

# Sustainable Colloidal-Silver-Impregnated Ceramic Filter for Point-of-Use Water Treatment

VINKA A. OYANEDEL-CRAVER AND JAMES A. SMITH\*

Department of Civil and Environmental Engineering,  
University of Virginia, P.O. Box 400742,  
Charlottesville, Virginia 22904-4742

Received May 29, 2007. Revised manuscript received September 21, 2007. Accepted November 12, 2007.

Cylindrical colloidal-silver-impregnated ceramic filters for household (point-of-use) water treatment were manufactured and tested for performance in the laboratory with respect to flow rate and bacteria transport. Filters were manufactured by combining clay-rich soil with water, grog (previously fired clay), and flour, pressing them into cylinders, and firing them at 900 °C for 8 h. The pore-size distribution of the resulting ceramic filters was quantified by mercury porosimetry. Colloidal silver was applied to filters in different quantities and ways (dipping and painting). Filters were also tested without any colloidal-silver application. Hydraulic conductivity of the filters was quantified using changing-head permeability tests. [<sup>3</sup>H]H<sub>2</sub>O water was used as a conservative tracer to quantify advection velocities and the coefficient of hydrodynamic dispersion. *Escherichia coli* (*E. coli*) was used to quantify bacterial transport through the filters. Hydraulic conductivity and pore-size distribution varied with filter composition; hydraulic conductivities were on the order of 10<sup>-5</sup> cm/s and more than 50% of the pores for each filter had diameters ranging from 0.02 to 15 μm. The filters removed between 97.8% and 100% of the applied bacteria; colloidal-silver treatments improved filter performance, presumably by deactivation of bacteria. The quantity of colloidal silver applied per filter was more important to bacteria removal than the method of application. Silver concentrations in effluent filter water were initially greater than 0.1 mg/L, but dropped below this value after 200 min of continuous operation. These results indicate that colloidal-silver-impregnated ceramic filters, which can be made using primarily local materials and labor, show promise as an effective and sustainable point-of-use water treatment technology for the world's poorest communities.

## Introduction

Untreated surface water or groundwater is often contaminated with pathogenic organisms of fecal origin. If not, it can become contaminated during transport and storage (1–4). Even water treated with a disinfectant often becomes contaminated when collected from a public standpipe and stored in the home. A recent review of the literature sponsored by the WHO concludes that simple, socially acceptable, and low-cost interventions at the household (point-of-use)

and community level have the potential to significantly improve the microbial quality of household water and reduce the risk of diarrheal disease, dehydration, and death, particularly among children (5, 6).

Beginning in the late 1980s and early 1990s, ceramic filters for point-of-use water treatment began appearing in third-world marketplaces and their performance has been evaluated in a small number of published studies (5, 7, 8). These studies have evaluated filters that are typically produced through an industrial design and manufacturing process (that does not use local labor) with high-purity ingredients. This often results in a filter price point that is beyond the reach of many residents of developing global communities.

In this study, point-of-use water treatment using a colloidal-silver-impregnated ceramic filter promoted by a U.S.-based nongovernmental organization (NGO) called Potters for Peace is investigated. Since 1998, Potters for Peace has been teaching communities to manufacture and distribute their water filters that retail for \$5–15 (U.S. \$). The filters look like simple ceramic pots. The filter pots are suspended in 5-gallon plastic containers. Water is then poured into the filter pot and flows by gravity through the ceramic filter and into the lower plastic container where the treated water can be accessed with a spigot.

The filters are typically made with local labor and materials (clay, water, and a combustible organic material such as sawdust, flour, or rice husks). The filter is formed using a filter press, air-dried, and fired in a flat-top kiln, increasing the temperature gradually to about 900 °C during an 8-h period. This forms the ceramic material and combusts the sawdust, flour, or rice husk in the filters, making it porous and permeable to water. After firing, the filters are cooled and impregnated with colloidal silver by either painting with, or dipping in, a colloidal-silver solution. The colloidal silver is hypothesized to act as a microbial disinfectant.

Each filter is tested by measuring the water flow rate to ensure it is between 1 and 2 L/hr. This test is the sole design criterion (other than the physical dimensions of the filter). A typical filter lifetime is 2–3 years; it must be periodically cleaned with a brush to maintain the design flow rate. Since 1998, Potters for Peace has aided NGOs in establishing filter factories throughout the world. They estimate that about 100,000 filters have been manufactured and distributed for use.

The Potters for Peace ceramic filter has many potential advantages as a point-of-use water treatment technology. It can be manufactured with mostly local materials and labor. Since clay pots are often used as storage containers for water, it is a socially acceptable technology that can work year round in different climates. It does not impart an objectionable taste to the treated water. It is designed to remove both turbidity and pathogens and its retail cost is low. No refereed journal publication has critically evaluated the performance of this filter. Lantagne (9) has published the most comprehensive report on the filter to date.

There are several critical knowledge gaps related to filter design and performance. There is no information available on how the manufacturing process or the composition and relative amounts of the raw materials used to make the filter affect its physical pore structure and treatment performance. The role of colloidal silver in the deactivation of pathogenic bacteria as they pass through the filter is poorly understood. It is uncertain if bacterial removal is caused by filtration/sorption, deactivation by colloidal silver, or some combination of these processes. Potters for Peace has chosen a specific

\* Corresponding author e-mail: jas9e@virginia.edu.

application rate of colloidal silver onto their filters, but they do not have any data to indicate that it is, or is not, appropriate.

