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Laboratory Investigation into the Effect of Silver Application on the Bacterial Removal Efficacy of Filter Material for Use on Locally Produced Ceramic Water Filters for Household Drinking Water Treatment

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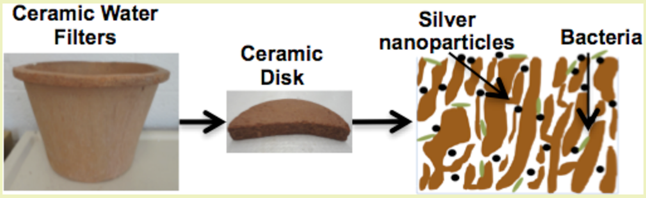
Supporting Information



ABSTRACT: Locally produced ceramic water filters (CWF) are an effective technology to treat pathogen-contaminated drinking water at the household level. CWF manufacturers apply silver to filters during production, although the silver type and concentration vary and evidence-based silver application guidelines have not been established. We evaluated the effects of three concentrations of two silver species on effluent silver concentration, *E. coli* removal, and viable bacteria retained on the surface and contained in the pores of ceramic disks manufactured with clay imported from three CWF factories using sawdust as the burn-out material. Additionally, we evaluated performance using water with three chemistry characteristics ($Na^+{-}NaCl$, $Ca^{2+}{-}CaCl_2$, and humic acid as natural organic matter) of disks made from the different clays using either sawdust or rice husk as the burn-out material. Results showed the following: (1) Silver desorption from disks coated with silver nitrate (Ag^+) was greater than desorption of silver nanoparticles (nAg) for all disks. (2) Effluent silver concentration, *E. coli* removal, and viable bacteria retention were dose-dependent on the amount of silver applied. (3) Neither water chemistry conditions (inorganic or organic compounds) nor burn-out material showed an effect on any of the parameters evaluated at the silver concentration tested. The recommendation for filter manufacturers to use only nAg and at a higher concentration than currently recommended is discussed.

KEYWORDS: *Ceramic pot filters, Ceramic water filters, Colloidal silver, E. coli removal, Household water treatment and safe storage, Point-of-use water treatment, Silver nanoparticles, Silver nitrate*

INTRODUCTION

Worldwide, an estimated 783 million people do not have access to an improved water source,[1] and hundreds of millions more drink water that is contaminated at the source or during collection, transport, or storage.[2] Drinking water contaminated by pathogenic microorganisms causes gastrointestinal infections, which account for 1.87 million childhood deaths each year, mostly in developing countries.[3] Potters for Peace (PfP) style ceramic water filters (CWF) are a low-cost technology produced at independently owned factories in developing countries by pressing a mixture of clay and an organic (burn-out) material into the filter shape and then firing it to a ceramic state. Combustion of the burn-out material during the firing process creates the porous structure. CWFs remove pathogens from water by retaining them on the surface or trapping them within the filter pores.

CWFs are effective at removing more than 99% of protozoan[4,5] and 90−99.99% of bacterial organisms from drinking water;[6] however, the removal of viruses remains a challenge. In the field, water treated by CWFs is often improved to the World Health Organization's (WHO) low-risk classification[6,8] of fewer than 10 CFU *E. coli*/100 mL,[7] and filter use has been associated with a reduction in diarrheal disease among users.[9]

Silver nanoparticles (nAg) and silver nitrate ($AgNO_3$, Ag^+) are known antimicrobial agents and are added to filters at all factories, mostly after the firing process.[10] Reported *E. coli* log

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reduction values (LRVs) by CWFs coated with nAg range from 2.5 to 4.56.[11,10] LRVs from 2.1 to 2.4 of *E. coli* have been measured using filters coated with Ag$^+$; however, similar LRVs were measured in CWFs without Ag$^+$ application.[6]

In production, 83% of factories use nAg and 17% use Ag$^+$.[12] Some factories use Ag$^+$ because it is cheaper than nAg and/or it is locally available. The concentration of silver applied at each factory varies. Reported nAg concentrations range from 107 to 288 ppm,[12] excluding probable outliers. The silver solution is applied to fired filters by brushing, dipping, or firing it into the filters. When applied with a brush, the volume and concentration of silver can be measured, whereas when filters are dipped, the amount of silver absorbed by the filter is not controlled and the amount of silver fired into filters is proprietary. Factories reported applying from 32 to 96 mg of nAg per filter when applied by brushing. The current guideline, which is experiential rather than evidence based, is 64 mg of nAg per filter.[13]

A variety of water sources are used at factories to prepare silver solutions, from untreated surface water to treated water.[12] Water characteristics at the filter user's home will also vary. Previous studies have reported a reduction in antibacterial properties of nAg with increased size of the nanoparticle clusters due to aggregation in the presence of divalent ions such as calcium (Ca$^+$) and magnesium (Mg$^+$).[14,15] In addition, water can contain organic compounds, such as humic acids (HA). These can rapidly coat the nanoparticle surfaces creating a physical barrier that prevents interaction between nanoparticles and bacteria.[14−16] While previous studies have reported that different water chemistry conditions can impact the disinfection performance of nAg in the aqueous phase, these parameters have not been evaluated on CWFs either in the field or in laboratory tests.

Desorption of silver from coated CWFs during the first flushes of water has been reported.[10] A study using a phosphate buffer as influent solution reported a decrease in silver concentration in effluent from nAg-impregnated CWFs to below the United States Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for silver in drinking water (0.1 mg/L or 100 ppb)[17] within a few flushes.[10] To our knowledge, no comprehensive study has evaluated the desorption of either nAg or Ag$^+$ from CWFs using different clays and water chemistry conditions.

