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PERFORMANCE OF SILVER NANOPARTICLE-IMPREGNATED CERAMIC
WATER FILTERS

BY:
ZACHARY SHEPARD

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
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IN
CIVIL AND ENVIRONMENTAL ENGINEERING

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2020

MASTER OF SCIENCE THESIS

OF

ZACHARY SHEPARD

APPROVED:

Thesis Committee:

Major Professor Vinka Oyanedel-Craver

Joseph Goodwill

Irene Andreu-Blanco

Nasser H. Zawia
DEAN OF THE GRADUATE SCHOOL

UNIVERSITY OF RHODE ISLAND
2020

ABSTRACT

Ceramic water filters (CWFs) are manufactured in developing communities worldwide and are designed to remove microorganisms from drinking water. These filters are low cost, point-of-use, and have been shown to reduce the prevalence of diarrheal disease. CWFs are manufactured at 50 locations around the globe, each factory using a different set of raw materials and manufacturing practices. In this study, the state of the literature encompassing CWF manufacturing and performance assessments was reviewed to determine areas of potential improvements. A modified form of one of the potential standard methodologies was then used to analyze the performance of a new style of CWF with ovoid (curved) walls.

The goal of the literature review was to demonstrate the need for a standardized performance assessment procedure in the testing of CWFs. The performance of CWFs can vary greatly between units manufactured in different areas. A standardized methodology for evaluating CWF performance is necessary in order to determine how manufacturing differences could change the performance of the final product. The many variables in manufacturing and testing that can affect the performance of CWFs were reviewed to determine the major contributors to variations in CWF performance. The USEPA and WHO performance assessments procedures that are available for CWFs are discussed and compared. The implementation of a standardized performance assessment procedure has the potential to improve the performance of CWFs, increase stakeholder involvement, and improve health in developing communities.

Experimentally, the performance of a ceramic water filter (CWF) with curved (ovoid) walls developed by Potters without Borders was evaluated. The modified

protocol used in this assessment was the USEPA *Guide Standard and Protocol for Testing Microbiological Water Purifiers*, which has yet to be utilized in the literature. Filters with/without silver nanoparticles (AgNPs) were evaluated for bacterial removal, turbidity removal, flow rate, and silver leaching. Bacterial and turbidity removal were high for the ovoid CWFs compared to previous studies. All the CWFs tested here had flow rates within the acceptable range after they had been saturated. Coated CWFs had a higher total effluent silver concentration compared to uncoated; coated CWFs also had increased silver release during testing phases with a higher concentration of total dissolved solids (challenge phase, 35 ppb). This was compared to the general phase that had a release of 13 ppb. The procedure demonstrated utility as a reproducible performance testing technique. X-ray diffraction and mercury intrusion porosimetry were used to study the ceramic structure in order to explain the high performance of the CWFs. X-ray photoelectron spectroscopy (XPS), was used to determine that the AgNP coating on the exterior of the CWFs leached off by the dissolution of the AgNPs during the general and challenge phases and the release of AgNPs from the ceramic during the leaching phase.

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PREFACE

This thesis is partially written in manuscript format and in accordance with the University of Rhode Island Graduate School guidelines. There are three sections: a review paper, a manuscript detailing experimental work performed on ovoid CWFs, and a conclusion. Chapter 1 is the review paper entitled *Performance Assessments of Point-of-Use Ceramic Water Filters: A Review*, which describes the current state of the literature surrounding the performance assessments of ceramic water filters and Chapter 2 is a manuscript, *Performance of Silver Nanoparticle-Impregnated Ovoid Ceramic Water Filters*, which details the study of a new type of ovoid ceramic water filter. Chapter 3 develops some ideas about future studies that could be completed under this research.

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PUBLICATION STATUS

This thesis has been used as the foundation for a manuscript submitted to *Environmental Science: Nano*. The literature review represents a review paper that has been submitted to *Journal of Hazardous Materials*.

CHAPTER 1

MANUSCRIPT-I: PERFORMANCE ASSESSMENTS OF POINT-OF-USE

CERAMIC WATER FILTERS: A REVIEW

Zachary Shepard¹, Vinka Oyanedel-Craver¹

¹Department of Civil & Environmental Engineering, University of Rhode Island,
Kingston, RI, 02881

*Corresponding author: Vinka Craver, craver@uri.edu

Abstract:

Ceramic water filters (CWFs) are manufactured in under-served communities across the world. The performance (measured by microbial removal) of CWFs varies widely depending on the manufacturing practices and testing conditions used in the performance assessment. The manufacturing and testing variables that impact CWF performance are reviewed here. The literature review showed that CWFs tested with synthetic solutions or manufactured with clay, sawdust, and silver nanoparticles have a higher removal of microorganisms (LRV) compared to CWFs tested with collected water or made with locally-sourced clay, rice husks, and silver nitrate. Currently available standardized performance assessment procedures from the USEPA and WHO are described and compared. The adoption of either of these procedures would likely improve the overall performance of CWFs by providing measurements that could guide the manufacturing process. A performance assessment procedure that could be applied in the field could increase stakeholder involvement in the study of CWFs, which could lead to increased use. The practical application of a standardized performance assessment procedure is also discussed. Overall, the application of a standardized performance assessment procedure has the potential to improve the performance of CWFs and lead to improved health in developing communities.

Introduction:

Point-of-use (POU) drinking water treatment technology is designed to provide safe drinking water at the household level.^{1,2} These technologies are an alternative in developing communities where other treatment technologies are costly or impractical. POU strategies involve treating and storing collected water at the point of consumption.³

Ideally, these technologies are low cost and prevent recontamination of the treated water.⁴ POU water treatment has been reported to reduce waterborne diseases (especially among children) by reducing the pathogenic load in drinking water.^{1,5-7} Ceramic water filters (CWFs) are a type of POU water treatment technology that has been studied in the literature. CWFs have been shown to be effective against a wide range of contaminants including bacteria⁸⁻¹¹, organic and inorganic chemicals⁸, protozoa¹², and viruses¹³⁻¹⁵. This reduction in pathogenic bacteria has led to reduced diarrheal rates in Colombia¹¹, South Africa⁹, and Cambodia², among others. CWFs are a socially acceptable alternative because they are easy to use, low cost, utilize local craftsmanship, and do not impart a smell or taste to the water.^{1,16-18} In terms of limitations, regular cleaning is required for appropriately functioning CWFs and the flow rate decreases over the lifetime (about 1-2 years) of the device.^{1,16,19,20} Also, microbial removal (the primary performance metric) of CWFs varies depending on the quality of the materials used in its construction.^{1,11,21}

