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ASSESSMENT OF CERAMIC WATER FILTERS AS A POINT-OF-USE WATER TREATMENT SYSTEM FOR TREAMENT OF MICROBIOLOGICAL, ORGANIC, AND INORGANIC CONTAMINANTS IN DRINKING WATER

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BY

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ABSTRACT

The use of ceramic water filters (CWFs) is common in many households in developing and rural communities worldwide. Currently, CWFs are a viable means of microbial contaminant removal from untreated drinking water sources, however, very little is known about their ability to remove other organic and inorganic contaminants, such as heavy metals and hydrocarbons. CWFs are also commonly impregnated with silver nanoparticle to increase antimicrobial properties. However, little is known about the effect of the surface functionalization of silver nanoparticles on the performance of ceramic water filters. Furthermore, CWFs are typically used as a household water treatment system, in the form of a large pot filter. The feasibility of CWFs as a portable, point-of-use system will be examined in this thesis.

The main objective of this research was to assess the implications and effects of the surface functionalization of silver nanoparticles on the performance of CWF in terms of organic and inorganic contaminant removal. Ceramic disks were manufactured, characterized and tested under laboratory and field conditions to determine the address the aforementioned knowledge gaps. We used silver nanoparticles functionalized with casein, maltose and phyto-extracts to study the effects of microbiological, organic and inorganic contaminant removal using disks manufactured in the laboratory. CWFs were functionalized with three nanoparticles synthesized using casein, maltose, and a extract from the rosemary plant as reducing agents, and were compared to unmodified CWFs manufactured from Red Art Clay. The disks were tested for their efficacy to remove from water

metal ions, polycyclic aromatic hydrocarbons (PAHs), and *E. coli* simultaneously. Results showed that removal of bacteria was highly dependent on the mass of silver retained in each disk after impregnation with the nanoparticles. Results suggested that silver nanoparticle (nAg) average size and size distribution were the controlling factors in ceramic disks performance in terms of both bacterial and lead removal efficiency. The nAg size and size distribution dictated the amount of nAg retained within the ceramic disks after treatment, where smaller average size and more monodisperse nanoparticles (in this case, the Maltose nanoparticles and Rosemary nanoparticles) were preferentially retained within the disks, whereas larger, and polydisperse nAg particles (Casein nanoparticles) were released after the impregnation process. Hydrocarbon removal was unaffected by the mass of silver retained within the filters, and appeared to be removed by size exclusion, and retention in dead-end pores of the disks. Furthermore the removal rate of lead through the CWFs increased when the filters were treated with the silver nanoparticle, with Casein nanoparticles being the most effective amendment of the three nanoparticles tested.

Laboratory and field trials conducted in the Soweto province of South Africa, in which a point-of-use water treatment system called the CleanSip bottle was tested in conjunction with the CWFs. Two environmental samples were run through the system. The bottle exhibited log removal values (LRV) of up to 3.87 and proved effective at removing microbial pollutants from surface water bodies. Rosemary-nAg functionalized CWFs performed better than any of the other CWFs in terms of bacterial removal performance.

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PREFACE

This thesis is partially written and organized in manuscript format and in accordance with the University of Rhode Island Graduate School guidelines. The thesis is divided into 3 sections, which consist of an introduction, one submitted manuscript, and additional field trials. Chapter 1 is an introduction to the work done throughout the thesis. Chapter 2 is a manuscript entitled *"Understanding the microbiological, organic and inorganic contaminant removal capacity of ceramic water filters doped with different silver nanoparticles"* with the authors R. K. Sullivan, M. Erickson, and V. Craver, and is under review by the journal Environmental Science: Nano. Chapter 3 title *"Field Trial of Ceramic Water Filters for use in CleanSip water bottle in Soweto, South Africa"* described the field trial of the ceramic water filters.

