# Performance of Silver Nanoparticle-Impregnated Ovoid Ceramic Water Filters

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# Performance of Silver Nanoparticle-Impregnated Ovoid Ceramic Water Filters

Zachary J. Shepard, Elizabeth M. Lux, Vinka A. Oyanedel-Craver*

Department of Civil & Environmental Engineering, University of Rhode Island, 2 East Alumni Ave, Kingston, RI, 02881

KEYWORDS: Ovoid ceramic water filters, silver nanoparticles.

**Environmental Significance Statement:** Ceramic water filters (CWFs) provide a sustainable source of safe drinking water in developing communities around the world. This study explores the performance of a new shape of CWF impregnated with silver nanoparticles in a manner that promotes the sustainable development and use of CWFs.

**Abstract:** A ceramic water filter (CWF) with curved (ovoid) walls has been developed by Potters without Borders, a nonprofit that provides technical assistance to CWF factories. Here, a modified version of the USEPA testing method was used to evaluate the performance of ovoid CWFs, which have yet to be studied in the literature. Filters with/without silver nanoparticles (AgNPs) were evaluated for bacterial removal, turbidity removal, flow rate, and silver leaching. Log removal values (LRVs) for *Escherichia coli* for AgNP coated CWFs were 9.5-10.9 LRV while uncoated achieved 8.0-9.8 LRV. All the CWFs tested here had flow rates between 0.8 and 1.3 L/h. The turbidity of the influent was reduced by the filters throughout the general and challenge water conditions with removal of 9.1-90.9% and 99.3-99.8%, respectively. Silver-coated CWFs had a higher total effluent silver concentration compared to uncoated (coated CWFs had 74% more total silver leaching on average) and had an increased silver release during the challenge phase (35 ppb) compared to the general phase (13 ppb). The exterior wall coated with AgNPs was shown to leach silver off the ceramic using X-ray photoelectron spectroscopy,

providing evidence that supports the recommendation to coat only the interior wall of CWFs with AgNPs. The procedure demonstrated utility as a reproducible performance testing technique. X-ray diffraction and mercury intrusion porosimetry were used to study the ceramic structure.

## Introduction:

Point-of-use (POU) water treatment technologies are recognized for providing low-cost water treatment in developing communities.[1] Ceramic water filters (CWFs) are a type of POU device applied in developing communities because they are manufactured locally, low cost, and provide effective pathogen removal.[2] Many microorganisms are retained/deactivated by CWFs including (but not limited to) *E. coli*[3], *C. parvum*[4], and MS2 bacteriophages[5]. Interventions with CWFs have reduced diarrheal rates in South Africa (80% reduction), Bolivia (75%), and Colombia (60%) by reducing the pathogenic load in drinking water.[2,6,7]

CWF factories have been established across the world with technical assistance provided by Potters without Borders (PWB) and Potters for Peace (PFP), well-established nonprofit organizations.[8,9] The CWF design utilized most widely in the field incorporates impregnated colloidal AgNPs and was developed by Dr. Fernando Mazariegos in Guatemala, 1981.[10,11] CWFs are manufactured from locally sourced materials (clay, sawdust, and water) and local infrastructure (kilns, mills, hydraulic presses).[10,12] Water is added to a mixture of clay and burnout material (usually sawdust or rice husks) and filters are press-formed from this mixture using a mold.[10,12] After molding, the filters are air dried and fired in a kiln, where peak temperatures can vary from 600-1000°C depending on the clay/burnout material.[3,10,12] Finally, the CWFs are coated with AgNPs or silver nitrate ($AgNO_3$), which prevent biofilm growth and provide residual disinfection.[10,12,13] Coating with AgNPs increases long term performance compared to $AgNO_3$, but is higher cost and difficult to purchase in developing communities.[12–14]

The primary mechanism for microbiological removal in CWFs is mechanical filtration; microorganisms are removed from the throughput when they are trapped on the surface and within the matrix of the ceramic.[4,5,15–18] Microorganisms are trapped by the small (1-5 μm in diameter) and tortuous pores of the ceramic matrix.[3,18,19] The second mechanism is inactivation with silver compounds, usually AgNPs. The inactivation of microorganisms using AgNPs is expressed through several mechanisms.[20] AgNPs release silver ions that target DNA and interfere with replication.[20] The nanoparticle form physically disrupts the cell membrane and produces reactive oxygen species at the surface of the organism.[20] While most of the silver released from AgNP-coated CWFs is in the dissolved form, there is evidence in the literature supporting the contribution of both ion and nanoparticle in the inactivation of microorganisms.[16,20]

According to PWB and PFP, there are about 40 CWF filter factories established in developing communities worldwide.[8,9] The geometry of the filter varies depending on where the filter was manufactured.[10] The new shape developed by PWB has curved (ovoid) walls, a flat bottom, and can hold 10L of water.[10] Ovoid CWFs are designed with a thicker wall cross section than a straight-walled filter.[21] The increased wall thickness could improve the durability and microbial removal of the CWF by increasing the length of the pores. Removal from the mold is easier because the ceramics can be inverted and dropped onto their lips instead of being pushed out of the bottom, which could reduce cracking and warping during production.[21]

Here, we utilize a modified version of the USEPA *Guide Standard and Protocol for Testing Microbiological Water Purifiers* in the performance assessment of ovoid CWFs.[22] While this standard operating procedure (SOP) has been available since 1987, to our knowledge it has not been used in the study of CWF performance. One study that evaluated CWFs did utilize the challenge water chemistry, but not the sampling schedule or the other influent chemistries of the EPA standard.[23] The World Health Organization (WHO) has also produced a performance assessment that is based on the EPA procedure.[24] One previous study used the WHO challenge water phase for testing CWF performance.[25]

The objective of this study was to characterize the performance (using a standardized performance assessment) and structure of the CWFs provided by PWB. The performance of the CWFs will be analyzed in terms of bacterial removal, turbidity reduction, flow rate, and silver leaching. The main objective of the structural characterization was to determine the fate of silver nanoparticles within the ceramic matrix. X ray photoelectron spectroscopy was applied to CWFs for the first time in this study. The minerology and pore size distribution of the ovoid CWFs were also studied during the characterization phase.