This research aimed to address some of the silver-related research needs outlined in the *Best Practice Recommendations for Local Manufacturing of Ceramic Pot Filters for Household Water Treatment*[13] with the objective of developing evidence-based recommendations for silver type, concentration, and dilution water characteristics that take into consideration variation in local material characteristics and potential silver exposure for filter users. In this study, we evaluated the performance of ceramic disks manufactured with clays from three different factories and two types of burn-out material, sawdust and rice husks. In phase I, disks manufactured with the different clays and sawdust were coated with three different concentrations of either nAg or Ag$^+$ and evaluated for (1) effluent silver concentration and silver retention, (2) *E. coli* removal, and (3) viable bacteria retained in disks. In phase II, the influence of three water chemistries (Na$^+$−NaCl, Ca^{2+}−CaCl$_2$, and humic acid as natural organic matter) on nAg and Ag$^+$ were evaluated on disks manufactured with each of the clays and each of the burn-out materials against the same outcome parameters.

EXPERIMENTAL SECTION

Disk Manufacturing and Pretreatment. While PFP-style filters are ~10 L capacity filter pots, in this study, to simplify manufacturing, transport, and testing, disks were pressed out of filter material. Disks were manufactured at Advanced Ceramics Manufacturing (Tucson, AZ) with clay imported from filter factories in Indonesia (Indo), Tanzania (Tanz), and Nicaragua (Nica). Factories were selected for geographical distribution, variation in manufacturing methods, and willingness to ship clay. Saw dust and rice husk, the primary burn-out materials used at factories,[12] were purchased in Arizona and processed between United States sieve numbers 16 and 30 (1.19 mm and 0.595 mm openings, respectively). The filter mixture comprised 15% burn-out to clay ratio by weight. Disks were pressed at 3.58 PSI and air dried. In order to achieve sufficient strength for testing, the Indonesian clay disks were fired to 800 °C peak firing temperature held for 180 min (800 °C/180 min), Tanzanian to 950 °C/60 min, and Nicaraguan to 1085 °C/60 min. Fired disk thickness was ~1.5 cm. Once fired, disks were boiled in water for 1 h, and the percent porosity of each disk was calculated by dividing the difference between saturated and dry weights by the geometric disk volume.

Disks were shipped to the University of Rhode Island (URI) where they were cut to 3.8 cm diameter to fit existing filter holders. To eliminate possible microbiological contamination, disks were heat treated to 550 °C/30 min and then allowed to cool at room temperature. The sides of the disks were sealed with silicone, allowed to dry, and then fixed in the filter holders with silicone. All tests were performed in duplicate.

Disk Characterization. Tracer experiments were conducted to determine the intrinsic characteristics of the disks and to identify possible anomalies in the porous matrix. Tracer tests and the subsequent determination of the advection and dispersion coefficients were performed using the procedure described in Oyanedel-Craver et al.[10] but with NaCl as a conservative tracer instead of tritiated water.

Study Phases. This study was carried out in two phases. In both phases, tests were conducted in duplicate, using two disks of each recipe. In phase I, a phosphate buffer solution was used to evaluate disks made with each of the clays and sawdust, coated with different concentrations of each type of silver. Phosphate buffer was selected to minimize natural decay of bacteria during the test period. Only disks manufactured with sawdust were tested in phase I due to limited availability of rice husk disks.

In phase II, the influence of three water chemistries, selected to mimic the ionic strength and organic carbon content in natural water, was evaluated with each of the silver types on disks manufactured with each of the clays and each of the burn-out materials (Table 1). The silver concentration was selected to minimize the effect of residual silver on bacteria deactivation.

Silver Release and Retention. Suspended silver nanoparticles (nAg) (70% silver) were purchased from Laboratorios Argenol and dissolved silver (Ag$^+$) from Sigma Aldrich. The majority of CWF factories use Argenol silver nanoparticles.[13] The few factories that use Ag+ purchase it from a variety of sources. Silver was applied by brushing each disk with a specific concentration of either nAg or Ag$^+$ in the appropriate electrolyte solution according to the procedure

Table 1. Experimental Conditions

study phase and burn-out	silver (nAg[a] or Ag^{+b}) concentration (mg/g[c])	water characteristics
I. sawdust	0.003	10% phosphate buffer solution
	0.03	
	0.3	
II. sawdust or rice husk	0.003	150 mg/L Na$^+$−NaCl
	0.003	150 mg/L Ca^{2+}−NaCl
	0.003	5 mg/L humic acid as total organic carbon

[a]Silver nanoparticles. [b]Ionic silver. [c]Milligrams of silver per gram of disk.

described in Oyanedel-Craver et al.[10] Physicochemical characterization details of nAg exposed to the different water chemistry conditions are presented in Table S1 of the Supporting Information. These results are similar to results from previous studies performed by the authors and other researchers[18−21] and show the impact that divalent ions have on the stability of nanoparticles suspensions. When Ca^{2+} was used as an electrolyte solution, the nanoparticles aggregated, forming clusters with an average hydrodynamic diameter 3 times greater than in the other solutions.

After silver application, disks were flushed for 24 h with a bacteria-free solution. Samples were preserved by adding 2% nitric acid, then effluent silver concentration was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) after 100, 200, and 300 min, and at 24 h. Percent retention of silver was calculated by dividing the difference between the mass of silver applied and the mass of silver released by the initial amount of silver added to the disk and then multiplying by 100 to obtain the percent value.

