or once collected into containers. The principal design studied consisted of a conventional porous ceramic filter coated internally with amorphous iron-oxide coating. The results of this research may be applied in various contexts including in-line filters in a pipe, disk filters, or pots. Most tests reported herein were conducted using 2.0-cm thick, 1.5-cm diameter ceramic plugs to simulate full-scale pots. While very limited tests with full-scale pots are reported herein, comprehensive field testing at full-scale is critical under a wide range of varied conditions.

Potentially the most important application of this surface modified ceramic filters (SMCF) is in filter pots (e.g. the form advocated by Potters for Peace) to provide simultaneous disinfection and arsenic removal in developing nations. Issues that impact all filtration technology, including Potters for Peace filters, such as iron or particulate fouling, are being studied at full scale in continuing work.

MATERIALS AND METHODS

Materials

Ceramic filters for laboratory testing were manufactured from clay, sawdust and water according to standard ceramic filter protocols (Potters for Peace 2005). A majority of the testing was conducted using a common 200-mesh Redart pottery clay (Resco Products, Pittsburgh, PA) used for ceramic filters (Oyanedel-Craver & Smith 2007; Yanez 2009). The burnout material used was 50-mesh-sieved sawdust (600 μm nominal) mixed into the clay at 27% by mass to create the porous pore structure after firing providing sufficient water flow rates with effective bacterial filtration.

As(III) and As(V) stock solutions were prepared frequently from reagent grade sodium arsenite (NaAsO2; Fisher Scientific, St Louis, MO) and sodium arsenate (HAsNa2O4; Sigma Aldrich, St Louis, MO). Na2SeO4, CdCl2, Cr2O3, and CuCl2 were purchased from Acros Organics (New Jersey). Ferric nitrate (Fe(NO3)3; MP Biomedicals) was used to prepare the iron-oxide coating on the ceramic filters. Colloidal silver was purchased from Argenol Laboratories (Spain) and mixed into a 0.023% (as Ag) suspension used to coat selected filters. Lab water (18 MΩ-cm) was produced using a Milli-Q (MilliPore Model Direct-Q) water system. Natural water was collected from Clinton Reservoir in Douglas County, KS (USA) for experiments examining competitive effects for water constituents potentially present in shallow groundwaters or surface water. Natural water was also collected from Potters Lake in Lawrence, KS (USA) for experiments confirming bacteriological removal effectiveness of the coated filters.

Analytical methods

Arsenic concentrations were determined using a Varian Spectra AA 240 graphite furnace atomic absorption spectrophotometer equipped with a GTA 100 graphite-tube analyzer and programmable sample dispenser. Verification of arsenic speciation in the influent solutions was performed by ion chromatography (IC) analysis using a Dionex ICS-2000 with an IonPac AS18 anion exchange column (Dionex). A KOH gradient of 6–52 mM in 15 min at a 1 mL/min flow rate was used as the eluent. Fe concentrations in the filtered effluent were determined using Hach Iron TNT 858 method. pH was determined using an Accumet Basic pH meter (Model AB15; Fisher Scientific). The total calcium hardness and alkalinity of the Clinton Lake water were determined using Hach digital titrator kits using Hach Methods 8329 and 8203, respectively. Phosphate (PO4-P) concentration in the natural water was determined using Hach Phosphorus TNT 843 method.
using a DR 5000 spectrophotometer (HACH). Dissolved organic carbon (DOC) was determined using a Teledyne Tekmar TOC Analyzer. Petrifilm plates (3M, St Louis, MO) were used to measure *Escherichia coli* and total coliform counts in unfiltered and filtered natural water.

Physical properties of uncoated and coated ceramic filters were determined in the Leventis Research Laboratory at the Missouri University of Science and Technology (Rolla, MO). Specifically, skeletal density was determined using helium pycnometry using a Micromeritics AccuPyc II 1340 (Norcross, GA). Surface areas and pore size distributions were determined using N2-sorption porosimetry using a Micromeritics ASAP 2020 Surface Area and Pore Distribution Analyzer.