## Experimental:

The CWFs used in this study were manufactured by PWB using a mix of commercial clays (see Table S1, Supplemental Information, for details) and sawdust from a milled hardwood pellet. The firing temperature for these CWFs was 900-925°C, which is hotter than usual for the PWB factory (usually 885-900°C depending on the clay/burnout mix).[21] The ovoid CWFs were fired using a pitet kiln setter which guarantees consistent air flow during the firing process and greater removal of carbon from burnout materials.[21] Pitet setters are interlocking cones that bear the weight of the CWF during firing.[21] The use of these setters increases the number of ovoid filters that can be fired in a single run by 30%.[21]

Four CWFs (used directly after manufacturing) with the new wall shape were evaluated using a modified version of the EPA protocol. Two of the filters were coated with 0.3 g AgNPs (roughly 0.2 g on the interior surface and 0.1 g on the exterior surface) and two were uncoated. The colloidal AgNPs used to coat the filters were Colargol produced by Argenol (Spain). Colargol silver nanoparticles are synthetized using a radiation method and are stabilized with casein (70-75% silver content).[26,27] These commercial nanoparticles are popular in the manufacture of CWFs and have been characterized in previous studies.[10,16,18,28–31] They have a surface charge ranging from -20 to -26 mV.[29,32,33] The hydrodynamic diameter of casein coated AgNPs has been measured with dynamic light scattering and ranges from 45 to 105 nm.[16,29,33,34] The surface charge and hydrodynamic diameter values are based on AgNPs in National Sanitation Foundation challenge water (pH 6.5 with 1.5 g/L sea salts), collected surface and ground water, and deionized water. TEM measurements have shown that these nanoparticles have a diameter between 7-15 nm.[18,29,30] CWFs manufactured for this study were made using between 17-21% wt. sawdust that was screened using a sieve with 595 and 250 µm openings (manufacturing details in SI).

*Performance testing*

EPA *Guide Standard and Protocol for Testing Microbiological Water Purifiers* dictates a 13 day testing period with three phases (general, challenge, and leaching) defined by the influent solution.[22] Table 1 contains the EPA requirements for the influent solutions required for each phase. Table S2 contains amounts of the reagents that were added to deionized water in order to meet the requirements in Table 1. The materials required for the influent water were purchased from Fisher Scientific and used as received. The temperature requirements of the EPA protocol (listed in Table 1) could not be met because of the large volume of influent required each day for testing. All of the solutions were prepared at room temperature (20-25°C). The influent water for the general and challenge phases was spiked with $10^{10}$ CFU/100mL *E. coli* K12 (ATCC 23716). Fresh cultured bacteria was added daily to the influent. The bacteria stock solution preparation and quantification were performed following methodology previously published.[35] The leaching phase is the final phase of the experiment (Days 12 and 13), designed so that researchers can ensure that excessive amounts of silver are not released from the CWF.[22] Before the beginning of the leaching phase, the CWFs were cleaned by scrubbing with a soft brush and backwashing with a solution containing 10 mM $NaNO_3$, which is has been shown to minimize the release of silver from the nanoparticles on the ceramic.[16]

**Table 1.** EPA Requirements and Inputs for Influent Solutions.

| | General (Days 1-6) | Challenge (Days 7-11) | Leaching (Days 12-13) |
|---|---|---|---|
| pH | 6.5-8.5 | 8.8-9.2 | 4.8-5.2 |
| Total Organic Carbon (mg/L) | 0.1-5.0 | >10 | 1.0 |
| Turbidity (NTU) | 0.1-5.0 | >30 | 0.1-5 |
| Temperature (°C) | 20 | 4 | 20 |
| Total Dissolved Solids (mg/L) | 50-500 | 1350-1600 | 100 |

CWF performance was determined in terms of bacterial removal, turbidity reduction, flow rate, and silver leaching. Flow rate and turbidity measurements are not required by the EPA protocol, but were performed in addition to EPA testing. CWFs are used to remove turbidity from water as well as microorganisms and flow rate measurements are a standard measure of quality control in CWF factories.[3,10,12,36] A total of 19 L of the influent solution was filtered in each filter each day. The influent addition was performed in four steps: first, 10 L were added during the morning, then 3 L at three hour intervals throughout the day. The level to which the filters were filled with influent solution during the experiment was kept constant throughout the testing. Samples for bacteria and turbidity determination and flow rate measurements were collected three times on the first day and once a day for the rest of the testing from the plastic buckets underneath the CWFs (Figure S1). Flow rate was calculated after the CWFs had been filled the second time. Sampling more frequently on the first day of testing captures the changing performance of the filter during start up. In this schedule, samples were acquired more frequently than required by the EPA protocol. The EPA protocol also requires samplings after 48 hours of stagnation, which was not possible in this case because filtration in the CWFs cannot be stopped.[22]

Bacterial concentrations were determined *via* membrane filtration and incubation with Millipore Sigma m-FC broth and rosolic acid overnight at 44.5°C. Colonies of bacteria were counted and results were reported as colony forming units per 100 milliliters (CFU/100 mL).[34,35] This methodology for bacterial culture and counting is allowed in the *Guide Standard and Protocol* (Section 3.4.1.1).[22] Turbidity was measured using a Hach Turbidimeter and reported in nephelometric turbidity units (NTU). Samples taken for silver concentration were stored in the refrigerator (or freezer for long term storage) in light proof containers until they were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) with a Thermo X series 2 quadrupole ICP-MS using a Nd-YAG laser ablation system. Effluent samples from days 4, 6, 8, and 13 were filtered using Amicon Ultracel Centrifugal Filters with a pore size of 3 kDa (UFC800324) in order to separate AgNPs and $Ag^+$. The concentration of silver in the filtered and unfiltered samples was analyzed *via* ICP-MS. Due to the high chloride concentrations in the throughput matrix, ICP-MS samples were acidified to 10% with hydrochloric acid before analysis.[37] Statistical significance was determined throughout performance testing using the Wilcoxon rank sum test, which allows the determination of statistical significance in smaller data sets.[38]