There are two main antimicrobial mechanisms involved in ceramic water filtration: physical filtration and inactivation through contact with silver (in nanoparticle or ionic form). Mechanical filtration is the main method by which water purification is achieved in CWFs.^{12-14,22-24} Bacteria are removed from the contaminated water when they are retained on the surface and within the matrix of the ceramic *via* size exclusion.^{8,25} Membrane filters operate in the same manner, using small pores to block contaminants that physically cannot fit through them.^{26,27} Sullivan *et al* demonstrated that there is an active layer on the surface of the ceramic that removes roughly 10^3

CFU/gram-ceramic while around 10^2 CFU/gram-ceramic can be found in the matrix of uncoated CWFs.⁸

Silver, usually in nanoparticle form, is added to CWFs in order to improve the reduction of the microbial load.^{24,28} Silver nanoparticles (AgNPs) release silver ions, which interact with thiol functional groups and prevent DNA replication.²⁹ Physical contact between microbes and AgNPs occurs on the ceramic element, where the coating prevents biofilm formation.^{13,24,30,31} AgNPs also release silver ions, which disrupt cellular functions such as respiration, electron transfer, and DNA replication.²⁹ Silver is mostly eluted in the ionic form from CWFs, which provides some residual disinfection in the water storage container.^{22,32}

Even though the performance of CWFs can vary widely, standardized performance assessment procedure to guide the manufacture of CWFs has yet to be universally adopted by the field.^{1,13–15,30,33–37} In this case, “performance assessment” refers to testing during the manufacturing stage. For CWFs, a standard performance assessment would guide the manufacturing process toward developing more robust units by creating a consistent data set for manufacturers and researchers, on which product improvements can be based. Establishing a standardized performance assessment would allow for easy comparisons between studies of filters produced at different factories under different conditions.

The goal of this review is to demonstrate the effect that the variables involved in manufacturing and testing CWFs have on the reported performance. The role that the water chemistry of the influent plays on the effectiveness and assessment protocols are reviewed here. Currently available performance assessment procedures will be

evaluated based on their influent chemistry and its potential effect on results, practicality on the field, and the data provided by following the procedure.

Current State of CWF Research

Many studies have assessed the performance and structure (mineralogy, pore size distribution, strength, silver sorption, etc) of CWFs. 67 studies were analyzed in this review. A breakdown of the types of studies, the filter types evaluated, and the microorganisms of interest can be found in Table 1.1. The percentages presented under the subcategories of the microorganisms of interest (i.e. *E. coli*, MS2 bacteriophages, etc.) are representative of the subcategory. This means that the papers written about *E. coli* make up 69% of the papers about bacteria, not 69% of the total.

While these studies have demonstrated the effectiveness of CWFs and provided important data (microbial removal, silver leaching, flow rate, turbidity reduction), the performance assessment process has been inconsistent among the studies. This variability has led to a wide range of microbial removal values while making difficult to determine the source of this variation. Table 1.2 presents *E. coli* log removal values (LRVs) for CWFs in laboratory performance studies. The results presented in Table 1.2 are for CWFs that have been coated in AgNPs. These studies have evaluated CWFs with a number of different shapes including straight walled (7), disks (3), and curved walls (1). Both the chemistry of the influent solutions used for the performance assessment and the production variables (clay source, burnout material, and silver coating) differ among the studies. Without a unified methodology for performance assessment, studies such as those presented in Table 1.2 cannot be directly compared.

Variability in CWF Structure and Performance:

Approximately 50 CWF factories operate around the globe with technical assistance provided by Potters for Peace and Potters without Borders.^{41,42} Local materials are utilized in the production of CWFs at each of the factories.^{30,33} The differences in the local materials used at each location can introduce variability into the performance of the CWFs.

Variability in manufacturing:

The manufacture of CWFs begins by conditioning both the burnout material and clay. Burnout materials are locally sourced, low cost, and include sawdust, flour, rice husks, or peanut shells.^{28,30} The clay utilized in a CWF is sourced from locally collected soil.^{30,33} Both the soil and the sawdust are sieved according to the requirements in each factory and the availability of sieves.³⁰ Since there is no standard for the sieves used to process the soil and sawdust, there is a great deal of variability in the grain sizes of those materials between factories. Factories usually process soil for clay and sawdust by sieving with meshes that have openings varying 177 to 2000 μm .³⁰ Clay is classified as soil with a grain size less than 2 μm and sand and silt have grain sizes between 2 and 2000 μm , so the clay utilized in CWF manufacturing is more of a clayey sand.^{43,44} Processing of the soil in this manner introduces variable sizes of grains into the mixture used for the filter, which could have an impact on the microbial removal.²⁸ The clayey sand and burnout are mixed after sieving and water is added to the dry mixture.³⁰ The amount of burnout material added to a CWF varies between factories and can range from 5-25% (by weight) of the clay/sawdust mixture.^{12,30,32,40} The filters are then press-formed into the correct shape, air dried, and fired in a kiln.^{30,33} Firing temperatures vary

between 600 and 1000°C depending on what the manufacturers find effective for their specific mix of local clay and burnout material.^{28,30,33}

The final step in the process is coating the filter with silver, which is meant to prevent the growth of biofilm on the ceramic and provide some residual disinfection.³⁰ Variability in this step comes from the type, amount, and method of silver application. CWFs are amended with silver nanoparticles (AgNPs) or silver nitrate (AgNO₃).^{30,33,40} In the field, CWFs are coated with solutions of between 100 and 300 ppm silver.^{30,33} Coating a filter is usually accomplished by painting or dip coating.^{30,33,45} Silver has also been fired into the ceramic matrix by mixing it with the clay/burnout mixture prior to firing.^{33,39} In the last poll CWF manufacturers (2011), 56% paint on, 33% dip in, and 11% firing in either AgNO₃ (17%) or AgNPs (83%).³⁰ More CWF factories utilize AgNPs compared to AgNO₃ because they are associated with better long term performance.^{33,39,40} Of the literature reviewed here, 47% of the studies used an AgNP coating and 22% used AgNO₃. The rest of the papers used uncoated CWFs (25%) or silver of an unidentified species (6%). CWFs in these papers were painted with (59%), dipped in (7%), or contained fired in (15%) silver. Several studies did not specify the manner of silver application (19%). As discussed in greater detail in the next section, the different silver types and application methods can affect the removal of microorganisms and retention of the silver on the CWF. This has implications for the health of the user and performance of the CWF.

Each material and process involved in the manufacture of CWFs introduces some variability into the final product. A discussion of the manner in which the materials and processes affect different areas of CWF performance and durability can

be found in the next section. The variations in each step make the filters produced at different factories entirely unique. The microbiological removal of filters can vary based on the variations in materials utilized in the construction phase. After construction and quality control testing (discussed in detail later), the CWF is ready to be deployed in the field.