**Ceramic filter fabrication**

A 73:27 (wt) clay: sawdust ratio was used in all filter experiments by mixing 4.55 kg of the dry clay/sawdust mix with 3.6 L tap water and kneading into a workable homogeneous consistency. Full-size ceramic filters were pressed using a hydraulic press and mold. However, most experiments were conducted on 2.0-cm thick, 1.3-cm diameter ceramic plugs in column experiments to simulate filter performance at full scale to allow the testing of a wide range of filters and experimental conditions. The filters were air dried for at least three days prior to firing in a Carbolite 3216 tube furnace in a ramp from 20 °C to a maximum of 900 °C where it was held for 6 hours before cooling. For preliminary full-scale pot tests, a mold and hydraulic press was used to create pots of 21-cm height, with internal diameter of 15 cm at the top tapering to 10 cm at the bottom. The thickness of the pots was the same as for the plugs described above (2 cm).

The Fe oxide coating on the ceramic filters was created in a process modified from sand coating procedures previously reported (Benjamin *et al.* 1996; Thirunavukkarasu *et al.* 2003). Ferric nitrate coating solutions were prepared at different concentrations including 0.026, 0.128, 0.51 and 2.0 M (depending on the experiment) to test the effect of different Fe coating mass and thicknesses. Specific Fe mass was estimated based on dry weight gain, and Fe oxide film thickness was estimated using mass and surface area estimates. Filter plugs were saturated in two ways with the ferric nitrate solution including extended submersion and mixing, and/or by passing the ferric nitrate solution through the plug using a syringe. Full-scale pots were coated by filling with iron nitrate solution once, and allowed to drain until most solution had passed through. Coated filters were baked at 110 °C for 4 hours to remove the water, and then at 550 °C for 3 hours. The filters were then allowed to cool to room temperature, and then rinsed with lab water to remove any colloidal fines. The ferric Fe coating procedure was then repeated for plugs. Colloidal silver was coated on a subset of filters by submersion in a 200 mg/L (as Ag) solution for 2 min according the procedure recommended by *Potters for Peace* (2005).

**Experimental filtration system**

For testing of various filter designs, filter plugs were encased using 10-mL Luer-lock syringes (BD, Franklin Lakes, NJ) using epoxy adhesive on the sides so that no water could bypass the filter plug. Four 8-channel Minipulse 3 peristaltic pumps (Gilson) were used to continuously pump water through the ceramic plugs. The flow rate through the ceramic plugs of 0.026 mL/min was used to approximate the typical flow rate through a gravity-fed, full-scale ceramic filter (of 2.5 L/h) by scaling surface areas of the full-scale filter to the plug. For purposes of calculating effective filter runs, a full-size pot of approximately 22 cm high by 25 cm diameter was assumed. A system of stainless steel hypodermic needles (Cadence Science, Cranston, RI), Tygon tubing (Masterflex, Kalamazoo, MI), and Luer fittings were used to pass solutions from the feed reservoirs, through the peristaltic pump, the filters, and finally into polypropylene test tubes in a Retriever II sample collector (ISCO, Lincoln, NE). The sample collector was set to advance after a time (and volume) scaled to correspond to one filter run.

For a preliminary full-scale pot test, Logan River (Utah) water was spiked with As(V) to a concentration of 283 μg/L as As. The pot was filled repeatedly and allowed to drain for 1 hour. Flow rate, arsenic concentrations and turbidity were measured for each run.