*Characterization of ceramic matrix*

Ceramic characterization was performed by analyzing the CWFs in terms of minerology (X ray diffraction, XRD), pore size distribution (mercury intrusion porosimetry, MIP), and distribution of AgNPs within the ceramic matrix (X-ray photoelectron spectroscopy, XPS). XRD analysis was performed on an Olympus Terra XRD between 2-theta angles of 5 and 55. The Olympus Terra XRD has an energy resolution of 200 eV and can detect minerals present at 1% of the sample.[39,40] Peaks acquired during testing were compared to reference peaks using XPowder software. MIP analysis was performed on an unused CWF with a Quantachrome PoreMaster *GT* series (0.2-60,000 psi). Samples (n=2) were taken from the bottom and at intervals up the wall of the filter. Pore size distributions were determined by calculating the size fractions as a percentage of the total volume of mercury intruded into the sample. Cross sectional pieces of the wall of used and unused silver coated and uncoated CWFs were analyzed to study the fate of AgNPs in the ceramic matrix with a Thermo Scientific K-Alpha XPS using an Al Kα source. Additional CWFs that were not used in the experiment and were specifically used for imaging supplied the samples from unused filters. XPS spectra were acquired from 380 to 360 eV at 300 μm intervals across the cross section. The presence of silver was indicated by peaks that appear at approximately 367 eV and 373 eV on the XPS spectra.[41]

## Results and discussion:

*Performance Analysis*

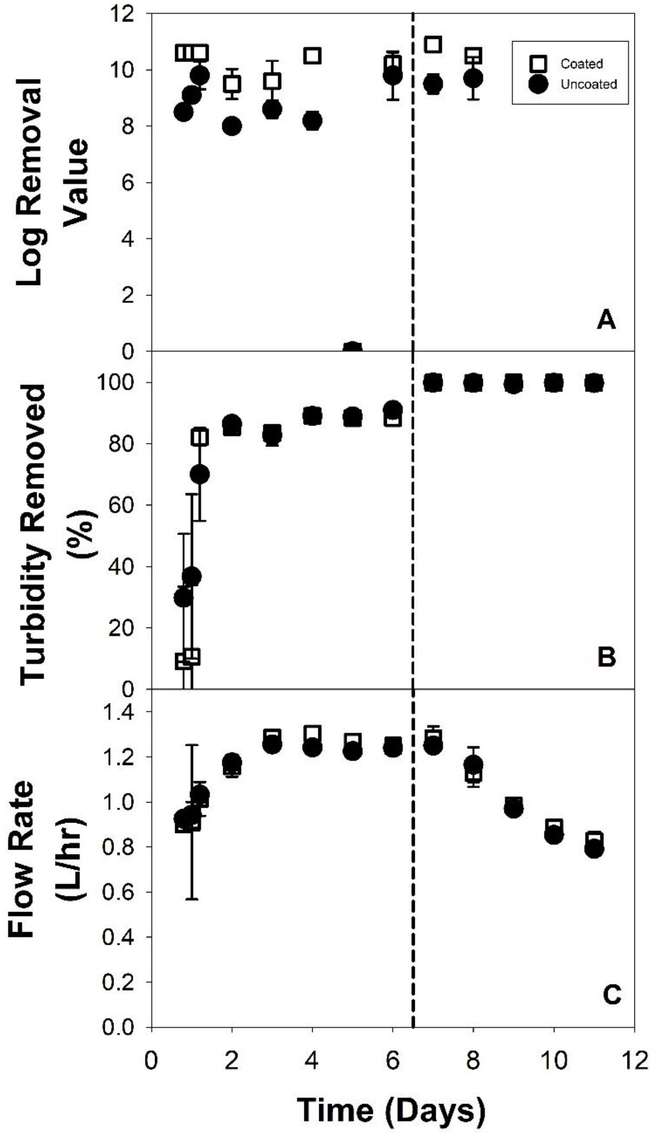

**Figure 1.** CWF performance data. (A) Removal of *E. coli* K12 (B) Turbidity removal (C) Flow rate. White squares are silver coated and black circles are uncoated. The vertical line marks the start of the challenge phase of testing. Error bars are standard error and points represent the average performance (n=2).

Figure 1A presents the LRVs for silver coated and uncoated ovoid CWFs. The silver coated filters had a higher *E. coli* removal than the uncoated filters ($p<0.01$). Previous studies have also reported that the presence of AgNPs increases bacterial removal.[3,5,15] The performance of the uncoated filters slowly improved during the first day of testing. Previous studies have also shown changes in LRV during the startup CWFs; however these experiments had a higher LRV at the beginning that decreased over time.[14,29] The decrease in performance was shown in ceramic disks, which could behave differently during startup compared to fully scale CWFs. Overall, the log removal values obtained in this study were higher than those reported in previous studies.[3,4,42] There have been many studies on CWFs in the literature, but, in general, LRVs for *E. coli* range between 1.0 and 6.0.[3,18,25,43] Reasons that the LRVs measured here are higher than in previous studies include: influent chemistry (specifically the concentration of bacteria and turbidity) and the construction of the CWF. The concentration of bacteria utilized in this study ($10^{10}$ CFU/100 mL) was higher than concentrations reported in previous studies, which Brown *et al* has correlated to larger LRVs.[44] With regard to the turbidity in the influent, high turbidity clogs the pores of CWFs and leads to higher removal rates of viruses and bacteria by improving size exclusion.[42,45]

