

DEVELOPMENT OF AN IRON-OXIDE COATED CERAMIC FILTER FOR REMOVAL OF AS(III) AND AS(V) IN DEVELOPING NATIONS

BY

EMILY ROBBINS

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Dr. Craig D. Adams, Chair

Dr. Edward F. Peltier

Dr. Stephen J. Randtke

Date Defended: _____

The Thesis Committee for Emily Robbins certifies that this is the approved version of the following thesis:

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Dr. Craig D. Adams, Chair

Date approved: _____

ABSTRACT

Over 4,000 children die each day due to diarrheal diseases which are often related to drinking unsafe water, and are often preventable with proper water treatment. Many regions of the world also suffer from high levels of arsenic due to natural and/or anthropogenic sources. Chronic arsenic poisoning leads to many maladies including skin, bladder and lung cancer, as well as non-carcinogenic arsenicosis symptoms including hyperpigmentation of skin, thickening hands and feet, and skin lesions.

A new point-of-use (POU) technology using conventional ceramic filters coated with a ferric-iron coating to achieve simultaneous arsenic (III) and (V) removal along with filtrative disinfection has been developed in the research for this thesis. The Iron-Oxide Coated Ceramic Filter (IOCCF) is produced using the standard ceramic filter methods (see www.pottersforpeace.org) leading to a porous clay pot that will filter out most pathogens. The iron was shown to bond strongly with the ceramic filter such that no iron leaching occurs. Experiments were conducted on ceramic micro-columns prepared to have the exact thickness and properties of a full-scale ceramic filter. While no significant arsenic removal is achieved in a traditional ceramic filter, the IOCCF was shown to be capable of filtering arsenic for long periods of time with essentially no As breakthrough. For example, As concentrations in source water can be easily reduced from 250 $\mu\text{g/L}$ to less than the 10 $\mu\text{g/L}$ WHO and EPA guideline for arsenic for over 365 effective filter runs. As(V) was sorbed more effectively at lower pH values while sorption of As(III) was not as sensitive to pH. However, there was not a large difference in As(V) or As(III) removal performance over a pH range of 6 to 9. Filtration of lake water containing NOM reduced performance of As(III) and As(V) removal, but the IOCCF still removed both As species from natural water for a significant number of filter runs. As(III) and As(V) remain strongly adsorbed at normal pH levels, however more research is needed on this topic. Results also showed that the IOCCF retained the bacterial removal capabilities of the Potters for Peace Filter.

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PUBLICATION THESIS OPTION

This thesis has been prepared in the form of a detailed literature review along with one journal article manuscript for peer review. The article presented in the manuscript has been prepared in the style utilized by Environmental Science and Technology and pages 33 to 55 will be submitted for publication in that journal.

The remaining material has been added for purposes normal to thesis writing in partial fulfillment of the requirements for the degree of Master of Science. The appendices have been added as supplemental information for the journal articles, regarding additional experiments, methods, and other useful information.

1. BACKGROUND AND LITERATURE REVIEW

1.1 THE NEED FOR DRINKING WATER TREATMENT IN DEVELOPING NATIONS

Every year 1.5 million children die from diarrheal diseases (WHO 2009), and many of these deaths can be attributed to unsafe drinking water. Lack of access to drinking water and exposure to waterborne diseases from unsafe drinking water are problems faced by many people in the developing world. The WHO/UNICEF (2010) estimates that 884 million people worldwide lack access to improved sources of drinking water defined as public taps or standpipes, tube wells or boreholes, protected dug wells, protected springs, rainwater collection, and piped household water connections located inside the user's dwelling, plot, or yard. Persons obtaining water from unimproved sources are at risk of drinking water contaminated with pathogens that may cause diseases such as cholera, enteric fever, dysentery, and hepatitis. Even people with access to so-called improved sources may not have microbiologically safe water and are at risk for developing the same diseases caused by drinking from unimproved sources. Boreholes and wells may also be fecally contaminated, and some urban water systems abstract water from contaminated sources and deliver water to customers with no or inadequate treatment (Sobsey 2002). With this in mind, it is likely that the number of people without access to safe drinking water is underestimated.

The global disease burden of diarrhea falls disproportionately on children living in developing countries where children experience on average three episodes of diarrhea per year (Kosek et al. 2003). Along with the high mortality rates, children experiencing chronic episodes of diarrhea throughout childhood due to inadequate safe drinking water and sanitation suffer growth stunting (Checkley et al. 2004) and impaired cognitive development (Guerrant et al.

2002) likely because of malnutrition caused in part by diarrheal disease. This translates to the potential for long-term disability and a decrease in quality of life for people experiencing these consequences of diarrheal disease. Diseases caused by pathogens in drinking water such as cholera and dysentery can kill adults as well as children. Along with the mortality and morbidity caused by water-related diseases, affected persons can lose vital income, which is especially problematic in poverty stricken areas of the developing world.

1.2 ARSENIC CONTAMINATION IN DRINKING WATER AND ITS EFFECTS ON HEALTH

Along with microbiological pathogens, many other contaminants can be present in untreated drinking water that are detrimental to human health. Arsenic is one such contaminant, and its incidence in drinking water has become a major public-health concern. In Bangladesh alone between 77-95 million of the 140 million inhabitants drink water contaminated with arsenic levels above the WHO's 10 µg/L maximum contaminant level (Hussam and Munir 2007). Much of the drinking water contaminated with arsenic throughout the world is groundwater (Mukherjee et al. 2006) contaminated by natural sources. Since many people obtain drinking water from groundwater wells, they are susceptible to drinking unsafe water in areas where arsenic contamination is present. Though most water is contaminated by natural sources, arsenic can also be introduced into water through anthropogenic sources such as insecticides, herbicides, and wood preservatives. Industries including glass manufacturing, paint, and electronics also use arsenic and its derivatives. A review of the world-wide arsenic contamination scenario by Mukherjee et al. (2006) determined that the major incidences of arsenic contamination occur in Bangladesh, West Bengal, India, China, Mongolia, Nepal, Cambodia, Myanmar, Afghanistan, DPR Korea, Pakistan, western Iran and Vietnam. Figure 1 shows the world-wide arsenic

contamination scenario as of 2006. The concentrations of arsenic in water for various locations throughout the world are summarized in Table 1.



Figure 1- World-wide arsenic contamination scenario as of 2006 (Mukherjee et al. 2006)
Contamination is a result of both natural and man-made sources. Locations listed in no particular order

Table 1 – Summary of waters with elevated arsenic concentrations throughout the world

Water Body and Location	Arsenic concentration, µg/L	
	Range	Typical
River water		
Baseline, various	0.13-2.1	0.83
Norway	<0.02-1.1	0.25
Southeast United States	0.15-0.45	0.30
Madison and Missouri Rivers, United States (geothermal influenced)	10-370	
United States		2.1
Dordogne, France		0.7
Po River, Italy		1.3
Polluted European rivers	4.5-45	
High-As groundwater influenced		
Northern Chile	190-21800	
Northern Chile	400-450	
Ron Phibun, Thailand (Mining influenced)	4.8-583	218
Ashanti, Ghana	<2.0-7900	284
British Columbia, Canada	<0.2-556	17.5
Lake Water		
Baseline	<0.2-0.42	0.28
France	0.73-9.2	
Japan	0.38-1.9	
Sweden	0.06-1.2	
Western United States (geothermal influenced)	0.38-1000	
Estuarine Water		
Oslofjord, Norway	0.7-2.0	
Saanich Inlet, British Columbia	1.2-2.5	
Rhone, France	1.1-3.8	2.2
Krka Estuary, Yugoslavia	0.13-1.8	
Seawater		
Deep Pacific and Atlantic Oceans	1.0-1.8	
Coastal Malaysia	0.7-1.8	1.0
Coastal Spain	0.5-3.7	1.5
Coastal Australia	1.1-1.6	1.3
Groundwater		
Baseline, United Kingdom	<0.5-10	
As-rich provinces: Bengal Basin, Argentina, Mexico, northern China, Taiwan, Hungary	10-5000	

Source: Adapted from Crittenden et al. (2005)

Exposure to arsenic can have serious negative health effects, the extent of which depends on the severity and duration of exposure (Mukherjee et al. 2006). Ingestion of large doses of arsenic, although rare from water sources, results in acute poisoning. Symptoms typically include vomiting, oesophageal and abdominal pain, and bloody “rice water” diarrhea. Coma, seizures, and fatality are possible in severe cases (Ratnaik 2003). Chronic exposure to arsenic can result in melanosis (hyperpigmentation of the skin) and hyperkeratosis (rough, dry papular

skin lesions that cause a thickening of the palms and soles), together known as arsenicosis (Ahsan et al. 2006; Mukherjee et al. 2006).



Figure 2 – Arsenicosis due to chronic exposure to arsenic in drinking water (EWB University of North Carolina - Chapel Hill 2011)

Certain neurological, reproductive, cardiovascular, respiratory, hepatic, haematological, and diabetic diseases are also associated with chronic exposure to arsenic (NRC 1999). The International Agency for Research on Cancer (IARC 2004) has classified arsenic as a group 1 human carcinogen and the ingestion of inorganic arsenic is an established cause of skin, bladder and lung cancer (NRC 1999; NRC 2001). Further research is necessary to define the dose-response relationships between arsenic ingestion and its associated diseases; however, one study found an increased risk of skin lesions at relatively low exposure (less than 50 $\mu\text{g/L}$) (Ahsan et al. 2006). The WHO guideline and EPA maximum contaminant level (MCL) are both set at 0.01 mg/L (or 10 $\mu\text{g/L}$) total arsenic.

1.3 POINT-OF-USE HOUSEHOLD WATER TREATMENT

As a means to improve the quality of water for the millions of people who do not have access to improved water sources, point-of-use (POU) water treatment technologies are being promoted. These technologies can provide families with a method for household water treatment (HWT), allowing them to obtain clean water in the home. Although universal access to safe, piped water is the ultimate goal, the prohibitively expensive costs of providing piped water to dispersed populations in rural areas and the inability of governments to plan and construct water supply and treatment facilities for the exploding populations in urban areas make decentralized POU treatment options a logical choice (Mintz et al. 2001). A systematic review and meta-analysis by Clasen et al. (2007) concluded that household interventions significantly reduced diarrhea episodes in both age groups studied – all ages and children under five. Source based interventions, however, did not show a statistically significant reduction in diarrheal episodes for the likely reason that water is being contaminated between source based treatment and arrival to households. Contemporary reviews estimate 30-40% reductions in diarrheal disease by improving household drinking water at the point-of-use, making HWTs more effective than treatment at the source (Esrey et al. 1985; Fewtrell et al. 2005; Clasen et al. 2007; Sobsey et al. 2008). The goal of HWT is to empower people in developing countries by giving them the means to obtain safe drinking water by treating and storing it in the home (Sobsey et al. 2008). A variety of HWT types have been tested and promoted, but not all have shown evidence of effectiveness or sustained use (Fewtrell et al. 2005; Clasen et al. 2007). Some common types of POU technologies currently being promoted include chlorination with safe storage, combined coagulant-chlorine disinfection systems, solar disinfection (SODIS), ceramic filtration, and biosand filtration.

Sobsey et al. (2008) evaluated the aforementioned types of POU water treatment technologies based on microbial efficacy, health impacts, sustainability, water quantity produced, treatment robustness, ease of process use and time treating water, cost to treat, supply chain requirements, and usage levels after cessation of monitoring and education efforts. Using criteria developed for each of these categories, the POU technologies were rated and a total score was calculated. Out of all the treatments, ceramic filtration scored the highest along with biosand filtration. The study concluded that ceramic filters are one of the most sustainable POU options because they produce adequate water supply for household use with minimum time and effort, and have also achieved large-scale adoption and continued, long-term use. Ceramic filters have also been shown to improve the microbial quality of water and decrease the incidence of diarrheal disease in rigorous epidemiological studies. It was determined that an average diarrheal disease reduction of 63% was achieved using ceramic candle filtration in a study by Clasen et al. (2007) and 46% reduction in diarrheal disease was achieved using ceramic water purifiers (such as the Potters for Peace filter) in a study by Brown et al. (2007). The Sobsey et al. (2008) also concluded that sustained, effective performance of the ceramic filters occurred long after implementation. The study suggested that ceramic filters have shown the potential for large scale adoption as approximately 500,000 people already use this type of POU treatment.

1.3.1 CERAMIC FILTRATION AND THE POTTERS FOR PEACE FILTER

The following section reviews the methods for fabricating the Potters for Peace filter and studies investigating the effectiveness, sustainability and social acceptability of ceramic filtration by users in the developing world.

1.3.1.1 FILTER FABRICATION METHODS

Since 1998, the Potters for Peace (PFP) organization has been assisting with the production of the low-tech, low-cost, colloidal silver-enhanced ceramic water purifier (CWP). The CWP is a bucket-shaped (11 in. wide by 10 in. deep with a wall thickness of $\frac{1}{2}$ to $\frac{3}{4}$ in.) clay vessel that is produced with clay and a combustible material such as sawdust or rice husks. The CWP can be produced using many different types of clay, and in most cases local soils with high clay contents can be used. The clay must be dry milled before use so that the clay can be mixed with the combustible material. The combustible material burns away during the firing process and leaves small pores behind in the ceramic material which allow water to pass through. The combustible material is sieved US standard 30 mesh (600 μm nominal size) sieve in order to obtain combustible particles of the proper size. The desired maximum pore size in the CWP is 1 μm . This pore size should be small enough to prevent the passage of many types of pathogenic bacteria through the filter. The PFP guidance documents recommend a 50:50 mix of clay to combustible material by volume, and a 60:40 mix if more plasticity is needed. Yanez (2009) found that a mixture of 73:27 mix of clay to combustible material by weight produced filters with the most optimal flow rates.



Figure 3 – Ceramic water purifiers (CWPs) promoted by the Potters for Peace organization (Safe Water Today 2009)

Once the clay and combustible material are combined, they must be mixed thoroughly to evenly distribute the particles. PFP suggests mixing in a container, a cement mixer (for larger batches), or a plastic sheet rolled back and forth (Potters for Peace 2005). Water is then added to the dry mix in order to create a plastic clay material. A 30% mix by weight of water to the dry mix is recommended (Potters for Peace 2005). The water added should give a moist consistency without obvious “drippiness”. The water should coat the particles and allow the clay mixture to hold shape. The clay is then further mixed in a process called “wedging”. The purpose of this process is to work in the moisture and remove air from the mixture. During wedging, the clay is folded over upon itself repeatedly while applying pressure (Potters for Peace 2005). After wedging, the clay can then be pressed into the ‘pot’ shape of the CWP. This is performed by placing clay into a pre-manufactured mold of the proper dimensions and pressing the mold together using a press. Presses can be operated by using a hydraulic jack or a type of motor. Figure 4 shows a hydraulic jack press in operation.