**Arsenic adsorption experiments**

The arsenic adsorption capacity of the SMCFs was tested under a wide range of coatings and conditions. Parameters
studied included the effect of: (1) arsenic species (i.e. As(III) versus As(V)) in the feed solution; (2) Fe coating solutions used to coat the filters of 0, 0.026, 0.128, 0.51 and 2 M, the amount of Fe coated on the filters is, respectively, 0, 0.96, 4.81, 19.25 and 36.07 mg/g; (3) standard versus no colloidal silver; and (4) feed solutions in lab water versus natural water with high DOC. As(III) and As(V) arsenic feed solutions were prepared at 250 μg/L in lab water buffered with 0.5 mM HCO₃⁻/CO₃⁻ at a pH of 7.5 generally (or 6.0 or 9.0 in selected experiments).

Selected experiments were conducted in natural waters (prefiltered through a 0.45-μm glass fiber filter) with a calcium hardness, total hardness and alkalinity of 113, 141, and 159 mg/L as CaCO₃, respectively. The lake water contained 4.98 mg/L DOC, 10.9 mg/L Cl⁻, 1.52 mg/L NO₃⁻-N, 1.3 mg/L PO₄-P, and 36.7 mg/L SO₄²⁻. The pH of the natural water solutions was adjusted from 8.3 to 7.5 using 10% HCl prior to the experiments.

In selected experiments, the filters were tested for their ability to adsorb other metals, specifically, cadmium (Cd²⁺; from CdCl₂), chromate (CrO₄²⁻; from CrNa₂O₄), copper (Cu²⁺; from CuCl₂), and selenate (SeO₄²⁻; from Na₂SeO₄). These experiments were conducted at pH 7.5 in lab water buffered with 0.50 mM HCO₃⁻.

**Arsenic desorption experiments**

The tendency for arsenic to desorb from coated filters was tested in order to investigate the safety of the filters both during use and after disposal, as well as the possible ability to regenerate the filters. In these experiments, filters loaded to 15% breakthrough with arsenic were then switched to a feed of pure bicarbonate buffered water at pH 7.5. The pH of the feed solution was then adjusted either downwards or upwards at 1.0 pH unit intervals to pH 2.5 or 12.5, respectively. Four equivalent filter bed-volumes were collected at each pH unit.

**Bacterial removal efficiency**

The bacterial removal effectiveness of the SMCFs was evaluated by filtering four equivalent filter volumes of natural water from Potter Lake with two SMCFs and colloidal silver. Filter influent and effluent samples were plated in triplicate on Petri film plates and incubated at 35 ± 1°C for 24 h for total coliform enumeration and for 48 h for E. coli enumeration.

**RESULTS AND DISCUSSION**

**Filter characterization**

The Brunauer–Emmett–Teller (BET) surface areas for each Fe coating concentration increased non-linearly with coating solution strength due to the creation of a significant microporous structure of up to 15.1% at the greater iron coating level (Table 1). Average pore size shifted downward from 22.5 nm for the uncoated ceramic to 9.7 nm for the highest coating level (Table 1). The porosity determined by water