Herein, we provide the first critical and mechanistic evaluation of the performance of ceramic filters manufactured according to the design guidelines specified by Potters for Peace. Using two well-characterized natural soils and commercial pottery clay, ceramic filters were manufactured and tested to quantify pore-size distributions, hydraulic conductivity, and bacteria transport (for filters with and without colloidal silver). The advection–dispersion–reaction equation was used to simulate bacteria transport through the filters and to quantify first-order bacterial decay coefficients for filters treated with colloidal silver.

## Materials and Methods

Ceramic filters for laboratory testing were manufactured from soil, grog (previously fired clay), flour, and water. Three different soil samples were studied: a commercial 200-mesh Redart pottery clay (Resco Products, Inc.) and natural soil samples (with significant clay contents) collected from San Mateo Ixtatán, Guatemala and Ciudad Juarez, Mexico. Soil samples from these two communities were chosen because the communities either already have a ceramic filter factory in operation (San Mateo Ixtatán) or they have a local brick-making community and could likely sustain a locally operated filter factory (Ciudad Juarez). The two natural soil samples were dried, ground in a jar mill for 24 h, and passed through a 60-mesh sieve. A commercial 48-mesh grog (Resco Products, Inc.) was used to prevent shrinkage of the ceramic filters during drying and firing and to improve the flow rate of water through the final filters. Grog is clay that has previously been fired and can be obtained by grinding clay bricks that were damaged and/or discarded after primary manufacturing. Flour was purchased from a local grocery store and was used as received.

The percent silt (2–20  $\mu\text{m}$ ) and clay (<2  $\mu\text{m}$ ) subfractions of each soil sample were quantified using a Micromeritics SediGraph 5100. The samples (2–3 g) were dispersed in 0.05% Calgon solution by shaking for 24 h prior to analysis. The surface area of the soil samples was measured using a multipoint BET method (Gemini 2360, Micromeritics) with  $\text{N}_2$  as the adsorbate. X-ray diffraction analysis was performed to determine the predominant clay mineral in each sample using the procedure developed by Ohtsuba et al. (10). The procedure employs a XDS Scintag 2000 diffractometer using monochromatic  $\text{Cu K}\alpha$  radiation at 40 kV and 40 mA over oriented specimens. The scanning speed was 1.5° (2 $\theta$ )/min.

Tritiated water ( $^3\text{H}$ ]H<sub>2</sub>O) was used as a conservative tracer for solute transport experiments to quantify advection velocities and coefficients of hydrodynamic dispersion for each filter. Tracer concentrations in water were quantified with a Packard 1900CA Liquid Scintillation Analyzer.

A nonpathogenic wild strain of *Escherichia coli* provided by IDEXX laboratories was used for bacteria transport experiments. This organism was selected because of its relatively small size (about 1  $\mu\text{m}$ ) and because it is a specific indicator of fecal contamination in drinking water. Bacteria were grown as described by Vigeant et al. (11). Cells were resuspended in a sterilized phosphate buffer (ionic strength = 0.2 M) to a concentration of  $(7 \pm 2) \times 10^9$  MPN/100 mL. Phosphate buffer solutions were prepared as described by Sherwood et al. (12). The concentration of *E. coli* in water was quantified using the Colilert Defined-Substrate Technology System (IDEXX Laboratories, Inc., Westbrook, Maine) (13).

Stable suspensions of zerovalent silver particles (e.g., colloidal silver) are generated by the aqueous phase reduction of silver nitrate by ascorbic acid (14, 15). In this investigation, a commercial solution of 7–8% colloidal silver from Argenol

Laboratories, Spain was purchased and was used as received. Filter factories established by Potters for Peace commonly use this commercial supplier. Silver concentrations were quantified using an acetylene–air flame atomic adsorption spectrometer (Perkin-Elmer model 5100PC) with a multi-element hollow cathode lamp.

**Ceramic Filter Synthesis and Characterization.** Ceramic filters were manufactured by combining 40% soil, 10% flour, and 50% grog on a weight basis. This combination of materials was selected after testing several ceramic filters prepared with different ratios of clay/flour/grog. Fired ceramic filters with higher percentages of flour were weak and broke easily, while those with a higher clay content presented a relatively low value of hydraulic conductivity and, therefore, an unacceptably low flow rate.

Clay, flour, and grog were combined and mixed until homogeneous. The dry mix (244 g) was combined with 75 mL of deionized water. The mix was separated into four portions and then molded by hand, placed in a 6.5-cm-diameter polyvinylchloride cylindrical mold, and compressed for 1 min at 1000 psi. The resulting cylindrical filters were approximately 1.5-cm thick after compaction. A cylindrical filter design was chosen to simplify the geometry (relative to a pot shape) and thereby facilitate one-dimensional hydraulic conductivity and bacteria transport experiments. The filters were air-dried at room temperature for 3 d 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 3 h.

After firing, the ceramic filters were treated with colloidal silver using two different procedures. The first treatment consisted of applying 6 mL of a 200 mg/L colloidal-silver solution to the surface of each ceramic filter using a brush (9). In the second method, the ceramic filters were submerged for 45 s in an 800-mg/L colloidal-silver solution (16). These silver application methods are currently being used or recommended for use by Potters for Peace. To better compare the effectiveness of the application method, a third 600-mg/L colloidal-silver solution was prepared. Ceramic filters manufactured with Redart clay were submerged in the 600 mg/L colloidal silver solution and the uptake volume of the colloidal silver solution was recorded. Other specimens were painted with the same amount of solution used in the submersion process.