Bacterial Removal Performance. After 24 h of flushing with a bacteria free solution, a concentration of 10^6 CFU/mL *E. coli* was prepared in water of the same chemical composition as used during the flushing stage (i.e., deionized water with a buffer solution, electrolytes, or humic acid) and continuously fed to the disks at a flow rate of 0.5 mL/min using a peristaltic pump. A fresh solution of bacteria was prepared daily for both phase I and phase II testing. Samples were taken daily for 10 days, and LRVs were calculated. The concentration of bacteria in the influent and effluent were measured using membrane separation followed by an incubation period in m-FC; specific substrate media (Millipore, Inc.) and colonies were counted after 24 h. A more detailed description of the procedure[22] is presented in the Supporting Information.

At a feed of 0.5 mL/min for 10 days, the total throughput for each disk over the study period was ~7.2 L, which equates to ~1300 L through a full-sized filter. This was calculated by multiplying the flow rate per cm^2 of the filter disk by the area of a full-sized Nicaraguan filter using filter dimensions presented in van Halem.[5] Using this calculation, the 10 day test period simulated approximately four months of a filter treating 10 L of water per day.

Bacteria Retention. After completing the bacterial removal tests, the concentration of viable bacteria retained on the surface and contained in the pores of the disks was determined. The disks were ground, and 10 g were transferred to a 50 ml flask. The bacteria were dispersed in the buffer solution by gentle sonication for 15 min to detach the bacteria from the ceramic material. The concentration of bacteria was determined using Vigeant et al.[22] as described above (additional details are provided in the Supporting Information).

RESULTS

Disks Characterization. A total of 144 disks were tested, including 30 each of Indo-sawdust, Tanz-sawdust, and Nica-sawdust and 18 each of Indo-rice husk, Tanz-rice husk, and Nica-rice husk. The average advection (v) (directly proportional to the fluid velocity) and dispersion (D) (directly proportional to the effective porosity) coefficients and geometric porosity values for the ceramic disks manufactured from each recipe were similar (Table 2). Results from disks manufactured with Indonesian and Tanzanian clays were also similar; however, disks manufactured with the Nicaraguan clay had higher advection and dispersion coefficients, indicating that the solute spread fastest through the Nicaraguan disks. For each of the clay groups, disks manufactured with rice husk had slightly lower porosities than disks manufactured with sawdust. This is likely because rice husk is denser than sawdust, so the same weight would result in a smaller volume ratio.

Phase I. *Silver Release and Retention.* For both types of silver and regardless of clay type, a higher concentration of silver was measured in effluent from disks coated with higher concentrations of silver (Figure 1). With the exception of 0.003 mg/g of silver, for each of the silver concentrations applied, a higher effluent concentration of Ag+ was measured in comparison with nAg. Silver concentration in the effluent reduced with solution throughput regardless of silver type. Effluent silver concentration from nAg-coated disks was below the USEPA MCL after 24 h in all but one case (disks made with Nicaraguan clay and impregnated with 0.3 mg/g nAg). After 24 h, the effluent concentration from disks impregnated with 0.3 mg/g Ag+ exceeded the USEPA's MCL in all cases and ranged from 797 ppb to 2697 ppb. Specific effluent values are presented in Table S2 of the Supporting Information.

Table 2. Physical Properties of Ceramic Disks Manufactured with Different Materials

clay source and burn-out material	firing temp and soak time (°C/min)	advection coefficient (cm/min)	dispersion coefficient (cm^2/min)	geometric porosity (%)
Indo sawdust	800/180	0.06 ± 0.01	0.01 ± 0.01	57 ± 1.5
Tanz sawdust	950/60	0.06 ± 0.01	0.01 ± 0.00	59 ± 1.8
Nica sawdust	1085/60	0.09 ± 0.01	0.05 ± 0.03	54 ± 1.5
Indo rice husk	800/180	0.05 ± 0.01	0.01 ± 0.00	54 ± 0.5
Tanz rice husk	950/60	0.06 ± 0.01	0.01 ± 0.00	54 ± 1.3
Nica rice husk	1085/60	0.10 ± 0.01	0.09 ± 0.05	49 ± 1.6

An increased concentration of silver resulted in increased silver retention in disks coated with nAg regardless of clay type (Figure 2). nAg retention did not vary widely between disks made with different clays. A greater percentage of nAg was retained in disks in comparison with Ag+, most notably in disks made with Nicaraguan clay. A greater difference in Ag+ retention between the different clays was observed. An increase in Ag+ concentration from 0.003 mg/g to 0.03 mg/g resulted in increased retention; however, the highest concentration of Ag+ 0.3 mg/g resulted in the lowest percent retention.

Bacterial Removal Performance. In all samples, a sharp reduction in LRV was observed from day 1 to day 4 of continued 0.5 mL/min throughput (Figure 3), which would be the equivalent to 520 L through a full-sized filter; however, the LRV leveled off from day 5. Thus, the LRV performance comparison is based on an average of the results from the last six days (days 5−10) of testing, the equivalent to an additional 780 L full-sized filter throughput.

Disks made with Indonesian and Tanzanian clays demonstrated an increased LRV with increased silver concentration, regardless of species applied (Figure 3). However, at lower silver concentrations, little LRV improvement over the control disks was measured in disks made with Indonesian clay. No change in LRV was measured from Nicaraguan disks regardless of silver species or concentration applied. Change in LRVs was similar as a function of time and magnitude between disks coated with nAg and Ag^+, with the exception of 0.3 mg/g Ag^+, which achieved substantially greater LRVs in both Tanzanian and Indonesian disks.

Disks made with either Indonesian or Tanzanian clay and coated with 0.3 mg/g nAg achieved >4 LRV on day 10 of testing (1−1.7 LRV improvement, respectively, over control disks without silver). A less than 1 LRV improvement over the control disks was measured with 0.03 mg/g of either silver. Disks coated with 0.003 mg/g of silver showed little or no improvement in LRV in comparison with the control disks by day 10 of testing.