Impacts of manufacturing variables in CWF performance

Each of the variables in CWF manufacturing (clay, burnout material, firing temperature, and application of silver) affect the performance of CWFs. Oyanedel-Craver *et al* demonstrated that clays with a smaller grain size produce filters with a smaller median pore size (2.03 μm pores for red art vs. 14.3 μm pores for a locally sourced Mexican clay) and a larger rejection of bacteria (rejection of 99.97% for red art and 97.86% for Mexico).²⁸ Rayner *et al* showed that the use of different clay materials in CWF manufacture can reduce bacterial removal by about 50%.⁴⁰ The presence of aluminum and iron oxides in ceramic media increases performance of CWFs by inactivating and adsorbing microorganisms.⁴⁶ Clay mineralogy has also been shown to effect the strength, plasticity, and sorption of silver of the ceramic.^{21,47–49} Table 1.3 shows the main mineral components of clays used in six studies of CWFs. The mineralogy of the clay used in a CWF affects the bonding of the clay particles and, therefore, the strength of the ceramic.²¹ The sorption of silver to the CWF has been shown to be affected by differences in the smectite fraction of the clay used in the construction of the filter.²¹ The cations in pyroxene and albitic phagioclase feldspar (minerals commonly found in the clays used to make CWFs) create localized positive charges that attract negatively charged AgNPs.²¹ Clays with higher amounts of these

minerals sorb AgNPs better. Increased sorption means better performance of the filter over the long term as the silver is released more slowly.

Burnout materials also have an impact on the performance of the filter. The quantity and grain size of the burnout material affect the porosity of the filter, which changes the flow rate and the ability of the filter to remove microorganisms.^{33,48,50} Increasing the amount of burnout material leads to an increased flow rate.^{32,38} CWFs made with burnout materials that have been sieved with a finer mesh have a smaller pore size and a higher removal of microorganisms.⁵¹ For example, Rayner *et al* showed that CWFs made with sawdust sieved between meshes with 2.38 mm and 1.19 mm openings have a lower LRV compared to CWFs made with sawdust sieved between meshes with 0.595 mm and 0.250 mm.⁵¹ The LRV for the CWFs made with the larger sawdust grains was 1.87 ± 0.261 while the CWF made with the smaller grains had an LRV of 2.06 ± 1.330 .⁵¹ There are several types of burnout materials (sawdust, rice or coffee husks, peanut shells, etc) and differences in the type of burnout material has been shown to affect the performance of the CWF.^{34,40,51} CWFs made with coffee or rice husks have a lower removal ($LRV = 0.96 \pm 0.079$) compared to CWFs made with sawdust ($LRV = 2.37 \pm 0.239$) because the husks tend to clump together and create larger pores.^{34,51}

Differences in the firing temperature have been shown affect the flow rate of CWFs.³⁸ Increasing the firing temperature can increase the flow rate by between 4-8 liters per hour.³⁸ The environment in which CWFs are fired also plays a role in the performance of CWFs.⁵² Black ceramics are fired in a reductive atmosphere and have been shown to have a higher removal of viruses and bacteria than CWFs fired in an

oxidative atmosphere.⁵² CWFs fired in a reductive atmosphere had an LRV of 2.32 ± 0.85 and the same type of CWF fired in an oxidative atmosphere only had an LRV of 0.68 ± 0.62 .⁵²

The type and method of silver application are also variables that change the performance of the filter. Silver is either applied to CWFs as AgNPs or silver nitrate, AgNO₃. There have been several studies examining the difference in performance between the two. AgNPs show improved performance over the long term when compared to AgNO₃.³⁹ CWFs release AgNO₃ rapidly, which increases initial removal of microorganisms.^{22,31,40} AgNPs remain adhered to the ceramic surface because they are trapped in nanoporous structures.⁴⁰ Ag⁺ from AgNO₃ is rapidly eluted from the ceramic because it is displaced by cations with a higher valence.⁴⁰ Rayner *et al* demonstrated the greater elution of AgNO₃ compared to AgNPs and the effect that it can have on LRV.⁴⁰ The desorption of silver from AgNO₃ was 20% greater compared to AgNPs in this study.⁴⁰ Removal of *E. coli* by ceramic disks with 0.3 mg silver/g ceramic was about 1-2 LRV higher for AgNO₃ compared to AgNPs coated.⁴⁰ The higher removal stems from the continued inactivation of bacteria *via* interactions with eluted silver in the effluent of the filter.^{13,40} This high removal does not last long because all of the silver ions are eluted from the filter quickly.⁴⁰ Rayner *et al* predicted that all of the silver desorbs in 1 year for a filter coated in AgNO₃ and 8 years for a filter coated in AgNPs.⁴⁰ These predictions demonstrate that AgNO₃ is eluted from the CWFs faster compared to AgNPs. A CWF coated with a monodisperse solution of small AgNPs more effectively removes bacteria than a polydisperse solution of large particles.⁸ Smaller AgNPs showed increased removal of microorganisms because they have more available

surface area.^{8,39} A monodisperse solution of AgNPs ensures that the majority of the AgNPs are in the desired size range, so the majority have the highest level of toxicity.⁸ Casein stabilized AgNPs in Sullivan *et al* had a higher poly-dispersivity index (PDI) compared to AgNPs made with rosemary and maltose: 0.58, 0.12, and 0.18 for casein, rosemary, and maltose AgNPs, respectively.⁸ Ceramic disks coated with casein AgNPs had about 0.5 LRV less *E. coli* removal than rosemary and maltose AgNPs (which had roughly the same performance) throughout the 11 day study.⁸

The method by which the silver is applied to the filter also affects its release and the performance of the filter. CWFs are painted with, dipped in, or fired with silver.³⁰ CWFs are usually painted with AgNPs; capillary action transports the silver nanoparticles into the small pores.⁴⁵ When CWFs are dipped into a solution of AgNPs, the pressure forces the particles into the pores of the ceramic.⁴⁵ The silver tends to segregate to the exterior surfaces near the pores in this production scenario.⁵³ No silver can be found on the inside of the ceramic when dip coating.⁵³ Dipping and painting release roughly the same amount of silver while firing in releases about 0.3% of that amount.⁴⁵ When using AgNO₃, the firing in technique has been shown to release less silver while still providing disinfection.³⁹ 5-10 times the amount of silver is required in order for filters with fired in AgNO₃ to have equivalent LRVs to filters with painted AgNPs.³⁹ This may be applicable in the field because AgNO₃ is less expensive than AgNPs.³⁹ The firing in technique prevents silver from being oxidized, eluted from the filter during use, or scrubbed off during cleaning.³¹ It also removes a step in the manufacturing process by eliminating the need for coating the ceramic.³⁹

The filter's users can also affect the performance of CWFs. Regular maintenance is essential for the continued use of CWFs.^{54,55} The microbial removal and flow rate of CWFs declines over time, but with maintenance this decline can be slowed.⁵⁵ The regular maintenance that is required by CWFs has the potential to lead to recontamination or breakage of the ceramic.²⁰ CWFs usually come with a safe storage container that holds a reservoir of treated water.^{9,17,20,24,32} Separating the ceramic from its safe storage container for cleaning exposes the treated water to recontamination.²⁰ Farrow *et al* demonstrated that there is a statistically significant difference between log removal of *E. coli* by CWFs studied in the field and in the laboratory.⁵⁶ One of the reasons for this difference was the users' interactions with the filter.⁵⁶ Recontamination of the water in the safe storage container associated with the CWF frequently occurs during cleaning of the filter element.⁵⁶ The manner in which users interact with a CWF is yet another variable that effects filter performance.