The hydraulic conductivity of the ceramic filters (prior to colloidal-silver application) was measured in triplicate using a changing-head flexible-wall permeameter test according to ASTM method D5084 (17). The ceramic filters were placed in flexible-wall permeameters and back-pressure saturated with 0.005 N  $\text{CaSO}_4$  solution at 5 psi for 24 h. The confining (cell) pressure was 5 psi. Following back-pressure saturation, the pressure at one end of the specimen was decreased to 3.5 psi to initiate fluid flow. Influent and effluent hydraulic heads were measured over time until the calculated hydraulic conductivity was approximately constant over time, the inflow rate was equal to the outflow rate, and at least three pore volumes of flow passed through the ceramic filter.

Porosity and pore-size distribution of 1-g samples of ceramic filters were characterized by low- and high- pressure mercury intrusion (Autopore II, Micromeritics), with intrusion pressures up to 8000 psi.

**Tracer and *E. coli* Transport.** Transport experiments were performed with ceramic filters without colloidal silver and after the two different colloidal-silver treatment procedures. The ceramic filters were placed in flexible-wall permeameters and a three-way stopcock was connected to the inflow valve of the permeameter chamber. A high-performance liquid chromatography (HPLC) pump (Acuflow series IV) and a 1-mL syringe were connected to the three-way stopcock. The

**TABLE 1.** Physical Properties and Bacteria-Transport Model Parameters for Ceramic Filters Fabricated Using Guatemalan, Redart, and Mexican Soils

	Guatemala	Redart	Mexico
hydraulic conductivity (cm/s)	$1.15 \times 10^{-5}$	$5.01 \times 10^{-5}$	$3.26 \times 10^{-5}$
porosity (%)	38.8	41.9	37.4
median pore diameter ( $\mu\text{m}$ )	8.21	2.03	14.3
	tracer transport		
linear velocity, $v$ (cm/min)	0.058	0.050	0.068
coefficient of hydrodynamic dispersion, $D$ ( $\text{cm}^2/\text{min}$ )	0.021	0.005	0.013
	bacteria transport through filters without colloidal silver		
rejection mass, $R_{\text{mass}}$ (dimensionless)	0.9867	0.9997	0.9786
retardation factor, $R$	1.04	0.68	0.79
	bacteria transport through filters with colloidal silver		
first-order decay coefficient for painted filters, $\mu$ ( $\text{min}^{-1}$ )	0.008	0.0008	0.008
first-order decay coefficient for submerged filters, $\mu$ ( $\text{min}^{-1}$ )	0.015	N.C.*	0.017

\* N.C. - Not Calculated (since no bacteria were detected in effluent).

HPLC pump maintained a 0.6-mL/min inflow rate to the chamber corresponding approximately to a whole-filter flow rate of 1.5 L/h (e.g., the average design flow of whole filters). The inflow solution was the phosphate buffer solution described in the bacteria preparation section. The effluent valve of the permeameter chamber was open to the atmosphere and used to collect effluent water samples for analysis of tracer and bacteria. The ceramic filters were saturated with the phosphate buffer solution prior to the transport tests by pumping the solution through the filter for 12 h. If the ceramic filters were treated with colloidal silver, effluent samples were sampled and analyzed to quantify the silver concentration as a function of time during the 12-h saturation period.

After the saturation period, a 1.0-mL syringe was used to inject a 0.6-mL pulse of  $4.3 \mu\text{Ci}$   $^3\text{H}$   $\text{H}_2\text{O}$  into the ceramic filter and effluent samples were collected over time to define the breakthrough of this conservative tracer. Transport of bacteria through each filter was quantified by methods similar to those used for the conservative tracer. A 0.6-mL pulse of  $(7 \pm 2) \times 10^9$  MPN/100 mL *E. coli* was passed through the filter and effluent samples were collected over time to define the breakthrough of the *E. coli*.

**Transport Simulations.** Effluent tracer and bacteria concentrations over time for ceramic filters with and without colloidal-silver treatments were simulated using the following transient one-dimensional form of the advection–dispersion equation with first-order decay:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \mu c$$

subject to the following initial and boundary conditions:

$$\begin{aligned} c(x, 0) &= 0 \\ c(0, t) &= c_0 \quad \text{for } t < t_0 \\ c(0, t) &= 0 \quad \text{for } t > t_0 \\ \frac{\partial c(L, t)}{\partial x} &= 0 \end{aligned}$$

where  $R$  is the retardation coefficient,  $c$  is the concentration of  $^3\text{H}$   $\text{H}_2\text{O}$  (counts per minute per mL) or *E. coli* (mpn/100 mL),  $t$  is time (min),  $t_0$  is the tracer or bacteria pulse injection time,  $D$  is the dispersion coefficient ( $\text{cm}^2 \text{min}^{-1}$ ),  $x$  is distance (cm),  $v$  is the linear velocity ( $\text{cm min}^{-1}$ ),  $\mu$  is the first-order decay coefficient ( $\text{min}^{-1}$ ), and  $L$  is the thickness of the filter. This model assumes local equilibrium sorption. The com-

puter program CXTFIT (18) was used to adjust the relevant model parameters to provide the optimum fit of the model to the experimental data.  $D$  and  $v$  for each column were determined from the  $^3\text{H}$   $\text{H}_2\text{O}$  transport experiments (with  $R = 1$  and  $\mu = 0$ ).  $R$  and  $\mu$  were determined from the *E. coli* transport experiments. For bacteria transport experiments through ceramic filters untreated with colloidal silver,  $\mu$  was assumed to equal zero.

