

Research Article

A New Method for the Deposition of Metallic Silver on Porous Ceramic Water Filters

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Received 8 November 2017; Revised 17 December 2017; Accepted 15 January 2018; Published 1 March 2018

Academic Editor: Farid A. Harraz

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A new method of silver application to a porous ceramic water filter used for point-of-use water treatment is developed. We evaluated filter performance for filters manufactured by the conventional method of painting an aqueous suspension of silver nanoparticles onto the filter and filters manufactured with a new method that applies silver nitrate to the clay-water-sawdust mixture prior to pressing and firing the filter. Filters were evaluated using miscible displacement flow-through experiments with pulse and continuous-feed injections of *E. coli*. Flow characteristics were quantified by tracer experiments using [³H]H₂O. Experiments using pulse injections of *E. coli* showed similar performance in breakthrough curves between the two application methods. Long-term challenge tests performed with a continuous feed of *E. coli* and growth medium resulted in similar log removal rates, but the removal rate by nanosilver filters decreased over time. Silver nitrate filters provided consistent removal with lower silver levels in the effluent and effective bacterial disinfection. Results from continued use with synthetic groundwater over 4 weeks, with a pulse injection of *E. coli* at 2 and 4 weeks, support similar conclusions—nanosilver filters perform better initially, but after 4 weeks of use, nanosilver filters suffer larger decreases in performance. Results show that including silver nitrate in the mixing step may effectively reduce costs, improve silver retention in the filter, increase effective lifespan, and maintain effective pathogen removal while also eliminating the risk of exposure to inhalation of silver nanoparticles by workers in developing-world filter production facilities.

1. Introduction

The World Health Organization (WHO) estimates that over 4 million deaths per year, of which more than 1.5 million involve children under the age of 5, are attributable to unsafe drinking water [1]. Centralized water treatment facilities, like those found in cities and suburban areas in the developed world, are not feasible for many developing communities due to the large infrastructure investment. Alternatively, the WHO has suggested a decentralized approach of treatment in home immediately prior to consumption—commonly referred to as point-of-use (POU) water treatment [2, 3]. POU technologies have the potential to significantly improve microbial quality of drinking water and reduce the risk of diarrheal disease and death, particularly in children [4]. A POU technology must be effective with respect to removal and/or deactivation of waterborne pathogens under a wide

range of water chemistries and must be simple to use to ensure long-term effectiveness and reduce risk of recontamination [3, 5]. The technology must also be socially acceptable and affordable, commonly achieved by the use of local labor and materials [6–8]. Ceramic water filters, produced with local labor and materials, are an appealing POU water treatment technology, and over 50 production facilities exist worldwide [9]. Clay, sawdust, and water are mixed and then molded into a pot shape. The filter is then fired in a kiln, causing the clay to sinter into a ceramic and sawdust to combust. This creates pore channels that allow water flow. After quality testing, the filter is painted with a silver nanoparticle solution, where the silver acts as a well-studied antimicrobial agent without changing the taste, color, or odor of treated water [10–14]. The ceramic filter is suspended inside a plastic bucket with a spigot on the bottom for personal use. Source water is poured into the

ceramic filter, then the water percolates through to the lower reservoir, and clean water is dispensed through the spigot. The relatively small pore size (mean around $10\ \mu\text{m}$) of the ceramic filter helps remove turbidity and larger particles [15]. The silver release rate has generally been reported to produce silver concentrations below the secondary drinking-water standard of $0.1\ \text{mg/L}$ set by the USEPA [16] and the World Health Organization [17]. The “nano” size of the silver particles results in a high surface area to volume ratio, leading to better bactericidal activity [18]. However, silver nanoparticles have poor retention in ceramic, shortening the effective lifespan of the filter and possibly causing silver levels in the effluent water above drinking-water standards [19]. Mixing silver nanoparticles into the clay mixture prior to firing has been shown to result in higher retention of silver in the ceramic and a potentially longer lifespan than filters made with the silver nanoparticle method—which release silver at high levels quickly during early use [19]. This method has not been tested for bacterial disinfection nor has it been field tested, but it could be a promising alternative, despite the fact that it still relies on silver nanoparticles as a raw material. The method of silver application does not appear to be a factor affecting disinfection efficiency [15, 20]. Instead, the mass of colloidal silver in the ceramic determines effectiveness.

Ehdaie et al. [21] reported on the formation of silver nanopatches in a ceramic porous tablet. In this work, they mixed silver nitrate, a Redart clay, sawdust, and water together in different proportions. The mixture was pressed into the shape of a disk of varying thickness and diameter and fired in a kiln at a final temperature of 900°C . Characterization of the resulting silver-ceramic tablet revealed patches of silver throughout the pore structure with mean diameters in the range of 2–3 nm.