<table>
<thead>
<tr>
<th>Ferric nitrate coating solution strength (M)</th>
<th>0</th>
<th>0.026</th>
<th>0.128</th>
<th>0.51</th>
<th>1.0</th>
<th>2.0</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface areas</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BET surface area (m²/g) (1.7–300 nm)</td>
<td>1.57</td>
<td>2.33</td>
<td>3.07</td>
<td>3.95</td>
<td>10.08</td>
<td>9.77</td>
</tr>
<tr>
<td>t-plot micropore area (m²/g)</td>
<td>0</td>
<td>0</td>
<td>0.30</td>
<td>0.225</td>
<td>0.88</td>
<td>1.48</td>
</tr>
<tr>
<td>Percentage micropores (% t-plot micropore to BET total) (%)</td>
<td>0</td>
<td>0</td>
<td>9.79</td>
<td>5.69</td>
<td>8.72</td>
<td>15.1</td>
</tr>
<tr>
<td><strong>Average pore diameter</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BJH desorption average pore diameter (nm)</td>
<td>22.5</td>
<td>19.7</td>
<td>12.5</td>
<td>14.8</td>
<td>12.7</td>
<td>9.7</td>
</tr>
<tr>
<td><strong>Hydraulic conductivity</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydraulic conductivity (cm/s)</td>
<td>0.0103</td>
<td>0.0103</td>
<td>0.0102</td>
<td>0.008</td>
<td>0.0065</td>
<td>0.0049</td>
</tr>
<tr>
<td>r (correlation coefficient)</td>
<td>0.9772</td>
<td>0.9823</td>
<td>0.9738</td>
<td>0.9815</td>
<td>0.9823</td>
<td>0.9778</td>
</tr>
</tbody>
</table>
uptake of the uncoated and 1.0 M SMCF was measured to be 60% and 58%, respectively, or nearly unchanged. Hydraulic conductivity decreased by approximately 50% with increasing Fe coating between the uncoated filter and the filter with the highest coating level (Table 1). The decreases in average pore diameter due to the iron-oxide coating would also likely improve microbial removal, unless the coating speeds up the clogging of filter pores. Hydraulic conductivity can be adjusted within limits by the size and weight percentage of the burnout material chosen.

**Arsenic adsorption in laboratory water**

Each plug filter was subjected to a flow rate of 0.026 mL/min, equivalent to a full-scale filter rate of 2.5 L/h. Each effective filter run was 6.45 mL [or 2.43 bed volumes (BV)] based on proportional surface area for a 14.7 L filter (or approximately a one-day drinking water requirement for a family). For influent feed solutions containing 250 μg/L As(III), the filters coated with 0, 0.026, 0.128, 0.51, and 2.0 M ferric nitrate solution produced approximately 0, 49, 262, 875, and 1619 BVs (i.e. 0, 20, 108, 360 and 666 equivalent filter runs), respectively, with effluent below the WHO guideline of 10 μg/L (Figure 1(a)). For As(V), very similar results were observed as for As(III) (Figure 1(b)). These results can be explained in terms of both increased BET surface area and total moles of Fe on the filters which both correlated \( (\alpha = 0.05) \) well with 10 and 50 μg/L breakthroughs for both As(III) and As(V). For example, by comparing the BET surface areas for the different coating strengths shown in Table 1 to the mass of As adsorbed per mass of Fe on the filters increase, the mass of arsenic per mass of Fe increases.

These results are very promising in that at one filtration per day at these conditions, the SMCF may operate for a year or more removing both As(III) and As(V) from very high levels (e.g. 250 μg/L) to below WHO guidelines of 10 μg/L. The high removal rates of arsenite are especially promising as arsenite is not typically removed as well as arsenate (and suggesting that arsenite may be being converted to arsenate on the filter). Comparison of filters with and without colloidal silver (as is sometimes coated on ceramic filters) showed no significant difference in capacity for As (results not shown).

The average specific adsorption was 21 and 29 mg As/mg Fe for 10 and 50 μg/L breakthroughs for both As(III) and As(V) (data from Table 2). Only for As(III) for 50 μg/L breakthrough was there a significant \( (\alpha = 0.05) \) trend of less Fe oxide correlating with greater specific adsorption. It is hypothesized that as more layers of the iron-oxide surface form during the coating process, a smaller proportion of available sorption sites are accessible.