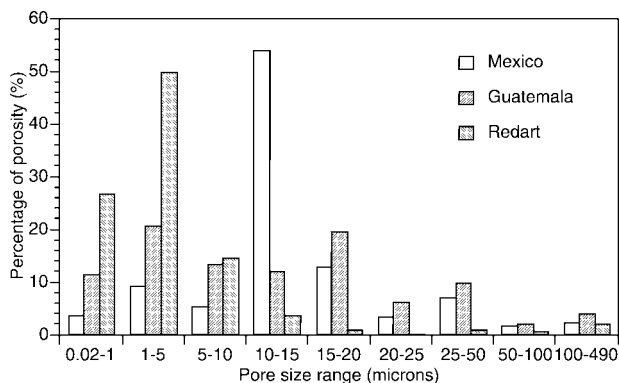
## Results

**Soil and Filter Characteristics.** The three soil samples tested had very different physical and mineralogic characteristics (Table S2-S2 in the Supporting Information). The particle-size distribution of the raw materials shows that the Redart soil had a higher clay content (particles  $< 2 \mu\text{m}$ ) than the soils from Guatemala and Mexico. The median grain sizes ( $d_{50}$ ) for Redart, Guatemala, and Mexico soils were 6.3, 12.3, and  $44.7 \mu\text{m}$ , respectively. The values of the uniformity coefficient ( $d_{60}/d_{10}$ ) were 5.1, 7.1, and 28.4 for Redart, Guatemala, and Mexico soils, respectively. The Redart clay also had the highest specific surface area of the three sample specimens.

The results of the XRD analysis are also summarized in Table S2-S2. Illite and kaolinite are the predominant clay minerals in the Redart soil, whereas illite is the predominant clay mineral for the Guatemalan soil. It was not possible to detect a predominant clay mineral for the Mexican soil; the absence of peaks in a XRD reflection can imply the presence of an amorphous material or a mixed-layer clay mineral base material. A quartz peak was detected in all three samples tested.

The hydraulic conductivities of the ceramic filters ranged from  $1.15 \times 10^{-5}$  cm/s (Guatemalan filter) to  $5.01 \times 10^{-5}$  cm/s (Redart filter) (Table 1). If we assume a whole filter constructed with these materials and a hydraulic head equal to half the height of the filter pot, resulting calculated flow rates are 0.5 (Guatemala), 1.3 (Mexico), and 2.1 L/hr (Redart). These values are close to the design flow rate of 1–2 L/hr specified by Potters for Peace. The porosities of the three filters were similar. However, the median pore size for each filter was distinctly different (Table 1). Figure 1 shows the pore-size distribution for the three ceramic filters.

**Tracer and Bacteria Transport Experiments.** Figure S4-S4 (Supporting Information) presents the results of tracer-transport experiments for the three filters (without silver impregnation) made from each soil type. Simulated concentrations of  $^3\text{H}$   $\text{H}_2\text{O}$  agree well with experimentally



**FIGURE 1.** Pore-size distribution for ceramic filters fabricated using Redart, Guatemalan, and Mexican soils.

observed effluent concentration data. The  $[^3\text{H}]\text{H}_2\text{O}$  was a conservative tracer in all ceramic filters; greater than 95% of all influent  $[^3\text{H}]\text{H}_2\text{O}$  was recovered during effluent sample collection for each test. Table 1 shows the fitted values of the linear velocity and dispersion coefficient for the three ceramic filters based on analysis of the tracer experiments.

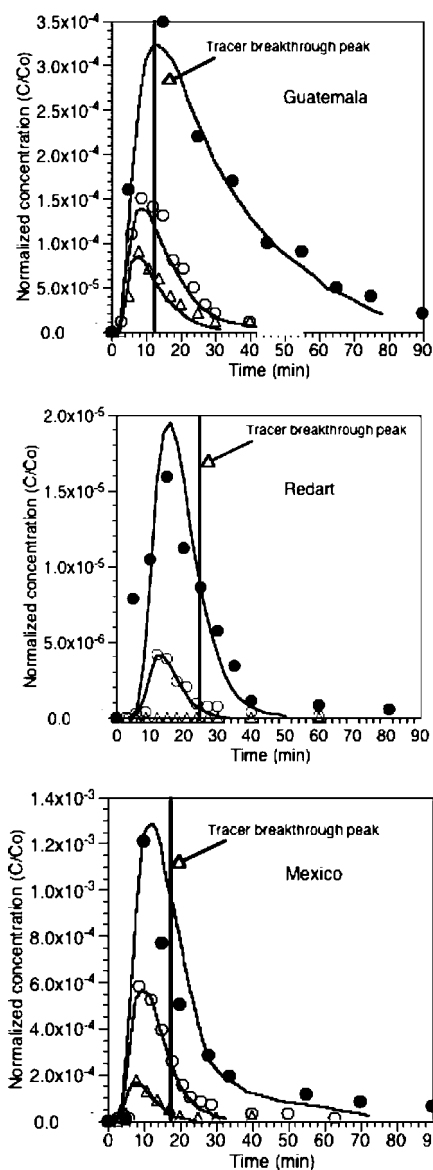
Figure 2 presents the results of the bacteria-transport experiments for each filter type. A global measure of rejection ( $R_{\text{mass}}$ ) was calculated for each filter without colloidal silver treatment.  $R_{\text{mass}}$  is based on the fractional mass of bacteria injected that did not pass through the ceramic filter (Table 1).  $R_{\text{mass}}$  is commonly used to compare removal efficiencies for microfiltration and ultrafiltration membranes (19). In all cases,  $R_{\text{mass}}$  values are greater than 0.97 (2.6 log reduction).