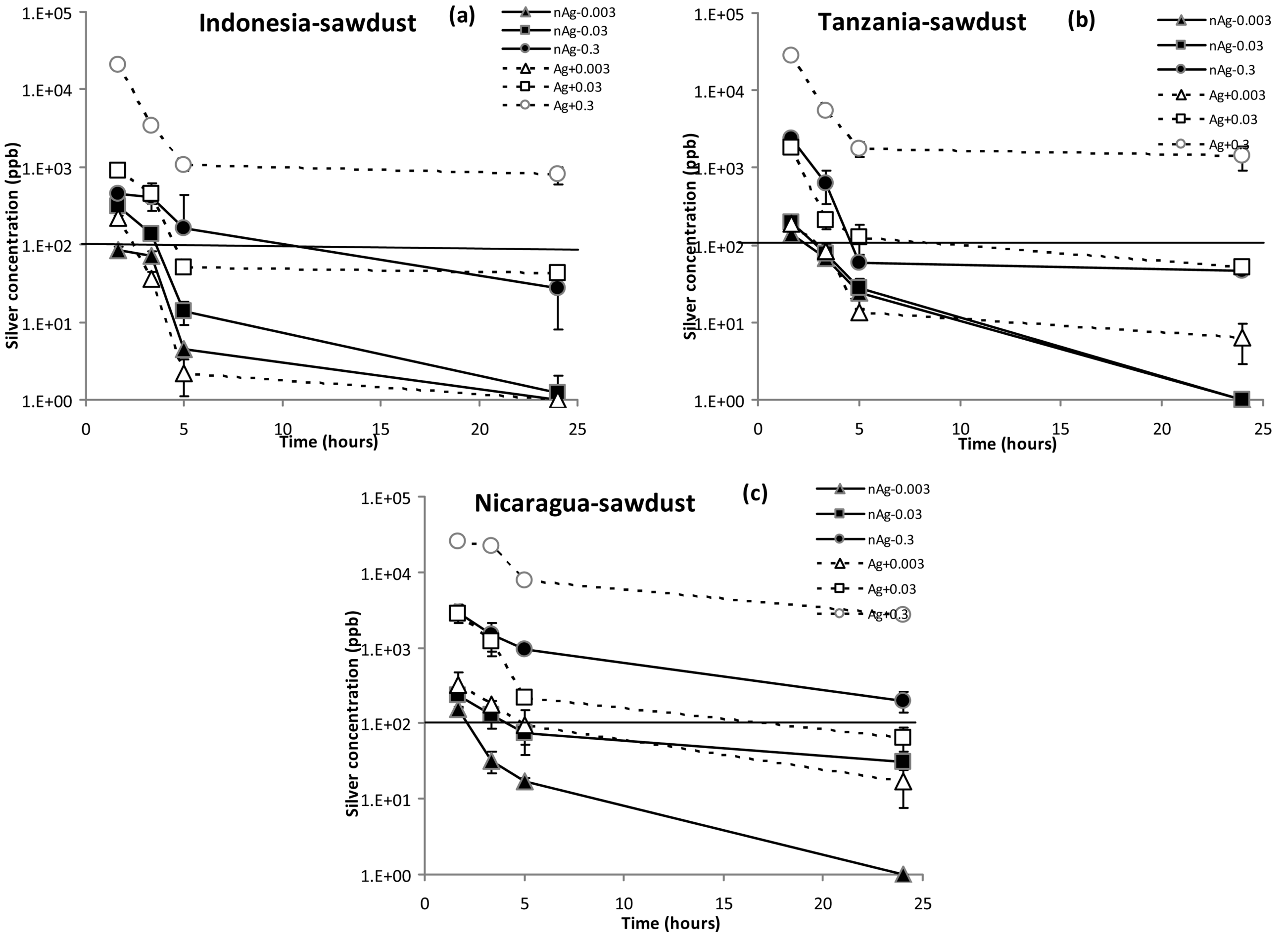

Figure 1. Concentration of silver in effluent from disks manufactured with Indonesian (a), Tanzanian (b), or Nicaraguan (c) clay and sawdust (with standard error bars) coated with different concentrations (mg/g) of either nAg or Ag^+ (horizontal line at 1.E+02 represents USEPA MCL for silver).

Viable Bacteria Retention. The concentration of viable bacteria measured from disks made with Indonesian and Tanzanian clays decreased with increased silver concentration for either nAg or Ag^+. In disks made with Nicaraguan clay, there was less than an order of magnitude decrease in bacteria retention between control disks and disks coated with 0.3 mg/g of either silver (Figure 4). Less bacteria retention could be due to the possibly larger pores in the Nicaraguan disks (Nicaraguan disks also had the lowest LRV values). Disks impregnated with either nAg or Ag+ resulted in similar bacteria concentration reduction per silver concentration applied, although disks coated with 0.3 mg/g of nAg had fewer viable bacteria than Ag^+. Negligible changes were detected between the amount of viable bacteria remaining in disks coated with 0.003 mg/g of either silver species and the control groups (without silver application) regardless of clay type.

Phase II. *Effect of Water Chemical Composition and Burn-Out Material.* Effluent concentration of silver from disks manufactured with rice husk or sawdust with 0.003 mg/g of either silver was below the MCL value of 100 ppb after 300 min of throughput with each water chemistry (Table S3 and Figure S1, Supporting Information). Variation in influent water characteristics resulted in little difference in silver retention among disks treated with nAg (Figure S2, Supporting Information). In disks coated with Ag^+, there was some variability in silver retention in disks manufactured with Tanzanian and Nicaraguan clays when HA was used as the influent solution. A difference in silver retention was not observed between disks manufactured with the same clay but different burn-out materials.