Herein, we evaluated an alternative silver application method to ceramic water filters that adds silver nitrate to the clay-water-sawdust mix, similar to the methodology described by Ehdaie et al. [21] for ceramic tablets and building on results from Nunnelley et al. [22]. During firing, we hypothesize the formation of silver nanopatches in the porous medium. Compared to silver nanoparticles, silver nitrate is less expensive, more accessible in developing regions of the world, and easier to apply to ceramic water filters. We hypothesize that our new application method will keep more silver in the filter compared to conventional methods. This may increase the effective performance lifespan of the filter and result in less ingestion of silver by the end users. We evaluate this method with a series of miscible flow experiments using $[^3\text{H}]\text{H}_2\text{O}$ as a conservative tracer and a nonpathogenic strain of *E. coli* as an indicator organism targeted for removal. Different formulations of the silver nitrate method are compared against the conventional silver nanoparticle application method.

2. Materials and Methods

2.1. Materials. For ceramic filters, 200-mesh Redart clay produced by Cedar Heights Clay Company and sawdust sieved to 20-mesh from a commercial lumberyard in Earlsville, Virginia (USA), were used. The clay has a particle-size

distribution (PSD) of 30.7%, 54.9%, and 14.4% for particles <2 , 2 – 20 , and $>20\ \mu\text{m}$, respectively [15]. For the silver nanoparticle method of production, silver proteinate (7–8% Ag by weight) from Argenol Laboratories was used.

For the silver nitrate method, 99.5% pure silver nitrate from Acros Organics was used for the ceramic filter disk fabrication. For bacterial tests, a nonpathogenic strain of *E. coli* was purchased from IDEXX Laboratories (cat. 982900700, Lot 042313) and cultured, used, and stored in the same method outlined in Ehdaie et al. [21]. A 10 mM phosphate buffer solution (PB) composed of 11.2 g/L of dipotassium phosphate, 4.8 g/L of potassium phosphate monobasic, 0.02 g/L of netetraacetic acid, and deionized, organic-free water was used to preserve viability of *E. coli* in solution while preventing growth. A 60 g/L solution of sodium thiosulfate, prepared by dissolving anhydrous sodium thiosulfate (Fisher Scientific) in deionized water, was used to treat samples at the collection time to inhibit continued disinfection during incubation. All materials and solutions used for microbial analyses were sterilized before use. $4.3\ \mu\text{Ci}\ [^3\text{H}]\text{H}_2\text{O}$ was used for conservative tracer tests.

2.2. Ceramic Filter Synthesis. Two types of filters were studied in this investigation, and they will be referred to as the following throughout the manuscript: (i) silver nanoparticle filters and (ii) silver nitrate filters. Silver nanoparticle filters use a conventional synthesis method similar to that described by Oyandedel-Craver and Smith [15]. Because of the results in Oyandedel-Craver and Smith [15] show that silver nanoparticles improve performance of ceramic water filters and that current production methods utilize silver nanoparticles, only filters with nanosilver were compared. 168.75 g of Redart clay and 18.75 g of sawdust (total mass of 187.5 g) were mixed by hand. Then 57 mL of deionized, organic-free water was added and thoroughly mixed by hand. This mix was then separated by hand into three portions of equal weight, placed in a 6.5 cm-diameter PVC mold, and compressed at 1000 psi for 1 minute. The resulting filter was an approximately 1 cm thick disk, providing a one-dimensional simplified geometry for lab testing (Figure 1). After air-drying for 48 hr, the ceramic filters were fired in a kiln with the following temperature program: increase temperature from 20°C at 150°C/h to 600°C , then increase at 300°C/h to 900°C , then isothermal for 3 h.

In order to produce the silver nanoparticle filter, a 496 mg/L silver nanoparticle suspension in deionized water was used. Silver amounts applied to the ceramic filter were chosen to be proportional to silver used in a full-size filter containing 0.3 g of silver. This ratio and silver amounts were chosen because of their current use at the PureMadi Mukondeni Production Facility in Mukondeni, Limpopo Province, South Africa. 10 mL of this solution was painted with a brush on both sides and the edges of the filter [23]. This impregnates 4.96 mg of Ag per filter.

For the silver nitrate filters, the same dry mix described above was combined with either 117 mg AgNO_3 (5x filters) or 234 mg AgNO_3 (10x filters) dissolved in 57 mL deionized water. These higher levels of silver were chosen since silver nitrate is much less expensive, and the removal of the painting



FIGURE 1: Ceramic filter disks used for laboratory testing.

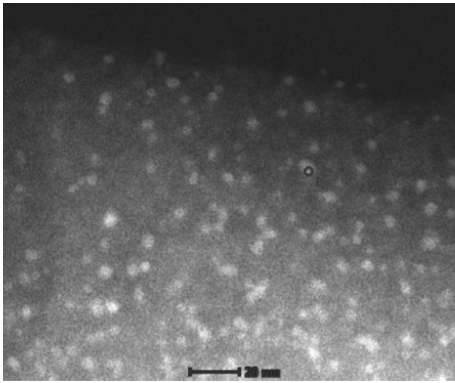


FIGURE 2: Transmission electron microscopy image of silver nanopatches in the center of a ceramic tablet using scanning electron microscopy mode. The scale bar represents 20 nm in length [21].

step saves labor costs, also, due to concern that some silver nitrate would end up in dead-end pore channels, having no contact with water as it filters through. The silver nitrate filters were then pressed into the shape of a cylinder, air-dried, and fired as described above for the silver nanoparticle filters.