As evidenced by the data in Figure 2 and the  $R_{\text{mass}}$  values in Table 1, the application of colloidal silver to the filter reduces bacteria transport, regardless of the application method used. However, the ceramic filters submerged in the colloidal-silver solution showed a higher level of bacteria removal than those painted with the colloidal-silver solution. For experiments with the Redart filter submerged in the colloidal-silver solution, no effluent bacteria were quantified at any time (e.g.,  $R_{\text{mass}} = 1.0$ ).

Figure 2 also shows the results of model simulations of the bacteria-transport experiments. For these simulations, the mass of *E. coli* that did not pass through the ceramic filters was subtracted from the injected mass. The linear velocity and dispersion coefficients determined from the tracer experiments were used as fixed parameters. For transport experiments on filters without colloidal silver, the retardation factor was the only fitting parameter. For bacteria-transport experiments on filters with colloidal silver, the retardation factor from experiments with untreated filters was also used as a fixed parameter and the first-order bacterial decay coefficient ( $\mu$ ) was the only fitting parameter. The retardation factors and decay coefficients for these simulations are shown in Table 1.

Simulated concentrations of bacteria agree well with the observed experimental effluent concentration data. The values of  $\mu$  for painted ceramic filters are lower than those obtained for submerged ceramic filters. For the Redart filter submerged in the colloidal-silver solution, it was not possible to quantify  $\mu$  because no effluent bacteria were detected. Figure 2 shows that the appearance of the peak effluent bacteria concentration from the Redart and Mexican ceramic filters consistently preceded the appearance of the concentration peak for  $[^3\text{H}]\text{H}_2\text{O}$ . For the Guatemalan filter, the peak effluent concentrations for the tracer and bacteria occur at about the same time.

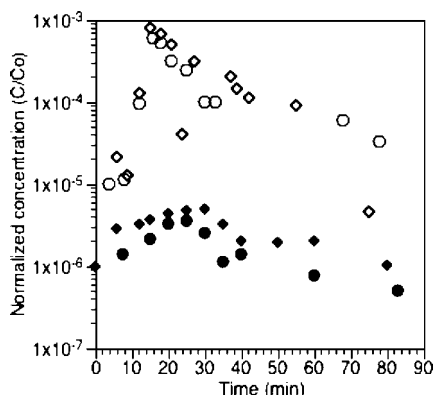
The concentration of colloidal silver in each ceramic filter for each application method is presented in Table S3-S3. Figure S5-S5 shows the effluent aqueous silver concentrations from the painted filters as a function of time during the



**FIGURE 2.** Effluent *E. coli* concentrations normalized to the influent pulse concentration as a function of time for ceramic filters fabricated with Redart, Guatemalan, and Mexican soils without colloidal silver (●), painted with colloidal silver (○), and submerged in colloidal silver (△). Lines represent optimized solute-transport model fits. Black vertical lines represents the tracer breakthrough peak for each experiment.

saturation period; similar profiles were obtained for filters submerged in the colloidal-silver solutions. The amount of colloidal silver removed from the ceramic filters was between 20 and 22%. The mass of colloidal silver remaining in each ceramic filter was calculated by subtracting the mass of colloidal silver collected in the effluent from the initial concentration of colloidal silver in the ceramic filter.

To compare the relative effects of the two colloidal-silver application methods (e.g., painting and submerging), additional bacteria transport experiments were carried out using filters fabricated from the Redart soil. Afterward, one filter was submerged in a 600 mg/L colloidal-silver solution. The volume of solution taken up by this filter was 15 mL. Then, the second filter was painted with 15 mL of a 600 mg/L colloidal-silver solution. After the saturation period, a bacteria transport test was performed on both filters using the same testing conditions used in previous experiments. Figure 3 shows the bacteria concentration in the effluent as a function



**FIGURE 3.** Effluent *E. coli* concentrations normalized to the influent pulse concentration as a function of time for ceramic filters fabricated with Redart soils without colloidal silver ( $\diamond$  and  $\circ$ ), and painted with ( $\blacklozenge$ ) and submerged in a 600-mg/L colloidal silver solution ( $\bullet$ )

of time for both filters. The results are presented using a logarithmic scale due to the low concentration of bacteria obtained in the effluent after the colloidal-silver treatments. Both application methods showed at least a five order-of-magnitude reduction in bacteria concentrations compared to the three order-of-magnitude reduction observed for earlier colloidal-silver applications.