While each of the variables discussed here has an effect on the performance of the CWF, the most profound variations in performance stem from differences in clay and burnout materials. The type and quality of clay and burnout materials vary widely between factories established across the world.^{30,40} As discussed previously, the variations in these materials have a large impact on the manufacturing process and the performance of the final product.

Performance Assessment of CWFs:

Effect of water chemistry variables on CWF performance

In order to study the implications of the current performance assessment procedures, it is essential to understand the potential effects of the influent water

chemistry. Important water chemistry parameters for CWF testing include turbidity, natural organic matter (NOM), total dissolved solids (TDS), microbial load, pH, and chlorine concentration. Of these parameters, turbidity, NOM, TDS, and microbial load have been studied within the context of their effect on microbial removal. Turbid water increases the removal of viruses by CWFs (*via* adsorption onto larger particles that are strained out).^{15,19} An increase the turbidity of the influent from 0 to 2 NTU leads to an increase in viral removal from 0.2-0.4 LRV to 1.3-1.4 LRV.¹⁵ NOM coats AgNPs, preventing dissolution and minimizing their toxicity and microbial removal.^{31,57} In controlled, laboratory scale testing, AgNPs exhibited lower toxicity in solutions with high concentrations of divalent cations.⁵⁸ The survival of *E. coli* increased from 9% at 10 mg/L Mg^{+2} to 20% at 1000 mg/L Mg^{+2} .⁵⁸ Increasing the concentration of Ca^{+2} from 10 mg/L to 1000 mg/L had a similar effect, increasing the survival rate of *E. coli* from 3.5% to 20%.⁵⁸ Differences in the microbial load in CWF testing can also affect microbial removal, where a higher microbial load increases the measured LRV.⁵⁹

Turbidity, TDS, pH, and chlorine concentration also have an effect on silver release. An increased turbidity has been shown to increase silver release.¹⁰ Mikelonis *et al* reported that the solids in turbid water form complexes with the silver on the filter, pulling the silver off of the filter.¹⁰ Increases in ionic strength (especially the concentration of divalent cations) and chlorine increase effluent silver concentrations.^{10,22,31} When the TDS of the influent solution was increased from 10 mM to 50 mM $NaNO_3$ in Mittelman *et al*, the concentration of effluent silver increased from about 0.1 mg/L to 0.8 mg/L.²² At a constant ionic strength of 10 mM, solutions containing Mg^{2+} and Ca^{2+} caused 2-4 times more silver leaching from AgNP coated

filters compared to solutions containing Na^+ .²² The silver eluted from the AgNP coated filters was mostly (>90%) ionic.²² An increase in free chlorine residual from 0 to 2 mg/L increases the effluent silver concentration from AgNP painted disks 2-5 times.³¹ Increasing the pH of the influent from 7 to 9 has been shown to decrease silver release by a factor of 7 for AgNP coated CWFs.²²

Each of these variables affects the performance of the filters in the field and during performance assessments. The TDS of the influent solutions is likely the most important factor in the performance of CWFs. It has a strong influence on the AgNP coating and can affect silver toxicity and release.^{22,57} Differences in influent chemistry between studies and performance assessments make it difficult to determine whether the source of differences in performance is the CWF or the influent solution.

Previous studies have reported the performance of CWFs under a range of water chemistry conditions (Table 1.4). Several of these have examined CWFs produced in the same country under different water chemistry conditions. The removal of *E. coli* by these filters ranged from 1.1 to 2.9 LRV.^{13,14,32} The differences in influent chemistry as well as manufacturing techniques make comparisons among the studies difficult. This is particularly apparent in the studies that use surface water for performance assessment. Table 1.4 shows the water chemistry conditions reported for the studies in Table 1.2 that utilize collected water. The studies in Table 1.2 that utilize a chemically-defined throughput, such as phosphate buffer solution, are not included in Table 1.4 As discussed previously, each of the variables reported in Table 1.4 can affect the performance of a CWF. As previously discussed, total dissolved solids has an impact on filter performance, but this parameter is not included in Table 1.4. This is because

none of the studies report this parameter. The *E. coli* LRVs for the filters in these studies range from 1.1 to 5.6. Since the water quality varies between the studies, it is difficult to determine if the variations in performance come from variations in the filters or the influent water chemistry.

Currently available standardized performance assessment procedures

There are two main performance assessment procedures that have been established: one by the USEPA and the other by the World Health Organization (WHO). The goals of these procedures are different from the quality control procedures currently utilized in the field. CWF manufacturers frequently employ a set of quality control techniques to ensure the quality of their filters before they are sold. These techniques do not inform the manufacturing process and, therefore, are not performance assessments as defined here. Most CWF factories perform visual inspections throughout the manufacturing process.³⁰ Some factories use acoustic quality control by tapping the filters and listening for resonance present if there are no cracks in the filter.³⁷ The flow rate of CWFs is used as the primary metric for quality control; CWFs need to have a flow rate between 1 and 5 L/hr in order to pass this quality control test (specific flow rate ranges vary by factory).^{15,20,28,30,36} Filters with flow rates above the acceptable range are likely cracked and therefore cannot effectively filter out microbial contaminants.³⁰ Quality control performed on the CWFs is important for the delivery of quality CWFs, but this does little to inform the manufacturing process. Performance assessments undertaken during the design cycle can improve the manufacturing process.