The CWFs used in this study were made with higher purity materials than CWFs manufactured in the field. PWB utilized a commercial clay for the filters they provided, which have a smaller particle size than clays sourced locally to CWF factories.[3] This smaller particle size leads to a higher LRV.[3] The burnout material used in manufacturing these filters could also affect performance. Burnout materials with smaller grain sizes leave smaller pores when incinerated during firing, leading to a higher LRV.[4,4618,42] Previous reports indicate that most CWF factories in the field utilize a sieve with a pore size larger than 595 μm.[10,28] The ovoid CWFs also have a thicker cross wall compared to previous styles of filters.[8] A thicker wall allows greater opportunity for microorganisms to adsorb to the ceramic or sediment within the tortuous pores of the ceramic.[12,19] Differences in influent solution and CWF construction techniques between studies makes it difficult to compare quantitative values with previous studies, however the higher LRVs reported here can be related to trends in influent and material characteristics seen in other studies.[3,5,15]

The microbiological removal testing lasted for 8 days instead of the full 11 days of the EPA test. This is because of an incubator malfunction that left us without microbiological removal data on the last three days. We could not redo the testing because our only available filters had already been used. On Day 5 of the testing, an incubator malfunction prevented the proper enumeration of bacteria in the influent of the filters. One of the other limitations of this study is in the decay that bacteria can experience in solutions with a reduced ionic strength. Previous studies have used influent solutions of this style before and Sullivan *et al* demonstrated that their solution, which had a similar ionic strength to the challenge influent and contained toxic heavy metals, had a 10% decrease in *E. coli* viability.[13,14,29,42,47] Based on this information, the decay of the bacteria in the influent solutions used here was assumed to be negligible. All the CWFs studied here were exposed to the same influent solutions, so, even if the bacteria experienced some osmotic shock, the coated CWFs still had a significantly higher LRV compared to the uncoated.

The reduction of turbidity by the filters can be found in Figure 1B. There was no significant difference between the removal of turbidity by the silver coated and uncoated CWFs ($p$=0.82). Physical filtration is the main mechanism to remove particulates in CWFs.[4,15] In CWFs, physical filtration is a function of the porosity and tortuosity of the ceramic matrix, not of the AgNPs, which is why coated and uncoated CWFs have similar effluent turbidities.[5] The influent turbidities reported during the general phase fall within the range in the literature, 0 to 60 NTU.[2,15,25,43,48] Some studies did not report the turbidity of their influent solutions, demonstrating the need for a more consistent testing and reporting procedure.[5,30] The challenge water turbidity (160-240 NTU) was much higher than prior studies. The effluent turbidity data presented here are within the established range of effluent turbidities reported in the literature which are usually between 0.09 and 27 NTU.[18,25,49] Removal of turbidity ranged from 9% during startup to 99% during the challenge water phase. The lower removal during start up could have originated from the filters, which were not flushed before use. Ashes or loose clay from the filter could have briefly increased the effluent turbidity. The turbidity of the throughput can affect the performance of a CWF by clogging pores and restricting water flow.[45,50] While pore clogging has negative effects (such as a reduction in flow rate), it also improves the removal of microorganisms.[42,45]

The flow rates of the sets of silver coated and uncoated CWFs displayed in Figure 1C were not significantly different throughout the testing ($p$=0.69). Over the first few days of use, the flow rate increases steadily until the filter becomes saturated and the rate stabilizes. Previous studies have reported a similar phenomenon, soaking their ceramics to achieve a consistent flow rate.[50] During the operation of the filters in the general water phase, the flow rates were within the range established in the literature: 1-5 L/hr.[12] This range was developed because of the relationship between the flow rate of a CWF and LRV.[10] Flow rate is a function of the porosity of the ceramic matrix; a CWF with larger pores will have a higher flow rate. Less bacteria are retained in a CWF with larger pores, so less bacteria are retained on a filter with a higher flow rate.[3] Flow rate could also directly influence some of the mechanisms (adsorption, diffusion, and sedimentation) that are involved in microbial removal because it affects the interaction with the ceramic matrix.[10,19]

The concentration of total silver in the influent and effluent of the CWFs in this study can be found in Figure 2A. The silver released into the effluent of the CWFs was never above the

WHO guideline for silver consumption (100 ppb).[51] Day 3 represents the concentration of silver released into the effluent during the general phase of testing, Day 7 is from the challenge phase, and Days 12 and 13 are the leaching phase. The concentration of total silver in the effluent of the coated CWFs was significantly larger than the concentration in the uncoated CWFs ($p$<0.01) and the influent ($p$<0.01). Total silver concentrations in the effluent of the uncoated CWFs were the same as the influent concentrations ($p$=0.60). The spike in total silver release during Day 7 is most likely due to the increase in salt concentration and turbidity of the influent during the challenge water phase.[16] Day 7 has a higher effluent total silver concentration than either of the leaching phase days (12 and 13). The leaching phase was meant to increase silver release, so there should have been a higher effluent silver concentration in this phase compared to others.[22] The water chemistry of the leaching phase is one reason that the silver release is higher during the challenge phase. Influent solutions with a higher turbidity and total dissolved solids (such as the challenge water solution) promote silver release from CWFs.[16,30] Another reason for the low release during the leaching phase could have been the use of the filters in the challenge water phase. The CWFs utilized in the leaching test had undergone challenge water testing which has a higher concentration of clay in the influent. This clay could have prevented the release of silver from the filters. The CWFs were also cleaned in order to prepare them for the leaching phase. It is possible that the cleaning removed some of the silver and reduced the effluent silver concentrations.