Figure 4 – Operation of a hydraulic filter press (Potters for Peace 2005)

After pressing the clay into the pot shape, it is carefully removed from the mold, cleaned up to remove any fringe clay and allowed to air dry. Air drying the green (unfired) clay pot is important to prevent excessive moisture in the clay from causing the pot to explode during the firing process. Approximately one day should be sufficient for air drying; however this depends on the humidity of the region where the pots are being manufactured. Once dried, the pots can then be fired in a kiln. PFP (2005) recommends that the kiln be fired very slowly up to the boiling point of water (100 °C) to allow the remaining water in the clay to evaporate before boiling and potentially cause cracks. After the boiling point is reached, the temperature in the kiln can be increased quickly to 890 °C and held there for several hours to form the ceramic material. Oyandel-Craver and Smith (2007) used the following firing schedule to produce ceramic filters for their research: increase temperature at a rate of 150 °C/h from room temperature to 600 °C, then increase at a rate of 300 °C/h to 900 °C, holding this final temperature for 3 hours before cooling.

1.3.1.2 LAB STUDIES

Oyanedel-Craver and Smith (2007) tested the laboratory performance of colloidal-silver impregnated ceramic filters with respect to flow rate and bacteria transport. The filters were manufactured by combining clay-rich soil, grog (previously fired clay), and flour and compressing the mixture into a 6.5-cm diameter mold at 1000 psi for 1 min. resulting in 1.5-cm thick cylindrical disks. Three different types of clay-rich soil were used in this study; a commercial 200-mesh Redart pottery clay, and two natural soils from Mateo Ixtatan, Guatemala and Ciudad Juarez, Mexico. The filters were air-dried at room temperature for three days and then fired in a muffle furnace. The temperature was increased at a rate of 150 °C/h from room temperature to 600 °C, and then increased at a rate of 300 °C/h to 900 °C, holding this final temperature for three hours. Filters were coated with colloidal silver either by painting with 6 mL of 200 mg/L colloidal silver solution or submerging the disks for 45 seconds in 600 mg/L or 800-mg/L colloidal silver solution. Results of the study showed that the hydraulic conductivity and pore-size varied with filter composition. Hydraulic conductivities were on the order of 10^{-5} cm/s, and the filter made with Redart clay had the highest hydraulic conductivity of 5.01×10^{-5} cm/s. More than 50% of the pores in each filter had diameters ranging from 0.02 to 15 μ m. The filters removed between 97.8% and 100% of the applied 6 mL pulse containing $7 \pm 2 \times 10^9$ MPN/100 mL *E. coli*. Colloidal silver application improved the filter performance, likely through the inactivation of bacteria. The quantity of colloidal silver applied to the filters was more important than the method of application. While this study did show high effectiveness of the colloidal-silver impregnated filter in the lab for pulse *E. coli* concentrations, it was not a long-term study and field performance is difficult to estimate from these results.

Laboratory experiments were conducted by Bielefeldt et al. (2009) to determine bacterial treatment effectiveness of POU ceramic water filters. Six filters were tested; two were used by families for approximately four years and the other filters had limited use in the lab. Water spiked with approximately 10^6 cfu/mL of *E. coli* served as the influent feed to the filters. *E. coli* removal efficiencies of the first batch (one full filter volume) ranged from 3 to 4 log, similar to the lab results of other studies (Brown 2007; Oyanedel-Craver and Smith 2007). Removal efficiency began to decline after the filtration of the second and third batches. The average *E. coli* removal was 3.8 log for the first batch, 2.4 log for the second batch, and 2.2 log for the third batch, indicating a cumulative bacterial loading effect on the filter performance. This study also investigated the effects of silver on bacterial removal effectiveness. A colloidal silver solution was prepared by mixing two mL of 3.2% silver with 300 mL deionized water. Four of the filters were painted with this solution using the PFP procedure. Three batches were run through each filter immediately after the recoating procedure using the same influent concentration of *E. coli* of the first experiment. The bacterial removal efficiency of these first three batches ranged from 3.2–4.2 log for the four filters recoated with silver. Effluent silver concentrations ranged from 36 to 63 ppb, compared to 1.8 to 0.04 ppb before recoating. Even after recoating, the effluent silver concentrations still fall below the USEPA’s secondary MCL for silver of 100 ppb, and this reapplication looks to have improved the performance of the ceramic filters.

The particle removal performance of POU ceramic filters was studied by Bielefeldt et al. (2010) to determine the filter’s effectiveness in removing particles ranging from virus to protozoan sized (0.02–100 μm). Carboxylate-coated polystyrene fluorescent microspheres, natural particles, and clay were used to characterize the particle removal capabilities of the ceramic filter. The study used six ceramic filters manufactured in Managua, Nicaragua. Four of

the filters had been previously used in lab experiments and two of the filters had been used for about four years by families in Nicaragua before being shipped to the researchers. Two of the lab filters had never been coated with silver, and since the other four had been previously used, it was assumed that most of the colloidal silver coating had leached out. The filters were not recoated for the first experiments performed in this study. Removal of virus-sized 0.02 and 0.1 μm spheres was highly variable between the six filters, ranging from 63 to 99.6%. Removal of 0.5 μm spheres was less variable, ranging from 95.1-99.6%. For the 1, 2, 4.5 and 10 μm spheres, removal was greater than 99.6%. Most pathogenic bacteria are sized 1 μm or greater, so the high removal of the 1 μm and greater particles in this study shows promise for bacterial removal capabilities.

USAID contracted with Jubilee House Community (JHC) and Daniele Lantagne, a consulting engineer, to complete a study of the Potters for Peace (PFP) filter. Lantagne completed two reports for the study. Report 1 investigated the intrinsic effectiveness of the PFP ceramic filter with lab studies and Report 2 focused on field testing of the PFP ceramic filter. One focus of Lantagne's lab study (2001a) was to determine the intrinsic properties of the PFP filter. The chemical composition, pore uniformity, and pore size of the PFP filter was evaluated using a Scanning Electron Microscope (SEM) with x-ray elemental analysis capability. The main chemical component of the filter was silicon, followed by oxygen and aluminum. Trace amounts of iron, magnesium, sulfur, and potassium were present. The chemical composition of filters will vary depending on the type of clay used to make the filter. The composition of the filter was not uniform with both cracks and spaces present. The cracks measured up to 150 μm in length and spaces measured up to 500 μm in length. Many of these cracks and spaces are not connected within the filter, serving only as reservoir space for water and do not allow bacteria to

pass completely through the filter. The pore sizes not within cracks or spaces ranged from 0.6 to approximately 3.0 μm . The PFP pore goal size is 1.0 μm in order to remove *E. coli* bacteria. The SEM results show that the filter analyzed was had pore sizes well within range of the 1.0 μm goal.

A series of “Microbial Challenge” tests were performed as a part of Latagne’s lab study (Lantagne 2001a). These tests investigated the capacity of the PFP filter to remove microbiological contaminants in different regions, use conditions, and through different filter designs. The results of the challenge study showed that many different filter designs over the years remove 98-100 percent of the indicator bacteria. The study compared the performance of filters that had been in use for two and seven years and determined that the filters still effectively remove microbiological contamination. These results indicate that the colloidal silver coating does not “wear out” and reapplication of colloidal silver throughout the lifetime of the filter does not seem to be necessary. Currently the PFP organization recommends reapplication of silver once per year to the filter. This does not seem to be necessary based on these results, but reapplication provides a safety factor and Latagne does not recommend discontinuation of this practice until further studies have been performed.

An “Arsenic Challenge” study was also conducted as part of Latagne’s Report 1 (Lantagne 2001a) to investigate the PFP filter’s arsenic removal capabilities. Water spiked with arsenic was run through two filters, and finished water samples were taken every five liters. Percentage retention of arsenic in the filter decreased significantly with sample volume. The filter coated with colloidal silver performed slightly better than the filter with no coating. After filtering five liters 88.75% of the arsenic was retained and after 20 liters only 58.78% of the arsenic was retained. The uncoated filter retained 81.79% of the arsenic after five liters and

63.06% of the arsenic after 10 liters. One hypothesis for the weak arsenic removal capability of the filter is that the small amount of activated carbon remaining after the firing process serves as a sorbent for arsenic. However, the amount of activated carbon present in the filters is small and only a small amount of arsenic can be retained before the carbon is saturated. Use of the filter in its current design as a POU technology for areas with arsenic contamination is not recommended.

1.3.1.3 FIELD STUDIES

As ceramic filtration has been promoted and its use by persons in developing countries has increased, a number of studies evaluating field performance have been published. Brown et al. (2008) conducted a randomized, controlled intervention trial of ceramic water purifiers in a rural village in Cambodia. The study documented significant reductions in diarrheal disease in households using the ceramic water purifiers. Use of the filters resulted in a mean reduction in diarrheal disease of 49% in all ages and both sexes compared to the control group. The filters used in the study reduced the *E. coli* in stored, untreated water by a geometric mean of 96% from pre-treatment levels. Turbidity levels after treatment using the ceramic filters were also lower compared to baseline levels of untreated water. Users of the ceramic filter reported a high level of compliance throughout the study, with 98% of filters in use at all visits and 100% of users reporting that the filter was used for treating all “household drinking water”.

Clasen et al. (2004) performed a study evaluating the effectiveness of ceramic filtration in households of a community in rural Bolivia. During a six-month trial, ceramic Katadyn[®] candle filters were distributed randomly to half of the 50 participating households while the other half continued to use customary water handling practices, serving as controls. An investigator returned to the community at approximately six-week intervals to record diarrhea prevalence

during the previous seven days (defined as three or more loose stools during a period of 24 hours) and to take drinking water samples. In the four rounds of sampling following the intervention, 100% of the 96 water samples from the intervention households were free of TTCs compared with 15.5% of the control household samples. Diarrheal disease risk for the intervention group was determined to be 70% lower than for individuals in the control group. For children less than five years old in the intervention group, diarrheal disease risk was 85% lower than the control group. The results of this study provide strong evidence that affordable ceramic filtration technology may be an effective method to improve the microbiological quality of drinking water and reduce the risk of diarrheal disease in low-income populations.

An independent study was commissioned by UNICEF and Water and Sanitation Program (WSP) – Cambodia and executed by Brown et al. (2007) to evaluate the characterize the microbiological effectiveness and health impacts of ceramic water purifiers (Potters for Peace filters) that were distributed to a number of Cambodian villages up to four years prior to the study. Approximately 25% of the 2000 households located in 13 villages and in three provinces in Cambodia that originally received the filters were randomly selected and visited. These households were matched with control households that had never received the filter. Selected households were followed for an additional three visits during which water samples and health data were collected. Results from the study showed that the filters can significantly improve the microbiological quality of drinking water, reducing *E. coli* by a mean of 98% with reductions as high as 99.99%. Use of the ceramic filters was associated with an estimated 46% reduction in diarrhea in filter users versus non-users. The study concluded that the ceramic filter's demonstrated effectiveness in improving water quality and health over a wide range of

conditions makes it an attractive option for POU treatment. The authors recommend future efforts to ensure continued effectiveness and sustained use of the filters.

In Report 2 of the joint USAID and JHC project investigating the Potters for Peace (PFP) filtration system, Latagne (Lantagne 2001b) details a three-week field study in rural Nicaraguan communities using the PFP system. This field study evaluated the use of the filter system in households and the system effectiveness in terms of water quality improvement. A total of 33 homes were visited in seven communities located in three geographical regions in Nicaragua. During the time of the unannounced visits, 24 of the 33 households were using the filter. From the field study results, Latagne concluded that community leadership and follow-up visits by educators were necessary for sustained use. Breakage of the filter was a common problem in households. Water samples were collected during household visits, and samples were tested for presence or absence of total coliform, H₂S producing and *E. coli* bacteria. Of the 24 samples collected, only one of possible 24 filters removed total coliform, six of a possible 22 filters removed H₂S-producing bacteria and 8 of a possible 15 filters removed *E. coli* contamination. Duplicate samples from two villages were enumerated by CIRA-UNAN (a Nicaraguan academic and research institute) and results show an increase in total coliform after filtration, indicating contamination was occurring due to storage in unclean receptacles. This study concluded that PFP filters in the field performed less optimally than in the lab studies, and better education on proper cleaning of the filter and safe storage of filtered water is recommended to improve performance.

Many of these studies do not attempt to perform direct observation on filter use and relied solely on user response, which has been shown to introduce reporting bias to results (Schmidt and Cairncross 2009). Reviews have also suggested that unblinded trials (with respect to the

study subjects and researchers) can introduce significant bias toward a certain result in studies. Therefore, it will be important to perform blinded trials or trials using an objective outcome in the future to determine the effectiveness of POU treatments, including the ceramic filter. Despite these considerations, Hunter (2009) determined that ceramic filtration significantly outperformed a number of other POU technologies using meta-regression that adjusted for bias due to a lack of blinding. With currently available evidence, the study found that ceramic filters are the most effective form of HWT in the long term. The author stated that “the clear effectiveness of the ceramic filter in this analysis would make further controlled trials unethical. Research should focus primarily on how to increase uptake and sustainability of the intervention.”

1.4 ARSENIC REMOVAL

As discussed previously, the arsenic contamination situation worldwide is a significant problem that is causing serious health problems for the people who have no choice but to drink arsenic contaminated water. Due to this situation, a large effort has been made to develop methods for removing arsenic from water. A number of methods have now been devised that are capable of reducing arsenic concentrations to a few parts per billion. The following section gives a brief review of the chemical properties of arsenic in water in order to better understand the possible treatment processes available for arsenic removal.

1.4.1 CHEMICAL PROPERTIES OF ARSENIC IN WATER

Arsenic is a metalloid element within Group Vb of the periodic table, but is often incorrectly referred to as a metal. It is ubiquitous in the environment and is usually present in small amounts in all rock, soil, dust, water, air and biological tissues (Thornton and Fargo 1997).

Arsenic can occur in four oxidation states in water (+5, +3, 0, -3) but is most commonly present only in the trivalent [arsenite, As(III)] and pentavalent [arsenate, As(V)] states. The predominance diagrams for As(III) and As(V) as a function of pH are shown in Figure 5. From pH 2 to 9, the undissociated form of arsenite (H_3AsO_3) is the predominate species. Therefore, most natural surface and groundwaters with pH ranging from 6.5 to 8.5 containing As(III) will have As in the H_3AsO_3 form. The arsenic in natural water containing As(V) will be in the form of HAsO_4^{2-} from pH 7 to 11.5. For water with pH values less than 7.0, H_2AsO_4^- will be the predominate form of arsenate.