For each clay, LRVs were in the same magnitude range regardless of influent water chemistry applied, the silver type or burn-out material used (Figure S3, Supporting Information). The amount of viable bacteria retained in disks coated with nAg or Ag^+ was within the same order of magnitude regardless of the influent water chemistry conditions or burn-out material (Figure S4, Supporting Information). The amount of viable bacteria retained in disks manufactured with clay from Nicaragua was almost an order of magnitude less than disks made with either Indonesian or Tanzanian clays regardless of silver type or influent water chemistry. These results are similar to phase I results at the same silver concentration and could be a result of bacteria passing through the possibly larger pores in the Nicaraguan disks.

■ DISCUSSION

In this study, nAg and Ag^+ performance at varying concentrations in disks manufactured with clays from different filter factories was evaluated. Additionally, silver was evaluated using different water chemistries on disks manufactured with different clays and different burn-out materials. Disks were used as a model for full-sized filters due to space, time, and laboratory constraints. The continuous flow rate was controlled at 0.5 mL/min to simulate four months of household use,

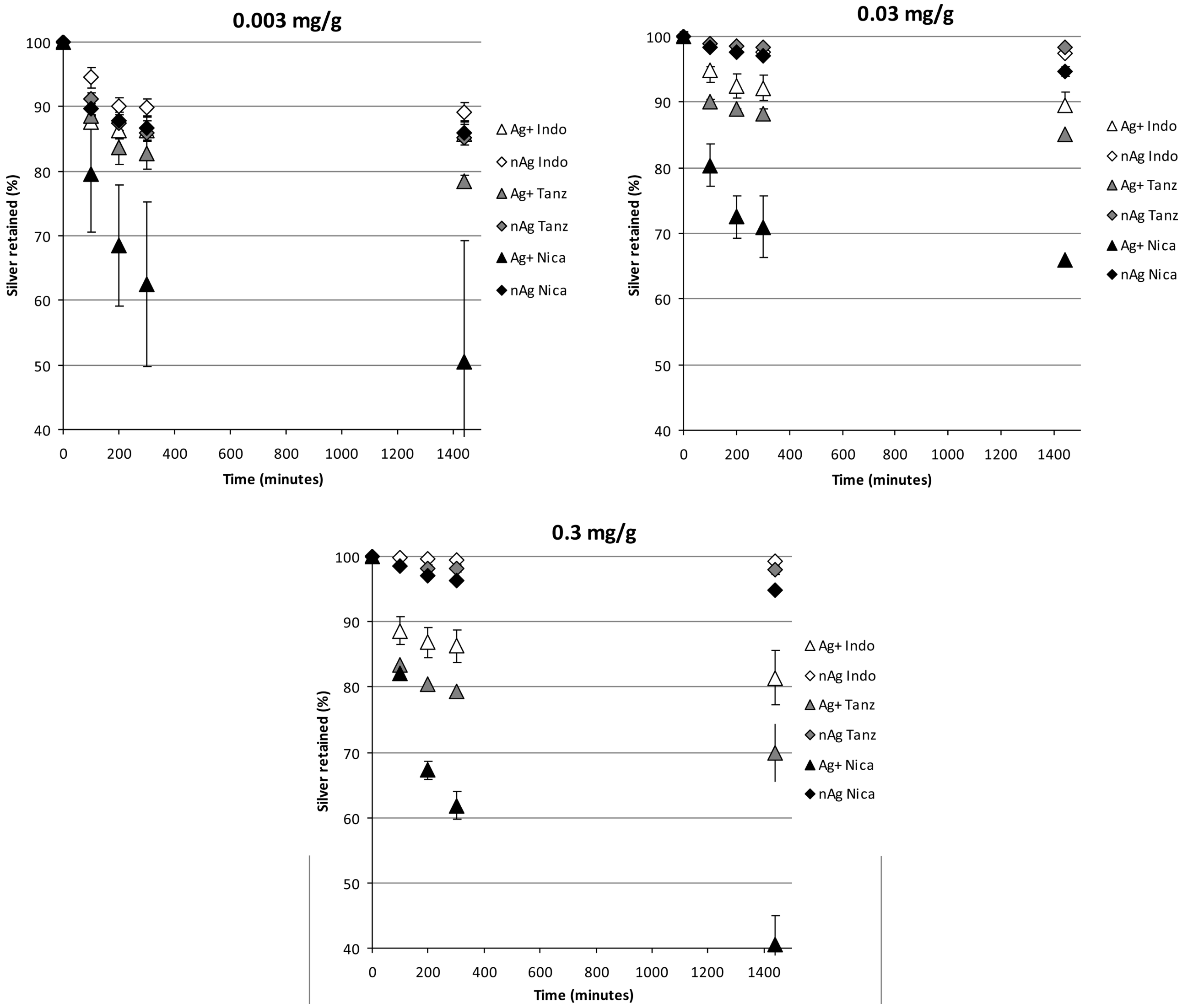

Figure 2. Percent silver retention and standard error over time in disks manufactured with different clays and sawdust coated with different silver species and concentrations (mg/g).

which is possibly the longest lab-scale materials evaluation on CWFs carried out to date. The main difference between our manufacturing specifications and full-sized filter manufacturing was the criteria used. At CWF factories, filter mixture recipes are established by selecting a ratio and firing temperature that, using the locally available materials, result in filters that meet specific quality criteria such as flow rate, LRV, and strength. In this study, rather than manufacture filter disks that met factory quality criteria, the ratio of clay to burn-out material was held constant regardless of the clay origin or burn-out type in order to control variables except for silver application. In order to achieve enough strength for testing, however, the firing temperature was adjusted for each clay. A protocol for establishing or evaluating firing temperature at filter factories has not been developed, and peak firing temperature ranges from 800 to 980 °C. Little research has been carried out on the effects of firing temperature on filter characteristics, and while its importance is recognized, firing temperature evaluation was beyond the scope of this research. Disks manufactured with the different clays likely varied in structure due to variability in the clay, burn-out material type, and firing temperature.