## Discussion

The experiments and analyses performed herein show that colloidal-silver-impregnated ceramic filters constructed from relatively heterogeneous, natural materials can effectively reduce the concentration of *E. coli* in water. Even without application of colloidal silver and using a relatively heterogeneous soil to manufacture the filter, the filters were able to remove between 97.86% and 99.97% of the total amount of *E. coli* in the influent water (Table 1). Treatment of the filters with colloidal silver further improved their performance. For the case of the Redart filter submerged in the colloidal silver solution, no effluent bacteria were detected (e.g., 100% removal).

Filter performance is also affected by the characteristics of the natural soil used in the manufacturing process. In this work, filter performance (with regard to flow rate and bacteria removal rate) increased in the order Mexico  $\approx$  Guatemala > Redart. This also corresponds approximately to increasing clay content and specific surface area for each soil type. Additionally, the same approximate trend was observed for the pore-size distribution of the filters and the coefficient of hydrodynamic dispersion. Soil samples with relatively uniform and fine-grained particle-size distributions will likely produce filters with better bacteria-removal efficiency, smaller pores, and lower dispersion than comparatively coarse-grained, heterogeneous soils. In our experiments, this is supported by data for the two ceramic filters with the highest and lowest performance. The Redart soil, with a  $d_{50}$  of 6.3  $\mu\text{m}$  and a uniformity coefficient of 5.1, had 75% of its pores with diameters smaller than 5  $\mu\text{m}$  and had a  $R_{\text{mass}}$  of 0.997, while the Mexico soil, with a  $d_{50}$  of 44.7  $\mu\text{m}$  and a uniformity coefficient of 28.4, only had 12% of its pores with diameters less than 5  $\mu\text{m}$  and had a  $R_{\text{mass}}$  of only 0.979. Soil samples with high clay contents also typically have a high plasticity, which may facilitate the manufacturing process of the filters (20).

The predominant clay mineral in the soil may also influence filter performance. At firing temperatures below 1000  $^{\circ}\text{C}$ , a smaller amount of amorphous material is produced from kaolinite relative to illite (21, 22). Amorphous material developed at this temperature has a lower porosity than

crystalline material. This may partially explain the higher hydraulic conductivity and porosity observed for the Redart clay, which contains a significant amount of kaolinite as determined by X-ray diffraction analysis.

Results of the solute- and bacteria-transport experiments provide improved understanding of the relative affects of filtration and colloidal-silver disinfection on bacteria removal by the ceramic filters. Bacteria transport data for the three filters prior to application of colloidal silver support the hypothesis that steric rejection or size exclusion chromatography is a significant mechanism of bacteria removal in the ceramic filters. Filters with smaller pores caused higher rejection of bacteria (Table 1 and Figure 1). It is also possible that bacteria removal is caused by bacterial sorption to the ceramic porous medium. However, if reversible sorption occurs, effluent bacteria-concentration peaks should appear after the effluent tracer peaks and bacteria retardation factors would necessarily be greater than unity. Our results show the peaks of bacteria breakthrough appeared before or coincident with the tracer peaks, and the bacteria retardation factors were less than or equal to one. Similar results have been observed for bacteria transport through natural soils (23–25). Although each filter has a significant percentage of pores with diameters greater than 1  $\mu\text{m}$  (the size of an *E. coli* bacterium), it is unlikely that many of these pores extend through the entire thickness of the filter. Therefore, most bacteria or clusters of bacteria likely encounter a pore opening that they cannot pass through and are removed from the flow field. The small fraction of bacteria that exit the filter are transported along the largest pore channels. These pore channels likely have water velocities greater than the average (linear) water velocity determined from the tracer experiments. Therefore, it is not unreasonable that bacteria peak concentrations occur at times less than tracer peak concentrations for a given filter. It is also possible that *irreversible* sorption partially contributes to bacteria removal.

Colloidal silver treatments significantly improved the quality of the ceramic filter effluent, and the experiments performed herein are the first to specifically identify the beneficial affects of colloidal silver (independent of physical filtration or sorption) for a ceramic water filter. Sondi and Salopek-Sondi (15) showed that silver nanoparticles were an effective bactericide against *E. coli*. Other recent studies have investigated the bactericidal properties of silver supported by polyurethane foam (26), a zeolite (27), alumina (28), and activated carbon (29, 30). Each of these studies demonstrated a beneficial bactericidal effect although none of the studies specifically elucidated the mechanism. Heinig (28) observed that as the dissolved oxygen concentration in influent water was increased, the bactericidal properties of silver-treated alumina increased. They suggested that the silver had a catalytic effect that promoted the oxidation of bacteria and viruses. More recently, Schmidt et al. (31) studied the interaction of oxygen and silver clusters. At temperatures between 77 and 105 K, molecular oxygen chemisorbed to the silver particles. At temperatures greater than 105 K, chemisorption transformed into oxidation, invoking the dissociation of the oxygen molecule and the release of a highly reactive oxygen atom (with a  $-2$  oxidation state). These studies suggest that oxygen is required for deactivation, and that other natural organic matter may compete with bacteria for oxidation. Further research on the disinfection mechanism of colloidal silver is needed to better understand this process and its potential limitations.