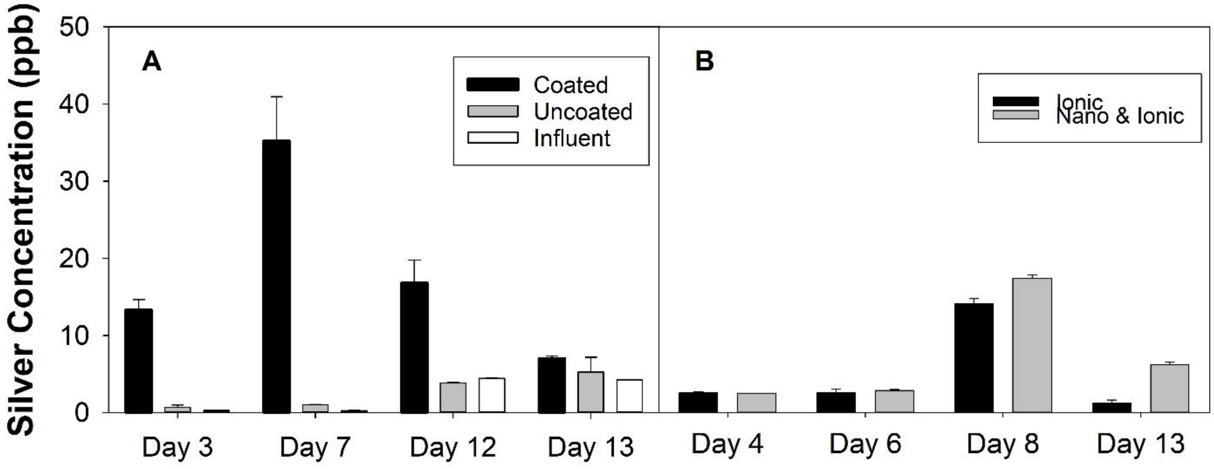

**Figure 2.** (A) Total silver concentration (B) Nano vs. ionic silver concentration. In 2A, black bars are silver coated filters, light gray bars are uncoated, and white bars represent the concentration of silver in the influent. In 2B, black bars are the concentration of ionic silver in the effluent and gray bars are the concentration of nanoparticle and ionic silver. Error bars for both are standard deviation (n=2).

Samples (n=2) from Days 4, 6, 8, and 13 were filtered using 3 kDa centrifugal filters and analyzed *via* ICP-MS to determine whether the silver in the effluent was in nanoparticle or ionic form (Figure 2B). AgNPs were retained on the 3 kDa filter while ionic silver passed through it. The concentration of silver in the filtered samples was not significantly different from the concentration of silver in the unfiltered samples ($p$=0.43). This indicates that most of the silver in the effluent was in the ionic form. Previous studies have shown the higher concentration of dissolved silver compared to the nanoparticle phase.[16] Figure 2B shows that the percentage of ionic silver as a proportion of total silver varies between Day 8 and Day 13. This change stems from the change in ionic strength of the influent solutions between the challenge and leaching phases. Negatively charged nanoparticles, such as the AgNPs used here, detach from quartz in transport columns due to a decrease in the ionic strength of the throughput.[16,52,53] The challenge influent had a higher ionic strength than the leaching influent and the main mineral in the CWFs studied here was determined to be quartz (see characterization section for more details). This decrease in ionic strength could have led to a greater elution of silver nanoparticles, which changed the ratio of ionic to total silver between days 8 and 13.

X ray photoelectron spectroscopy (XPS) was used to determine the fate of the AgNPs painted on the surface of the ceramic filters. Cross sectional pieces of the wall from used and unused CWFs were analyzed using this technique. The used samples had undergone the performance assessment described within this paper. XPS spectra were acquired at 300 µm intervals over the entire cross section. Selected XPS spectra acquired in this analysis can be found in Figures 3 and S2. XPS analysis of a silver-coated, unused CWF (Figure S2A) indicates surface layers that are 2419 µm and 1512 µm deep on the interior and exterior, respectively, of the CWF wall. These results agree with information provided by the manufacturer and previous studies. PWB applies most of the colloidal silver to the interior of the filters.[21] One previous study used EDS SEM to show that silver tends to segregate to a 50-180 µm surface layer in unused ceramic filters.[54] A cross section of a silver coated filter that had been used in the performance assessment showed silver peaks for the first 1524 µm on the interior side and a band of silver in the middle of the ceramic wall from 10368 to 11283 µm. Figure 3 shows a selection of the spectra that were collected from the used, silver coated cross section. The peaks in Figure 3A and C indicate the presence of silver nanoparticles with peaks at 367 eV and 373 eV. The band of silver was located in the middle of the cross section and was much more concentrated than the other bands. The silver peaks from this band were much more clearly defined than the other peaks (Figure 3C). The band on the exterior surface layer was missing from the sample from the used CWF (Figure 3D). This was most likely washed away during testing and cleaning. This result is supported by a prior study by Mittelman *et al,* which demonstrated that the initial elution of silver comes primarily from the exterior surface of the CWF.[16] The elution of silver from the exterior surface indicates that manufacturers may be able to skip this step of the process. CWFs with an AgNP coating on the interior of the CWF may be just as effective as those with both interior and exterior surface coatings. Uncoated CWFs (both used and unused) did not indicate the presence of silver.