After firing, silver nitrate filters do not require any additional fabrication steps, as the silver forms metallic silver nanopatches like those seen in the TEM micrograph in Figure 2.

The porosity of each filter was measured gravimetrically by weighing a dry filter, saturating in deaired, deionized water for 24 h and then reweighing. The difference in mass equates to the volume of water inside the filter. The porosity is then calculated as the volume of water divided by the volume of the filter.

2.3. Miscible Displacement Transport Experiments with *E. coli*. The cylindrical ceramic filters were loaded into a flexible-wall permeameter, holding a 10 psi pressure on the cell to ensure flow through the filter, rather than around. A high-performance liquid chromatography (HPLC) pump (Acuflo series IV), a 1.0 mL syringe, and the inflow valve of the permeameter chamber were connected with a three-way stopcock. The HPLC pump maintained a constant flow rate of 0.6 mL/min to mimic the average flow of pot filters (1.5 L/h). For initial bacterial pulse testing, 10 mM phosphate buffer solution was used as the inflow solution. The effluent valve of the permeameter chamber was open to the atmosphere for

collection of effluent water samples. Filters were saturated by pumping inflow solution through the filter for 24 hours prior to the experiment. During the saturation period, effluent water samples were collected for silver analysis.

After the saturation period, a 1.0 mL syringe was used for a pulse injection of approximately 10^{10} MPN/100 mL *E. coli*. Effluent samples were collected and analyzed over time to define the breakthrough of the *E. coli*. Viable *E. coli* were quantified in each sample using the Colilert Defined-Substrate Technology System, a method approved by the U.S. EPA and recommended by the WHO for microbiological testing [24–26]. Colilert media (cat. WP200I) was added to 100 mL of sample and mixed thoroughly, before being poured into IDEXX Quanti-trays (cat. WQT-2K) and incubated for 24 hours at 37°C. A fluorescent UV lamp was used to count the number of fluorescing wells in the tray and correlated to *E. coli* concentrations using a most-probable-number table provided by the manufacturer. Samples were taken over time to measure nitrate in the effluent with Hach TNT835 Kit and the DR 3900 bench top spectrophotometer. Total silver was tested with a graphite furnace atomic adsorption spectrometer (PerkinElmer HGA 900). Upon collection, bacteria samples were treated with a 60 g/L solution of sodium thiosulfate, prepared by dissolving anhydrous sodium thiosulfate (Fisher Scientific) in deionized water, to deactivate silver from continuing to disinfect during sample incubation. Silver methods were tested in triplicates.

2.4. Long-Term Performance Evaluation with Constant Exposure. To evaluate the performance of each filter type over an extended period of time, silver-ceramic filters were again loaded in to a flexible-wall permeameter with a 10 psi cell pressure. The saturation period was performed as described above, with one HPLC pump providing a constant feed of 10 mM phosphate buffer solution for 24 hr. After 24 hr of saturation, hydraulic conductivity was measured using a falling head analysis. Then, as in Oyanedel-Craver and Smith [15], 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 disk. Effluent samples were collected over time and measured by a liquid scintillation counter to define a conservative tracer breakthrough curve. Effluent tracer concentrations were simulated using a transient one-dimensional form of the advection-dispersion equation with first-order decay:

$$R \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \mu c. \quad (1)$$

Subject to the following initial and boundary conditions:

$$\begin{aligned} c(x, 0) &= 0, \\ c(0, t) &= c_0 \quad \text{for } t < t_0, \\ c(0, t) &= 0 \quad \text{for } t > t_0, \\ \frac{\partial c(L, t)}{\partial x} &= 0. \end{aligned} \quad (2)$$