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CHAPTER 1

INTRODUCTION

It is estimated that 884 million people do not have access to improved drinking water sources [1]. The World Health Organization reported that 80% of gastrointestinal disease is caused by contaminated drinking water [2]. Pathogens such as *Vibrio cholera, Escherichia coli,* and *Shigella dysenteriae* are commonly found in drinking water in developing communities and can cause diseases such as diarrhea, that could lead to dehydration, malnutrition and death [3] [4]. Gastrointestinal infections result in nearly 1.87 million children deaths yearly, of which 99.8% happen in developing countries. Ceramic water filters (CWFs) are simple and effective devices for providing people with safe drinking water. This technology is currently used in more than 50 countries as point-of-use water treatment option [5].

The purpose of this study is to evaluate the simultaneous chemical and bacterial removal efficiency of CWFs functionalized with silver nanoparticles with various surface modifications. Previous research has primarily focused on the effectiveness of ceramic water filters to remove microbiological contamination; however, chemical pollutant removal has been scarcely evaluated [6] [7]. In this study, CWFs were amended with three types of silver nanoparticles including commercial grade casein functionalized nanoparticles, and two silver nanoparticles with polyvinyl-pyrrolidone (PVP) as stabilizer agent and analyzed for their effectiveness in biological, **organic**, and inorganic contaminant removal.

Although bacterial reduction performance for silver impregnated CWFs has been published in previous studies [6], few studies have been done regarding the amount of viable bacteria retained on the surface and inside the CWF [2], or the effect of nanoparticles synthesized using different techniques, and their antimicrobial properties.

Chapter 2 of this thesis is a manuscript entitled "Understanding the microbiological, organic and inorganic contaminant removal capacity of ceramic water filters doped with different silver nanoparticles" in which we examined the effect of surface modification of silver nanoparticles when applied to ceramic water filters, and the implications that the surface modifications have on the contaminant removal efficiency of the CWFs. The study utilized a modified version of standardized challenge water designed by the National Sanitation Foundation recommended for the testing of point-of-use water treatment systems. Several contaminants commonly found in surface water were examined including *E. coli*, lead, and the hydrocarbons acenaphthene and fluorene.

Chapter 3 is entitled "*Field Trial of Ceramic Water Filters for use in CleanSip water bottle in Soweto, South Africa*" in which the performance of the CWFs utilized in Chapter 2 in conjunction with the CleanSip water bottle developed at the University of Johannesburg is examined. In this chapter, the bacterial removal performance of the CWF was evaluated using the challenge water mentioned above, as well as at two local drinking water sources used by citizens of the community.

The communities in and around Soweto, South Africa have access to improved drinking water sources within the informal settlements in the form of a community tap; however, the lack of sanitation facilities, stormwater management, and density of the population often times leads to secondary contamination of drinking water [8]. Furthermore, many locations where residents are employed, such as farms or mines, lack access to improved drinking water, forcing workers to resort to surface water bodies for their drinking water [1]. The goal of the work done in Chapter 3 was analyzes the efficacy of the CleanSip bottle as a point-of-use water treatment device.

The overall goal of this work was to make advances in the use of ceramic water filters in rural communities. The intended focus of this study was aimed at addressing the lack of information regarding the organic and inorganic contaminant removal of ceramic water filters functionalized with silver nanoparticles. Although the variation in performance of the CWFs was not able to be linked directly to the surface modification of the nAgs, the average size and size distribution of the nAgs were shown to have an effect on the contaminant removal performance of the CWFs by influencing the amount of nAg retained within the disks.

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CHAPTER 2

MANUSCRIPT - I: UNDERSTANDING THE MICROBIOLOGIAL, ORGANIC AND INORGANIC CONTAMINANT REMOVAL CAPACITY OF CERAMIC WATER FILTERS DOPED WITH DIFFERENT SILVER NANOPARTICLES