The disinfection efficiency of the colloidal-silver treatments appears to depend primarily on the mass of colloidal silver that remains in the filter after the saturation period rather than the method of application (e.g., painting versus submerging). The first-order bacteria decay coefficients for filters submerged in the 800 mg/L colloidal-silver solution

are double ( $0.016 \text{ min}^{-1}$ ) the value of decay coefficients for filters painted with the 200 mg/L colloidal-silver solution ( $0.008 \text{ min}^{-1}$ ) (Table 1). However, when these decay coefficients are normalized by the colloidal silver mass on the filters (1.2 mg for painted and 12 mg for submerged filters) the results are reversed. The specific first-order decay coefficient obtained for painted filters was five times higher ( $0.0067 \text{ min}^{-1} \text{ g}^{-1}$ ) compared to those filters submerged in colloidal silver solution ( $0.0012 \text{ min}^{-1} \text{ g}^{-1}$ ). It is possible that the disinfectant capacity of the colloidal silver increases up to some threshold concentration, above which no additional increase in disinfection can be obtained. When similar Redart filters were painted and submerged in the same colloidal-silver solution, similar levels of bacteria removal were achieved (Figure 3).

It is possible that treatment of the ceramic filters by colloidal-silver suspensions improves bacterial removal efficiency by physically clogging pores that could be used by bacteria for transport. However, tracer transport experiments conducted on select filters before and after colloidal silver application did not show any significant differences (data not shown). Furthermore, the model formulation used to simulate *E. coli* breakthrough employs a standard, first-order decay coefficient as the only fitting parameter. This model was able to effectively simulate the observed experimental data (Figure 2). These observations, coupled with the established disinfectant properties of colloidal silver, indicate that colloidal silver treatments improve filter performance by a disinfection mechanism.

Release of colloidal silver from the filters will likely depend on water chemistry (32), the amount of colloidal silver applied, and the pore structure of the filters. The regulatory limit for silver in drinking water is 0.1 mg/L, and this level was not exceeded for any of the filters tested after passing water through the filter for about 200 min (Figure S5-S5).

Future studies need to extend the experiments and analyses presented here to quantify removal rates of other pathogens, including viruses and protozoa, for different water-quality conditions. In addition, the long-term field performance of locally produced filters and their effects on human health must be quantified.

## Acknowledgments

This research was partially supported by a grant from the Environmental Sustainability Program of the National Science Foundation (CBET 651996). We thank Ron Rivera, Sophie Johnson, Dara Philips, and Maria Takahashi for technical assistance.

## Supporting Information Available

Table S2-S2 shows the particle size, specific surface area, and predominant clay mineral for Guatemalan, Redart, and Mexican soils used to fabricate ceramic filters; Table S3-S3 shows the colloidal silver masses applied to and retained by ceramic filters manufactured using each of three types of soil samples; Figure S4-S4 shows the effluent [ $^3\text{H}$ ]H<sub>2</sub>O concentrations normalized to the influent pulse concentration as a function of time for ceramic filters, without silver impregnation, fabricated with Redart, Guatemalan, and Mexican soils; Figure S5-S5 shows the silver concentrations in effluent water from painted ceramic filters as a function of time. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## Literature Cited

- (1) Quick, R. E.; Kimura, A.; Thevos, A.; Tembo, M.; Shamputa, I.; Hutwagner, L.; Mintz, E. Diarrhea prevention through household-level water disinfection and safe storage in Zambia. *Am. J. Trop. Med. Hyg.* **2002**, *66* (5), 584–589.