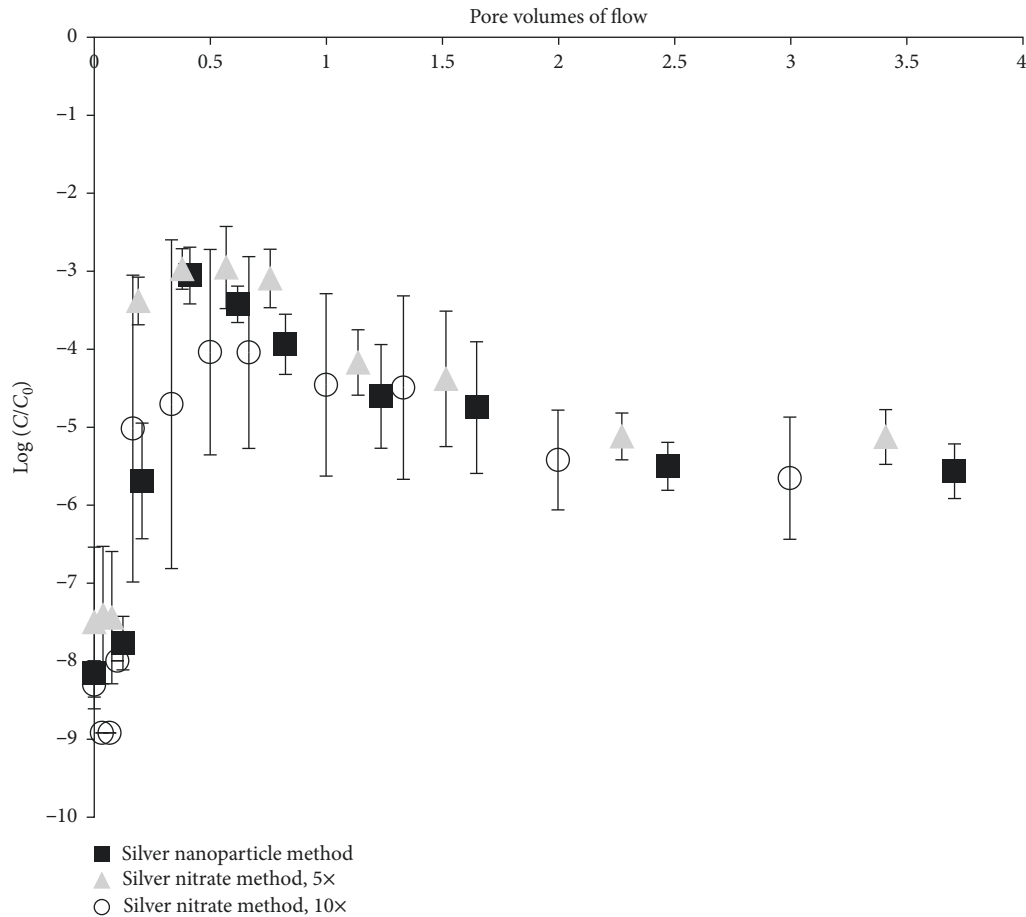


FIGURE 3: Average log change of *E. coli*, $\log(C/C_0)$, versus pore volumes of flow after an one-min pulse injection of *E. coli* to ceramic filters manufactured using the silver nanoparticle method and the silver nitrate application method. Error bars show one standard error above and below the mean. For the silver nitrate application method, the mass of added silver was five times (5x) or ten times (10x) the mass of silver applied to the ceramic filter fabricated using the silver nanoparticle method. Samples were taken at the same time for each disk and converted to pore volume. Since pore volumes varied minimally (3%) between disks, samples at the same time were averaged.

R is the retardation coefficient, c is the concentration of $[^3\text{H}]\text{H}_2\text{O}$ in counts per minute per mL, t is time in minutes, t_0 is the tracer injection time, D is the dispersion coefficient in cm^2/min , x is distance in cm, v is the linear velocity in cm/min , μ is the first-order decay coefficient, and L is the thickness of the disk. CXTFIT [27] was used to provide the optimum fit of the model to experimental data. D and v were determined with $R = 1$ and $\mu = 0$ from the $[^3\text{H}]\text{H}_2\text{O}$ transport experiment.

After the completion, two high-performance liquid chromatography (HPLC) pumps (Acuflow series IV) were connected and mixed at a three-way push to connect fitting immediately before the inflow valve of the permeameter chamber maintaining a constant flow rate of $0.6 \text{ mL}/\text{min}$ to mimic the average flow of pot filters ($1.5 \text{ L}/\text{h}$). For these experiments, one pump contained an inflow of EPA semi-hard synthetic groundwater solution plus acetate at a concentration of $6 \text{ mg}/\text{L}$ (to allow bacterial growth similar to natural water) [28]. The other pump contained $\sim 10^6 \text{ MPN}/100 \text{ mL}$ *E. coli* in synthetic groundwater without the added acetate. The growth medium was kept separate from the *E. coli* until immediately prior to entering the cell,

which ensued a constant influent concentration. The effluent valve of the permeameter chamber was open to the atmosphere for collection of effluent water samples. Pumping and sampling of effluent for silver levels and *E. coli* concentration continued for 2 weeks. A final hydraulic conductivity was measured, and another $[^3\text{H}]\text{H}_2\text{O}$ breakthrough experiment was performed to compare initial and final porous medium flow characteristics. For *E. coli* concentration, the same quantifications were used as described above. A graphite furnace atomic adsorption spectrometer (PerkinElmer HGA 900) was used for total silver quantification. Silver methods were tested in duplicate.