In six separate experiments, removal of As(V) at three different influent concentrations (507, 240 and 122 μg/L) was studied on plugs coated with 1 M ferric nitrate. Each concentration was conducted in duplicate. The As(V) mass removal was consistent with lower concentrations correlating to nominally equivalent increase in the BVs treated to 10 μg/L As breakthrough.
To examine the effect of pH on adsorption, the sorption capacity for arsenic for the low-Fe, 0.128 M coated filters was tested at pH 6.0, 7.5 and 9.0 at otherwise the same conditions as described above. In the pH range 6–9, As(III) exists primarily in the neutral H₃AsO₃ form, while As(V) exists primarily as the anionic mono- and divalent H₂AsO₄⁻ and HAsO₄²⁻ species. Adsorption of the neutral As(III) was greatest at pH 7.5, and was less for pH 6 and 9 (Figure 2(a)). Specifically, the capacity of the filter for As(III) at pH 6.0, 7.5, and 9.0 was 124, 77, and 60 μg As/g filter at 10 μg/L breakthrough (Table 2), or 296, 187, and 195 BVs (i.e. 122, 77 and 59 effective filter runs) (Figure 2(b)). As pH increases from 6 to 9, the net surface charge of the iron oxide coating would tend to become more negative. Based on electrostatic sorption interactions, this should tend to decrease sorption of the increasingly anionic As(V) due to increased electrostatic repulsive forces (which is the result observed).

**Table 2 | Adsorption capacities for As(III) and As(V)**

<table>
<thead>
<tr>
<th>Ferric nitrate coating strength (M)</th>
<th>As species filtered</th>
<th>pH</th>
<th>As adsorbed at 10 μg/L breakthrough (μg/g filter)</th>
<th>As adsorbed at 50 μg/L breakthrough (μg/g filter)</th>
<th>Mass As/mass Fe at 10 μg/L breakthrough (μg/mg)</th>
<th>Mass As/mass Fe at 50 μg/L breakthrough (μg/mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>As(III)</td>
<td>7.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.026</td>
<td>As(III)</td>
<td>7.5</td>
<td>2</td>
<td>38</td>
<td>21</td>
<td>39</td>
</tr>
<tr>
<td>0.128</td>
<td>As(III)</td>
<td>7.5</td>
<td>115</td>
<td>160</td>
<td>24</td>
<td>33</td>
</tr>
<tr>
<td>0.51</td>
<td>As(III)</td>
<td>7.5</td>
<td>369</td>
<td>561</td>
<td>19</td>
<td>29</td>
</tr>
<tr>
<td>1.0</td>
<td>As(III)</td>
<td>7.5</td>
<td>562</td>
<td>631</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>2.0</td>
<td>As(III)</td>
<td>7.5</td>
<td>677</td>
<td>708</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>0</td>
<td>As(V)</td>
<td>7.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.026</td>
<td>As(V)</td>
<td>7.5</td>
<td>26</td>
<td>53</td>
<td>27</td>
<td>55</td>
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<tr>
<td>0.128</td>
<td>As(V)</td>
<td>7.5</td>
<td>77</td>
<td>119</td>
<td>16</td>
<td>25</td>
</tr>
<tr>
<td>0.51</td>
<td>As(V)</td>
<td>7.5</td>
<td>376</td>
<td>453</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>1.0</td>
<td>As(V)</td>
<td>7.5</td>
<td>597</td>
<td>631</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>2.0</td>
<td>As(V)</td>
<td>7.5</td>
<td>675</td>
<td>708</td>
<td>19</td>
<td>20</td>
</tr>
<tr>
<td>0.128</td>
<td>As(III)</td>
<td>6</td>
<td>77</td>
<td>108</td>
<td>16</td>
<td>22</td>
</tr>
<tr>
<td>0.128</td>
<td>As(III)</td>
<td>9</td>
<td>71</td>
<td>142</td>
<td>15</td>
<td>30</td>
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<tr>
<td>0.128</td>
<td>As(V)</td>
<td>6</td>
<td>124</td>
<td>207</td>
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<tr>
<td>0.128</td>
<td>As(V)</td>
<td>9</td>
<td>60</td>
<td>128</td>
<td>12</td>
<td>27</td>
</tr>
<tr>
<td>0.128</td>
<td>As(III)</td>
<td>7.5</td>
<td>32</td>
<td>162</td>
<td>7</td>
<td>34</td>
</tr>
<tr>
<td>0.128</td>
<td>As(V)</td>
<td>7.5</td>
<td>29</td>
<td>59</td>
<td>6</td>
<td>12</td>
</tr>
<tr>
<td>1.0</td>
<td>As(III)</td>
<td>7.5</td>
<td>243</td>
<td>251</td>
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<td>13</td>
</tr>
<tr>
<td>1.0</td>
<td>As(V)</td>
<td>7.5</td>
<td>238</td>
<td>318</td>
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<td>415</td>
<td>441</td>
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<tr>
<td>2.0</td>
<td>As(V)</td>
<td>7.5</td>
<td>420</td>
<td>474</td>
<td>12</td>
<td>13</td>
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</tbody>
</table>