The USEPA *Guide Standard and Protocol for Testing Microbiological Water Purifiers* was published in 1987, but has yet to receive much attention from the CWF

field.⁶⁰ The USEPA guide dictates a 13 day testing period with three different influent chemistries: general (normal operation), challenge (worst case scenario), and leaching (stressful conditions for silver coated units).⁶⁰ The conditions for testing can be found in Table 1.5. The general water phase was designed to simulate normal operation.⁶⁰ The normal operation of a CWF utilizes an influent solution that does not promote the dissolution of AgNPs or have a detrimental effect on the water production or microbial removal of the filter. This phase has a low TDS, turbidity, and concentration of NOM and a roughly neutral pH.⁶⁰ The challenge water has a higher pH, total organic carbon (TOC), turbidity, and TDS than the other two testing waters. Increasing the turbidity can decrease the flow rate and increase removal of microorganisms.^{15,19,61} The predicted effect that this influent will have on the release of silver is interesting because of the pH, turbidity, and TDS. The increased turbidity and TDS will likely increase the release of silver, but increased pH has been shown to prevent that release.^{10,22} In our previous work, we demonstrated that the increase in turbidity and TDS has more of an effect on silver release than the pH. The leaching phase is the final phase of the USEPA testing. This phase is designed to test the leaching of the silver on the CWF and ensure that excess silver will not be leached into drinking water.⁶⁰ The pH is slightly lower in the leaching phase compared to the general water phase (5.0 ± 0.2), which encourages the release of silver from the nanoparticles.⁶⁰ Our previous research using this protocol has demonstrated that the procedure allows a framework for producing data on a number of performance metrics including flow rate, turbidity reduction, removal of microorganisms, and release of silver. One complete performance assessment using the USEPA protocol CWFs costs \$60 USD per filter (based on the cost of the reagents

required to complete the analysis). This value reflects the cost of the influent solution constituents and not the general laboratory equipment required to complete the procedures.

The World Health Organization (WHO) has also released a performance assessment procedure similar to the one created by the USEPA (*General Testing Protocol #6: Ceramic Pot Gravity Flow Mechanical Filtration Batch System Technology (with and without a silver component)*).⁶² The time commitment is slightly shorter than the USEPA procedure (11 days compared to 13 days). One trial of the WHO protocol costs \$67 USD per filter (under the same assumptions as the USEPA protocol). The WHO procedure provides a framework for data collection that is similar to the USEPA protocol. A comparison between the influent chemistries used in the USEPA and WHO performance assessments can be found in Table 1.5. There are several differences between the USEPA and WHO protocols.^{60,62} One of the most notable differences between the two protocols is the difference in influent chemistry. The WHO protocol calls for the addition of alkalinity using sodium bicarbonate, NaHCO_3 . The addition of alkalinity in the WHO protocol is designed to buffer the pH of the influent.⁶² The pH values for the general and challenge influents in the WHO protocol are 7.0 ± 0.5 and 9.0 ± 0.2 , respectively.⁶² The addition of sodium bicarbonate allows the buffering of the influent pH at the required values for the general and challenge phases.^{63,64} Only inorganic acids and bases are allowed to adjust the pH of the USEPA protocol which makes the targets more difficult to reach. Buffering the influent makes it easier to reach a consistent pH value.

The WHO procedure begins with a conditioning phase. During this phase, 200L of dechlorinated tap water local to the CWF manufacturer is filtered through the CWF.⁶² This does not count toward the volume of water filtered during testing and there is no microbial addition during this phase.⁶² The addition of the conditioning phase is interesting because it allows the flow rate to stabilize without requiring labor intensive sampling. Reducing the amount of sampling reduces the intensity of the work required.

The USEPA and WHO protocols also require the use of different microorganisms for their performance assessment. The USEPA protocol dictates the use of *Klebsiella terrigena* (ATCC 33257), poliovirus 1 (LSc) (ATCC-VR-59), rotavirus Wa (ATCC-VR-899) or SA-11 (ATCC-VR-2018), and *Giardia muris* or *Giardia lamblia*.⁶⁰ The WHO requires *E. coli* (ATCC 11229), MS-2 coliphage (ATCC 15597-B1) or *Salmonella typhimurium* (WG4 NCTC 12484) and phiX-174 coliphage (ATCC 13706-B1), and *Cryptosporidium parvum* oocysts.⁶² The WHO procedure also requires a smaller amount of bacteria added to the influent: 10⁵ CFU/100 mL compared to 10⁷ CFU/100 mL in the EPA study.^{60,62} The differences in microorganisms between these two procedures has some implications for their applicability in the field. *Klebsiella terrigena* was reclassified *Raoultella terrigena* after the creation of the EPA document and is now considered as biosafety level 2 organism by the ATCC.^{65,66} The strain of *E. coli* utilized in the WHO procedure is a biosafety level 1 organism and could safely be used at a CWF factory. Of course, the EPA protocol could be adapted to incorporate a safer bacterium as we have done in our previous research.

The final difference between the USEPA and WHO protocols is the presence of a leaching phase in the USEPA guide. There is no equivalent phase in the WHO

protocol. This helps lower the amount of time invested in the performance assessment testing by two days. The silver leaching phase is, however, an important part of the CWF performance assessment. Silver coatings are an essential part of the performance of CWFs and need to be measured in any performance assessment. While accurately determining the concentration of silver in the effluent of the CWF usually requires specialized equipment, such as inductively coupled plasma-mass spectrometry^{19,30}, optical emission spectroscopy⁸, or atomic emission spectroscopy⁴⁰, there are other alternatives. Spectrophotometric techniques can be used to quantify silver concentrations to below the WHO silver consumption limit of 100 ppb.^{67,68} This means that silver concentration measurements could be taken at CWF factories during the design phase to ensure high removal throughout the unit's lifetime.

Discussion of the benefits of standardized performance assessments:

Important variables in the manufacturing and testing of CWFs

The previous sections have discussed the variables that effect the microbial removal of CWFs. Table 1.2 contains comparisons between laboratory studies that examine the ability of CWFs to remove *E. coli*. Figure 1.1 shows the effect of manufacturing and testing conditions on measured performance. The types of clay, burnout material, and silver coating were examined as the manufacturing conditions of interest. Of the manufacturing parameters examined in Figure 1.1, the clay source creates the largest variability in LRV. CWFs made with local clays had a range of LRVs between 1.2 and 5.6. Red Art clay is a commercial blend with a smaller grain size than the local clays that are normally used in CWF manufacture.²⁸ The studies that utilized this clay had a much smaller distribution (3.7-4.3 LRV). This distribution is based on

the LRVs from two studies examining five CWF samples. The burnout material used in the construction of a CWF has the most potential to improve the LRV. CWFs made with sawdust have an average LRV two times that of CWFs made with rice husks. Figure 1.1 demonstrates that a CWF made with clay with a smaller grain size (like Red Art clay), sawdust, and AgNPs will likely have a higher LRV than a CWF made with different components.