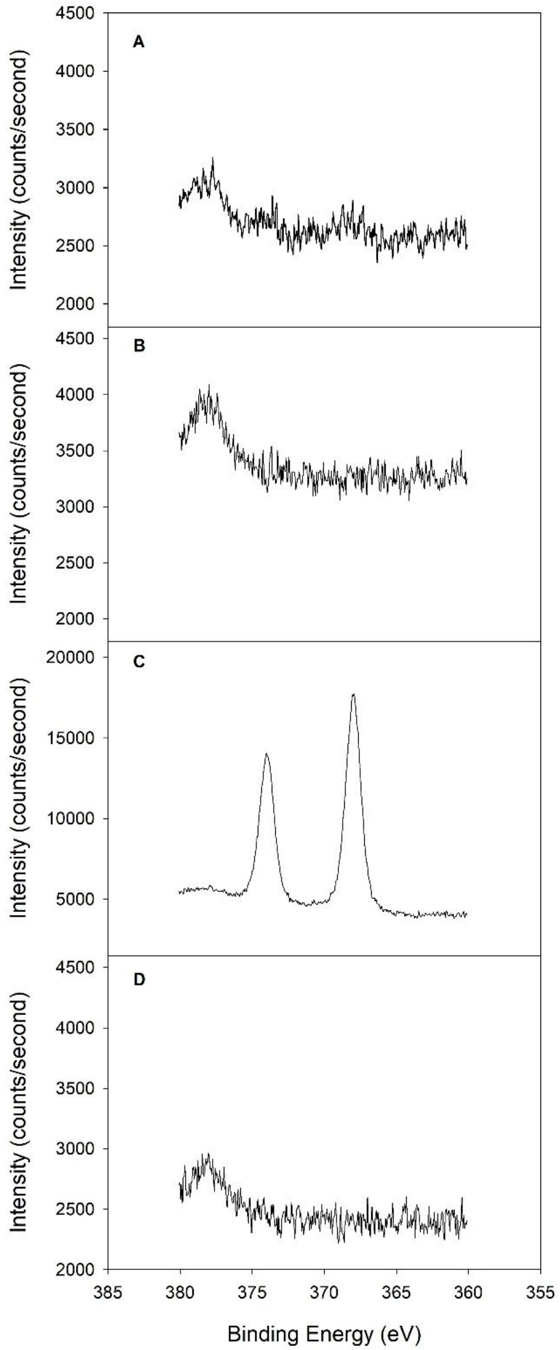

**Figure 3.** Sequence of XPS spectra from a used CWF with an AgNP coating. Panels are spectra acquired at (A) 600 µm (B) 3300 µm (C) 10700 µm (D) 13400 µm from the interior surface of the CWF. A schematic version of this plot as well as the schematics from the other samples can be found in SI.

*Ceramic Characterization*

XRD results showed that the main mineral in the CWF was quartz ($SiO_2$). Our results agree with previous research, which has shown that the main mineral in most CWFs is quartz, regardless of where the clay is mined.[27] Other minerals found in the CWFs studied here include: muscovite ($KAl_2(SiAlO_{10})(OH)_2$), hematite ($Fe_2O_3$), and albite ($NaAlSi_3O_8$). Illites are hydrated muscovite and incorporation of this class of clay minerals imparts a high flexural strength to CWFs.[27] Clays enhanced with hematite have an increased sorption of bacteriophages in small scale, batch adsorption testing and the presence of albite in the CWF matrix can affect the sorption of AgNPs.[27,55] Albite has a negative surface charge that adsorbs cations, which, in turn, attract AgNPs.[27] The XRD results show that the CWFs studied here are made using a more highly purified type of clay than would normally be found in the field. As mentioned previously, CWFs made with more highly purified clays are more effective at removing microorganisms.[3] CWF factories usually utilize locally sourced, low purity clays.

The pore size distribution of a CWF is an important parameter because size exclusion is one of the two main mechanisms by which bacteria are removed from the influent.[2,4] Filters with smaller pores have been shown to remove more bacteria than those with larger pores.[3] Pore sizes are affected by a number of variables including the type and quantity of burnout material and the particle size of the clay.[3,18] Figure S3 shows that most of the pores in the CWFs are less than 2 μm in diameter, which is in the size range of bacteria that are removed by CWFs. The pore size distributions measured here are similar to those that have been established in the literature and do not vary greatly as a function of wall height.[3,11,18,19] 80% of the pores in the CWF were less than 5 μm in diameter, which is similar to the 75% pore fraction previously established for Red Art ceramic filters.[3] Red Art ceramic filters are made of Red Art clay, which is a commercial clay blend with a very narrow grain size distribution. CWFs and ceramic disks made with Red Art clay have been used as control samples in many studies.[3,14,29,56] Table S3 presents the average pore diameters (1.87 to 2.56 µm) of the samples taken from an unused CWF.

## Conclusion:

The first objective of this study was to analyze the performance of ovoid CWFs as designed and manufactured by PWB. The ovoid CWFs produced by PWB exhibit a greater removal of *E. coli* compared to previously studied models. The flow rates were within the appropriate range and the turbidity was reduced drastically by the filters. Silver leaching never exceeded the WHO standards during the testing of the filters. The XPS characterization demonstrated the distribution of silver nanoparticles through the matrix of the CWF. The exterior surface coating of AgNPs leached off of the CWF, indicating that this coating could be eliminated from the CWF without diminishing the performance of the filter. A modified version of the USEPA *Guide Standard and Protocol for Testing Microbiological Water Purifiers* was used to analyze the performance of the ovoid CWFs. The consistency of this performance assessment would allow researchers to build up a body of knowledge that could be used to target improvements in manufacturing. The characterization data was able to describe the mineralogical composition and pore size distribution, which informed the mechanisms involved in the microbiological removal of the CWFs.

## Supporting Information:

Supplementary images, procedure details, and data can be found online.

## Corresponding Author:

* Dr. Vinka Oyanedel-Craver: craver@uri.edu.

## Conflicts of Interest:

There are no conflicts of interest to declare.

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References:

1 D. Ren, L. M. Colosi and J. A. Smith, Evaluating the sustainability of ceramic filters for point-of-use drinking water treatment, *Environ. Sci. Technol.*, 2013, **47**, 11206–11213.

2 L. S. Abebe, J. A. Smith, S. Narkiewicz, V. Oyanedel-Craver, M. Conaway, A. Singo, S. Amidou, P. Mojapelo, J. Brant and R. Dillingham, Ceramic water filters impregnated with silver nanoparticles as a point-of-use water-treatment intervention for HIV-positive individuals in Limpopo Province, South Africa: A pilot study of technological performance and human health benefits, *J. Water Health*, 2014, **12**, 288–300.

3 V. A. Oyanedel-Craver and J. A. Smith, Sustainable colloidal-silver-impregnated ceramic filter for point-of-use water treatment, *Environ. Sci. Technol.*, 2008, **42**, 927–933.

4 L. S. Abebe, Y. Su, R. L. Guerrant, N. S. Swami and J. A. Smith, Point-of-Use Removal of Cryptosporidium parvum from Water: Independent Effects of Disinfection by Silver Nanoparticles and Silver Ions and by Physical Filtration in Ceramic Porous Media, *Environ. Sci. Technol.*, 2015, **49**, 12958–12967.

5 H. Van der Laan, D. van Halem, P. W. M. H. Smeets, A. I. A. Soppe, J. Kroesbergen, G. Wubbels, J. Nederstigt, I. Gensburger and S. G. J. Heijman, Bacteria and virus removal effectiveness of ceramic pot filters with different silver applications in a long term experiment, *Water Res.*, 2014, **51**, 47–54.