2.5. Performance Evaluation after 2 and 4 Weeks of Flow. To evaluate the long-term performance of the ceramic filters under conditions mimicking real-world use, we conducted experiments using 2- and 4-week pulse injections of *E. coli* without an added growth substrate. Ceramic filters were again in to a flexible-wall permeameter with a 10-psi cell pressure. Like above, a HPLC pump, a 1.0 mL syringe, and the inflow valve of the permeameter chamber were

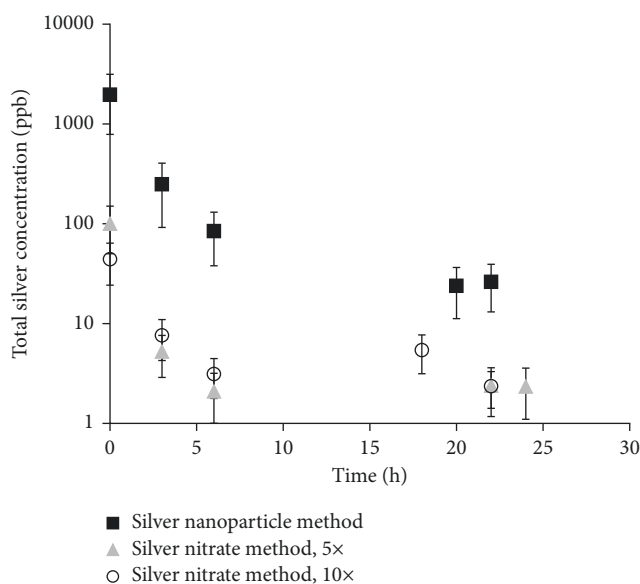


FIGURE 4: Total silver concentration as a function of time in effluent from silver-ceramic filter media. Data is for three filter types with varying silver application methods and amounts. Error bars show one standard error above and below the mean.

connected with a three-way stopcock. The HPLC pump maintained a constant flow rate of 0.6 mL/min this time with an EPA semi-hard synthetic groundwater solution as the inflow solution [28]. The effluent was collected the same as before for silver and *E. coli* sampling. After two weeks, a 0.6 mL pulse of $\sim 10^9$ *E. coli* was injected through the filter via the syringe. Effluent samples were collected to trace the bacterial breakthrough. The pump was left to continually pump synthetic groundwater for another two weeks with effluent sampling for silver levels. After a total of four weeks of pumping, another 0.6 mL pulse of $\sim 10^9$ *E. coli* was injected through the filter via the syringe. Effluent samples were collected to trace the bacterial breakthrough. For *E. coli* concentration, Colilert medium (cat. WP200I) was added to 100 mL of sample and mixed thoroughly, before being poured into the IDEXX Quanti-trays (cat. WQT-2K) and incubated for 24 h at 37°C. A fluorescent UV lamp was used to count the number of fluorescing wells in the tray and correlated to *E. coli* concentrations using a most-probable-number table provided by the manufacturer. A graphite furnace atomic adsorption spectrometer (PerkinElmer HGA 900) was used for total silver quantification. Silver methods were tested in duplicate.

3. Results and Discussion

3.1. Miscible Displacement Transport Experiments with *E. coli*. The results of the *E. coli* pulse injections into the ceramic filter disks are shown in Figures 3 and 4. Figure 3 shows the log removal of *E. coli* versus the pore volumes of flow. Both methods of silver application, silver nanoparticle and silver nitrate, performed similarly. Further, both levels of silver nitrate application (5x and 10x) performed similarly, showing the potential of the new method as a viable substitution. To calculate results, the effluent concentration

(C) was divided by influent concentration (C_0), followed by taking the log of C/C_0 .

Figure 4 shows the total silver measured in the effluent from the ceramic filters over time. The effluent from filters made with the silver nanoparticle method has the highest silver levels—even above the drinking-water standard for sampling times less than 5 hr—while the new silver nitrate method results in lower levels. These lower silver levels, while still an effective antimicrobial agent, suggest a safer filter with a longer lifespan because silver is retained in the filter media rather than released into the treated water.

These graphic results suggest that, at least during short-term experiments, the new silver nitrate method provides no benefit in regard to bacterial removal since the error bars overlap. However, in Figure 4, the error bars do not overlap between the silver nanoparticle and silver nitrate methods, showing a statistical difference. Water chemistry will effect the rate of silver release from the ceramic filter [29]; however, under the same conditions, the silver nitrate application method results in lower silver effluent levels, potentially improving long-term silver retention in the filter and the overall useful filter lifetime. This fits well with literature that a significant fraction of silver nanoparticles is being washed off over time, decreasing the long-term effectiveness of ceramic water filters [19]. This is particularly notable since there is five and ten times as much silver in the silver nitrate filters as the silver nanoparticle filters. New filters commonly require the first few liters be discarded in case of high silver levels [30], and these silver levels are safely below the drinking-water standard quickly after first use.

3.2. Long-Term Performance Evaluation with Constant Exposure. In response to the bacterial tracer testing results, a longer-term experiment was performed in order to evaluate the hypothesis that ceramic filters made with the silver