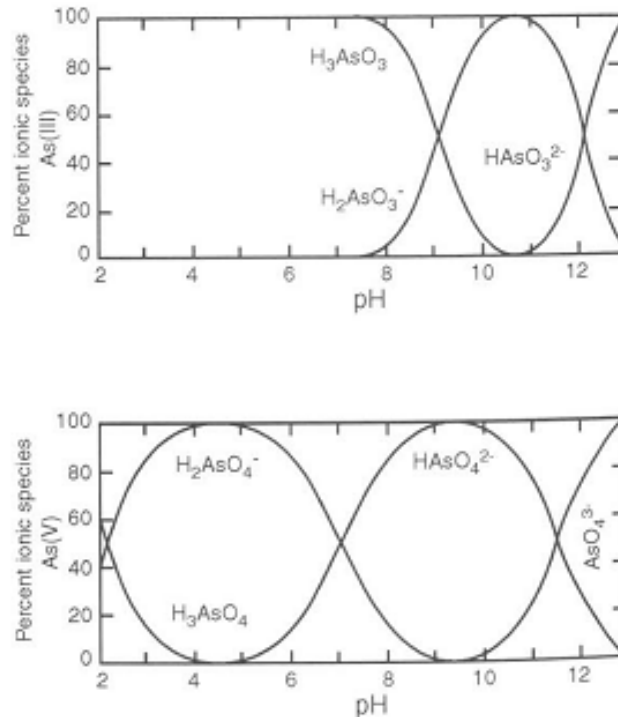


Figure 5 – Predominance diagram for As(III) and As(V) as a function of pH (MWH (2005), adapted from Gupta and Chen (1978))

The E_H -pH diagram for arsenic in the presence of oxygen and water at 25 °C is presented in Figure 6. This diagram represents the equilibrium condition of arsenic under various redox

potentials and pH conditions (MWH 2005). Under oxidizing or high E_H conditions (aerated waters), the $H_2AsO_4^-$ form of arsenate becomes the dominant species at pH values less than approximately 6.9. At pH values greater than approximately 6.9, $HAsO_4^{2-}$ becomes the dominant species. Usually little or no As(III) is present under oxidizing conditions. For groundwaters that contain little dissolved oxygen (mildly reducing or low E_H values), the H_3AsO_3 form of arsenite becomes the dominant species at pH values less than 9.2. Dissolved arsenic-sulfide species can be present in water containing relatively high concentrations of reduced sulfur. Reducing, acidic conditions will favor the formation of sulfur compounds such as orpiment (As_2S_3), realgar (AsS), or other sulfide-arsenic species (MWH 2005).

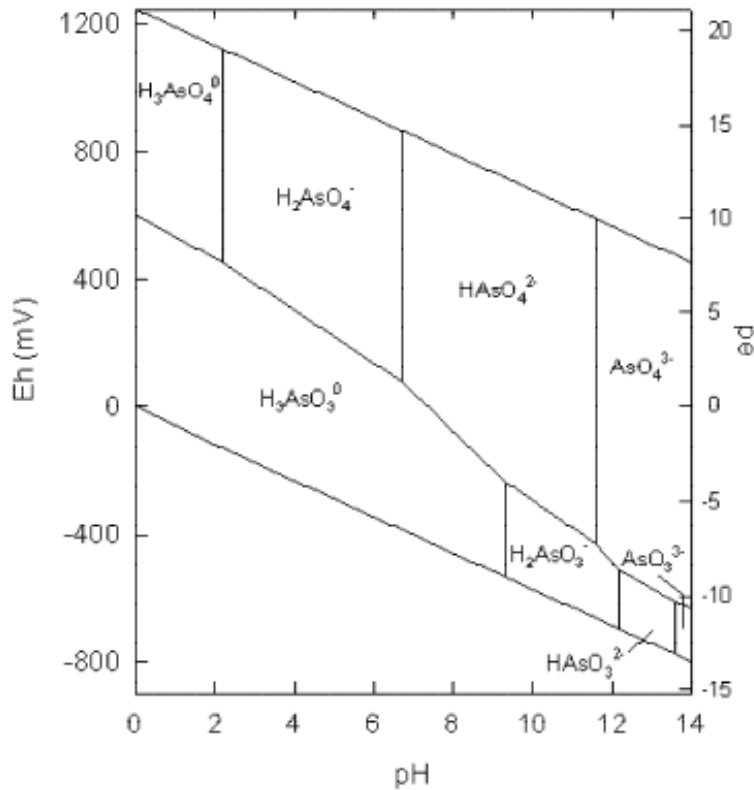


Figure 6 – E_h -pH diagram for Aqueous Arsenic Species in the System As-O₂-H₂O at 25 °C and 1 bar total pressure (WHO 2002)

1.4.2 ARSENIC MOBILITY IN GROUNDWATER

Because most arsenic contamination occurs in groundwater, it is important to understand the mobility of arsenic in these systems. Arsenic mobility in groundwater is mainly governed by adsorption and desorption processes. The mobility of arsenic depends on the type and amount of adsorbing compounds, pH, and the redox potential (Bissen and Frimmel 2003). Arsenic compounds can adsorb to oxides and hydroxides of Fe(III), Al(III), Mn(III/IV), humic substances and clay minerals (Bissen and Frimmel 2003). Natural geochemical weathering is the cause for much of the elevated arsenic levels in groundwater around the world.

1.4.3 ARSENIC REMOVAL TECHNOLOGIES

A number of methods for removing arsenic from water have been developed. These methods include conventional coagulation, reverse osmosis, ion exchange and adsorption (Crittenden, Trussell et al. 2005). Granular activated carbon (GAC) is the most conventional type of adsorbent used for arsenic removal, however novel adsorbents such as ferric and aluminum oxides are now known to be very effective in removing arsenic. Many studies have demonstrated the effectiveness of iron oxides, oxyhydroxides and hydroxides as adsorbents (all are called 'iron oxides') (Pierce and Moore 1980; Edwards and Benjamin 1989; Robins et al. 2001; Dixit and Hering 2003; Thirunavukkarasu et al. 2003; Frazer 2005; Jessen et al. 2005; Leupin et al. 2005; Jang et al. 2006; Kundu and Gupta 2006; Ko et al. 2007; Maiti et al. 2010). Adsorption of arsenic using iron oxides is considered to be one of the most promising technologies because it is both economical and effective (Gupta and Chen 1978; Frazer 2005; Jessen et al. 2005; Leupin et al. 2005).

The literature suggests that the mechanisms for the sorption of these two naturally occurring arsenic species are as follows: arsenate forms inner-sphere surface complexes on amorphous iron oxide while arsenite forms both inner- and outer-sphere complexes on the adsorbent (Manceau 1995; Goldberg and Johnston 2001; Bissen and Frimmel 2003; Sherman and Randall 2003). The redox state of arsenic can affect the removal effectiveness of iron oxide adsorbents. Generally it is assumed that iron oxides have a higher affinity for As(V) than As(III) and it is thought that the oxidation of As(III) to As(V) on the iron oxide surfaces can aid in arsenite removal. However, more recent studies have demonstrated greater adsorption of arsenite than arsenate on ferrihydrite surfaces (pH range 3-11) at relatively high initial As concentrations (Raven et al. 1998). Studies have also shown that pH can affect the As species preference of iron oxides. Raven et al. (1998) demonstrated that adsorbed arsenate concentrations were relatively greater than adsorbed arsenite at lower pH values whereas more arsenite was adsorbed at higher pH values. Dixit and Hering (2003) also demonstrated this result. For amorphous iron oxides (HFO), the crossover pH (i.e., the pH at which As(III) and As(V) are equally sorbed) is about 6.5 with 50 or 10 μM total As and pH 8.5 with 100 μM total As (Dixit and Hering 2003). Amorphous iron oxides tend to be better adsorbents than more crystalline solids such as goethite and hematite due to the higher surface areas of these compounds (Dixit and Hering 2003). Other effects from the conversion of amorphous to crystalline surfaces on adsorption could be observed. Other adsorbates (such as phosphate, NOM, silicate, and bicarbonate) are known to compete with arsenic for sorption sites on amorphous iron oxides (Meng et al. 2002; Dixit and Hering 2003). In recent times, researchers have focused significant efforts on developing a number of different methods for utilizing iron

oxides as an adsorbent for removal of arsenic from drinking water. The following section will review a number of these studies.

1.4.3.1 IRON OXIDE ADSORBENT TECHNOLOGIES FOR THE REMOVAL OF ARSENIC

A study by Benjamin et al. (1996) was one of the first to investigate the removal of arsenic from water using a material coated with iron oxides. The surface of ordinary filter sand was coated with iron oxide using either FeCl_3 (IOCS-1) or $\text{Fe}(\text{NO}_3)_3$ (IOCS-2) and heating the media to high temperatures in a number of different steps to produce an amorphous iron oxide surface that was a good adsorbent for dissolved metals. The BET surface areas of IOCS-1 and IOCS-2 were $5.8 \text{ m}^2/\text{g}$ and $9.1 \text{ m}^2/\text{g}$, respectively. Fixed bed column studies were performed to test metals removal effectiveness of the iron-oxide-coated sand (IOCS). A 1.8-cm ID column was packed with 250-mL of IOCS-2. The influent flow rate was 125 mL/min, yielding an empty bed contact time (EBCT) of 2 min. The media was regenerated using a solution near pH 2.0. The IOCS was effective in removing uncomplexed and ammonia-complexed metals (Cu, Cd, Pb, Ni, Zn) as well as some oxyanionic metals (SeO_3 and AsO_3). The IOCS-2 removed influent levels of $75 \text{ }\mu\text{g/L}$ of As(tot) to less than $10 \text{ }\mu\text{g/L}$ for over 600 bed volumes (BVs).

Thirunavukkarasu et al. (2003) used a slightly different high temperature coating process than Benjamin et al. (1996) for coating sand with iron oxide in order to study its effectiveness in removing arsenic from water. The surface area of the iron oxide coating on the sand was $10.6 \text{ m}^2/\text{g}$. An isotherm study was performed and showed that the observed data fitted well with the Langmuir model. The adsorption maximum for the iron oxide-coated sand (IOCS-2) at pH 7.6 was estimated to be 42.6 and $41.1 \text{ }\mu\text{g As/g IOCS}$ for As(V) and As(III), respectively, at an initial As concentration of $100 \text{ }\mu\text{g/L}$ (a mid-level As concentration for contaminated areas). The

performance of IOCS-2 as column media was also evaluated in this study. Five cycles of column tests were performed at an initial As concentration of 500 $\mu\text{g/L}$, a flow rate of 21.5 mL/min, 90 g IOCS-2 (volume 57 mL) and EBCT of 2.7 min. In the first cycle of the column tests, 1403 and 1244 BVs were achieved with less than 5 $\mu\text{g/L}$ As effluent for As(III) and As(V) influent, respectively. A slight decrease in the number of BVs achieved before an effluent level of 5 $\mu\text{g/L}$ As was reached occurred in subsequent cycles. The authors attribute this result to the possibility that iron may be detaching from the sand particles and escaping with the effluent during backwashing. This study demonstrated that IOCS-2 was capable of removing As(III) and As(V) to levels less than 5 $\mu\text{g/L}$ (each) in both the batch and column studies.

A study performed by Ko et al. (2007) tested the arsenic removal capacity of a colloidal iron oxide coated sand media. Both batch and column studies were performed. In this study, As(III) was removed through adsorption less effectively than As(V). The K_d value (moles sorbed species per mass unit/moles species in solution per volume unit) from the column experiments were 0.016-0.37 L/kg for As(III) and 0.023-0.85 L/kg for As(V). Arsenate was removed more effectively in the batch experiments, with K_d values of 0.50 L/kg for As(III) and 1.30 L/kg for As(V). This is likely due to the lower availability of adsorption sites in the packed columns. The effects of oxyanion competition on the removal of arsenic in the column were investigated and it was determined that the presence of sulfate and nitrate caused breakthrough to the MCL to occur more quickly relative to the breakthrough point without these oxyanions. Bicarbonate and chloride had lesser effects on the breakthrough point.

Filter columns containing zero-valent iron filings and sand were evaluated as a treatment method for removing arsenic from Bangladesh tube well water in a study by Leupin et al. (2005). Filter columns with 3-4 filters, containing 2.5 g iron filings and 100-150 g of sand, or containing

sand only were tested.. The sand and iron filings were either homogeneously mixed in the whole filter or layered with a homogeneous mixture of sand with iron filings on a layer followed by a layer of only sand. The columns containing iron filings and sand were able to treat 75-90 L of well water with 440 µg/L As, 1.8 mg/L P, 4.7 mg/L Fe, 19 mg/L Si, and 6 mg/L dissolved organic carbon (DOC) to below 50 µg/L As(tot) at a flow rate of 1 L/h without the addition of an oxidant. DOC did not appear interfere with arsenic removal in the filter columns. The filter columns containing sand only, however, did not provide sufficient arsenic removal. Only 37% of influent arsenic was removed in the first filter of the column, and just 5% was removed after the subsequent filters.

Jang et al. (2006) incorporated hydrous ferric oxide into porous diatomite and studied the arsenic removal capabilities of the material. A pH-controlled differential column batch reactor (DCBR) was used to determine the rate constants, initial sorption rates, and arsenic sorption capacities rather than a typical batch test because the diatomite media floats. The maximum sorption capacity for arsenite of the diatomite with iron oxide (Fe (25%)-diatomite) was about 0.4 mmol/g at pH 8.2. For As(III), the sorption capacity increased up to pH 8, but significantly decreased after pH > 9. The As(V) sorption capacities of Fe (25%)-diatomite were 0.45 mmol/g and 0.32 mmol/g at pH 4 and 8, respectively. The maximum capacity for As(V) occurred at pH 4 and significantly decreased as pH increased. The arsenite and arsenate sorption capacities of Fe (25%)-diatomite were 2-7 and 1.2 times greater, respectively, than those of AAFS-50, a proprietary activated alumina sorbent used for arsenic removal. Small-scale column tests were performed to determine the arsenic removal efficiencies for both Fe (25%)–diatomite and AAFS-50. The columns were 1.5-cm internal diameter and 15-cm in length and packed with 1.5 g of Fe (25%)–diatomite or AAFS-50. The influent contained 500 µg/L of arsenate or arsenite at pH 6.5.

The Fe (25%)–diatomite treated about 1100 and 2200 BVs at target concentrations of 10 µg/L and 50 µg/L, respectively of As(III). About 1100 and 2100 BVs were achieved for As(V) below 10 and 50 µg/L, respectively. AAFS-50 only treated about 150 and 350 BVs of As(III) and As(V) below 50 µg/L, respectively. Therefore, Fe (25%)-diatomite performed similarly for As(III) and As(V) removal, and much better than the conventionally used AAFS-50 adsorbent.

Sarkar et al. (2008) studied the effectiveness of 175 well-head community-based arsenic removal units in operation in remote villages of the Indian subcontinent. These arsenic removal units utilize naturally occurring iron in groundwater by oxidizing Fe^{2+} using a splash plate to aerate the water in order to form hydrous ferric oxide (HFO) capable of removing As(III) and As(V). These units also contain a bed of activated alumina (AA) or hybrid anion exchanger (HAIX) (essentially spherical anion exchange resin beads containing dispersed nanoparticles of HFO) with a specific affinity toward dissolved As(V) and As(III) species. Each well-head unit contains 100 L of AA or HAIX. Influent and effluent arsenic concentrations from an existing well-head unit were measured, and it was determined that for groundwater containing well over 200 µg/L As, the concentration in the treated water was consistently less than 50 µg/L (the MCL permitted in the Indian subcontinent) for over 13000 BVs. The filtration unit was regenerated using two cycles of 2% NaOH solution of pH ~12-13 followed by an acid rinse. The performance of the filtration unit was similar after regeneration. A large fraction of the influent As was removed with these units, however epidemiological studies have shown risk of cancer at As levels above 10 µg/L (the WHO MCL). The first run before regeneration only achieved approximately 2000 BVs less than 10 µg/L, and effluent concentrations after regeneration were never below 10 µg/L.