6 T. F. Clasen, J. Brown, S. Collin, O. Suntura and S. Cairncross, 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**, 651–657.

7 T. Clasen, G. Garcia Parra, S. Boisson and S. Collin, Household-based ceramic water filters for the prevention of diarrhea: A randomized, controlled trial of a pilot program in Colombia, *Am. J. Trop. Med. Hyg.*, 2005, **73**, 790–795.

8 B. Cohen, Potters Without Borders, http://www.potterswithoutborders.com/aboutus-2/, (accessed 3 September 2018).

9 J. Mally, Potters for Peace, https://pottersforpeace.org/?page_id=8, (accessed 2 May 2019).

10 The Ceramics Manufacturing Working Group, *Best Practice Recommendations for Local Manufacturing of Ceramic Pot Filters for Household Water Treatment*, Atlanta, GA, 2011.

11 D. S. Lantagne, *Investigation of the Potters for Peace Colloidal Silver Impregnated Ceramic Filter Report 1: Intrinsic Effectiveness*, Allston, MA, USA, 2001.

12 J. Rayner, B. Skinner and D. Lantagne, Current practices in manufacturing locally-made ceramic pot filters for water treatment in developing countries, *J. Water Sanit. Hyg. Dev.*, 2013, **3**, 252–261.

13 J. Rayner, H. Zhang, J. Schubert, P. Lennon, D. Lantagne and V. Oyanedel-Craver, 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, *ACS Sustain. Chem. Eng.*, 2013, **1**, 737–745.

14 K. N. Jackson and J. A. Smith, A New Method for the Deposition of Metallic Silver on Porous Ceramic Water Filters, *J. Nanotechnol.*, 2018, 1–9.

15 J. Brown and M. D. Sobsey, Microbiological effectiveness of locally produced ceramic filters for drinking water treatment in Cambodia, *J. Water Health*, 2010, **8**, 1–10.

16 A. M. Mittelman, D. S. Lantagne, J. Rayner and K. D. Pennell, Silver Dissolution and Release from Ceramic Water Filters, *Environ. Sci. Technol.*, 2015, **49**, 8515–8522.

17 J. Huang, G. Huang, C. An, Y. He, Y. Yao, P. Zhang and J. Shen, Performance of ceramic disk filter coated with nano ZnO for removing Escherichia coli from water in small rural and remote communities of developing regions, *Environ. Pollut.*, 2018, **238**, 52–62.

18 E. N. Kallman, V. A. Oyanedel-Craver and J. A. Smith, Ceramic Filters Impregnated with Silver Nanoparticles for Point-of-Use Water Treatment in Rural Guatemala, *J. Environ. Eng.*, 2011, **137**, 407–415.

19 D. van Halem, Delft University of Technology, 2006.

20 L. M. Stabryla, K. A. Johnston, J. E. Millstone and L. M. Gilbertson, Emerging investigator series: It's not all about the ion: Support for particle-specific contributions to silver nanoparticle antimicrobial activity, *Environ. Sci. Nano*, 2018, **5**, 2047–2068.

21 Personal communication with Burt Cohen, Potters without Borders.

22 S. A. Schaub, C. Gerba, R. Tobin and F. A. Bell, *Guide Standard and Protocol for Testing Microbiological Water Purifiers*, 1987.

23 A. Pérez-Vidal, J. Diaz-Gómez, J. Castellanos-Rozo, O. L. Usaquen-Perilla, A. Perez-Vidal, J. Diaz-Gómez, J. Castellanos-Rozo and O. L. Usaquen-Perilla, Long-term evaluation of the performance of four point-of-use water filters, *Water Res.*, 2016, **98**, 176–182.

24 World Health Organization, *General Testing Protocol #6: Ceramic Pot Gravity Flow Mechanical Filtration Batch System Technology (with and without a silver component)*, Geneva, 2014.

25 K. J. Lucier, S. E. Dickson-Anderson and C. J. Schuster-Wallace, Effectiveness of silver and copper infused ceramic drinking water filters in reducing microbiological contaminants, *J. Water Supply Res. Technol. - AQUA*, 2017, **66**, 528–536.

26 Potters without Borders, 2018, 1–2.

27 V. Oyanedel-Craver, S. Narkiewicz, R. Genovesi, A. Bradshaw and D. Cardace, Effect of local materials on the silver sorption and strength of ceramic water filters, *J. Environ. Chem. Eng.*, 2014, **2**, 841–848.

28 J. Rayner, Loughborough University, 2009.

29 R. K. Sullivan, M. Erickson and V. A. Oyanedel-Craver, Understanding the microbiological, organic and inorganic contaminant removal capacity of ceramic water filters doped with different silver nanoparticles, *Environ. Sci. Nano*, 2017, **4**, 2348–2355.

30 A. M. Mikelonis, D. F. Lawler and P. Passalacqua, Multilevel modeling of retention and disinfection efficacy of silver nanoparticles on ceramic water filters, *Sci. Total Environ.*, 2016, **566**–**567**, 368–377.

31 H. Zhang, V. Oyanedel-craver and A. M. Asce, Evaluation of the Disinfectant Performance of Silver Nanoparticles in Different Evaluation of the Disinfectant Performance of Silver Nanoparticles in Different Water Chemistry Conditions, *J. Environ. Eng.*, , DOI:10.1061/(ASCE)EE.1943-7870.0000460.

32 F. Faghihzadeh, N. M. Anaya, C. Astudillo-Castro and V. A. Oyanedel-Craver, Kinetic, metabolic and macromolecular response of bacteria to chronic nanoparticle exposure in continuous culture, *Environ. Sci. Nano*, 2018, **5**, 1386–1396.

33 H. Zhang, V. A. Oyanedel-Craver and J. A. Smith, The effect of natural water conditions on the anti-bacterial performance and stability of silver nanoparticles capped with different polymers, *Water Res.*, 2012, **46**, 691–699.

34 N. M. Anaya, F. Faghihzadeh, N. Ganji, G. Bothun and V. Oyanedel-Craver, Comparative study between chemostat and batch reactors to quantify membrane permeability changes on bacteria exposed to silver nanoparticles, *Sci. Total Environ.*, 2015, **565**, 841–848.