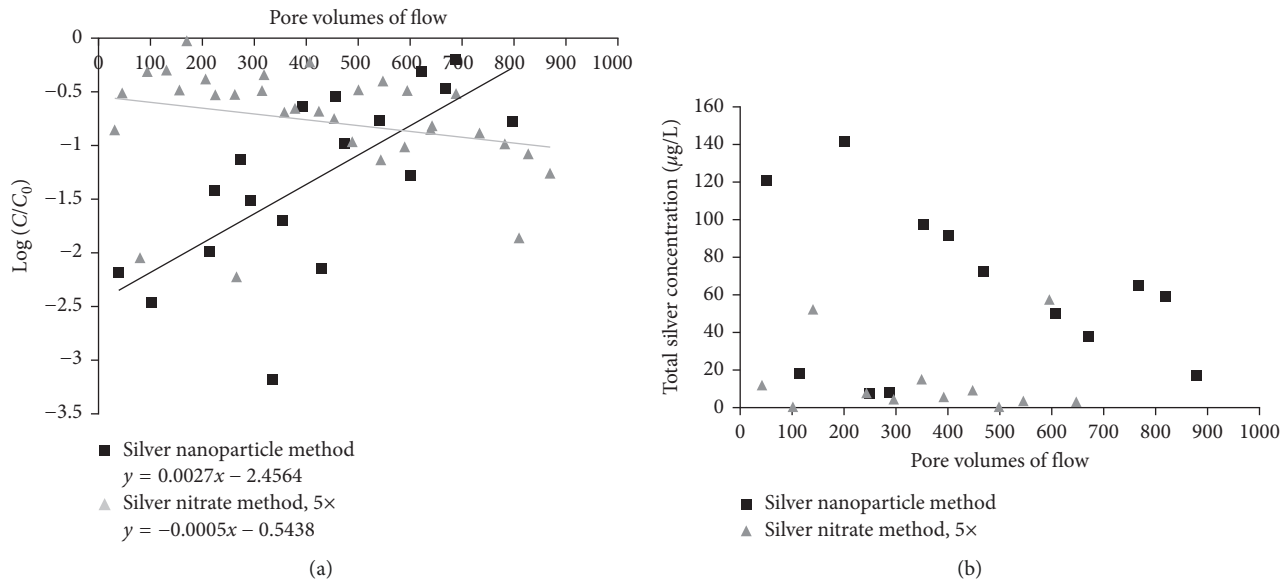


FIGURE 5: (a) Average log change of *E. coli*, $\text{Log}(C/C_0)$, versus pore volume of flow with a long-term constant exposure to *E. coli* by silver application method. Trend lines show the change in performance of *E. coli* removal over time. The slope of the trend line for the silver nanoparticle filters 0.0027 shows a decrease in performance. While the silver nitrate filter trend line has a slope of -0.0005 , meaning at least consistent performance. (b) Total silver concentration in effluent from silver-ceramic filter media as a function of pore volumes of flow with a long-term constant exposure to *E. coli*. Data are for two filter types with varying silver application methods and amounts.

nanoparticle method have longer lifespans. Figure 5 shows the results of exposing the ceramic filter disks to a constant flow of *E. coli* with synthetic groundwater and an added carbon source. This ensures maximal bacterial growth and can potentially cause biofilm formation and bacteria growth. Each point represents a single data point due to the nature of sampling over such a large time scale with slight variance in pore volume between replicates. Replicates of the same silver method had data pooled together to present the trends seen in Figure 5.

Figure 5(a) shows the log removal of *E. coli* versus pore volumes of flow. The silver nanoparticle method of silver application shows better performance initially, but then inconsistent performance over time. This could potentially be explained by *E. coli* growth in the filter. The bacteria may cause clogging in the filter but the HPLC pump used to maintain constant influent flow rates might be increasing pressure in an attempt to keep a constant flow rate, dislodging the bacteria growth. This could cause bacteria to be released in clumps, creating low removal rates after continued use. The silver nitrate filter performed more consistently, slightly increasing in performance over time and possessing a longer effective lifespan. Figure 5(b) shows the silver results over the same time period. As expected, the silver nanoparticle method resulted in much higher silver levels than the silver nitrate filters, with average effluent concentrations of 64 and 18 $\mu\text{g/L}$, respectively. Additionally, some of the early time points for the filters made with the silver nanoparticle method feature silver levels in the effluent above drinking-water standards. Silver concentrations in the effluent seem to vary some; this may be due to silver sloughing off close to a sampling time. Silver may not come out of the filter at a perfectly consistent rate; it may be

releasing as pressure builds up and requires more pore channel space for flow. A mass balance of silver release over the course of the experiment shows that an average of 0.63 mg of silver have come out of the silver nanoparticle filters versus 0.29 mg of silver that have come out of the silver nitrate filters. The silver nanoparticle filters only started with 4.96 mg of silver per filter, while the silver nitrate filters had five times as much. The silver nitrate method shows up to a ten times longer lifespan with a silver loss rate about half that of the silver nanoparticle method and containing five times as much silver.

Hydraulic conductivity, K , was measured before and after the *E. coli* exposure to quantify clogging in the filters. Hydraulic conductivity decreased by an average of 38.89% and 75.15% for the silver nanoparticle and silver nitrate filters, respectively. This decrease was expected, as bacterial growth promoted by the influent would likely cause clogging of the filter. Silver nitrate filters have more silver and therefore might be causing more microbial death in the filter. However it is important to note that this is a relatively small change, but could affect performance in actual use.

Tritiated water was used as a conservative tracer in pulse injections both before and after the *E. coli* exposure to estimate the change in the linear velocity (v) and dispersion coefficient (D). Table 1 shows the model output values generated for v and D by CXTFIT from the experimental results.