*aClinton Lake NOM experiments.*

**Effect of pH on arsenic adsorption**

To examine the effect of pH on adsorption, the sorption capacity for arsenic for the low-Fe, 0.128 M coated filters was tested at pH 6.0, 7.5 and 9.0 at otherwise the same conditions as described above. In the pH range 6–9, As(III) exists primarily in the neutral H₃AsO₃ form, while As(V) exists primarily as the anionic mono- and divalent H₂AsO₄⁻ and HAsO₄²⁻ species. Adsorption of the neutral As(III) was greatest at pH 7.5, and was less for pH 6 and 9 (Figure 2(a)). Specifically, the capacity of the filter for As(III) at pH 6.0, 7.5, and 9.0 was 124, 77, and 60 μg As/g filter at 10 μg/L breakthrough (Table 2), or 296, 187, and 195 BVs (i.e. 122, 77 and 59 effective filter runs) (Figure 2(b)). As pH increases from 6 to 9, the net surface charge of the iron oxide coating would tend to become more negative. Based on electrostatic sorption interactions, this should tend to decrease sorption of the increasingly anionic As(V) due to increased electrostatic repulsive forces (which is the result observed).

**Arsenic adsorption in natural water**

As adsorption was studied in 0.45-μm filtered Clinton Lake water (Lawrence, KS, USA) containing 4.98 mg/L DOC, 113 mg/L as CaCO₃ calcium hardness, 141 mg/L as CaCO₃ total hardness, 159 mg/L as CaCO₃ alkalinity,
10.9 mg/L Cl, 1.52 mg/L NO₃⁻N, 1.3 mg/L PO₄-P, 36.7 mg/L SO₄²⁻ and a pH of 7.5 (after adjustment from 8.3 using HCl). For the 0.51 and 2 M ferric nitrate coated filters, As(III) and As(V) adsorption capacity were both observed to decrease from 34 to 38%, respectively, due to this relative high level of DOC for both As(III) and As(V) based on the 10 μg/L breakthrough threshold (Table 2, Figure 1). For the lightly coated, 0.128 M coated filter, a greater impact of the NOM was observed. For these experiments, the lab water used for comparison was formulated to contain the same ion concentrations as the Clinton Lake water (cited above) such that the key difference was the NOM present. It is hypothesized that the impact of NOM on As sorption capacity was due to some combination of competition at adsorption sites and pore blockage by the NOM. This result suggests that the SMCF may successfully remove both As(III) and As(V) from water with typical lake DOC levels for a significant period.

Desorption of arsenic from loaded filters with pH

Of considerable interest was the reversibility of the adsorption of As on the Fe-coated filters for both reasons of safety (e.g. inadvertent release of As into filtered water) and regenerability of the filter (e.g. to be able to reuse filters after saturation). To examine potential desorption of As(III) and As(V) from the filters, 0.51 M ferric nitrate coated filters were loaded to 15% BT (with an influent concentration of 250 μg/L) for desorption studies. The initial pH of the feed solutions was pH 7.5, which was then increased or decreased in one-pH units for a duration of four effective filter volumes.