In 2007, a POU arsenic treatment technology called the SONO filter won the Grainger Challenge top award for developing an innovative, economical, socially acceptable device for arsenic removal. The SONO filter was developed by Hussam and Munir (2007) and consists of a two bucket system capable of removing arsenic to less than 10 µg/L for an extended time period. The top bucket contains coarse river sand used as a particulate filter, disperser, and flow stabilizer. High soluble iron in groundwater is oxidized and precipitates as Fe(OH)₃(s) in this media. The top bucket also contains a composite iron matrix (CIM) that serves as the active surface for complexation and immobilization of inorganic arsenic. The CIM is manufactured from various iron turnings obtained from local foundries or machine shops. A proprietary process is performed to enhance HFO formation. The bottom bucket also contains coarse river sand to retain any residual iron that leaches from the first stage as HFO. Wood charcoal is incorporated in the second bucket to adsorb any organics (odor causing compounds, pesticides, etc.). Fine river sand is used as a fine filtration media to remove any residual particulates. Brick chips are used in the second bucket for flow stabilization. Field testing of the SONO filter has demonstrated filtration of 25000 L of water containing 1139-1600 µg/L As(tot) to levels below 14 µg/L until reaching the detection limit of 2 µg/L. The SONO filter produces effluent with progressively decreasing arsenic levels due to the generation of new complexation sites on the CIM due to insitu iron oxidation and surface chemical reactions. So far, filters in the field have been in use for 5 years without breakthrough.

While the arsenic removal performance of the SONO filter is impressive, some issues should be addressed. Tests have shown that the filter itself does not foster the growth of pathogenic bacteria, but no tests were performed to determine if the filter can effectively remove pathogens capable of causing diarrheal diseases and the devastating effects of these diseases

(discussed previously). Some studies have shown that sand filtration alone is not adequate for complete pathogen removal (Clasen et al. 2007; Elliott et al. 2008; Hunter 2009). Another possible issue with the SONO filter is the cost. The five-year cost of the SONO filter is \$35-40. While this is more affordable than many technologies, the cost may still be prohibitive for some families living in the most impoverished regions.

The results of these studies clearly demonstrate that iron oxides, including iron oxides incorporated into other media are effective sorbents for both As(III) and As(V). These technologies are already being used successfully in industrial and municipal water treatment operations, but there is still great need for economical, socially acceptable, and sustainable methods for removing arsenic from water in impoverished such as Bangladesh where the arsenic contamination situation is dire. This research attempts to incorporate the successful use of iron oxides as an adsorbent into ceramic filtration technology – one of the most effective and socially acceptable POU water treatment technologies available – to create a filter capable of removing both pathogens and elevated levels of arsenic to produce safe drinking water for people living in developing regions who would not otherwise have access to water treatment technologies.

2. OBJECTIVES

The objectives of this study were (1) to develop a method for coating the Potters for Peace (PFP) filter with iron oxide and determine the resulting surface characteristics, (2) evaluate the arsenic adsorption capabilities of the iron-oxide coated ceramic filter (IOCCF) by simulating the typical usage conditions of the PFP filter, (3) determine the effects of pH and NOM on arsenic removal performance of the IOCCF, (4) investigate desorption of arsenic from the

IOCCF and the implications for safety and regeneration, and (5) determine if the bacterial removal capabilities of the PFP filter are retained with the addition of the iron-oxide coating.

2.1 EXPERIMENTAL PLAN

The experimental plan focused on designing and testing a modified Potters for Peace ceramic water purifier (CWP) capable of removing levels of arsenic typical of contaminated sources. Filters were coated with one of three different concentrations of ferric nitrate solution and tested to determine the optimal coating solution concentration. Some of the filters were also coated with the concentration of colloidal silver recommended by Potters for Peace to determine if silver affects the arsenic removal capability of the iron-oxide coating. The removal of the two common forms of arsenic found in water, As(III) and As(V), was studied.

2.2 EXPERIMENTAL APPROACH

This study consisted of five experiment phases performed in order to determine the arsenic and bacteria removal effectiveness of iron oxide coated ceramic filters (IOCCFs) under different test conditions as well as the regeneration capability of the IOCCFs. In Phase 1 of this research, 16 combinations of iron coating solution concentration, silver or no silver coating, and two arsenic species (As(III) or As(V)) were tested. The arsenic feed solutions were all buffered with 0.5 mM NaHCO₃ maintaining a pH between 7 and 8. The experimental matrix for Phase 1 is shown in Table 2.

Table 2 – Phase 1 Experimental Matrix

Filter No.	Ferric nitrate coating solution conc. (M)	Silver coating	Arsenic species
1	0	N	As(III)
2	0	Y	As(III)
3	0	N	As(V)
4	0	Y	As(V)
5	0.026	N	As(III)
6	0.026	Y	As(III)
7	0.026	N	As(V)
8*	0.026	Y	As(V)
9*	0.128	N	As(III)
10	0.128	Y	As(III)
11	0.128	N	As(V)
12	0.128	Y	As(V)
13	0.510	N	As(III)
14	0.510	Y	As(III)
15	0.510	N	As(V)
16	0.510	Y	As(V)

*Ran in duplicate (randomly selected)

Phase 2 of this research focused on the effects of pH on arsenic removal capability of the filter. Filters coated with a 0.128 M ferric nitrate solution and colloidal silver filtered water at spiked with either As(III) or As(V) at either pH 6.0 or pH 9.0. All filters were coated with silver in order to model a typical Potters for Peace CWP. Table 3 shows the experimental matrix for the Phase 2 experiments.

Table 3 - Phase 2 Experimental Matrix

Filter No.	Ferric nitrate coating solution conc. (M)	Silver coating	Arsenic species	pH of influent water
1	0.128	Y	As(III)	6.0
2	0.128	Y	As(III)	9.0
3	0.128	Y	As(V)	6.0
4	0.128	Y	As(V)	9.0

Phase 3 investigated the ability of the IOCCF to remove arsenic from natural water containing NOM and other constituents that may compete with arsenic for sorption sites. The influent water was taken from Clinton Reservoir, a lake near Lawrence, KS. The pH of the Clinton Lake water spiked with 250 ppb arsenic was adjusted to 7.5 using HCl. Filters coated with 0.128 M ferric nitrate coating solution and colloidal silver were used in this experiment. Removal of both As(III) and As(V) was tested. All filters were coated with silver to model the Potters for Peace CWP. Table 4 shows the experimental matrix for Phase 3.

Table 4 – Phase 3 Experimental Matrix

Filter No.	Ferric nitrate coating solution conc. (M)	Silver coating	Arsenic species	pH of Clinton Lake influent
1	0.128	Y	As(III)	7.5
2	0.128	Y	As(V)	7.5

In order to evaluate the tendency of the adsorbed arsenic that had adsorbed to the iron coating of the filters to desorb under different pH conditions, several experiments were performed. Understanding the desorption of arsenic from these filters due to changes in pH will be important for safety (preventing desorption during use) and also for the possibility of filter

regeneration and extended filter lifetime. These desorption experiments made up Phase 4 of this study.

Table 5 shows the experimental matrix of Phase 4. Filters coated with a 0.026 M ferric nitrate solution were used to obtain fast breakthrough, and the filters were coated with silver to model the PFP filter. The desorption of both As(III) and As(V) was studied by passing water containing no arsenic through the filters at either very high or low pH. In order to determine the pH level at which desorption occurs, pH of the influent was increased or decreased in a stepwise fashion.

Table 5 – Phase 4 Experimental Matrix

Filter No.	Ferric nitrate coating solution conc. (M)	Silver coating	Arsenic species	Desorption method
1	0.026	Y	As(III)	Increase pH to 12.5
2	0.026	Y	As(III)	Increase pH to 12.5
3	0.026	Y	As(V)	Decrease pH to 2.5
4	0.026	Y	As(V)	Decrease pH to 2.5

Phase 5 consisted of an experiment performed to investigate the microbial removal effectiveness of the IOCCF. Natural lake water containing *E. coli* and total coliforms was filtered by two 0.510 M coated filters and influent and effluent samples were plated to determine removal efficiency.

Removal of As(III) and As(V) in iron-oxide-coated ceramic filters for developing nations

Emily C. Robbins and Craig D. Adams

Department of Civil, Environmental, and Architectural Engineering, University of Kansas, Lawrence, KS 66045, USA

Corresponding author phone: (785) 864-1921; Fax: (785) 864-5631; email: cadams@ku.edu

Abstract

Over 4,000 children die each day due to diarrheal diseases which are often related to drinking unsafe water, and are often preventable with proper water treatment. Many regions of the world also suffer for high levels of arsenic due to natural and/or anthropogenic sources leading to many negative human health effects caused by chronic arsenic poisoning. The Iron-Oxide Coated Ceramic Filter (IOCCF) has been developed as a new point-of-use (POU) technology using conventional ceramic filters coated with a ferric-iron coating to achieve simultaneous arsenic (III) and (V) removal along with filtrative disinfection. Experiments were conducted on ceramic micro-columns prepared to have the exact thickness and properties for a full-scale ceramic filter. The IOCCF was shown to be capable of removing arsenic for over 365 effective filter uses to less than 10 $\mu\text{g/L}$ (the WHO and EPA guideline). As(V) was sorbed more effectively at lower pH values while sorption of As(III) was not as sensitive to pH. However, there was not a large difference in As(V) or As(III) removal performance over a pH range of 6 to 9. Filtration of lake water containing NOM reduced performance of As(III) and As(V) removal and more research is needed on the effects of competitive adsorbates. As(III) and As(V) remain strongly adsorbed

over a range of pH levels such that the used filters may be used and safely disposed of without the likelihood of As leaching under typical natural conditions. Results also showed that the IOCCF retained the bacterial removal capabilities of the Potters for Peace Filter.

Introduction

Millions of people around the world drink water contaminated with arsenic at levels hazardous to human health. These high arsenic levels are found naturally in the groundwater of many countries, most notably Bangladesh, West Bengal, India, China, and several other East-Asian countries (1). In Bangladesh alone between 77-95 million of the 140 million inhabitants drink water contaminated with arsenic concentrations above the World Health Organization (WHO) 10 µg/L drinking water guideline. Epidemiological studies have determined that chronic exposure to arsenic causes hyperpigmentation and hyperkeratosis of the skin (together known as arsenicosis) (1-3); skin, bladder, and lung cancer; and certain neurological, reproductive, cardiovascular, respiratory and other diseases (4,5). In addition, millions of people drink water containing harmful levels of pathogenic bacteria, viruses and parasites including many of sources co-contaminated with arsenic. Biologically unsafe drinking water contributes to the 1.5 million annual childhood deaths from diarrheal diseases (6). Significant research efforts have focused on developing point-of-use (POU) treatment methods appropriate for pathogens or arsenic control in developing nations. Few of these technologies simultaneously address concurrent removal of both pathogens and arsenic in an effective, economical, and socially acceptable manner.

Among a number of methods effective in removing arsenic from water is adsorption using novel sorbents including iron and aluminum oxides, phyllosilicates, porous diatomite, soil organic matter, and whole soils. Amorphous iron oxide as an adsorbent has been researched and implemented extensively in recent years. Adsorption using iron oxides is considered to be one of

the most promising technologies because it is both economical and effective (7-16). These sorbents can successfully remove both arsenate (AsV) and arsenite (AsIII), the two naturally occurring oxidation states of arsenic in water. While both forms are harmful to human health, the As(III) redox state is considerably more toxic. The literature suggests that the mechanisms for the sorption of these two naturally occurring arsenic species are as follows: arsenate forms inner-sphere surface complexes on amorphous iron oxide while arsenite forms both inner- and outer-sphere complexes on the adsorbent (17-20). Amorphous iron oxides tend to be better adsorbents than more crystalline solids such as goethite and hematite due to the higher surface areas of these compounds (7). Other sorbates (such as phosphate, NOM, silicate, and bicarbonate) are known to compete with arsenic for sorption sites on amorphous iron oxides (7, 21). The pH and redox potential of water can significantly affect arsenic adsorption onto iron oxides (7, 11, 18, 22-24).

To create a useful media for adsorption of arsenic, many researchers have focused on coating or impregnating different materials such as sand, cement, porous diatomite, and activated carbon with amorphous iron oxides. Studies have shown that coating these materials with iron oxide can produce materials with high adsorption capacity (10, 13, 25-27). While these materials may be effective for use in municipal treatment systems, they are not necessarily economical or socially acceptable for use in developing nations and may not provide adequate biological treatment. Contemporary reviews estimate 30-40% reductions in diarrheal disease by improving household drinking water at the point-of-use (28-31). Of all the POU treatment methods, several researchers have concluded that ceramic filtration (specifically the Potters for Peace (PFP) type filter) is one of the most effective, economical, socially acceptable, and sustainable drinking water treatment technologies for use by people in developing nations (28, 32-36). This research

has taken the concept of the iron-oxide coating for arsenic adsorption and combined it with Potters for Peace ceramic filter to produce a water treatment technology capable of simultaneously treating water for arsenic and biological contamination. The objectives of this study were (1) to develop a method for coating the Potters for Peace (PFP) filter with iron oxide and determine the resulting surface characteristics, (2) evaluate the arsenic adsorption capabilities of the iron-oxide coated ceramic filter (IOCCF) by simulating the typical usage conditions of the PFP filter, (3) determine the effects of pH and NOM on arsenic removal performance of the IOCCF, (4) investigate desorption of arsenic from the IOCCF and the implications for safety and regeneration, and (5) determine if the bacterial removal capabilities of the PFP filter are retained with the addition of the iron-oxide coating.

Materials and Methods

Materials. Ceramic filters for laboratory testing were manufactured from clay, sawdust, and water according to standard Potters for Peace protocol. Commercial 200-mesh Redart pottery clay (Resco Products, Inc.) was used based on its optimal performance with respect to bacterial removal and flowrate in other studies (36-37) and because of its similarity in composition to the earthenware clays in many parts of the world available for use in ceramic filter manufacturing. Sawdust was sieved through a 30-mesh (600 μm nominal size openings) sieve to create a pore structure that insures bacteria would be effectively removed while allowing sufficient water filtration rates.