The linear velocity and dispersion coefficient decreased for both silver methods. The silver nanoparticle filter caused decreases of 10.3% and 50.2% for v and D , respectively, while the silver nitrate disk saw a decrease of 17.73% and 46.01% for v and D , respectively. A decrease in diffusion coefficient, D ,

TABLE 1: Linear velocity, dispersion coefficient, and hydraulic conductivity for silver nanoparticle and silver nitrate filters before and after 2 weeks of constant flow of *E. coli*.

	v (cm/min)	Δv (%)	D (cm ² /min)	ΔD (%)	K (cm/min)	Average porosity (%)
Silver nanoparticle initial	3.17×10^{-2}		1.52×10^{-2}		3.62×10^{-4}	33.48
Silver nanoparticle final	2.84×10^{-2}	-10.3	7.58×10^{-3}	-50.2	1.84×10^{-4}	
Silver nitrate initial	3.02×10^{-2}		9.41×10^{-3}		7.64×10^{-4}	32.24
Silver nitrate final	2.48×10^{-2}	-17.73	5.08×10^{-3}	-46.01	1.82×10^{-4}	

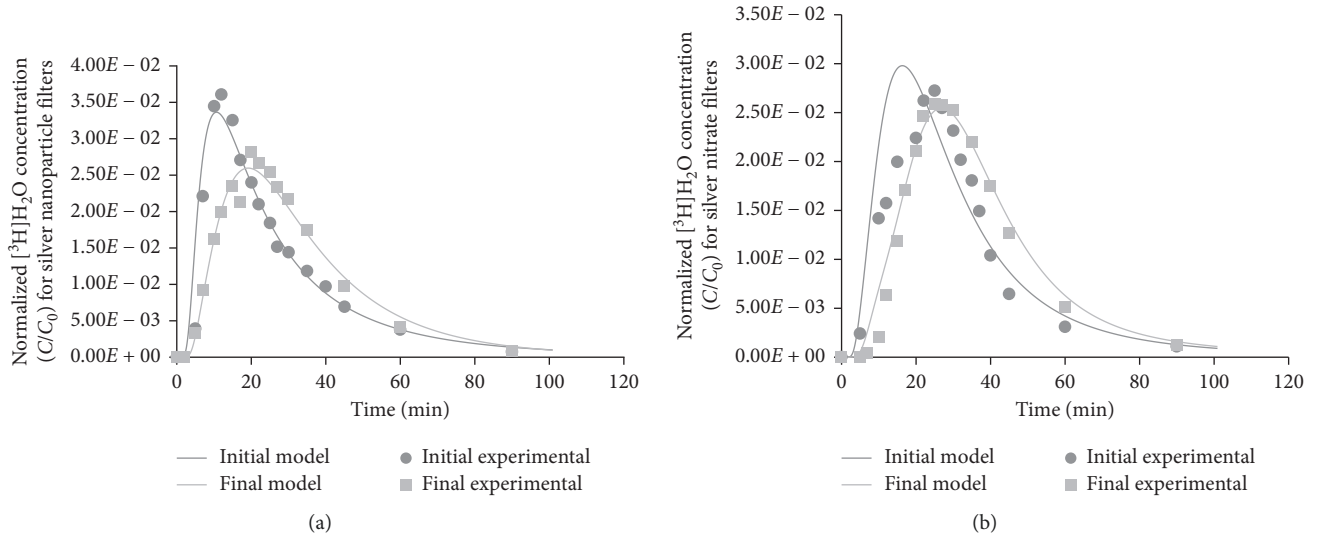


FIGURE 6: Results of $[^3\text{H}]\text{H}_2\text{O}$ transport experiments and simulations through (a) silver nanoparticle ceramic filters and (b) silver nitrate ceramic filters (b). Tracer experiments and simulations are shown for experiments conducted at the start and end of a two-week period of constant flow of synthetic groundwater containing *E. coli*.

would be indicative of a less tortuous path for flow. This could be due to dislodging of loose ceramic particles and nanosilver along pore channels. The output model with these v and D values and an assumed $R = 1$ and $\mu = 0$ can be seen in Figure 6.

The changes of v and D between initial and final measurements for silver nanoparticle and silver nitrate filters are similar, showing the silver nitrate method maintains performance of flow over time equal to the current production protocol.

3.3. Performance Evaluation after 2 and 4 Weeks of Flow. This experiment was performed to further evaluate the longer-term performance of the two different silver applications in the ceramic filters. Filters had synthetic groundwater flowing through for two weeks, and then an *E. coli* pulse was injected. Then, after two more weeks of synthetic groundwater flowing, another *E. coli* pulse was injected. The results of this experiment are found in Figure 7.

Again, using the graphed data and error bars for analysis, the filters with silver nanoparticle method perform better initially, allowing less *E. coli* to pass through the filter during the pulse after two weeks. But after four weeks of use, the same filter showed a large decrease in efficacy. The silver nitrate filters were consistent and showed almost identical performance after two and four weeks of use.