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ABSTRACT

Pathogen removal efficacy of ceramic water filters (CWF) impregnated with silver nanoparticles (nAg) has been well studied, however scarce information is available about the impact of nAg surface functionalization and removal of inorganic and organic pollutants. In this study, we examined the effect of nAg functionalized with casein, maltose and phyto-extracts on the microbiological (Escherichia coli), organic (polycyclic aromatic hydrocarbon, PAH) and inorganic (heavy metals) simultaneous removal using disks manufactured in the laboratory. Results showed that the mass of nAg retained on each disk varied depending on the nanoparticles used (casein-nAg: 80%, maltose-nAg: 93%, and rosemary-nAg: 95%). Untreated CWF disks had a bacterial mass rejection (Rmass) of 96%, while nAg impregnated showed values above 99%. Bacteria log removal values (LRV) varied with the type of nanoparticle applied to the disks, rosemary-nAg impregnated disks attained the highest value among all the nAgs tested. In terms of lead removal, non-impregnated Red Art disks had a Rmass of 61%, while the nAg impregnated filters removed 74%, 72%, and 69%, for disks impregnated with casein-nAg, rosemary-nAg, and maltose-nAg, respectively. PAH removal was most effective in unmodified clay (72%), while modified disks had removal of 72% for casein-nAg, 67% for rosemary-nAg, and 69% for maltose-nAg. Mass removal rates of fluorene were determined at 73% for unmodified disks, while 74% for casein-nAg, 69% in rosemary-nAg, and 72% in maltose-nAg modified disks. nAg treated disks exhibited no statistical difference in PAH removal when compared to untreated. Application of nAg reduced the amount of culturable

bacteria extracted from the surface an interior of the disks compared with unmodified disks. Results show that nAg impregnation increased the removal rates of E. coli and lead in the disks and that nAg average size and size distribution is an important factor in the removal rate of bacteria and lead in CWF.

INTRODUCTION

Outbreaks of waterborne diseases are prevalent throughout the world, with an estimated 10% of the world population lacking access to improved sources of drinking water [1]. Furthermore, over 2.4 billion people live without access to improved sanitation facilities [1]. Even in the presence of a centralized water source, contamination by waterborne pathogens can occur during collection, transportation, or storage of water [2]. Household level water treatment (point-of-use) systems are a promising low-cost, and socially acceptable means of preventing water-borne diseases in rural and urban developing communities.4 Although pathogens are the main contaminant of concern in most drinking water networks, chemical contamination by heavy metals and hydrocarbons can also occur [1]. Drinking water can be impaired with these pollutants through mixing with stormwater runoff [4,5]. Ceramic water filters (CWFs) are a point-of-use water treatment alternative used in more than 20 countries [2,6–9]. CWFs are produced using locally sourced materials such as clay and sawdust. CWFs have been proven to remove more than 99% of particles with an average diameter greater than 1 μm, and thus remove pathogens above that size threshold [10]. CWFs impregnated with antimicrobial agents such as silver nanoparticles (nAg) exhibited up to 5 log of bacteria removal (99.999%) [6, 10]. Previous studies have extensively evaluated CWFs for pathogen removal, however, little is known about their organic and inorganic contaminant removal capacity [2,8]. Additionally, there is a lack of systematic assessment about the use of nAgs with different surface functionalization within the context of CWF. The surface of the nanoparticles can be functionalized with different agents which can determine the size and surface charge of the nanoparticles [11]. The chemical properties of the surface functionalization agent can have implications in the contaminant removal of the CWFs, including the sorption of organic and inorganic contaminants, and the bacterial removal efficiency of the filter. Surface functionalization influences nanoparticles interaction with other molecules and media, as well as surface charge, and particle size. These factors have been shown to affect the amount of silver released from the nanoparticles, contaminant sorption, and nanoparticle stability [14,15] The surface modification of nanoparticles can also change the antimicrobial properties of the nanoparticles [16]. Previous studies have shown that nAg surface functionalization agents can enhance the microbiological removal performance of the CWFs due to the factors such as surface charge, silver ion release, agglomeration and particle size [12,13] . However, these studies do not cover the organic and inorganic contaminant removal of CWFs treated with different nAgs. To address these knowledge gaps, in this study disks were manufactured using Red Art clay and impregnated with silver nanoparticles with different surface functionalization. Red Art is readily available and commonly used by potters worldwide, therefore it can be used as control material to compare results among clays sourced in different geographical locations. Finally, since Red Art is a commercial product its properly are less variable than locally source clays. The disks, both with and without nAg amendments, were tested for their removal performance of heavy metals, organic contaminants (PAH), and Escherichia coli (E. coli) using a synthetic water.