The testing condition evaluated in Figure 1.1 is the influent solution, comparing natural water (surface or well water) with synthetic solutions (phosphate buffer solution, WHO challenge water, etc). Studies utilizing simple, synthetic solutions tend to overestimate the LRV of CWFs that are deployed in the field and evaluated using natural water. CWFs studied using synthetic solutions, such as WHO challenge water or phosphate buffer solution, had a higher average LRV (4.2) compared to CWFs studied with natural water (2.6). These studies also had a smaller range of LRVs (3.0-5.6) compared to CWFs that were evaluated using natural water (1.2-4.6). The natural waters have a range in water chemistry conditions (Table 1.4), which could increase the variability in LRV measurements. The smaller range of LRV in the synthetic solutions category shows that a standardized performance technique could be used to reduce variability in performance assessments. The studies that utilize a chemically defined throughput eliminate some of the variability seen in studies using natural water and improve the precision of the LRV. A standardized performance assessment with a standard influent chemistry, such as the WHO or USEPA protocols, could reduce the variability even more.

Standardization in testing CWFs

The goal of a standardized performance assessment for CWFs is to guide the manufacturing process in order to improve microbial removal. This review addressed the many manufacturing and performance assessment variables that can affect the performance of CWFs. Manufacturing and performance assessment variables lead to differences in measured removal, evidenced in Table 1.2 where *E. coli* removal is shown to range between 1.1 and 5.6 LRV. The studies included in Table 1.2 had variability in the influent solution, clay origin, burnout material, type of silver, and testing procedures. With all of these variables present, it is not possible to determine whether the testing procedure or the CWFs themselves create differences in LRV.

The implementation of a standardized performance assessment procedure, such as the USEPA or WHO protocols discussed previously, could highlight differences in CWF performance that are attributable to the manufacturing process.^{13,36} As discussed in previous sections, both the manufacturing differences and testing conditions can affect CWF performance. Standardized testing conditions highlight the manner in which differences in manufacturing lead to differences in performance. The USEPA and WHO protocols also provide a framework for testing that allows the evaluation of a number of different performance metrics. Traditional quality control testing for CWFs only involves the measurement of flow rate.^{15,20,28,30,36} The performance assessment procedures discussed here provide a framework for measuring microbial removal, turbidity reduction, flow rate, and silver leaching.^{60,62} The information collected during the performance testing would improve CWF performance by assisting CWF manufacturers in selecting raw materials that impart a higher performance to the final

product. Performance comparisons between filter factories will help set a standard to which the manufacturers can hold themselves. A standardized performance assessment would help manufacturers identify the weaknesses in their process by allowing them to compare performance data with other manufacturers. When incorporated into the evaluation of CWFs, these protocols could help shape the manufacture of CWFs by relating improved performance to manufacturing practices that might differ between factories.

Both the USEPA and WHO procedures could be applied in the field. The materials utilized in the protocols can be acquired easily online and all the required measurements are easy to take with some technical training. The implementation of either the USEPA or WHO procedures would improve CWF and drinking water quality in developing communities.³⁰ Focusing on variability in the CWF itself will allow researchers to guide changes to manufacturing that can improve the microbial removal of the CWFs. It is difficult to guide manufacturing changes given the current state of the literature because there is too much variability in the testing solutions.

Improving stakeholder involvement in CWF testing

Social acceptance and education are key factors in the use of CWFs.³⁵ In many areas, people do not use a CWF because they believe that their water is safe to drink without treatment.³⁵ In others, they do not know where they could purchase a CWF.⁶⁹ This demonstrates a lack of stakeholder involvement and understanding in the use of CWFs. The studies reviewed here have demonstrated a lack of stakeholder involvement in the assessment of CWF performance, which leads to a disparity between the groups who analyze CWFs and those who utilize them.

The currently available literature evaluates CWFs from around the world on a variety of different performance metrics including microbial removal, flow rate, and ceramic strength among many others. 34% of these studies use CWFs or the raw materials used to make CWFs from Asia, 32% from Central and South America, and 34% from Africa. These are areas in which CWFs are manufactured and used frequently. Studies on CWFs are rarely developed by communities that manufacture and utilize CWFs. Figure 1.2 is a geographic breakdown of the areas where studies on CWFs are performed. This was determined by looking at the contact information for the final author on the paper. 90% of the publications on CWFs were guided by researchers from the United States, Canada, and Europe. Only 10% of the studies that evaluate CWFs have last authors with contact information matching the field study location or the source of the ceramic materials used in testing. This means that stakeholder involvement in the development of CWFs is severely limited.

Ideally, the stakeholders would evaluate the performance of a CWFs and guide the manufacturing process in order to improve the performance based on their goals. A standardized performance assessment could help increase stakeholder involvement by empowering filter manufacturers and local researchers to analyze the performance of CWFs. The members of the community would be able to set and achieve their own performance goals by evaluating the performance of the filter using a consistent standard. This would allow community members greater access to the science behind CWF manufacture and greater control over the valued performance metrics. Increased stakeholder involvement in the production and performance assessment of CWFs could lead to greater social acceptance, increased CWF use, and improved health in

developing communities. If either the USEPA or WHO procedures were applied at the factory level, then CWFs could be studied, designed, manufactured, and evaluated by the stakeholders.

Practical application of a standardized CWF testing protocol

While useful, the USEPA and WHO protocols require a great deal of resources and time. CWF factories will not be able to test every unit that they produce. The standard protocols should be utilized at least during factory start up and whenever there are changes in the manufacturing process (different sources of raw materials, a change in firing time/temperature, etc.). Ideally, the performance would be measured at regular intervals specified by the manufacturer. The testing should occur at local laboratories or universities. If this is not possible, filters could be sent to laboratories abroad. This should be reduced as much as possible because one of the goals of a standardized performance assessment is to incorporate the stakeholder in the process. Since the performance assessments are standardized, manufacturers can be confident that their filters are being treated the same at any laboratory they choose.

Data sharing is an important aspect of the implementation of a standardized performance assessment procedure. CWF manufacturers need a method of reporting their data and making comparisons with other manufacturers. An internet forum is likely the best way for manufacturers to communicate and share information. This would allow them to post their data and coordinate with research groups or other manufacturers. Research groups outside of the stakeholder communities could assist with higher level measurements and characterization (such as mercury intrusion porosimetry or X-ray diffraction). An internet forum would also increase access to data

for modelling studies. Only 7.5% of the CWF studies reviewed here involved modelling. Greater access to data sets gathered using standardized methods could provide the opportunity for more modelling studies to be performed on CWFs. Appropriate data sharing would allow manufacturers to communicate the processes that improve microbial removal, which would bring about greater access to clean water and improved health in developing communities.

Conclusion:

A standardized performance assessment procedure for CWFs has the potential to positively impact health in developing communities worldwide. The performance of CWFs varies depending on the materials used in production and the chemistry of the testing solution. It would be impractical to study the effect of each of the possible combinations of CWF production materials in a single study. About 40 factories produce CWFs worldwide and each one utilizes a different set of raw materials. The standardized performance assessments described here could help manufacturers recognize practices that improve the performance of CWFs. Standardization of the protocol used to assess performance would highlight the differences between filters produced at different factories. This assessment would lead to the production of higher quality CWFs, which would, in turn, produce higher quality drinking water and improved health in developing communities. In this review, we explored the many variables involved in the manufacture and evaluation of CWFs. The benefits of currently available performance assessment procedures were evaluated. Standardized performance assessment procedures have the potential improve health in developing

communities by improving stakeholder involvement and ensuring the development of manufacturing processes that produce high quality CWFs.