Disks manufactured from Indonesian and Tanzanian clays had comparable advection and dispersion results, and their porosity and strength were suitable for testing. The higher advection and dispersion coefficients in disks manufactured with Nicaraguan clay suggested the solute spread faster, possibly due to larger or more interconnected pores. The Nicaraguan clay was exceptionally challenging to work with during manufacturing, and the firing temperature (1085 °C) likely resulted in excessive vitrification (overfired) in comparison with filters. A separate particle size analysis was carried out on samples of the raw clays used in this research by taking periodic density measurements of a soil and water suspension. The United States Department of Agriculture (USDA) particle size classification system was used to ascertain the relative sand, silt, and clay content. Results showed that the material from Nicaragua had a very low clay (<2 μm) content in comparison with the Tanzanian and Indonesians clays (0.5%, 28.5%, and 31%, respectively).[23] Results from the Nicaraguan disks in this study should therefore be interpreted with caution.

The results of our study showed (1) increased desorption of Ag^+ compared with nAg, (2) variation in LRV of *E. coli* depending upon silver concentration, (3) a difference in the

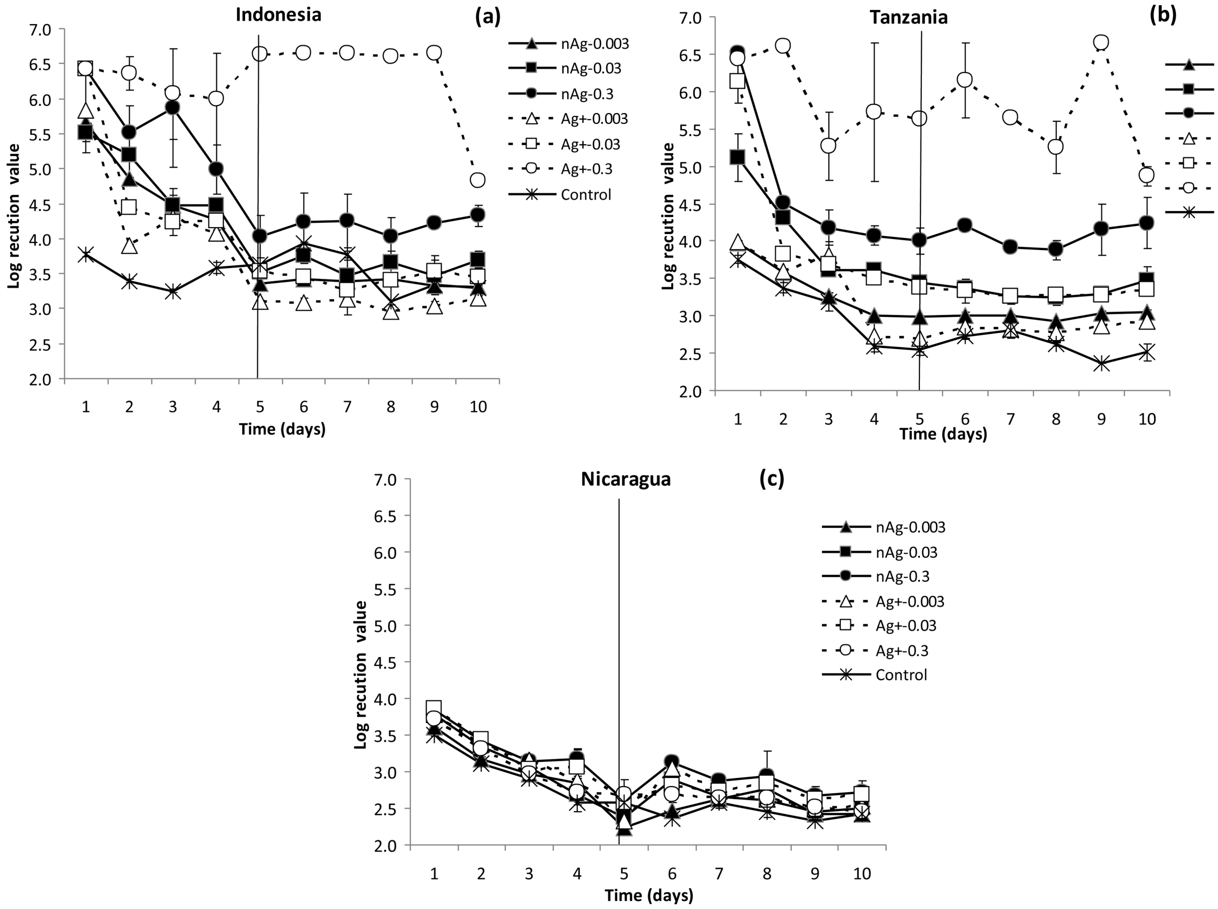

Figure 3. LRV of disks manufactured from Indonesian (a), Tanzanian (b), and Nicaraguan (c) clay (with standard error bars) and sawdust coated with varying amounts (mg/g) of either nAg or Ag^+. Vertical lines indicate day 5 of operation.