The results showed that essentially no As desorbed from the filters between pH 3.5 and 8.5, with very limited desorption at pH 2.5 and 9.5. At pH 10.5 and above, however, significant desorption occurred for both As(III) and As(V). These results suggest that at high pH (e.g. greater than 10), sorption of As may be significantly diminished, and further that if a loaded filter were subjected to such high pH water, significantly elevated As levels could result. Further, these results suggest the possibility of regenerating filters once loaded at lower pH by treatment with caustic or lime (though replacement of the inexpensive filter would be the more likely scenario). Specifically, the need for regeneration may be limited because the filtrative capacity for turbidity removal may be exhausted at a similar time resulting in the advisability of simply discarding the filter.

Sorption of other metals

Other heavy metals in addition to As also cause health threats to people in developing and developed nations. Initial experiments to examine the removal of Cd²⁺, CrO₄²⁻ and Cu²⁺, and SeO₂²⁻ were conducted to explore the performance of the SMCF. Specifically, filters coated with 0, 0.128, 0.51, and 2.0 M ferric nitrate were loaded with a mix of 3.34 μmol/L (each) of SeO₂²⁻, Cd²⁺, CrO₄²⁻ and Cu²⁺ and As⁵⁺ in pH 7.5 lab water. The results showed that the order of preference of the SMCFs for these metals was Cu > As > Cd > Cr > Se. Specifically, for the 2.0 M...
coated filter, breakthrough of Cu, As, Cd, and Cr reached 1480, 570, 564, and 207 BVs prior to 10 μg/L breakthrough (with Se breaking through immediately). These results demonstrate that the SMCF is effective at removal of other heavy metals in addition to As, and current studies are focused on these and other systems.

Bacterial removal

Because of the key importance of simultaneous filtrative disinfection along with As (and other heavy metal) removal, studies were conducted to confirm the retention of the disinfection capability of the SMCF. In these studies, natural water from Potters Lake (Lawrence, KS) containing an average of 2 CFU/mL E. coli and 15 CFU/mL total coliforms was filtered. The SMCF (0.51 M) achieved results of 0 cfu per 1 mL for both E. coli and total coliforms when 34.7 mL was filtered (the equivalent of four full-sized filter volumes). While the filters in this study were not subjected to rigorously microbial testing, these results suggest that the bacterial removal effectiveness of the Potters for Peace filter would not be reduced by the modifications performed to produce the SMCF. In fact, as the pore size was reduced by the Fe coating, increased microbial filtration would be expected.

Preliminary full-scale pot study

In preliminary full-scale experiments, arsenic in Logan River water spiked to 283 μg/L was removed by over 99.6% to below 2 μg/L in each of ten sequential runs filtering nearly 2.5 L of water in one hour per run. Prior to iron coating of the filter, turbidity was reduced in the filter from an average of 2.65 to 0.34 NTU, while the flow rate in the filter averaged 1.6 L/h with no significant reduction over 10 filter runs. After iron coating, turbidity was reduced in the filter from an average of 0.50 to 0.07 NTU, while the flow rate in the filter averaged 1.7 L/h with no significant reduction over the next 10 filter runs. Current experiments are ongoing to take filters to arsenic breakthrough. Full-scale testing of coated filters under a wide range of field conditions would provide critical data needed to examine the long-term effectiveness of the SMCF for arsenic removal. Application of this technology in in-line filters, disks and (especially) pots at full scale are needed to optimize performance. Many configurations of the technology may be easily designed depending on the application and process needs (e.g. pressure drop, hydraulics, physical characteristics and other parameters). The SMCF may be constructed in a Potters for Peace filter fashion with little more effort that the PFP filter itself, such that application in developing nations for simultaneous disinfection and arsenic removal is a highly achievable and valuable application. In surface waters, the SMCF provides arsenic removal with little enhanced filter fouling due to iron precipitate. For groundwater with reduced iron present, issues regarding fouling from precipitated iron are being examined with respect to reduced filter life, and the effectiveness of prefiltration with cloth and by other means. These studies need to occur at full-scale in varied field situations.

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