MATERIAL AND METHODS

CERAMIC DISK MANUFACTURING AND CHARACTERIZATION

Similar to previous studies, disks of 5.5 cm in diameter and a thickness of 1.5 cm were used instead of pot shaped filters to simplify the geometry of CWFs used in real conditions. The mix to manufacture the disks consisted of 80% Red Art clay and 20% sawdust by weight [9]. Both sawdust and clay were sieved using screens with 60 and 100 opening per inch mesh to collect the fraction that remained between both sieves [9]. Clay and sawdust were dry mixed and then combined with distilled water [17]. Afterward, the mixture was placed into a cylindrical mold (diameter 6 cm) and pressed to 1000 psi for 1 minute. The disks were air dried at room temperature for three days and then fired in a kiln (Skutt KM1027: Single phase kiln). In brief, the firing program consists of temperature increasing at a rate of 150 °C h−1 until a temperature of 600 °C was reached, when the rate was increased to 300 °C h−1 until the temperature of 900 °C where it was maintained for 12 h [17]. After firing, the disks were glazed to prevent short flow out the side of the disks. The edges of the disks were coated with Amaco LM-13 food safe glaze. The glazed disks were fired again in a process similar to the on noted above, until a final temperature of 1050 °C to fully cure the glaze. The glazing process was repeated twice. The disks were then sealed onto plastic holders using food-grade silicon. Physical properties of the ceramic disks such as porosity, advection and dispersion coefficients were measured by tracer transport tests [17]. KBr was used as a conservative tracer. A calibration curve of different concentrations of KBr and conductivity readings was used to follow the profile of KBr in the over-time. The disks sealed to the holders where connected to a Masterflex peristaltic pump set to maintain a flow rate of 30.24 cm per day (0.5 ml min−1). This was calculated by taking the flow rate per cm2 of a full sized ceramic water filter and adjusting proportionally based on surface area of the disk [17]. The filters were saturated with de-ionized (DI) water overnight. At the start of the tracer experiment, DI water was collected for approximated ten minutes to determine the background conductivity reading. Then, 10 mL pulse of a 10 g L−1 KBr solution was injected, followed by DI water until the background conductivity reading was reached. STANMOD19 was used to fit the obtained breakthrough curve to the transient one-dimensional form of the advection– dispersion equation (eqn (1)): Equation 1:

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

The Initial boundary conditions [18] were:

$$c(x,0) = 0$$

$$c(0,t) = c_0\, for\, t < t_0$$

$$c(0,t) = 0\, for\, t > t_0$$

$$\frac{\partial c(L,t)}{\partial x} = 0$$

where R is the retardation coefficient, D is the dispersion coefficient (cm2 min−1), c is the concentration of KBr, v is the linear velocity (cm min−1), t is the time (min), x is distance (m), t0 is the tracer pulse injection time (min), and L is the thickness of the disk (cm).

CHALLENGE WATER

A standardized synthetic water recommended by the National Sanitation Foundation (NSF) for testing point-of-use water treatment technologies was used [4]. The challenge water was modified with a mixture of heavy metals and hydrocarbons as used in previous studies to mimic the chemical constituents found in a water body impaired by surface water runoff [5]. To the author's knowledge, this is the first study in which NSF challenge water were used for testing CWFs. Previous studies used either natural or different synthetic water recipes [7,19,20]. The used of a standardized water chemistry recipe for the testing of ceramic water treatment technologies would allow for the direct comparison of results and trials on a large scale.

SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES

Casein-nAg were obtained from Argenol laboratories with a silver content of 70.37% w/w Ag0 . The silver nanoparticles bind to the casein polymers via complexation with the carboxylate or amino groups [21]. Maltose-nAgs were synthesized using a modified Tollen's method [23]. in which silver nitrate is reduced using maltose. Poly-vinyl pyrrolidone (PVP) was added to the solution as a coating agent which interacts with the surface of the nanoparticles acting as a steric barrier against agglomeration. Rosemary-nAgs were synthesized using a modified Tollen's method, which uses an extract of the rosemary bush. In this method, rosemary leaves (Rosmarinus officinalis) were washed in distilled water and dried at 50 °C. Dried leaves were then added to an Erlenmeyer flask with distilled water and boiled to release compounds into solution. Rosemary extract was then cooled and filtered to obtain a clear yellow extract [11]. This solution served as a reducing agent, and was used in place of maltose in the modified Tollen's method. Both maltose-nAgs and rosemary-nAgs were filtered using a Spectrum Laboratories tangential flow filtration system (KR2i TFF) using a 0.05 µm polysulfone hollow fibre membrane. After filtration, the nanosuspension was concentrated using a 500 kD membrane. This ensured a suspension of pure nAgs without excess PVP or reducing agents from the synthesis procedure. Casein-nAgs were used as received by manufacturer. Silver nanoparticle stock solutions of 4 mM were prepared using both deionized (DI) and the challenge water (Table 1). A Joel JEM-2100 TEM transmission electron microscope was used to image the nAgs after suspension in the challenge water solution without bacteria. It is important to note that the images were taken of dried nanoparticles, not nanoparticles in solution. The hydrodynamic size and zeta potential of nAgs were determined using dynamic light scattering (DLS; Malvern Zetasizer Nano ZS, ZEN 3600) at 25 °C. Total silver concentration was determined using inductively coupled plasma optical emission spectrophotometer (ICPOES; Perkin Elmer Optima 3100 XL) [6]. The concentration of silver ions was measured by filtering samples through Amicon ultra-14 centrifugal filters (Millipore) at 3500 rpm for 30 minutes [4]. The solution was then measured with ICP-OES.

BACTERIAL CULTURES

A non-pathogenic strain of Escherichia coli (E. coli) K12 was used as model microorganism due to its relevance as indicator of fecal contamination in drinking water [8,17]. It has been used in several other studies involving nAg, allowing a direct comparison of results with previous works[6,8,17,19]. Bacteria were grown and harvested daily according to Vigeant et al. [22]. The E. coli concentration was determined by the membrane filtration technique [24].

ANTIMICROBIAL PROPERTIES OF SILVER NANOPARTICLES

The antimicrobial properties of each nAg variety were measured in terms of lethal dose 50% (LD_{50}) before application to the ceramic disks. Challenge water conditions were used for these tests. Triplicate batch tests were conducted to assess the deactivation of bacteria when exposed to various nAg concentrations (5.0-45.0 mg/L nAg) using a microplate reader (Biotek Synergy MX). Details of methodology are described in the supplemental information [11]. A BacLight kit containing propidium iodide fluorescent nucleic acid stains and SYTO 9 dyes was used to determine the ratio between live and dead bacteria after a 24 hr contact time. Equation 2 was used to determine the percentage of live bacteria.

Equation 2:

$$\% \, Live \ Bacteria = \frac{P_t}{P_c} \times 100$$

where P_t is the green/red fluorescence ratio for bacteria exposed to nAg and P_c is the is the green/red fluorescence ratio for unexposed bacteria.

ORGANIC AND INORGANIC CONTAMINANTS

Metal concentrations were analyzed using a PerkinElmer inductively coupled plasma optical emission spectrophotometer (ICP-OES; Perkin Elmer Optima 3100 XL25). The PAH samples were prepared according to EPA method 610 and analyzed using a gas chromatograph coupled with a mass spectrophotometer (Shimadzu GC-MS QP2010).[26]

IMPREGNATION AND RETENTION OF SILVER NANOPARTICLES IN THE CERAMIC DISKS

Upon completion of the tracer experiments, the ceramic water filters were amended with nAg on a 0.3 mg g−1 basis,[9] which is the recommended dose of silver nanoparticles. A stock nanosuspension of each nanoparticle was prepared, and the respective nanosuspension applied pipetting it onto the surface of the disk. One side of the filter was treated at a time, and allowed to dry overnight. The surface of each disk was divided into quarters, each receiving the appropriate mass of nAg for the eight of the filter. The mass of nAg remaining in each filter after the experimental period was calculated by subtracting the mass of nAg collected in disk effluent from the mass of silver applied to the disks.