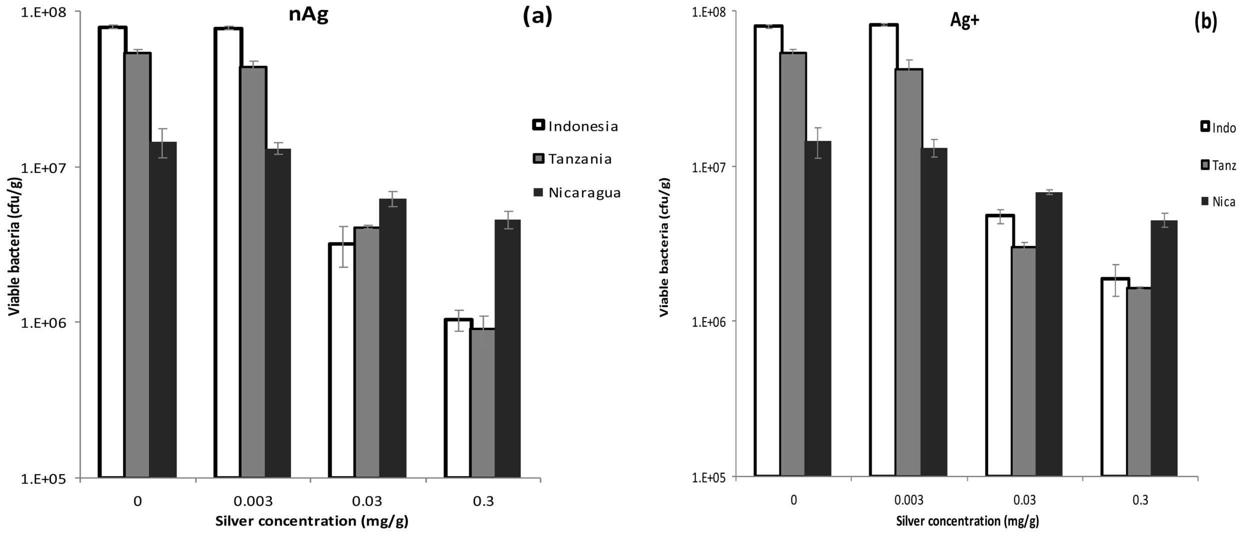

Figure 4. Viable bacteria detected in disks (with standard error bars) manufactured with sawdust coated with varying amounts of nAg (a) or Ag^+ (b).

amount of viable bacteria remaining in the disks depending upon silver concentration, and (4) at the concentrations tested, no impact of water chemistry on the efficacy of silver. These results are discussed in the following paragraphs.

Using a phosphate buffer influent, disks retained nAg more efficiently that Ag^+. Desorption of nAg ranged from 5% to 10% for all disks tested, while for Ag^+, 10–30% desorbed from Tanzanian and Indonesian clay disks and 30–40% from Nicaraguan clay disks. This effect has been reported by other authors who evaluated sorption of silver species on unfired clays using batch systems with equilibrium time of 24 h.[24] Ag^+ can be displaced by cations with higher valence or higher charge density, while nAg are trapped in the nano- and microporous structure of the filter allowing for a slow release of silver ions as the surface of the nanoparticles is oxidized by the dissolved oxygen in water.[25] With the exception of disks manufactured with Nicaraguan clay (with 0.3 mg/g), after 24 h, the concentration of nAg in filter effluent was below the EPA MCL for each concentration tested, and therefore, compliant under the current drinking water recommendation. The concentrations released from nAg-coated disks after 24 h of operation were similar to results presented in other laboratory studies using full-sized CWFs.[26−28]

A rough projection of how long silver could potentially last in filters if the same amount of silver measured in the effluent at 24 h continued to release at the same rate over time was calculated. Because the concentration of silver after 24 h of operation was used as the end point of concentration released, the projected time to exhaust the silver is a conservative estimate. Results are presented in Figures S5 and S6 of the Supporting Information. At the application strength of 0.003 mg/g, nAg or Ag+ could last for less than 4 years in the filter regardless of influent characteristics. At 0.03 and 0.3 mg/g of nAg, the silver could last in filters for more than 8 years, whereas the application of Ag+ at 0.03 and 0.3 mg/g could last for less than 1 year. Calculation methods and assumptions to this projection are presented in the Supporting Information.

While little change in LRV was measured regardless of the type or concentration of silver applied in Nicaraguan disks, with the Indonesian and Tanzanian clays, for either silver species, a dose−response relationship was observed; an increased concentration of silver resulted in an increased LRV of *E. coli*. Disks coated with 0.3 mg/g Ag^+ resulted in the highest LRV. This was likely the effect of the high concentration of silver in the effluent (1 order of magnitude above the EPA MCL); therefore, bacteria deactivation was partially achieved by residual silver in the effluent rather than contact with the silver sorbed/trapped in the porous structure of the disks. With lower concentrations of silver, comparable bacterial reduction was achieved between nAg and Ag^+; however, less silver was measured in the effluent of disks coated with nAg. The application of high concentrations of Ag^+ in filters causes concern about (1) the time that Ag^+ remains in the filter material, thus having implications on the length of time silver can impact filter efficacy, and (2) potential health concerns associated with Ag^+ ingestion by filter users.

The application of 0.003 mg/g of either silver did not demonstrate improved LRV over the control disks (without silver) after 10 days of testing (equivalent to 1300 L throughput in a full-sized filter). This data is consistent with another study that compared CWF performance with and without Ag^+ application.[6] In disks manufactured with Indonesian and Tanzanian clays, in comparison with the control group, 0.03 mg/g of nAg resulted in a 0.4 and 1.0 LRV improvement, and 0.3 mg/g of nAg resulted in a 1 and 1.7 LRV by day 10 of testing, respectively. Disks made from Indonesian and Tanzanian clays coated with 0.3 mg/g nAg achieved similar LRVs (>4) on day 10 of testing. The application of nAg resulted in a slightly greater improvement in LRV for the Tanzanian disks than the Indonesian disks.