Fresh As(III) and As(V) stock solutions were prepared frequently from reagent grade sodium arsenite (NaAsO_2 ; Fisher Scientific) and sodium arsenate ($\text{HAsNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$; Sigma Aldrich), respectively. Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; MP Biomedicals) was used in solutions used to

prepare the iron-oxide coating on the ceramic filters. Powdered colloidal silver (Argenol Laboratories, Spain) was used to produce a 0.023% (200 mg/L) colloidal silver solution used to coat and test selected filters per specifications by Potters for Peace (38). Reagent water (18 M Ω -cm) was prepared using a Milli-Q Direct-Q 3 system. All plasticware and glassware was washed in a 5% sulfuric acid bath between uses. Natural water was collected from Clinton Reservoir near Lawrence, KS for experiments examining effects of competition from natural constituents. Water was collected from Potter Lake (Lawrence, KS, USA) for experiments confirming bacteriological removal effectiveness of the ceramic filters.

Analytical Methods. Arsenic concentrations were determined using a Varian SpectraAA 240 graphite furnace atomic absorption (GFAA) spectrophotometer equipped with a GTA 100-graphite-tube atomizer and programmable sample dispenser (MDL 2.6 μ g/L). Pyrolytically coated partitioned graphite tubes (Agilent Technologies) were used with argon gas (Linweld) to sheath the atomizer and purge internally. A 500-mg/L palladium solution (Fluka) was prepared and used as a matrix modifier to decrease interferences and stabilize the analyte to higher temperatures (39). Verification of arsenic speciation in the influent solutions was performed by ion chromatography (IC) analysis (Dionex ICS-2000) using an IonPac AS18 anion exchange column (Dionex). Arsenic speciation was not determined for the effluent. A KOH gradient of 6–52 mM in 15 min at 1 mL/min was used as the eluent. Iron concentration in the filtered effluent was determined with the Hach Iron TNT 858 method using a DR 5000 spectrophotometer (HACH). pH was determined using an Accumet Basic pH meter (Model AB15; Fisher Scientific). The total and calcium (Ca) hardness and alkalinity of the Clinton lake water were determined using the Hach digital titrator kit (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 Torch instrument (Teledyne Tekmar) with the pre-programmed TOC–TN Drinking Water method. Petrifilm plates (3M) were used to determine the *E. coli* and coliform counts of the filtered and unfiltered Potter Lake water.

Skeletal densities, pore volumes and pore surface areas of prepared filters were determined in Dr. Leventis' laboratory at the Missouri University of Science and Technology (Rolla, MO, USA). Skeletal density was determined using helium pycnometry using a Micromeritics AccuPyc II 1340 instrument. Surface areas (σ) were measured by N₂-sorption porosimetry using a Micromeritics ASAP 2020 Surface Area and Pore Distribution Analyzer. Samples for surface area and skeletal density determinations were out-gassed for 24 h at 80 °C under vacuum before analysis.

Filter Fabrication. An optimized mixture of 73% dry Redart clay and 27% sawdust (by weight) (37) was combined and mixed until homogenous. The dry mix (4.55 kg) was combined with 3.6 L of tap water and mixed until a workable clay consistency was reached. Small, circular cross sections of the filter material were made for ease of fabrication and testing. Clay was pressed by hand into 1.5-cm thick, 2-cm diameter plastic molds and further compressed using a plastic plate. These molds produce cylindrical sections that are the same thickness as the Potters for Peace filter to accurately model the flow through the filter. The filters were air-dried at room temperature for 3 d and then fired in a Carbolite 3216 tube furnace. The temperature in the tube furnace was increased from room temperature to 80 °C at a rate of 60 °C/hr and held for 3 hours so that the water in the clay would evaporate slowly in order to prevent cracking (40). The temperature was then increased to 150 °C at a rate of 60 °C/hr and held for 3 hours, increased to

600 °C at a rate of 150 °C/hr, and finally increased to 900 °C at a rate of 300 C/hr and held for 6 h at this temperature.

To produce an iron oxide surface for arsenic adsorption, the filters were coated with a ferric nitrate solution through an adapted process (25, 27). Three iron coating solutions were prepared in order to test the effect of the iron concentration of the coating solution on arsenic removal. Filters were soaked in the iron coating solutions and agitated on a shaker table set at 100 rpm for 18 h to achieve full saturation of the pore spaces. The filters were then removed from the coating solutions and heated in a 110 °C oven for 4 hours, then heated at 550 °C for 3 hours. The filters were removed allowed to cool and were then rinsed with reagent water to wash away any loose particles. The filters were again soaked in the ferric nitrate coating solutions for 18 h as previously described and then heated 110 °C for 20 hours. A number of the filters (both non iron-oxide coated and iron-oxide coated) were coated with a colloidal silver by submerging filters for 2 min in a 200 mg/L solution as recommended by Potters for Peace (38).

Filtration Apparatus. An eight-channel Minipulse 3 peristaltic pump (Gilson) continuously pumped water through the ceramic filters. An equivalent gravitational flowrate through the filter section was calculated by multiplying the ratio of the filter section surface area to the surface area of the full-size Potters for Peace filter (ratio = 0.0006) by a flowrate of 2.5 L/hr to give 1.48 mL/hr through the filter sections. Filters were encased using 10-mL luer-lock syringes (BD) and secured with epoxy glue so that no water could bypass the filter. A series of 30-gauge hypodermic needles (Cadence Science, Inc.), 0.8-in. ID Tygon LFL tubing (Masterflex), and 1/16-in. barb plastic connectors (Cole-Parmer) were used to connect the filters to the pump and the pump to the influent solutions. Effluent from the filters dripped into 15-mL centrifuge tubes (BD) placed in a Retriever II sample collector (ISCO). The sample collector was set to advance

at the equivalent amount of time for the volume of water contained in a full-size Potters for Peace filter (~ 15 L) to pass through. Therefore, the water collected in each sample tube represents a full filter run.

Arsenic Sorption Studies. The arsenic sorption capacity of the iron-oxide-coated ceramic filters (IOCCFs) was studied by testing 16 combinations of iron coating solution concentration, silver or no silver coating, and arsenic species (As(III) or As(V)). The influent solutions contained approximately 250 ppb As(III) or As(V) (verified by IC analysis) and were buffered with 0.5 mM NaHCO₃ to maintain pH between 7 and 8. To study the effects of pH on arsenic sorption, filters coated with the 0.128 M ferric nitrate solution and colloidal silver filtered water spiked with 250 ppb As(III) or As(V) at either pH 6.0 or pH 9.0. pH was adjusted using either 10% HCl or 1 M NaOH.

Arsenic Sorption in the Presence of NOM. To investigate the ability of the IOCCF to remove arsenic from natural water containing NOM and other constituents that may compete with arsenic for sorption sites, natural lake water (from Clinton Reservoir) was used as the influent. This water was spiked with 250 ppb of either As(III) or As(V) and the pH was lowered to 7.5 using HCl. Filters coated with 0.128 M ferric nitrate solution and colloidal silver were used.

Desorption Studies. The tendency of arsenic to desorb from the filters was tested in order to investigate the safety (preventing desorption during use), and also for the possibility of filter regeneration and extended filter lifetime. Filters coated with 0.026 M ferric nitrate solution were loaded to ~15% breakthrough and then were switched to an influent of reagent water buffered with 0.5 mM NaHCO₃ at pH 7.5 which was then either increased or decreased by 1 unit in a step-

wise fashion to an endpoint of pH 2.5 or 12.5. Four equivalent filter volumes were filtered at each pH step.

Bacterial Removal. The bacterial removal effectiveness of the IOCCFs was evaluated by filtering four equivalent filter volumes of natural water collected from Potter Lake (Lawrence, KS) with two filters coated with the 0.510 M ferric nitrate solution and colloidal silver. Filter influent and effluent was plated on Petrifilm plates in triplicate and incubated at $35 \pm 1^\circ\text{C}$ for 24 h for total coliform enumeration and 48 h for *E. coli*.

Results and Discussion

Properties of Iron-oxide Surface and Pore Volume. The BET surface areas for each Fe coating concentration determined using N_2 -sorption porosimetry are shown in Table 6. Surface area was positively correlated ($\alpha = 0.05$) with increasing ferric nitrate coating solution strength, as the 0.510 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ coated filters had the largest surface area while the filter with no iron oxide coating had the lowest. Surface area did not increase linearly with increasing ferric nitrate coating strength (i.e. the 0.510 M coating solution did not produce a surface area 20X larger than that of the 0.026 M solution). This result is likely explained by the fact that as the filter surface becomes coated, additional iron added produces a smaller fraction of surface area compared to the base coating. The porosity of the 0.510 M IOCCF was measured to be approximately 58%. This porosity was only slightly lower than the uncoated filter porosity of 60%. Li et al. (2010) produced an iron-oxide coated porous ceramic filter (IOCPCF) with very similar properties to the 0.510 M IOCCF produced in this study. The IOCPCF had an average pore diameter, specific surface area and porosity of 11.36 nm, $4.987 \text{ m}^2/\text{g}$, and 58.63% respectively compared to 14.8 nm, $3.95 \text{ m}^2/\text{g}$ and 58% for the IOCCF.

Benjamin et al. (1996) developed two types of iron-oxide coated sand with surface areas of 5.8 and 9.1 m²/g, and Thirunavaukkarasu et al. (2003) produced iron-oxide coated sand using a slightly different method with a surface area of 10.6 m²/g. These surface areas are greater than those achieved on the ceramic filter, possibly due to the surfaces on to which the iron was coated (small particles of sand vs. the surface and inner pores of the ceramic filter) or due to the strength of the iron coating solutions used. Benjamin et al. and Thirunavaukkarasu et al. both used coating solutions of at least 2 M strength of either Fe(NO₃)₃·9H₂O or FeCl₃, while this study only used a Fe(NO₃)₃·9H₂O coating solution strength of 0.510 M at most in an attempt to make the filters as economical as possible. It may be possible to produce an iron-oxide coating for the ceramic filter with a similar surface area to that of iron-oxide coated sand, or at least increase it by using a higher strength iron coating solution. Results from analysis of the filter effluents showed that levels of iron were below 0.2 mg/L indicating that leaching of the iron coating was not occurring. Allowing the iron coating to flow completely through the filter pores rather than simply soaking the filters would also likely increase the amount of iron coating on the surface of the ceramic filter.

Table 6 also gives measures of the IOCCF pore volume and pore diameter at each Fe coating strength. As expected, the pore size decreased with increasing Fe coating strength with the exception of the 0.510 M coating. The average pore size of the filters coated with 0.510 M ferric nitrate was slightly higher but similar to that of the filters with 0.128 M coating strength. While these are average pore size measurements and do not rule out the presence of pores greater than 1 µm, the average pore sizes indicate that the filters will be effective in removing pathogenic bacteria and other larger pathogenic organisms (helminthes, protozoa, etc.). 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.

TABLE 6 – MATERIAL PROPERTIES OF IRON-OXIDE COATED CERAMIC FILTERS^{a, b}

	Ferric nitrate coating solution strength, M			
	0.000	0.026	0.128	0.510
Surface Areas				
BET Surface Area (m ² g ⁻¹) (1.7 - 300 nm)	1.57	2.33	3.07	3.95
t-plot Micropore Area (m ² g ⁻¹)	0.000	0.000	0.300	0.225
Percent micropores (% t-plot micropore to BET total) (%)	0.000	0.000	9.791	5.692
Average Pore Diameter				
BJH desorption average pore diameter (nm)	22.5	19.7	12.5	14.8

^aFilters were also coated with 0.023% colloidal silver

^bMeasured by N₂ BET

Arsenic Sorption Performance. Each filter was subjected to a flowrate of 0.026 mL/min, equivalent to a full size filter rate of 2.5 L/h. The arsenic concentration in the filter effluents are shown in Figure 7 as a function of effective filter runs. The volume of a filter run for these scaled down filters is 8.67 mL, which is equivalent to the 14.7 L that a full-size Potters for Peace filter can treat in one run. Tests confirmed that ceramic filters with no coating removed essentially no arsenic. For influent containing ~250 µg/L arsenite the filters coated with 0.026 M, 0.128 M, and 0.510 M ferric nitrate solution produced approximately 20, 38, and 366 filter runs, respectively, with effluent below the WHO MCL of 10 µg/L (Figure 7A). The performance of the 0.510 M coated filter was far superior to that of the other coating strengths. The 0.128 M ferric nitrate coated filter experienced breakthrough at 10 µg/L occurred not long after the breakthrough of the 0.026 M coated filter, but then As concentrations began to decrease

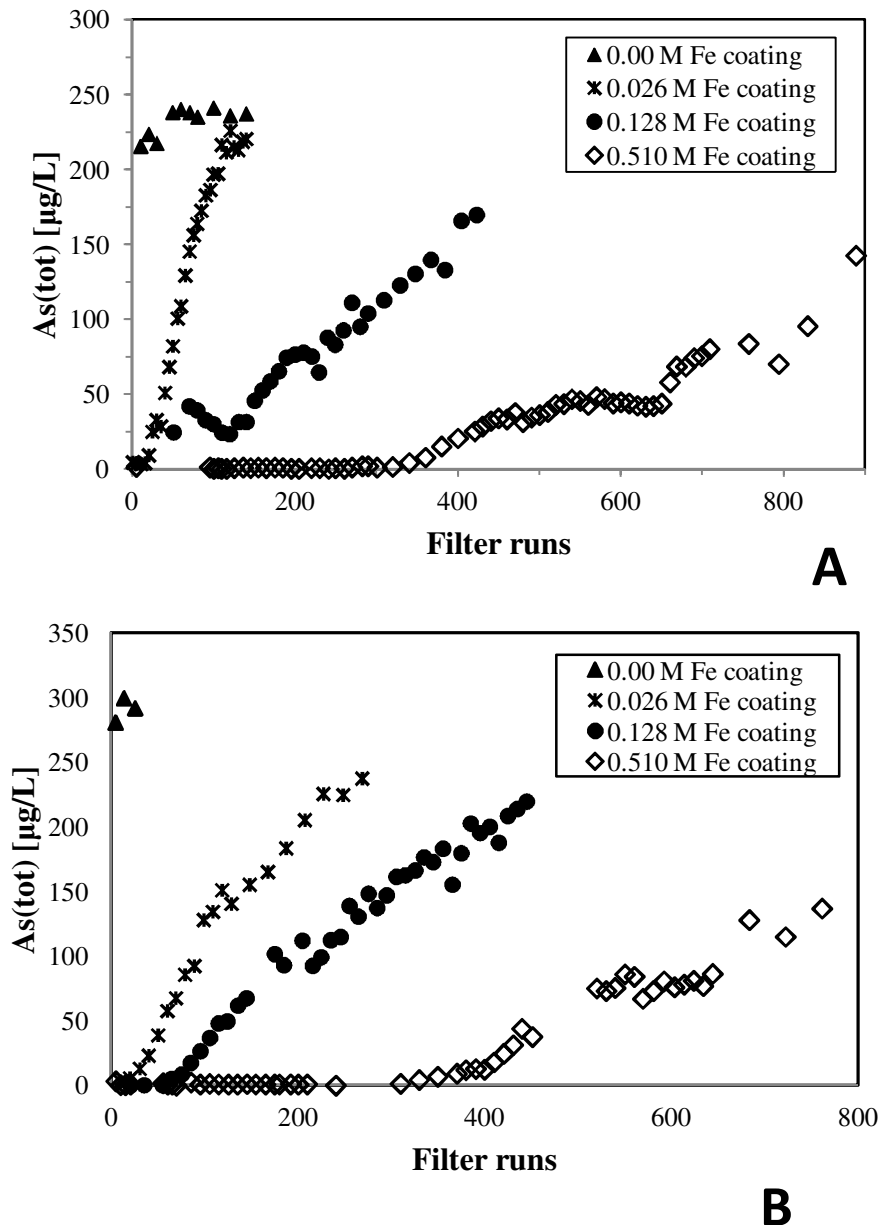


Figure 7 –Sorption of [A] arsenite and [B] arsenate (pH 7.5; arsenic concentration ~250 µg/L) under different coating conditions. All filters were also coated a with 200 mg/L colloidal silver solution.