4. Conclusions

The silver nitrate method presented here presents another potential benefit in that it reduces possible exposure of workers to silver nanoparticle inhalation. A recent article by Fewtrell et al. [31] assessed the safety of using silver nanoparticles in household water treatment and noted that one of the most significant silver exposure risks could be to workers fabricating the filters and inhaling the silver nanoparticles. They noted that occupational safety procedures in developing-world work environments may not be sufficient to protect the workers. They based their assessment of a study that observed genotoxic damage to silver workers [32].

Furthermore, filters manufactured using the silver nitrate method release lower levels of silver into the treated water, and the form of the silver is Ag^+ (e.g., ionic silver) [21]. Some studies show genotoxic effects caused by exposure to silver nanoparticles, albeit at silver doses that are orders of magnitude greater than what is found in drinking water treated with silver-ceramic water filters. If an adult weighing 50 kg were to consume 2 liters of water per day with 0.018 mg/L of silver (the mean silver concentration in water treated with filters manufactured using the silver nitrate method evaluated in this manuscript), 0.00072 mg/kg of body weight will be consumed per day. This level is far

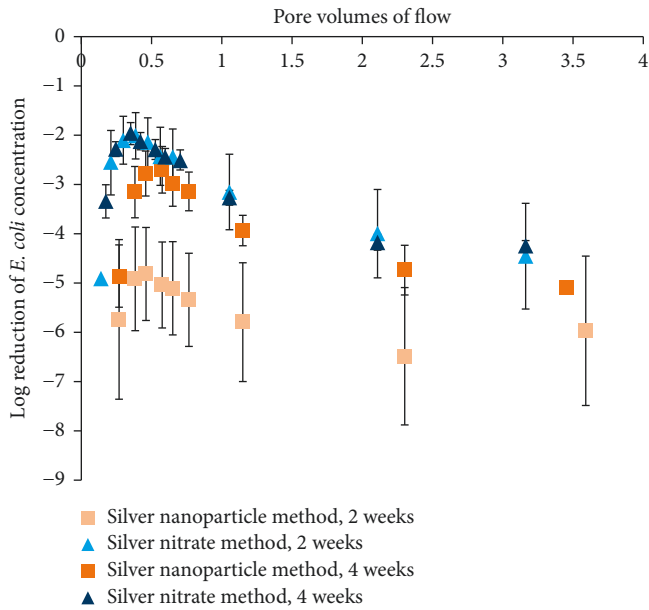


FIGURE 7: Average log change of *E. coli*, $\text{Log}(C/C_0)$, versus pore volume after a pulse injection of *E. coli* over 1 min by silver application method and time of saturation. Error bars show one standard error above and below the mean.

below the conservative Tolerable Daily Intake value of 0.0025 mg/kg of body weight per day suggested by Hadrup and Lam [33]. The levels presented in Table 1 of Fewtrell et al. are 0.25 to 500 mg/kg, 125 to 250,000 times greater than the doses found in water treated by our filters [31]. Studies with lower doses of silver show no genotoxic effects, and studies with ionic silver show no genotoxic effects at any reported concentration. Silver-ceramic water filters have been shown to release silver ions, not silver nanoparticles [21, 34]. Fewtrell et al. [31] and the response by Lantagne et al. [34] state that studies of silver ion toxicity have shown no adverse effects. Therefore, the silver nitrate method helps to insure the microbiological safety of the treated water while releasing only extremely low levels of ionic silver (more than 5 times below the EPA and WHO suggested permissible levels). At the same time, the method reduces the risks of exposure to workers in developing-world production facilities.

Each of the experiments points to a similar result when comparing the conventional method of painting on silver nanoparticles after firing and the new method of embedding silver nitrate prior to firing in ceramic water filters. The silver nanoparticle method may perform better initially, but decreases in antimicrobial efficacy over time and commonly releases silver at rates above the drinking-water standard. The silver nitrate application method produced filters that release lower amounts of silver and performed more consistently in bacterial removal over time. These results indicate that the silver nitrate application method is a viable substitute to painting on silver nanoparticles for the production of ceramic water filters. However, there are some concerns that this may not be ideal for all filter production facilities. Conventionally, filters that are manufactured will

not receive the silver nanoparticle application until after passing quality control tests. With the new method of silver application prior to firing, filters that do not pass these pressure and flow rate tests will be wasting the silver applied to them. Therefore, the new silver nitrate method of application may only be a good option to be incorporated at filter production facilities with relatively high pass rates for quality control tests. These results from experiments in clean lab conditions are promising, but are not a perfect indicator of how silver nanoparticle and silver nitrate filters would perform in expected in home use. In homes, there will be varying flow rates, turbidities, ionic strengths, temperatures, and many more variables that could affect performance. The next experiments to be done are to test the application of full-size filters and with real-world use, rather than simplified lab conditions.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors thank Dr. David Kahler, Genevieve Jordan, and Jamie Woodall for technical assistance in the laboratory. This work was supported by the U.S. National Science Foundation (CBET-1438619).

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