CONTAMINANTS REMOVAL EVALUATION

Before the start of the contaminant removal experiment, challenge water without contaminants was pumped through the disk to verify that the concentration of silver in the effluent was below the WHO safe draining water limit of 0.1 mg L−1 . [27] Contaminant removal experiments were conducted over a period of 13 days. Challenge water solution was prepared daily and kept at 10 °C to minimize decay of bacteria and volatilization of PAH compounds. Samples were taken at 3 h, 6 h 9 h, 24 h, and every 24 h thereafter until the end of the 13th day. At each sampling period, separate samples for PAHs, metals, and bacteria were taken and process according to procedures described in above. At 24 h, bacterial decay of 10% was detected in the feed solution and taken into consideration in bacterial removal efficiency calculations. At the end of the sampling period, to determine the distribution of bacteria throughout the disks, bacteria on the surface and interior pores of the disks were quantified. To accomplish this, the intact disks were submerged in phosphate buffer solution5 and sonicated twice for 10 min at 20% amplitude using an ultrasound probe (QSonica Q125). To quantify bacteria trapped in the interior pores of the disks, the filter was cut into quarters and sonicated similarly as described previously. Bacteria concentration was determined.

RESULTS AND DISCUSSION

CERAMIC DISK MANUFACTURING AND CHARACTERIZATION

Table 2.2 shows the results of tracer transport experiments as well as the fitted values for linear velocity, and dispersion coefficients determined using STANMOD. An acceptable recovery rate of more than 95% of KBr mass injected was obtained during sample collection for tracer tests. Parameters fitted with R2 values ranging from 0.95 to 0.97 were used to prevent over fitting. Results showed similar characteristics among all Red Art clay disks manufactured, also disks exhibited hydraulic characteristics (advection and dispersion coefficients, retardation factors, and effective porosity) similar to previously reported data using Red Art disks as well [8,28] or with other natural clay sources [19,29,30] Results in Table 2.2 show that the impregnation of silver nanoparticles did not impacted the hydraulic characteristics of the disks. Compared to CWFs manufactured from natural clay sources, such as Guatemalan and Mexican clay sources, the Red Art clay exhibits a higher hydraulic conductivity of 4.99 × 10−5 cm s−1 , compared to Guatemalan filters (1.15 × 10−5 cm s −1) and Mexican filters (3.26 × 10−5 cm s−1).9 Red Art disks also exhibited a similar linear velocity when compared to Guatemalan and Mexican filters, and had a porosity of 43.2%, compared to literature values of 38.8% for Guatemalan filters, and 37.4% for Mexican filters. [8]. Ceramic filters made from Moroccan clay exhibit a median pore size of 11 micrometers and a porosity of 43%.29 Furthermore, CWFs manufactured from clay sourced in Cambodia, Nicaragua, and Ghana exhibit porosity values of 43%, 38%, and 34% respectively.[30] Pore size was not measured in this study however, all other physical characteristics agree with Red Art clay filters from literature values [9] in which median pore diameter was 2.03 micrometers. This value is important to ensure the removal of bacteria due to size exclusion process and tortuosity of the porous matrix. Fig. 1 shows a SEM image revealing the porous nature of the disks formed from the combustion of the burnout material.

SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES

Table 2.3 shows the hydrodynamic size, size distribution, and zeta-potential values for the three nAgs in challenge water conditions, without the presence of bacteria. Both Rosemary-nAg and Maltose-nAg have similar average hydrodynamic diameter and zeta potential, while Casein-nAgs presented larger diameters. The size distribution of each nanoparticle is displayed in Figure 2.1. It is important to notice the tailing displayed in the Casein nanoparticles, as there is a proportion of the Casein-nAg that reach sizes up to 700 nm in diameter. When Figure 2.3 is examined, it shows that all nanoparticles are spherical in shape.. The poly-dispersivity index (PDI) of the Rosemary and Maltose-nAg are in the acceptable range to be deemed monodisperse, whereas Casein-nAg can be classified as polydisperse (>0.2 PDI). Casein-nAg were not filtered using membrane filtration.

All zeta potentials are highly negative (-28.6 mV for Rosemary, -27.8 mV for Maltose, and -21.3 mV for Casein), meaning the nAgs are less prone to aggregation.