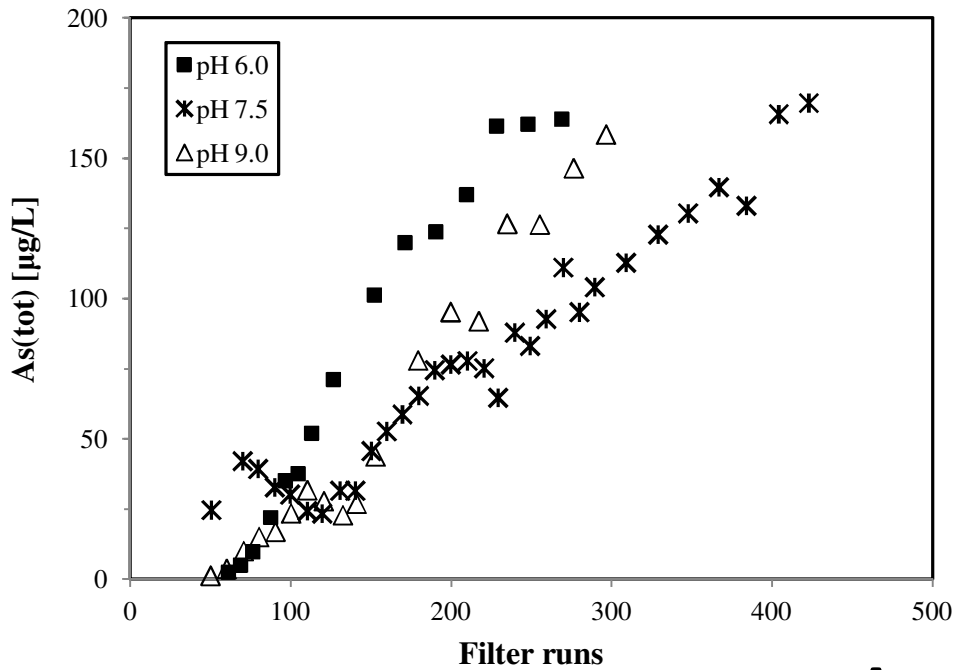
before increasing again. Further study must be performed to explain this occurrence. Figure 7B shows arsenate removal performance of the filters under the same conditions of the arsenite experiments. The filters had a slightly higher, but similar, removal capacity for arsenate

compared to arsenite, with the 0.026 M, 0.128 M, and 0.510 M ferric nitrate solution coated filters treating about 26, 77, and 373 equivalent filter runs, respectively to below 10 µg/L. Similar arsenite versus arsenate performance has been demonstrated in other studies (10, 27). Slightly better removal of As(V) than As(III) at pH 7.5 has been demonstrated with iron-oxide coated sand by Dixit and Hering (2003). The filter effluent had a normal drinking water pH of ~7.

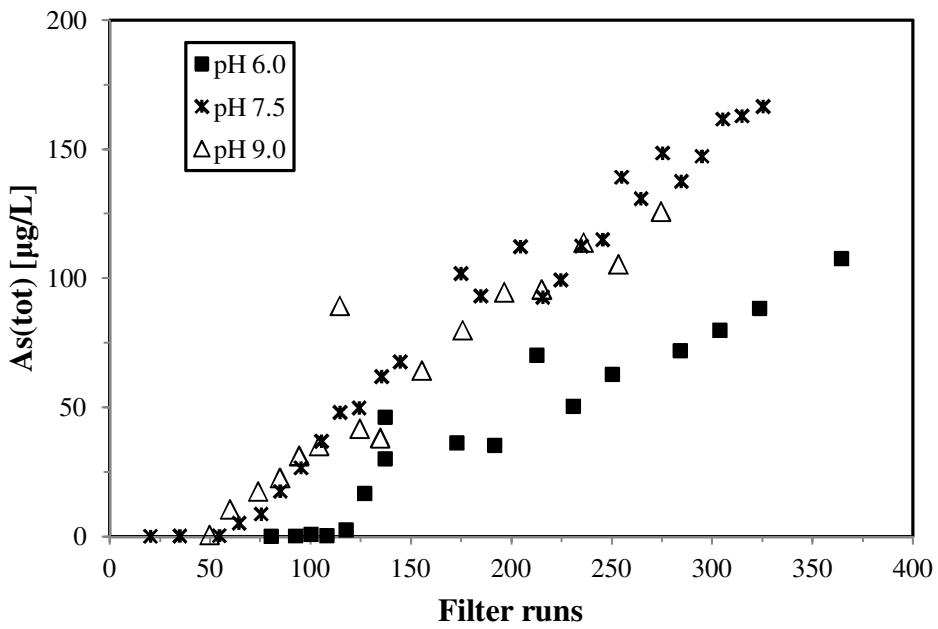
Table 7 shows the total mass of As sorbed and the mass As sorbed per mass of iron coated on the filters at the 10 and 50 µg/L breakthrough points. An increase in ferric nitrate coating solution strength corresponded to an increase in As sorbed at both 10 and 50 µg/L breakthrough. The increase in sorption capacity was not linear with the increase in coating strength. This result is likely due to the fact that surface area (and sorption sites) did not increase linearly with Fe coating strength. In general, the filters coated with less iron oxide removed more As per mass of iron but their overall arsenic removal performance was unsatisfactory. It is likely that as more layers of the iron-oxide surface form during the coating process, a smaller proportion of available sorption sites form. An overall increase in capacity occurred with greater Fe coating concentration, but the removal efficiency decreased. While the 0.026 and 0.128 M ferric nitrate solutions used to produce an iron-oxide coating on the ceramic filter surface did not offer promise for extended use, the filters coated with the 0.510 M solutions were capable of treat water containing 250 µg/L arsenate and arsenite to less than the WHO MCL of 10 µg/L for at least 365 uses. Therefore, if this filter is used once per day it could produce safe drinking water for 1 year. Breakthrough points of the IOCCFs coated with silver were similar to those with no silver, indicating that the 200 mg/L colloidal silver coating used on the Potters for Peace did not significantly affect the arsenic removal performance of the IOCCFs.

Effect of pH on As Removal. Filters coated with 0.128 M ferric nitrate solution treated influent at either pH 6.0 or pH 9.0 to investigate the effects of pH on the sorption capacity of the IOCCF. Other than pH, these tests were run with the same conditions as the sorption studies at pH 7.5. The effluent arsenic concentrations with respect to filter runs at pH 6.0, 7.5, and 9.0 are shown in Figure 8. For arsenite influent (Figure 8A) the filter runs performed with effluent As concentrations below 10 $\mu\text{g/L}$ at pH 6.0, 7.5, and 9.0 were 76, 38, and 70 respectively. Performance at pH 6.0 and 9.0 was similar while arsenite removal at pH 7.5 was less effective at 10 $\mu\text{g/L}$ BT. Filter runs achieved under 50 $\mu\text{g/L}$ at pH 6.0, 7.5, and 9.0 were all near 160. The 0.128 M ferric nitrate coated filters removed arsenic to below 10 $\mu\text{g/L}$ for 122, 77, and 59 filter runs at pH 6.0, 7.5, and 9.0 respectively (Figure 8B). Dixit and Hering (2003) reported a crossover pH (the pH value at which As(III) and As(V) are equally sorbed) was 8.5 with 10 μM (~750 total $\mu\text{g/L}$ As) with As(V) better adsorbed at pH levels below 8.5 and As(III) better adsorbed at pH higher than 8.5. The results from the As(V) tests of this study are consistent with this finding, with As removal decreasing with increasing pH. The results from the arsenite tests, however, did not correlate as well.

Table 7 shows the mass As adsorbed and the mass As adsorbed per mass Fe at 10 and 50 $\mu\text{g/L}$ breakthrough at pH 6.0 and 9.0. The mass of As(V) adsorbed and removal capacity (mass As/mass Fe) at pH 6.0 influent at both the 10 and 50 $\mu\text{g/L}$ breakthrough points were greater than at pH 7.5 and 9.0 indicating that As(V) is removed better at a lower pH value. The removal capacity and mass of As(III) adsorbed at pH 6.0 and 9.0 were similar at 10 $\mu\text{g/L}$ BT while at pH 7.5 the capacity and mass of As(III) removed were less. However, at 50 $\mu\text{g/L}$ BT, the mass of As(III) and capacity were very similar at pH 7.5 and 9.0, and lower at pH 6.0.



A



B

Figure 8 – [A] pH effects on As(III) adsorption, [B] pH effects on As(V) adsorption. All filters coated with 0.128 M ferric nitrate solution and 200 mg/L colloidal silver

Arsenic Sorption in the Presence of NOM. Water from Clinton Lake (Lawrence, KS, USA) containing 4.98 mg/L DOC (0.45- μm filtered), 113 mg/L as CaCO_3 calcium hardness, 141 mg/L as CaCO_3 total hardness, 159 mg/L as CaCO_3 alkalinity, and <0.05 mg/L $\text{PO}_4\text{-P}$, and having a pH of 8.3, was filtered by 0.128 M ferric nitrate coated filters at the same flow rate as previous tests to study the effects of NOM on As removal.

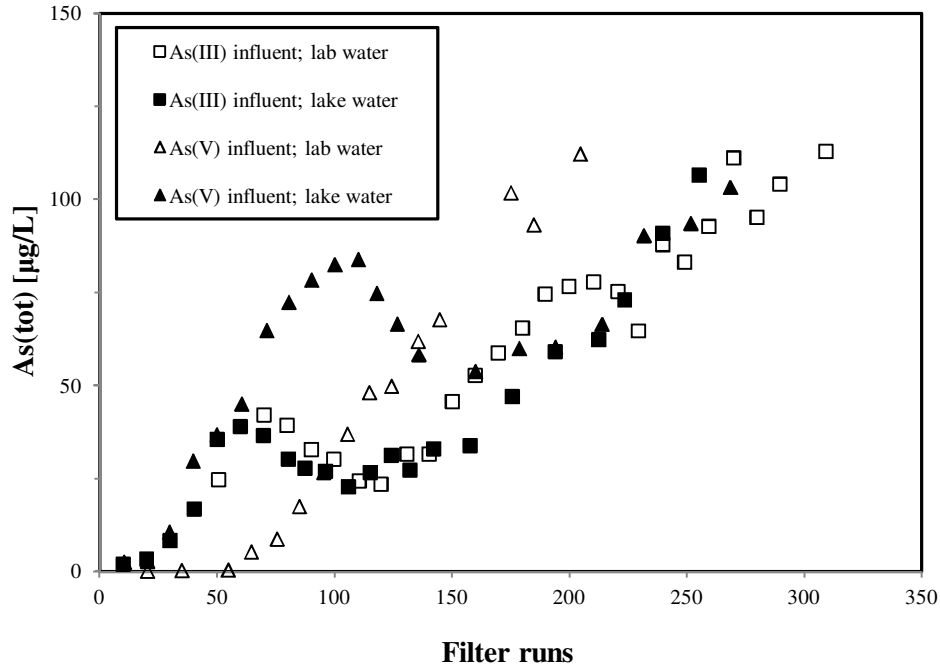


Figure 9 – Effects of NOM on As(III) and As(V) sorption. All filters coated with 0.128 M ferric nitrate solution and 200 mg/L colloidal silver; pH adjusted to 7.5.

pH was adjusted to 7.5 using 10% HCl to replicate conditions in the initial sorption experiments.

Figure 9 shows effluent As(III) and As(V) concentrations of lab water or Clinton Lake water versus filter runs performed. At 10 $\mu\text{g/L}$ BT 32 and 62 filter volumes were achieved for lake water containing As(III) and As(V), respectively compared to the 38 and 77 filter runs achieved with lab water containing As(III) and As(V) respectively. Table 7 also shows the mass As adsorbed and mass As per mass Fe of As(III) and As(V) adsorbed in the NOM experiments.

Performance of the IOCCFs decreased when filtering lake water, due presumably to some

combination of surface adsorption competition and pore blockage by natural organic matter or other anions present. This result indicates that the IOCCF can successfully remove both As(III) and As(V) from water with typical lake DOC levels for a significant period, but more research is needed on the competitive effects of NOM and inorganic anions in relation to As adsorption capacities.

TABLE 7 - BREAKTHROUGH CAPACITY SUMMARY

Ferric nitrate coating strength (M)	As species filtered	pH	Mass adsorbed at 10 µg/L BT (µg)	Mass adsorbed at 50 µg/L BT (µg)	Mass As/Mass Fe at 10 µg/L BT (µg/mg)	Mass As/Mass Fe at 50 µg/L BT (µg/mg)
0.026	As(III)	7.5	43.2	80.6	21.0	39.1
0.128	As(III)	7.5	82.1	305.3	8.0	29.6
0.510	As(III)	7.5	788.7	1200.0	19.1	29.1
0.026	As(V)	7.5	55.2	113.2	26.8	55.0
0.128	As(V)	7.5	165.2	255.2	16.0	24.7
0.510	As(V)	7.5	805.4	969.3	19.6	23.5
0.128	As(III)	6.0	164.4	231.9	15.9	22.5
0.128	As(III)	9.0	151.6	304.6	14.7	29.5
0.128	As(V)	6.0	264.8	444.0	25.7	43.1
0.128	As(V)	9.0	128.2	273.2	12.4	26.5
0.128	As(III)*	7.5	68.0	347.6	6.6	33.7
0.128	As(V)*	7.5	61.6	126.0	6.0	12.2

*Clinton Lake NOM Experiments

Desorption Experiments. Filters coated with 0.026 M ferric nitrate were loaded with arsenite and arsenate to approximately 15% BT (influent 250 µg/L) and then began filtering lab water containing no arsenic at pH 7.5. pH was then increased or decreased in one-unit increments and the effluent arsenic concentration was measured at each pH step. Four filter volumes were passed through the filters at each pH step. Figure 10 shows the effluent As concentrations vs. pH. Essentially no As desorbed from the filters at pH 3.5 to pH 8.5. Some arsenic began to desorb at pH 2.5 and 9.5, but the most significant desorption occurred at pH 10.5. Increases in pH at 11.5

and 12.5 caused additional As to desorb. When raising pH to 12.5, regeneration efficiencies of 70% and 94% were achieved for the As(III) and As(V) sorbed on to the filters, respectively.