Supporting Information:

Supplementary 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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CHAPTER 1 TABLES:

Table 1.1: Studies, filters, and microorganisms featured in papers evaluated in this review

Type of Study		
	Number of papers	Percent
Laboratory	37	55
Field studies	19	28
Modelling	5	8
Field/laboratory	3	5
Review	3	5
Type of Filter		
	Number of papers	Percent
Straight walled	28	42
Disks	17	25
Candles	10	15
Bowl	3	4
Curved	3	4
Not reported	7	10
Microorganism of Interest		
	Number of papers	Percent
Bacteria	36	72
<i>E. coli</i>	31	69
Total coliform	6	13
Thermotolerant coliform	6	13
Other species	2	4
Viruses	10	20
MS2 Bacteriophages	9	90
ϕ X-174	1	10
Protozoa	4	8
<i>Cryptosporidium parvum</i>	2	50
Protozoan oocysts	1	25
Protozoan-sized microspheres	1	25

Table 1.2: CWF performance data summary

Study	Influent Solution	Clay source	Burnout material	Silver coating	When was LRV measured?	LRV (number of units)
50	Well water or collected rain water	Cambodia	Rice husks	70 mg AgNO ₃	N.R.	3.0±2.1 (n=6)
32	Chlorine-free tap water or surface water (the Netherlands)	Cambodia	Rice husks	110 mg AgNO ₃	60-85L 125-160L 240-320L	1.7±1.5 1.1±0.4 1.4±0.6 (n=4)
13	Surface water (the Netherlands)	Cambodia	Rice husks	36 mg AgNO ₃ 110 mg AgNO ₃	N.R.	1.2±0.6 1.5±1.2 (n=6)
14	Rainwater and surface water (Cambodia)	Cambodia	Rice husks	110 mg AgNO ₃	<100L >100L	2.9±0.5 2.1±0.1 (n=4)
44	Phosphate buffer solution	Red art clay	Sawdust	4.96 mg silver per clay disk	2-4 pore volumes	4.3±1.7 (n=3)
8	National Sanitation Foundation challenge water	Red art clay	Sawdust	0.3 mg AgNP/g ceramic	12 days	3.75±1.1 (n=2)
16	Deionized water with dissolved solids, turbidity, and <i>E. coli</i> additions	Colombia	N.R.	Colloidal silver (Concentration not reported)	18 months	4.5±0.7 (n=1)
25	Dechlorinated tap water spiked with <i>E. coli</i>	Nicaragua	Sawdust	2 mL of 3.2% colloidal silver (Microdyne) solution	8-120L	3.8±1.1 (n=2)
42	Phosphate buffer solution	Indonesia Tanzania Nicaragua	Sawdust	0.3 mg nAg/g	7.2L	4.1±0.6 4.3±0.6 3.0±0.7 (n=2)
34	Surface water (Saucon Creek, Bethlehem, PA)	Nicaragua	Sawdust	2 mL of 3.2% colloidal silver (Microdyn) solution	5 weeks	4.6±2.1 (n=3)
37	WHO Challenge water	Dominican Republic	Sawdust	Variable amounts of silver nanoparticles	8-11 days	5.6±1.7 (n=2)

*N.R.-not reported. All LRV are reported for *E. coli*. When possible, steady state LRV reported. Results from laboratory made ceramics reported when applicable.

Table 1.3: Clay minerals and their effect on performance

Study	Major minerals in clays used to make CWFs	Effect on performance
45	Kaolinite clay doped with metal oxide additives (FeOOH, goethite; Fe ₂ O ₃ , hematite; Fe ₃ O ₄ , magnetite; Al ₂ O ₃ , alumina)	Fe ₂ O ₃ , FeOOH, and Al ₂ O ₃ increase the amount of virus removal 2-14 times kaolinite alone
21	Quartz, smectite clays, pyroxene, albite, and illite	Pyroxene and albite increase silver sorption
12	Smectite	N.R.
28	Illite and kaolinite	N.R.
46	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃	Decreasing the amount of quartz increases the fracture toughness
48	SiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃	Differences in clay minerals can lead to changes in the plasticity index, porosity, and CWF flow rates

Table 1.4: Water quality differences in performance studies

Study	Water source	pH	Turbidity OR Total Suspended Solids	Natural Organic Matter
50	Well water or rain water	N.R.	N.R.	N.R.
32	Surface water	7.9	14.9 mg/L	N.R.
13	Surface water	7.9	14.9 mg/L	N.R.
14	Surface water	7.8	8.4 NTU	0.05*
	Rain water	7.0	1.1 NTU	0.01*
25	Dechlorinated tap water	6.0-8.0	N.R.	1-4**
34	Surface water	N.R.	30 NTU	N.R.

*NOM concentration reported as absorbance at 254 nm.

**NOM concentration reported in mg/L.

Table 1.5: USEPA and WHO Influent Chemistries

Constituent	USEPA General	WHO General	USEPA Challenge	WHO Challenge	USEPA Leaching
Bacteria (CFU/100 mL)	10^7	$\geq 10^5$	10^7	$\geq 10^5$	0
Chlorine (mg/L)	0	<0.05	0	<0.05	0
pH*	7.5 ± 1.0	7.0 ± 0.5	9.0 ± 0.2	9.0 ± 0.2	5.0 ± 0.2
TOC (mg/L)	2.55 ± 2.45 (Humic acid)	1.05 ± 0.95 (Tannic acid)	>10 (Humic acid)	15 ± 5 (Humic acid)	1.0 (Humic acid)
Turbidity (NTU)	2.55 ± 2.45	<1	>30 (A.C. Fine Test Dust)	40 ± 10 (ISO spec. 12103-A2 fine test dust)	2.55 ± 2.45
Temperature (°C)	20 ± 5	20 ± 0.3	4 ± 1	4 ± 1	20 ± 5
TDS (mg/L)	275 ± 225 (Sea salts)	275 ± 225 (Sea salts)	1500 ± 150 (Sea salts)	1500 ± 150 (Sea salts)	100 (Sea salts)
Alkalinity (mg/L as CaCO_3)	N/A	100 ± 20 (Sodium bicarbonate)	N/A	100 ± 20 (Sodium bicarbonate)	N/A

*Inorganic acids/bases are allowed by both the USEPA and WHO procedures to make pH adjustments.