BACTERIAL REMOVAL EVALUATION

Silver ions dissolution in challenge water without bacteria present was determined to be less than 1% of the total nAg concentration for the three nAg (Table 3). Silver ion concentrations were supported by the fact that all nAgs exhibit similar antimicrobial properties (Fig. 4), and the only difference in filter performance was attributable to the size and retention rates of nAgs in the disks. The concentrations of bacteria in the surface and inside the porous matrix of the disks were measured at the end of each test (Fig. 6). Control disks (no nAgs) exhibited higher concentration of both superficial and matrix bound bacterial concentrations than disks treated with nAgs. For all the disks tested, higher concentrations of bacteria were detected on the surface than in the matrix of the disks. The results showed that the disks surface characteristics is the main contributor to process of bacterial removal. To our knowledge, this is the first study that clearly shows the importance of the disk surface on the overall microbiological removal process. This result also shows that ceramic disks perform in comparable manner to other membrane technologies in which the active filtration layer is the surface layer of the membrane [14]. Similar than with the effluent concentrations, rosemary nAgs amended disks had the lowest concentration of growing bacteria on their surface and interior compared to other two nAgs modifications. This implied that rosemary-nAg were the most effective amendment for disks, likely due to the higher nAg's mass retention compared with other nAgs amendments. The resultant bacteria removal efficiency of these nAgs and filter conditions were similar to findings made by Craver and Smith9 in which they attribute the variance in nAg microbiological removal performance amongst various filter types to the mass of nAg retained in each filter after treatment using the same type of nanoparticle. The greater mass retention of nAg resulted in a higher LRV of bacteria. Compared with other studies, the LRV value observed are within the expected range [8,20] Several mechanisms contribute to the microbiological removal/inactivation by CWFs treated with nAg including, damage to bacteria by pitting of the cell membrane, lysis of cells caused by silver ion release, or damage of the cell by reactive oxygen species formed on the surface of nAg. Bacterial removal by unmodified CWFs is due to physical straining, exclusion based on pore size, or entrapment in dead end channels in the porous matrix of the CWF [8].

INORGANIC AND ORGANIC CONTAMINANT REMOVAL

Table 4 shows mass rejection (Rmass) coefficient for all contaminant for all filters tested. Rejection coefficients reflect the percentage by mass that was able to be transported through the filter and was detectable in the effluent. Rmass is a widely used value to compare removal efficiencies on filtration processes.32 Lead removal can be attributed to hydroxyl groups, oxygen and nitrogen present in the nanoparticles surface coating compounds can form metal complexes30 (Fig. 7). The higher Pb sorption compared to other metals could be due bonding with hydroxyl groups and formation of complexes with the nanoparticle surface functionalization. Finally, the bare clay surface area could also provide some sorption sites for these metals, explaining the lead sorption without nanoparticle impregnation. All disks modified with nAg exhibited no difference in PAH removal compared to unmodified disks (Table 3, Fig. 8). PAH removal may be attributable to entrapment in dead-end pore spaces in the ceramic filter matrix. PAHs were removed at the same level throughout the entire time trial. Similarly, to other studies, it is hypothesized that the removal of organic contaminants was largely attributable to the partition of these materials onto the organic phase present on the surface of coated of silver nanoparticles in the CWFs.9 While there was no variation in removal of PAHs by modified and unmodified filters, the removal mechanism is thought to be due to both adsorption and entrapment of the molecules in dead-end channels in the porous matrix of the CWFs.