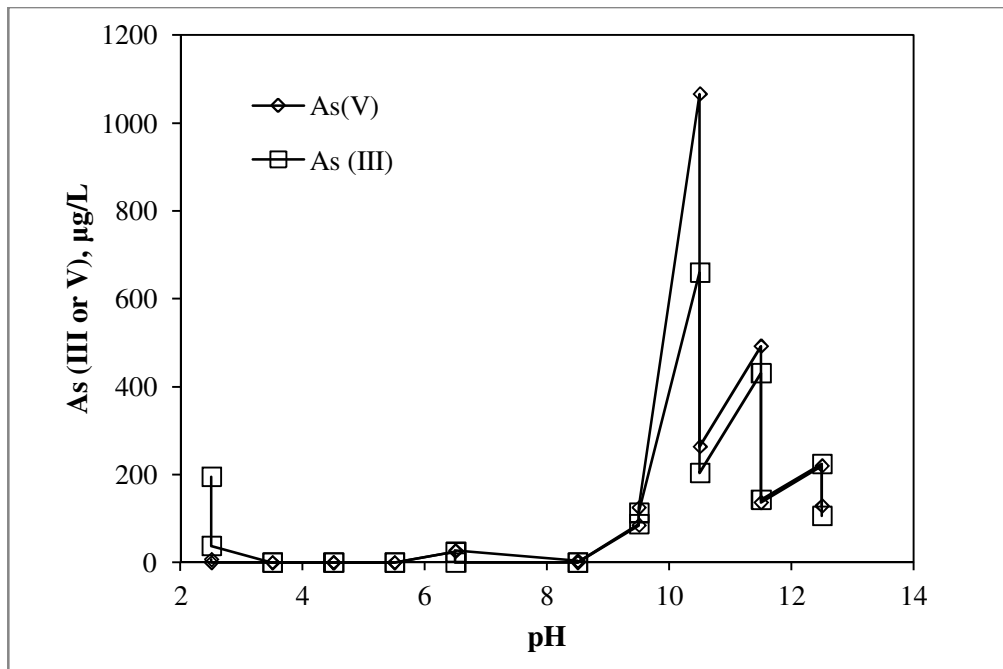


Figure 10 – Desorption of adsorbed arsenic at different pH steps - either decreasing from 7.5 to 2.5 or increasing from 7.5 to 12.5. All filters coated with 0.128 M ferric nitrate solution and 200 mg/L colloidal silver

When lowering pH to 2.5 only 21% and 7% regeneration efficiencies were achieved for As(III) and As(V), respectively. Regeneration of iron-oxide coated surfaces has been performed at similar pH levels in other studies (25, 27). These results indicate that unsafe levels of arsenic would not desorb from the IOCCF unless water pH shifted from lower levels to about 9.0 under normal use conditions. This effect requires more study to confirm performance, and determine appropriate operating requirements.

Regeneration, if desired, could be achieved by filtering water with pH 11.5 or 12.5 and possibly below 2.5. However it would be safer to dispose of the filters in a safe manner rather than producing water with extremely high As concentrations during regeneration.

Bacterial Removal. Water from Potter Lake (Lawrence, KS) contained on average of 2 CFU/mL *E. coli* and 15 CFU/mL total coliforms. One hundred percent removal of *E. coli* and total coliforms was achieved when filtered through the 0.510 M IOCCFs also coated with silver. While the filters in this study were not subjected to vigorous microbial testing, these results indicate that the bacterial removal effectiveness of the Potters for Peace filter has been not been reduced by the modifications performed to produce the IOCCF.

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4. CONCLUSIONS

Results from this research project have shown that the IOCCF coated with 0.510 M ferric nitrate (the highest coating strength used) is capable of removing both As(III) and As(V) from water at influent levels as high as 250 µg/L to effluent levels below the WHO and USEPA MCL of 10 µg/L for up to a year if the filter is used once per day. The filter produced water at normal drinking water pH levels (~ pH 7) and no leaching of the iron-oxide coating into the effluent was observed. pH had some effect on the sorption of the different arsenic species on to the iron-oxide coating. As(V) was sorbed more effectively at lower pH (7.5 and below) while pH had a lesser effect on As(III) sorption. Even so, there was not a large difference in As(V) or As(III) removal performance over a pH range of 6.0 to 9.0. The As(III) and As(V) removal performance of the IOCCF was slightly reduced when filtering lake water as compared with the As spiked reagent water, mostly likely due to a combination of blockage of surface adsorption competition and pore blockage by NOM and other adsorbates. However, the IOCCF removed both As(III) and As(V) for a significant number of filter runs. As(III) and As(V) remain strongly adsorbed over a range of pH levels such that the used filters may be used and safely disposed of without the likelihood of As leaching under most natural conditions, however more study of desorption effects is necessary. Results also showed that the IOCCF retained the bacterial removal capabilities of the Potters for Peace Filter.

5. ENVIRONMENTAL ENGINEERING IMPLICATIONS & RECOMMENDATIONS FOR FUTURE RESEARCH

This research has shown that ceramic filters coated with iron-oxide may be capable of removing arsenic at typical groundwater concentrations in regions with arsenic contamination to safe levels for up to one year. This filter could produce safe water by removing harmful levels of

pathogens and arsenic. It would be possible to incorporate the iron-oxide coating of the filter in to the normal manufacturing process of the Potters for Peace filter and other ceramic filters of similar design. After the filters are fired in a kiln, the coating process described in this research could be used to produce IOCCFs. The same kiln used for firing the filters can be used for the iron coating process so the purchase of additional equipment will not be necessary. The iron oxide coating should not add significantly to the normal cost of \$4 to \$6 (\$USD) for a Potters for Peace ceramic filter, continuing to make this filter one of the most economical POU water treatment technologies.

Further research is necessary before this technology is implemented in the field. Most importantly, the performance of the filter under differing influent water conditions should be examined. The arsenic removal capacity of the device should be determined for a range of different natural waters, and the competitive effects of NOM and other inorganic anions such as phosphate, nitrate, carbonate and silicate should be better understood. Other clay types, firing methods and iron coating techniques could be studied in order to fine tune the fabrication methods of the IOCCF for optimal As removal performance. Allowing the iron coating solution to fully flow through the filters rather than soaking just soaking them in the solution (and possibly only soaking the outer-most pores) should be performed to attempt to increase the amount of iron coated on the ceramic surface and create more sorption sites. More study of the desorption effects is necessary to ensure the safety of this device. Because tests were only performed at one influent arsenic concentration (~250 µg/L) it will be necessary to investigate As removal at higher influent concentrations since these high levels do occur in some regions. Results from this study showed that arsenic removal performance increased with increasing iron coating strength, so tests of filters produced with higher coating strength (>0.510 M

$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ should be performed. Benjamin et al. (1996) and Edwards and Benjamin (1989) have demonstrated removal of other metals such as Cu, Cd, Pb, Ni, Zn, Se, and Cr using iron-oxide coatings. The presence of these elements in drinking water may be due to either anthropogenic sources such as mines, or natural sources originating from rocks and other minerals. Therefore their removal performance using the IOCCF should be investigated.

APPENDIX A – SUPPLEMENTAL DATA

Additional sorption results

The following charts show the results of the sorption experiments testing filters not coated with colloidal silver.

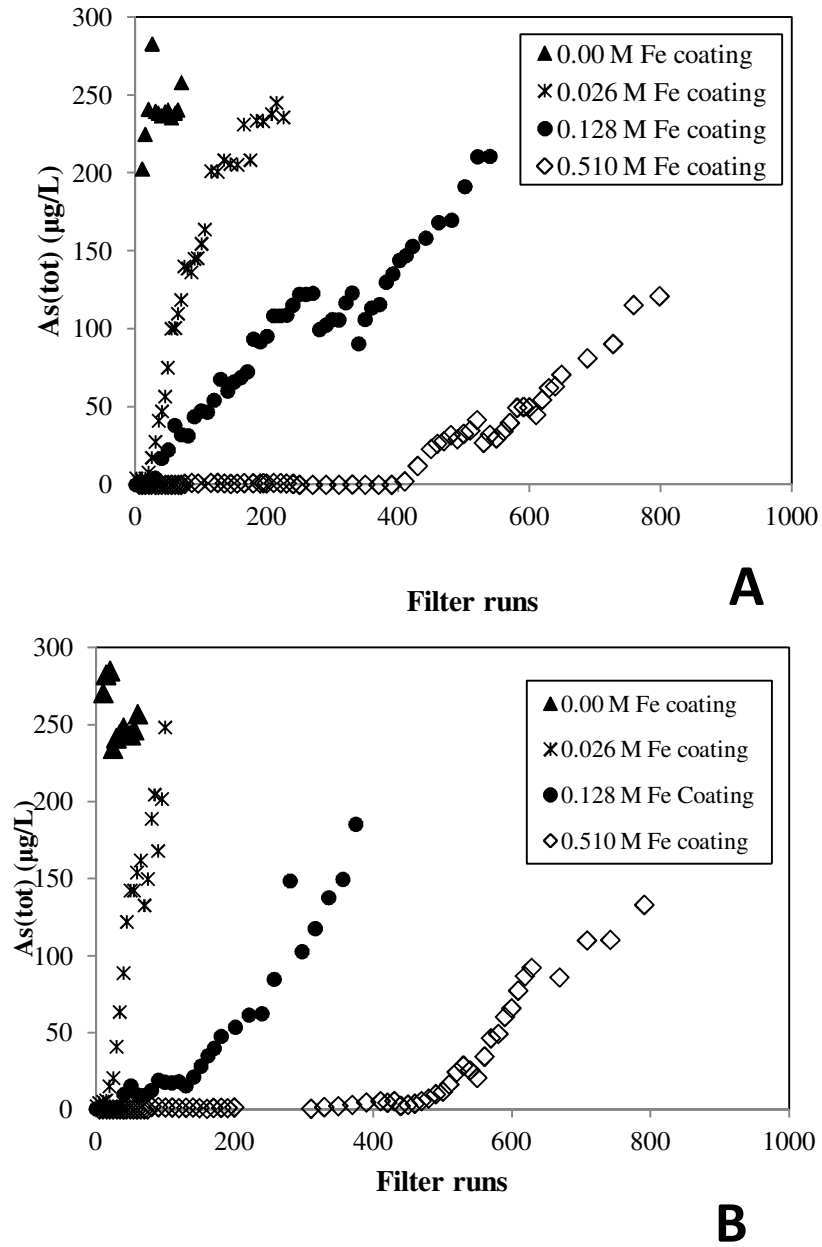


Figure 11 –Sorption of [A] arsenite and [B] arsenate (pH 7.5; arsenic concentration ~250 µg/L) under different coating conditions. Filters were not coated with colloidal silver.

Filter effluent pH and iron leaching tests

The following table shows the results of tests on filter effluent to determine effluent pH and iron concentration (to investigate whether the iron coating was leaching)

Table 8 – Filter effluent pH and dissolved iron concentration of filter with [A] 0.026 M ferric iron coating, As(III) influent, w/ silver coating; [B] 0.510 M ferric iron coating, As(III) influent, w/o silver coating; [C] 0.128 M ferric iron coating, As(V) influent, w/ silver coating. Influent pH to all filters was ~7.5

Filter run	As filter effluent conc. (µg/L)	Effluent pH	Dissolved Fe (mg/L)
[A]			
11	3.5	7.4	< 0.2
105	197.2	7.47	< 0.2
215	185.5	7.04	< 0.2
324	183.9	7.18	< 0.2
[B]			
10	0.0	7.11	< 0.2
130	1.1	7.1	< 0.2
230	0.0	7.5	< 0.2
329	1.6	7.3	< 0.2
430	5.6	7.09	< 0.2
520	24.3	7.17	< 0.2
619	86.6	7.08	< 0.2
708	109.8	7.2	< 0.2
[C]			
10	0.0	7.4	< 0.2
105	37.0	7.15	< 0.2
225	99.4	7.04	< 0.2
315	162.8	6.85	< 0.2
415	188.0	6.98	< 0.2
505	200.1	6.96	< 0.2

APPENDIX B – FILTER FABRICATION SUPPLEMENTAL INFORMATION

Filter fabrication

Dry, powdered Redart clay was selected as the base clay for the ceramic filters in order to test a material similar in composition to the earthenware clays available in many parts of the world. Redart clay is an earthenware clay composed of cristobalite, tridymite and quartz. An optimal mixture of 73% dry Redart clay was combined with 27% sawdust (by weight) (Yanez 2009). Sawdust is added to the clay to provide a combustible material that will leave small pores in the ceramic material after the firing process is complete. The sawdust was sieved through a 30-mesh sieve to obtain the correct particle size to ensure the pores that the sawdust will produce will be small enough to remove bacteria as small as 1 μm in size. The dry clay and sawdust were thoroughly mixed together until all particles were evenly distributed. Water was then added and mixed until a workable clay consistency was reached. The proper consistency is not too moist or sticky but moist enough to be pliable. For a 10-lb total dry weight (clay plus sawdust), approximately 3.6 liters of water were added to achieve the proper consistency. The newly mixed clay was placed in a plastic bag that was tied to retain the moisture in the clay. The clay was then allowed to “cure” for one week. Potters claim that bacteria grow on the clay body during the curing process and increase the acidity in the clay. This reportedly improves the plasticity and workability of the clay (Potters for Peace 2005).

Rather than fabricating full size Potters for Peace filters, small, circular cross sections of the filter material were made for ease of fabrication and testing. Molds for the filter sections, were constructed by cutting 1.5-cm sections from 2-cm diameter plastic syringes. These molds produce cylindrical sections that are the same thickness as the Potters for Peace filter. This was done to accurately model the flow through the filter. The clay was pressed into the molds by

hand and then further compressed by pressing a plastic plate on top of the molds. The plastic plate is used in order to evenly distribute the clay in the molds and fill all voids. The exposed top and bottom clay surfaces were then smoothed and leveled. The filters were allowed to air dry for at least 12 hours. After 12 hours, the filters shrink slightly and can be easily removed from the molds.