The viable bacteria quantification both on the surface and inside the disks supports and expands upon the LRV results. An increase in silver concentration resulted in reduced viable bacteria retained in disks, and disks with a higher concentration of nAg retained fewer viable bacteria than disks with a higher concentration of Ag^+. The results of this study demonstrated that a silver coating of 0.3 mg/g can reduce, by up to 2 orders of magnitude, the viable bacteria retention in disks. To our knowledge, this is the first study providing quantitative information about viable bacteria retention inside ceramic filter material.

Phase II focused on evaluating the impact of (1) inorganic and organic compounds present in natural water and (2) burn-out materials on silver sorption, bacterial removal, and viable bacteria retained in disks. The silver concentration (0.003 mg/g) used in this phase was selected to minimize the effect of residual silver (silver in the filtrate), either nAg or Ag^+, on bacteria deactivation. At the selected test conditions, a difference was not observed between the clays, burn-out material, or the silver species with the water chemistries evaluated in terms of silver retention, LRV, or concentration of viable bacteria remaining in the disks. This could be due to the low concentration of silver used considering that little impact was seen at this concentration using phosphate-buffered water and several other studies have shown the influence of the chemical characteristics of the solution on nAg aggregate size.[15,25] On the basis of current knowledge about the aggregation of nanoparticles in different electrolyte solutions, water containing a low concentration of divalent ions (soft water) should be used to prepare the silver solution used to coat filters. Additionally, the presence of natural organic matter, such as humic acids, can reduce the antimicrobial properties of nAg as they can interact with the surface of the nanoparticles, reduce silver ion release, and prevent direct contact between the nanoparticles and the bacteria.[29,30]

Recommendations resulting from this research include the following. (1) Factories should use nAg rather than Ag^+ due to better silver retention. Ag^+ is not recommended for filter application as it can lead to silver concentrations that exceed guideline values in filtered water. (2) Factories could increase the nAg concentration to 0.3 mg/g (approximately 640 g/filter) to achieve improved microbiological performance without compromising the quality of filter effluent. (3) Although this study did not show significant differences in terms of performance with water chemistry, evidence from other studies suggest that organic and inorganic compounds present in natural water can affect nAg performance, and therefore, soft water should be used in silver solution preparation.

We recognize that these results and recommendations will have an impact on factories. In some countries, Ag^+ is locally available (however, in some cases, information about quality or concentration may not be available) and significantly cheaper, and in some cases, importing nAg can be a challenge. Therefore, the recommendation to use only nAg and to increase nAg concentration by 10 times the current recommendation will add a cost burden to the manufacturers. The cost of silver nanoparticles from Argenol Laboratorios has increased to €1400.00/kg (70% total silver). Implementing this recommendation would result in an increase in cost from €0.13 to €1.30 per filter. The manufacture of high quality filter material remains important in achieving high performing filters, and while silver application improves bacteriological removal effectiveness, the lower concentrations showed little improvement over disks without silver.

We also note that previous research has not always documented sufficient detail required to compare research results including type of silver, silver concentration, dilution, and throughput water characteristics. In some cases, this may be attributable to a lack of documentation or information about silver type or concentration. Previous research should therefore be compared with caution, and future research should attempt to include these details.

The limitations in this study include the use of a controlled 5.4 L/h flow rate, which is about 2−3 times the flow rate used in the field. This flow rate was selected to achieve throughput equivalent to represent long-term operation within a short period of time. The results could underestimate microbiological performance and either under or overestimate viable bacteria retention due to faster water velocity, constant pressure, and reduced contact time between silver and bacteria. The same filter material subject to a slower (1−3 L/h) flow rate would likely result in similar trends and possibly improved performance.

Extrapolation of results to full-sized filters may be as (1) the volume of water fed through disks was consistent per cm^2, whereas at the household level, continuous exposure to water at different heights in the filter will vary depending upon the pattern of use in each household and (2) if structural or hydraulic differences exist between filter base and sides, the disks are more likely similar to a filter base due to the amount and/or direction of pressure applied during manufacture. The flow rate through filter walls and base, however, is likely comparable as approximately 83% more water flowed through the sides than the bottom of two Nicaraguan experimental filters,[4] and the surface area distribution of a Nicaraguan filter is approximately 81% and 19%, sides and base, respectively.

This study identified several key parameters that require more detailed studies, such as silver concentration, the effects of various influent water characteristics, and the nature of clay and other manufacturing variables. Future studies should measure influent pressure and the hydraulic conductivity of filter material. Further research recommendations include (1) evaluation of higher concentrations of nAg under a selection of water chemistry conditions to evaluate nanoparticle aggregation and silver particle size distribution in filter effluent, (2) evaluate effects of water characteristics separately on silver dilution and filter use (influent solutions), (3) evaluate how silver sorption and LRV are affected by physicochemical interaction between clay and silver species and the physical properties of the porous matrix, (4) carry out a pore-size comparison between disks with and without silver application, (5) investigate the influence of the amount and direction of pressure applied during manufacturing on pore structure and hydraulic properties to better understand whether or how this may influence the extrapolation of results from disks to full-sized filters, (6) characterize the influence of manufacturing variables on pore structure and hydraulic properties, including pore formation resulting from firing temperature, burn-out material size and type, and clay characteristics, and the influence of these variables on filter criteria including flow rate, microbiological removal, and strength, and (7) work toward the identification of indicator(s) to classify and compare filter material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Tables and graphs referred to in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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