- (2) Mintz, E. D.; Reiff, F. M.; Tauxe, R. V. Safe water treatment and storage in the home. *J. Am. Med. Assoc.* **1995**, *273* (12), 948–953.
- (3) Luby, S.; Agboatwalla, M.; Raza, A.; Sobel, J.; Mintz, E.; Baier, K.; Rahbar, M.; Qureshi, S.; Hassan, R.; Ghouri, F.; Hoekstra, R. M.; Gangarosa, E. A low-cost intervention for cleaner drinking water in Karachi, Pakistan. *Int. J. Infect. Dis.* **2001**, *5* (3), 144–150.
- (4) Esrey, S. A.; Potash, J. B.; Roberts, L.; Shiff, C. Effects of improved water-supply and sanitation on ascariasis, diarrhea, dracunculiasis, hookworm infection, schistosomiasis, and trachoma. *Bull. WHO* **1991**, *69* (5), 609–621.
- (5) Clasen, T. F.; Brown, J.; Collin, S.; Suntura, O.; Cairncross, S. Reducing diarrhea through the use of household-based ceramic water filters: A randomized, controlled trial in rural Bolivia. *Am. J. Trop. Med. Hyg.* **2004**, *70* (6), 651–657.
- (6) Sobsey, M. D. *Managing water in the home: Accelerated health gains from improved water supply*; World Health Organization, 2002; [http://www.who.int/water\\_sanitation\\_health/dwq/wsh0207/en/](http://www.who.int/water_sanitation_health/dwq/wsh0207/en/).
- (7) Chaudhuri, M.; Verma, S. R.; Gupta, A. Performance evaluation of ceramic filter candles. *J. Environ. Eng.* **1994**, *120* (6), 1646–1651.
- (8) Kulkarni, D. N.; Tajne, D. S.; Parhad, N. M. Performance of domestic water filters. *Indian J. Environ. Health* **1980**, *22* (1), 30–41.
- (9) Lantagne, D. S. *Investigation of the Potters for Peace colloidal silver impregnated ceramic filter*; USAID; 2001; p79.
- (10) Ohtsubo, M.; Egashira, K.; Tanaka, H.; Mishima, O. Clay minerals and geotechnical index properties of marine clays in East Asia. *Mar. Geores. Geotechnol.* **2002**, *20*, 223–235.
- (11) Vigeant, M. A.; Ford, R. M.; Wagner, M.; Tamm, L. K. Reversible and irreversible adhesion of motile *Escherichia coli* cells analyzed by total internal reflection aqueous fluorescence microscopy. *Appl. Environ. Microbiol.* **2002**, *68* (8), 2794–2801.
- (12) Sherwood, J. L.; Sung, J. C.; Ford, R. M.; Fernandez, E. J.; Maneval, J. E.; Smith, J. A. Analysis of bacterial random motility in a porous medium using magnetic resonance imaging and immunomagnetic labeling. *Environ. Sci. Technol.* **2003**, *37* (4), 781–785.
- (13) George, I.; Petit, M.; Servais, P. Use of enzymatic methods for rapid enumeration of coliforms in freshwaters. *J. Appl. Microbiol.* **2000**, *88*, 404–413.
- (14) SonDI, I.; Goia, D. V.; Matijevic, E. Preparation of highly concentrated stable dispersions of uniform silver nanoparticles. *J. Colloid Interface Sci.* **2003**, *260*, 75–81.
- (15) SonDI, I.; Salopek-SonDI, B. Silver nanoparticles as antimicrobial agent: A study on *E. coli* as a model for gram-negative bacteria. *J. Colloid Interface Sci.* **2004**, *275*, 177–182.
- (16) Holtslag, H. Colloidal silver application (personal communication), 2006.
- (17) Bartelt-Hunt, S. L.; Burns, S. E.; Smith, J. A. Nonionic organic solute sorption to two organobentonites as a function of organic-carbon content. *J. Colloid Interface Sci.* **2003**, *266*, 251–258.
- (18) Toride, N.; Leij, F. J.; Genuchten, M. T. V. The CXTFIT code for estimating transport parameters from laboratory or field tracer experiments, Version 2.0; Research Report 137; U.S. Salinity Laboratory, USDA: Riverside, CA, 1995.
- (19) Wiesner, M. R.; Buckley, C. A. Principles of Rejection in Pressure-Driven Membrane Processes. In *Water Treatment: Membrane Process*; McGraw-Hill: New York, 1996.
- (20) Souza, G. P.; Souza, S. J. G.; Terrones, L. A. H.; Holanda, J. N. F. Mineralogical analysis of Brazilian ceramic sedimentary clay used in red ceramic. *Ceramica* **2005**, *51*, 381–386.
- (21) Murad, E.; Wagner, U. Clay and clay minerals: the firing process. *Hyperfine Interact.* **1988**, *117*, 337–356.
- (22) McConville, C. J.; Lee, W. E. Microstructural development on firing illite and smectite clays compared with that in kaolinite. *J. Am. Ceram. Soc.* **2005**, *88* (8), 2267–2276.
- (23) Kretzschmar, R.; Barmettler, K.; Grolimund, D.; Yan, Y.; Borkovec, M.; Sticher, H. Experimental determination of colloid rates and collision efficiencies in natural porous media. *Water Resour. Res.* **1997**, *33* (5), 1129–1137.
- (24) Jewett, D. G.; Hilbert, T. A.; Logan, B. E.; Arnold, R. G.; Bales, R. C. Bacterial transport in laboratory column and filters: influence of ionic strength and pH on collision efficiency. *Water Res.* **1995**, *29* (7), 1673–1680.
- (25) Fontes, D. E.; Mills, A. L.; Hornberger, G. M.; Herman, J. S. Physical and chemical factors influencing transport of microorganism through porous media. *Appl. Environ. Microbiol.* **1991**, *57* (9), 2473–2481.
- (26) Jain, P.; Pradeep, T. Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. *Biotechnol. Bioeng.* **2005**, *90* (1), 59–63.

- (27) Rivera-Garza, M.; Olguin, M. T.; Garcia-Sosa, I.; Alcantara, D.; Rodriguez-Fuentes, G. Silver supported on natural Mexican zeolite as an antibacterial material. *Microporous Mesoporous Mater.* **2000**, *39*, 431–444.
- (28) Heinig, C. F. O<sub>3</sub> or O<sub>2</sub> and Ag: A new catalyst technology for aqueous phase sanitation. *Ozone Sci. Eng.* **1993**, *15*, 533–546.
- (29) LePape, H.; Solano-Serena, F.; Contini, P.; Devillers, C.; Maftah, A.; Leprat, P. Evaluation of the anti-microbial properties of an activated carbon fibre supporting silver using a dynamic method. *Carbon* **2002**, *40*, 2947–2954.
- (30) LePape, H.; Solano-Serena, F.; Contini, P.; Devillers, C.; Maftah, A.; Leprat, P. Involvement of reactive oxygen species in the bactericidal activity of activated carbon fibre supporting silver: Bactericidal activity of ACF(Ag) mediated by ROS. *J. Inorg. Biochem.* **2004**, *98*, 1054–1060.
- (31) Schmidt, M.; Masson, A.; Brechignac, C. Oxygen and silver clusters: Transition from chemisorption to oxidation. *Phys. Rev. Lett.* **2003**, *91* (24), 3401–3405.
- (32) Lui, A.; Gonzales, R. D. Adsorption/Desorption in a System Consisting of Humic Acid, Heavy Metals, and Clay Minerals. *J. Colloid Interface Sci.* **1999**, *218* (1), 225–232.

ES071268U