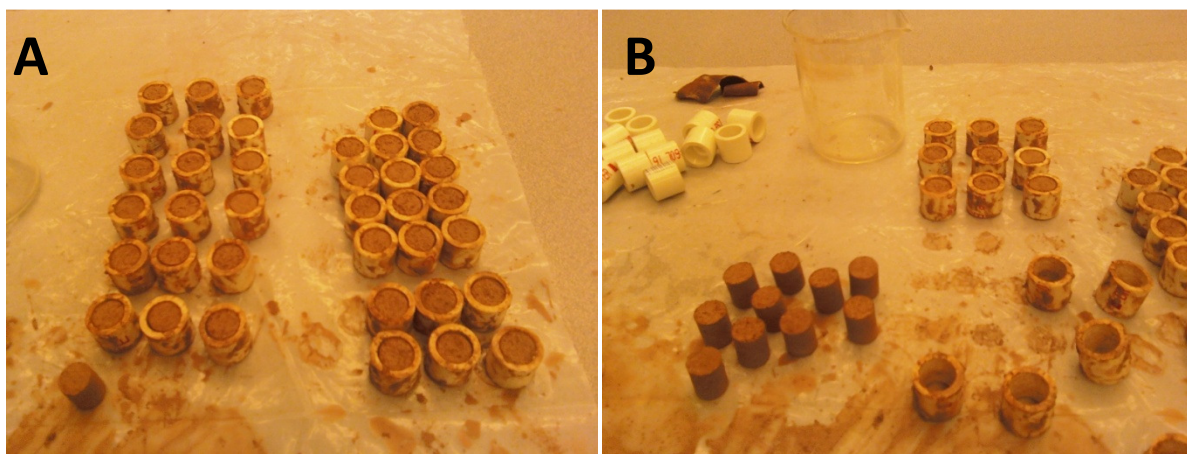


Figure 12 – [A] Filters drying in molds and [B] filters after being removed from molds

The filters were air dried for another 3 days and then fired using a Carbolite 3216 tube furnace to produce a ceramic material. Air was used as the carrier gas to allow for combustion and to remove products from the furnace. The air flowrate was set to $233 \text{ cm}^3/\text{min}$ during the firing process. The temperature in the tube furnace was increased from room temperature to $80 \text{ }^\circ\text{C}$ at a rate of $60 \text{ }^\circ\text{C}/\text{hr}$ and held for 3 hours so that the water in the clay would evaporate slowly in order to prevent cracking (Vertacnik 2010). The temperature was then increased to $150 \text{ }^\circ\text{C}$ at a rate of $60 \text{ }^\circ\text{C}/\text{hr}$ and held for 3 hours, increased to $600 \text{ }^\circ\text{C}$ at a rate of $150 \text{ }^\circ\text{C}/\text{hr}$, and finally increased to $900 \text{ }^\circ\text{C}$ at a rate of $300 \text{ }^\circ\text{C}/\text{hr}$ and held for 6 hrs at this temperature. The filters were allowed to cool for another 6 hours before being removed from the furnace. The firing schedule used for this project was adapted from (Oyanedel-Craver and Smith 2007).

Iron Coating Procedure

To produce an iron oxide surface for arsenic adsorption, the filters were coated with a ferric nitrate solution through a process adapted from Benjamin et al. (1996) and Thirunavukkarasu et al. (2003). Three 100-mL iron coating solutions were prepared in order to test the effect of the iron concentration of the coating solution on arsenic removal. Ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; MP Biomedicals) served as the iron species in all coating solutions. The composition of the coating solutions is listed in Table 9. The solid ferric nitrate crystals were first added to the reagent water and stirred on a stir plate until they dissolved. The NaOH was added and a black precipitate formed. The solution was again stirred on a stir plate until the precipitate was dissolved. The 0.510 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution had an approximate pH of 2 after the NaOH was added. Filters were placed in beakers containing the coating solutions that were placed on a shaker table at a speed of 100 rpm for 18 hrs to thoroughly saturate the filters with the coating solution. The filters were then removed from the coating solutions and placed in an oven set to 110 °C for 4 hours. The filters were removed from the 110 °C oven and placed in a muffle furnace set to 550 °C for 3 hours.

Table 9 - Composition of iron coating solutions

	Coating Solution 1	Coating solution 2	Coating Solution 3
Iron concentration of 100 mL solution	0.510 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.128 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0.026 M $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Volume of 10 M NaOH added	0.3 mL	0.3 mL	0.3 mL

The filters were then removed from the muffle furnace and placed in a heat-resistant Pyrex glass container to cool for an hour. After the filters had cooled, they were then rinsed with reagent water to wash away any loose particles. At this point, the filters were placed back into the coating solutions in which they had previously been soaked. The beakers containing the coating solutions and filters were again placed on a shaker table set at 100 rpm for 18 hours. The filters were then removed from the coating solutions and heated at 110 °C for 20 hours. The filters were removed from the oven and allowed to cool before further use.

Colloidal silver coating

To study the effects of colloidal silver that is used as a bactericidal and viricidal (Yahya et al. 1992) coating on the Potters for Peace filter on arsenic removal, a number of filters were also coated with colloidal silver. Powdered colloidal silver (Argenol) was added to reagent water to produce a 0.023% colloidal (200 mg/L) silver solution recommended by Potters for Peace (2006). The solution was mixed using a stir plate to evenly suspend the colloidal particles. Filters were submerged in the silver solution and stirred in the solution with a stir plate set to low for 2 minutes. The filters were then removed from the colloidal silver solution and allowed to air dry.

APPENDIX C – EXPERIMENTAL APPARATUS SUPPLEMENTAL INFORMATION

Filtration Apparatus

An eight channel Minipulse 3 peristaltic pump (Gilson) continuously pumped water through the ceramic filters. The optimal gravitational flowrate through the Potters for Peace filter is 1–3 liters per hour, however it is important to note that the flowrate varies with depth in a full size Potters for Peace filter. The bottom of the filter will see the highest flowrate until it begins to clog due to biofilm and/or other particulates filling in the pores. An equivalent gravitational flowrate through the filter section was calculated by multiplying the ratio of the filter section surface area to the surface area of the full-size Potters for Peace filter (0.0006) by a flowrate of 2.5 L/hr. This gives a flowrate of 1.48 mL/hr or 0.025 mL/min through the filter sections, which is within the optimal range. The peristaltic pump was calibrated by measuring the flowrate at several different pump set points to produce a linear pump calibration curve. The equation from this curve was used to calculate the pump set point for a flowrate of 1.48 mL/hr.

In order to pump water through the filters, they were encased using 10-mL luer-lock syringes (BD). To encase each filter, the luer-lock ends of two syringes were cut off. The luer-lock ends were placed on each end of a filter, and were glued on by coating the outer surface of the filter and syringe ends with 10-minute quick-set epoxy glue. Care was taken to avoid coating the top or bottom surface of the filter with epoxy glue so that the no filter surface area would be lost. The glue was allowed to air dry for at least an hour. After the glue had dried, the filters were wetted by connecting a 50-mL syringe to one luer-lock end and slowly squeezing the plunger to pass water through the filter. This process also served as a way to test for leaks

through the glued portions. If any leaks were found, the filter was again coated with epoxy glue until no leaks were present.

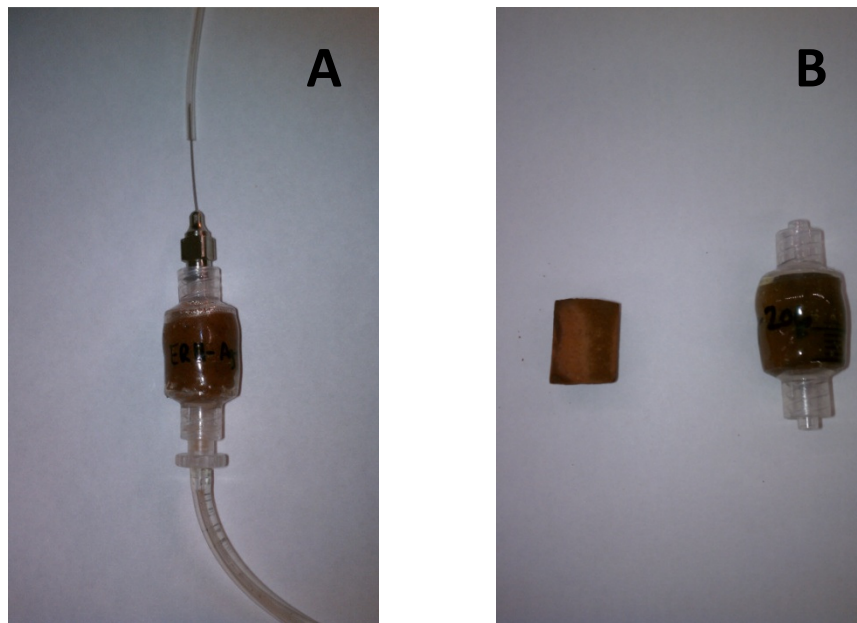


Figure 13 – [A] Filter before and after glued with epoxy into luer-lock syringe ends; [B] Filter connected to tubing using a 30-gauge hypodermic needle (top of filter) and barb plastic connector (bottom of filter)

To connect the filters to the pump, one of the luer-lock ends was connected to a 30-gauge hypodermic needle (Cadence Science, Inc.) that was inserted into the pump tubing. The other luer-lock end of the filter was connected to 0.8-in. ID Tygon LFL tubing (Masterflex) using a female luer thread style to 1/16-in. barb plastic connector (Cole-Parmer). The Tygon tubing attached to each filter was placed above one of the eight channels of a Retriever II sample collector (ISCO). This allowed the water passing through the filters to flow through the Tygon tubing and drip into 15-mL centrifuge tubes (BD) placed in the sample collector.



Figure 14 – [A] Pump setup - influent arsenic solutions connected to pumps connected to sample collector; [B] Close-up view of filters connected to Minipulse 3 peristaltic pump (Gilson)

The sample collector was set to advance every 353 minutes, which is the amount of time a filter run would take through a full size Potter for Peace at 2.5 L/hr. Therefore, the water collected in each sample tube represents a full filter run. Tygon tubing was used to connect the peristaltic pump tubing using another 30-gauge hypodermic needle and female luer thread style to 1/16-in. barb plastic connector. The other end of the Tygon tubing was placed in the arsenic feed solutions. Samples were checked to ensure that volume reduction through evaporation was not occurring.

APPENDIX D – ANALYTICAL METHODS SUPPLEMENTAL INFORMATION

Sampling for analysis

Sample volumes were recorded and every 20th sample (equivalent to every 20th filter use) was analyzed for arsenic unless breakthrough was occurring. During filter breakthrough, every 5th, 10th, 20th, or 40th sample was analyzed depending on the desired detail. Analysis for iron concentration and pH was performed on random samples. The 15 mL sample collection tubes were washed in a 5% sulfuric acid bath between uses.

Graphite Furnace Atomic Absorption (GFAA) Method for Arsenic Analysis

Arsenic concentrations were determined using a Varian SpectraAA 240 GFAAS equipped with a GTA 100-graphite tube atomizer and programmable sample dispenser. The method detection limit (MDL) was determined to be 2.6 µg/L using Method 1030C of Standard Methods for the Examination of Water and Wastewater (APHA 2005). Pyrolytically coated partitioned graphite tubes (Agilent Technologies) were used for analysis, and argon gas (Linweld) was used to sheath the atomizer and purge internally. An arsenic hollow cathode lamp (Varian Canada Inc., Toronto) was used at a wavelength of 193.7 nm with a slit width of 0.5 nm. A 500 mg/L palladium solution (Fluka) was prepared and used as a matrix modifier to decrease interferences and stabilize the analyte to higher temperatures (Michon et al. 2007). An external 1000 mg/L arsenic reference solution (Fisher Scientific) was used for instrument calibration. A quadratic calibration curve was used over a range of 0-50 µg/L total arsenic for this analysis. Three replicates were analyzed for each sample and only samples with relative standard deviation (%RSD) below 5% were accepted.

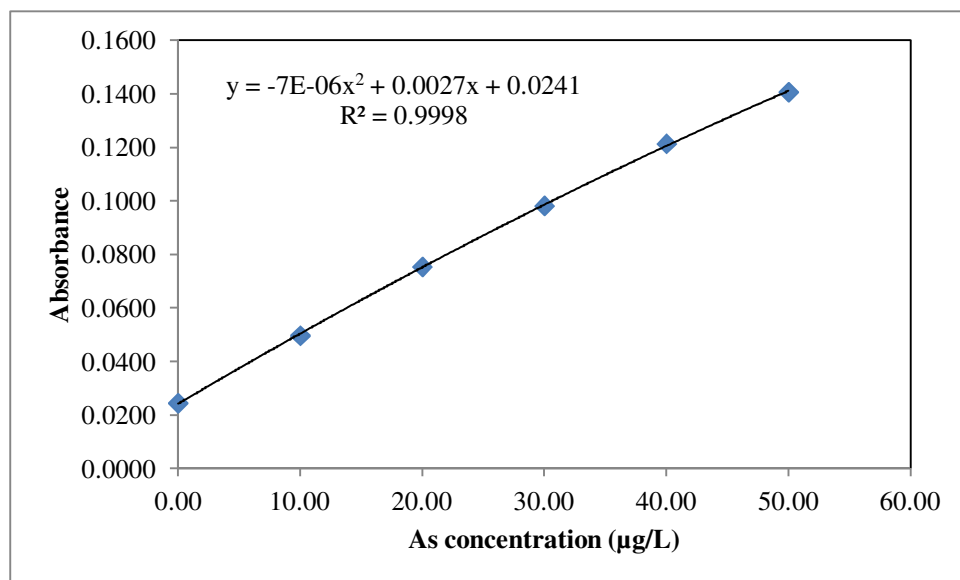


Figure 15 – Sample GFAA quadratic calibration curve for arsenic

Ion Chromatography method for speciation of As(III) and As(V)

Verification of arsenic speciation in the influent solutions was performed by IC analysis (Dionex ICS-2000) using an IonPac AS18 anion exchange column (Dionex). 10 mg/L standards were prepared from 200 mg/L As(III) (NaAsO_2 ; Fisher Scientific) and As(V) ($\text{HAsNa}_2\text{O}_4 \cdot 7\text{H}_2\text{O}$; Sigma Aldrich) stock solutions. A self-regenerating suppressor (ASRS Dionex) was used. A KOH gradient of 6-52 mM in 15 min at 1 mL/min was used as the eluent. The suppressor was set to 135 μS for this gradient. An elution time of 15 min was used for each sample.

Dissolved organic carbon (DOC)

Water was first vacuum filtered through Whatman GF/F 0.45 μm glass microfiber filters to remove particulate matter. A Torch instrument (Teledyne Tekmar) with a pre-programmed TOC-TN Drinking Water method was determined DOC concentration. A 500 ppm TOC

standard (SpectroPure, “Carbon Standard Organic (TOC) 500ppm” Part #SC021490-500C) was diluted to 2 ppm for this analysis. Three replicates were analyzed for each sample.

Total and calcium hardness, alkalinity, phosphate, and dissolved iron analysis

Dissolved iron concentration in the filtered effluent was determined with the Hach Iron TNT 858 method using a DR 5000 spectrophotometer (HACH). The total and calcium (Ca) hardness and alkalinity of the Clinton lake water were determined using the Hach digital titrator kit (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).

Enumeration of E. coli and Total Coliforms

One-mL aliquots of filter influent from Potter Lake (Lawrence, KS USA) and filter effluent were plated on Petrifilm (3M) plates. The plates were incubated at 24 h at 35°C ± 1°C for total coliforms and 48 h at 35°C ± 1°C. Only colonies with gas bubbles were counted.

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