CHAPTER 1 FIGURES:

Figure 1.1: Comparing the effect of manufacturing/testing variables on LRV

Figure 1.2: Geographic distribution of publications on CWFs

CHAPTER 2

MANUSCRIPT-II: PERFORMANCE OF SILVER NANOPARTICLE- IMPREGNATED OVOID CERAMIC WATER FILTERS

Zachary Shepard¹, Elizabeth Lux¹, Vinka Oyanedel-Craver¹

¹Department of Civil & Environmental Engineering, University of Rhode Island, Kingston,
RI, 02881

*Corresponding author: Vinka Craver, craver@uri.edu

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.

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.

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 bacteriophages⁵. 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 (AgNO₃), which prevent biofilm growth and provide residual disinfection.^{10,12,13} Coating with AgNPs increases long term performance

compared to AgNO₃, 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 2.1, 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 synthesized 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 2.2 contains the EPA requirements for the influent solutions required for each phase. Table 2.3 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 NaNO₃, which has been shown to minimize the release of silver from the nanoparticles on the ceramic.¹⁶

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 2.1). 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 mineralogy (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 X Powder 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 K α 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 μ m 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 2.2A 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.^{4,46,18,42} 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 2.2B. 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 2.2C 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 2.3A. 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.

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 2.3B). 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 2.3B 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 Figure 2.4A-D. XPS analysis of a silver-coated, unused CWF (Figure 2.4A) 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 2.4B shows a selection of the spectra that were collected from the used, silver coated cross section. The peaks in the spectra collected at 1100 μm and 10700 μm 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 2.4B, 10700 μm). The band on the exterior surface layer was missing from the sample from the used CWF (Figure 2.4B). 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.

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 ($\text{KAl}_2(\text{SiAlO}_{10})(\text{OH})_2$), hematite (Fe_2O_3), and albite ($\text{NaAlSi}_3\text{O}_8$). 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 2.5 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 2.4 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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CHAPTER 2 TABLES:

Table 2.1: Clay constituents of ovoid CWFs

Clay	Percent
Plainsman 3D Clay Ore	33.7
Plainsman M2 Clay Ore	33.7
Kentucky OM 4 Clay Ore	11.1
Kyanite (refractory sand)	3.2

This clay mixture makes up 83-79% of the weight of the final product with 30+ mesh sawdust making up the final 17-21%.

Table 2.2. EPA requirements and inputs for influent solutions.

	General	Challenge	Leaching
	(Days 1-6)	(Days 7-11)	(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

Table 2.3. Reagents for influent solutions

	General Input	Challenge Input	Leaching Input
Days	1-6	7-11	12-13
pH	N/A	adjusted with NaOH	adjusted with HCl
<i>E. coli</i> K12 (ATCC 25404)	10 ⁹ CFU/L	10 ⁹ CFU/L	0 CFU/L
Total Organic Carbon	3 mg/L humic acid	15 mg/L humic acid	1.0 mg/L humic acid
Turbidity	N/A	330 mg/L kaolinite	N/A
Temperature (°C)	N/A	N/A	N/A
Total Dissolved Solids	300 mg/L sea salt	1500 mg/L sea salt	100 mg/L sea salt

Table 2.4: Average pore sizes as determined by mercury intrusion porosimetry.

Sample*	Average (μm)
0 cm	2.49 ± 0.01
5 cm	2.56 ± 0.10
15 cm	1.87 ± 0.03
25 cm	2.19 ± 0.01

*Measurements refer to the distance from the bottom of the filter to the location from which samples were extracted.

CHAPTER 2 FIGURES:

Figure 2.1: Experimental set up

Samples were collected from the plastic buckets underneath the CWFs.

Figure 2.2. 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 2.3. Silver leaching. (A) Total silver concentration (B) Nano vs. ionic silver concentration. White bars are silver coated filters, light gray bars are uncoated, and dark gray bars represent the concentration of silver in the influent. Error bars are standard deviation (n=2).

Figure 2.4. Selected XPS spectra

The following figures showcase the distribution of silver nanoparticles through the matrix of the ceramic. The presence of silver was determined by peaks on the XPS at 367 and 373 eV. The signal to noise ratio is high due to the complex minerology of the clays used in the CWFs. Each cross section is presented as a bar with the interior and exterior surfaces labelled. The total length of the cross section is noted as well. Note that while the cross sections may differ in thickness, XPS analysis was of the entire cross section. Gray sections indicate areas where silver was found. A selection of spectra are presented as representative samples for different areas of the cross section. Dotted lines indicate roughly where the spectra was acquired on the cross section.

(A) Cross Section of Unused, Silver Coated CWF
Total length: 16632 μm

(B) Cross Section of a Used, Silver Coated CWF
Total length: 14637 μm

(C) Cross Section of Unused, Uncoated CWF
Total length: 16300 μm

(D) Cross Section of a Used, Uncoated CWF
Total length: 14393 μm

Figure 2.5. Pore size distributions.

Samples shown here were removed from an unused ovoid CWF. Results were calculated as the volume intruded over a given pore size fraction divided by the total volume intruded. White indicates pores with a diameter greater than 10 μm . Light gray bars represent diameters 2-10 μm . Dark gray bars are pores with a diameter less than 2 μm . Error bars are standard deviation ($n=2$). The measurements on the X axis of Figure 2.5 refer to the distance a sample was taken from the bottom of the filter. Samples were taken from different locations going up the wall of the CWF to determine if the pore size distribution changes as a function of wall height.

CHAPTER 3: OVERALL CONCLUSION AND RECOMMENDATIONS

Chapters 1 and 2 reviewed the potential for standardized ceramic water filter (CWF) testing and examined the performance of a novel ovoid CWF. While these manuscripts contribute to the literature on CWFs, there is still more that can be done in this field. Future projects along the same themes as the previous work might involve applying standardized CWF performance testing in the field, the evaluation of produced at different factories using a standardized assessment procedure, or the study of the structure of CWFs using X-ray photoelectron spectroscopy (XPS).

Chapter 1 discusses the importance of utilizing a standardized CWF performance testing system during the manufacturing process. These assessments would ideally be performed in the communities in which the CWFs are made. The implementation of standardized performance assessments at CWF manufacturers and the initiation of a data sharing network would be an interesting project. Coordination between CWF manufacturers could improve the performance of CWFs and the health of developing communities. It would also be interesting to utilize a standardized performance assessment to evaluate filters produced at different filter factories. This would demonstrate the way a standardized assessment could highlight the differences in manufacturing that lead to differences in performance.

XPS was first applied to CWFs in the work presented in Chapter 2 and it has more to offer the field. Under the right experimental conditions, XPS could be used to track the movement of silver nanoparticles (AgNPs) through the ceramic matrix over time. Ceramic disks could be set up so that they are exposed different amounts of a

throughput of interest. The migration of AgNPs as a function of throughput volume would be an important addition to the present literature.