35 US EPA, *Method 1604: Total Coliforms and Escherichia coli in Water by Membrane Filtration Using a Simultaneous Detection Technique (MI Medium)*, Washington, DC, 2002.

36 M. du Preez, R. M. Conroy, J. A. Wright, S. Moyo, N. Potgieter and S. W. Gundry, Short Report: Use of Ceramic Water Filtration in the Prevention of Diarrheal Disease: A Randomized Controlled Trial in Rural South Africa and Zimbabwe, *Am. J. Trop. Med. Hyg.*, 2008, **79**, 696–701.

37 P. Gaines, Common Problems with Ag, As, S, Ba,, Pb, and Cr, https://www.inorganicventures.com/common-problems-ag-s-ba-pb-and-cr, (accessed 19 December 2018).

38 P. D. Bridge and S. S. Sawilowsky, Increasing Physicians' Awareness of the Impact of Statistics on Research Outcomes: Comparative Power of the t-test and Wilcoxon Rank-

Sum Test in Small Samples Applied Research, *J. Clin. Epidemiol.*, 1999, **52**, 229–235.

39 Olympus Corporation, Terra Portable XRD, https://www.olympus-ims.com/en/xrf-xrd/mobile-benchtop-xrd/terra/, (accessed 31 May 2019).

40 D. Blake, D. Vaniman, C. Achilles, R. Anderson, D. Bish, T. Bristow, C. Chen, S. Chipera, J. Crisp, D. Des Marais, R. T. Downs, J. Farmer, S. Feldman, M. Fonda, M. Gailhanou, H. Ma, D. W. Ming, R. V. Morris, P. Sarrazin, E. Stolper, A. Treiman and A. Yen, Characterization and calibration of the CheMin mineralogical instrument on Mars Science Laboratory, *Space Sci. Rev.*, 2012, **170**, 341–399.

41 A. Zielińska, E. Kowalska, J. W. Sobczak, I. Łacka, M. Gazda, B. Ohtani, J. Hupka and A. Zaleska, Silver-doped TiO2 prepared by microemulsion method: Surface properties, bio- and photoactivity, *Sep. Purif. Technol.*, 2010, **72**, 309–318.

42 D. van Halem, H. van der Laan, A. I. A. Soppe and S. G. J. Heijman, High flow ceramic pot filters, *Water Res.*, 2017, **124**, 398–406.

43 D. Lantagne, M. Klarman, A. Mayer, K. Preston, J. Napotnik and K. Jellison, Effect of production variables on microbiological removal in locally-produced ceramic filters for household water treatment, *Int. J. Environ. Health Res.*, 2010, **20**, 171–187.

44 D. Brown, C. Farrow, E. A. McBean, B. Gharabaghi and J. Beauchamp, Advancing performance evaluation standards for household water treatment technologies, *J. Water Health*, 2019, **17**, 266–273.

45 H. Salsali, E. McBean and J. Brunsting, Virus removal efficiency of Cambodian ceramic pot water purifiers, *J. Water Health*, 2011, **9**, 306–311.

46 J. Rayner, X. Luo, J. Schubert, P. Lennon, K. Jellison and D. Lantagne, The effects of input materials on ceramic water filter efficacy for household drinking water treatment, *Water Sci. Technol. Water Supply*, 2017, **17**, 859–869.

47 A. R. Bielefeldt, K. Kowalski and R. S. Summers, Bacterial treatment effectiveness of point-of-use ceramic water filters, *Water Res.*, 2009, **43**, 3559–3565.

48 J. Brown, M. Sobsey and S. Proum, *Use of Ceramic Water Filters in Cambodia*, 2007.

49 C. Salvinelli, A. C. Elmore, B. R. García Hernandez and K. D. Drake, Ceramic pot filters lifetime study in coastal Guatemala, *J. Water Health*, 2017, **15**, 145–154.

50 C. Salvinelli, A. C. Elmore, M. R. Reidmeyer, K. D. Drake and K. I. Ahmad, Characterization of the relationship between ceramic pot filter water production and turbidity in source water, *Water Res.*, 2016, **104**, 28–33.

51 World Health Organization, *Guidelines for Drinking-water Quality*, Geneva, 4th edn., 2017.

52 Y. Wang, Y. Li, J. D. Fortner, J. B. Hughes, L. M. Abriola and K. D. Pennell, Transport and retention of nanoscale C60 aggregates in water-saturated porous media, *Environ. Sci. Technol.*, 2008, **42**, 3588–3594.

53 T. Phenrat, J.-J. Kim, F. Fagerlund, T. Illangasekare, R. D. Tilton and G. V. Lowry,

Particle size distribution, concentration, and magnetic attraction affect transport of polymer-modified Fe(0) nanoparticles in sand columns, *Environ. Sci. Technol.*, 2009, **43**, 5079–5085.

54 C. Larimer, N. Ostrowski, J. Speakman and I. Nettleship, The segregation of silver nanoparticles in low-cost ceramic water filters, *Mater. Charact.*, 2010, **61**, 408–412.

55 J. Brown and M. D. Sobsey, Ceramic media amended with metal oxide for the capture of viruses in drinking water, *Environ. Technol.*, 2009, **30**, 379–391.

56 D. Ren and J. A. Smith, Retention and transport of silver nanoparticles in a ceramic porous medium used for point-of-use water treatment, *Environ. Sci. Technol.*, 2013, **47**, 3825–3832.

# Performance of Silver Nanoparticle-Impregnated Ovoid Ceramic Water Filters

Zachary J. Shepard, Elizabeth M. Lux, Vinka A. Oyanedel-Craver*

Department of Civil & Environmental Engineering, University of Rhode Island, 2 East Alumni Ave, Kingston, RI, 02881.

**Table of contents entry:** This work presents the first performance evaluation of ovoid CWFs designed by Potters without Borders. Performance analysis and characterization data are presented here to inform manufacturing decisions and research methods.