CONCLUSION

The results show that ceramic disks designed for water filtration are not only effective biological filtration devices, but also have the potential to remove other organic and inorganic contaminants from drinking water. This study reinforced the proven effectiveness of nAg to enhance bacterial removal rates on CWFs, however we were unable to demonstrate that changes in disks performance were due to different surface functionalization of nAgs. nAg impregnation increased the sorption capacity of lead in comparison to unmodified filters. nAg application did not affect the removal rates of PAH compounds, which were more influenced by filter material and hydraulic properties. The most important factor in the variation of bacterial removal rates was the size of the nanoparticle (in terms of range, average size, and polydispersivity) in which a monodisperse solution of small nanoparticles added to disk yield higher LRV values than disk impregnated with larger and polydisperse nanoparticles. This paper also determined that the most important barrier to bacteria was the surface of the ceramic disks, where the greatest portion of the viable *E. coli* were found. If

CWFs could be produced to have a well defined surface in terms of pore size distribution and median pore sizes, a more efficient filter for bacteria removal could be produced. In the interest of improving the performance of ceramic water filtration performance in CWF factories worldwide, understanding the effects of size and polydispersivity of nanoparticles on the contaminant removal is essential. This study showed that both the average size, and size distribution of nanoparticles applied to ceramic water treatment affect the removal of various compounds commonly found in drinking water.

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TABLES

2.1 Challenge water chemistry

Constituent	Value
E. coli	$7.3*10^6$ CFU/100 mL
Sea Salts (Sigma Aldrich)	1.5 g/L
Zinc (ZnO)	10.0 mg/L
Copper ($CuSO_4$)	2.5 mg/L
Nickel ($Pb(NO_3)_2$)	2.5 mg/L
Cadmium ($Cd(NO_3)_2$)	1.2 mg/L
Lead ($Pb(CH_3COO)_2$)	3.6 mg/L
Acenaphthene	0.871 mg/L
Fluorene	1.11 mg/L
pH	6.5

Table 2. 1. Ceramic water filter characterization

x

	Control	0.3mg/g Rosemary	0.3 mg/g Maltose	0.3 mg/g Casein
hydraulic conductivity (cm/s)	4.99E-05	4.99E-05	4.99E-05	4.99E-05
porosity (%)	43.2	43.2	43.2	43.2
linear velocity (cm/min)	0.021	0.021	0.021	0.021
coefficient of hydrodynamic dispersion, D (cm^2/min)	0.0048	0.0048	0.0048	0.0048

Table 2. 2 Physical and hydraulic characteristics of nAgs

	Rosemary	Maltose	Casein
Hydrodynamic Diameter (nm)	46.7 +/- 7.8	56.2 +/- 8.1	104.5 +/- 11.5
Zeta Potential (mV)	-28.6	-27.8	-21.3
Poly Dispersivity Index (PDI)	0.12	0.18	0.58
Percent silver ions (%)	0.87%	0.92%	0.98%
LD_{50} (mg/L)	13.98	13.87	14.5

Table 2.3 Mass rejection values exhibited by the Read Art Clay filters for various contaminants.

	Control	0.3 mg/g Casein	0.3 mg/g Rosemary	0.3 mg/g Maltose
E. coli	0.95	>0.99	>0.99	>0.99
Lead	0.61	0.74	0.72	0.69
Fluorene	0.73	0.74	0.69	0.72
Acenaphthene	0.72	0.72	0.67	0.69

FIGURES

Figure 2.1 SEM image of the surface of a ceramic water filter at 859X magnification, EHT setting of 5.00 kV and imaged using backscatter mode.

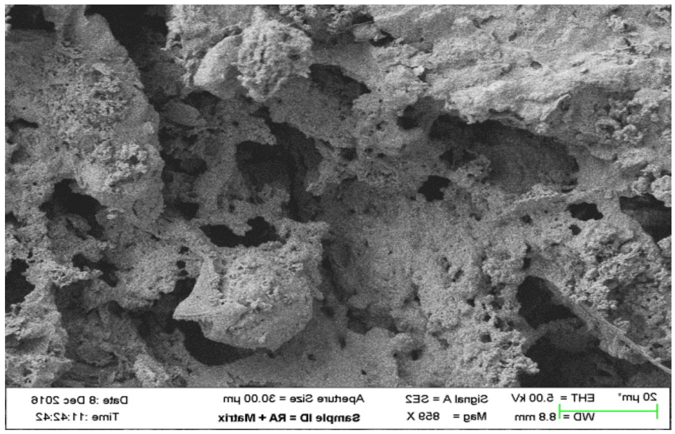


Figure 2.1 Nanoparticle size distribution in challenge water for three species of nanoparticles.

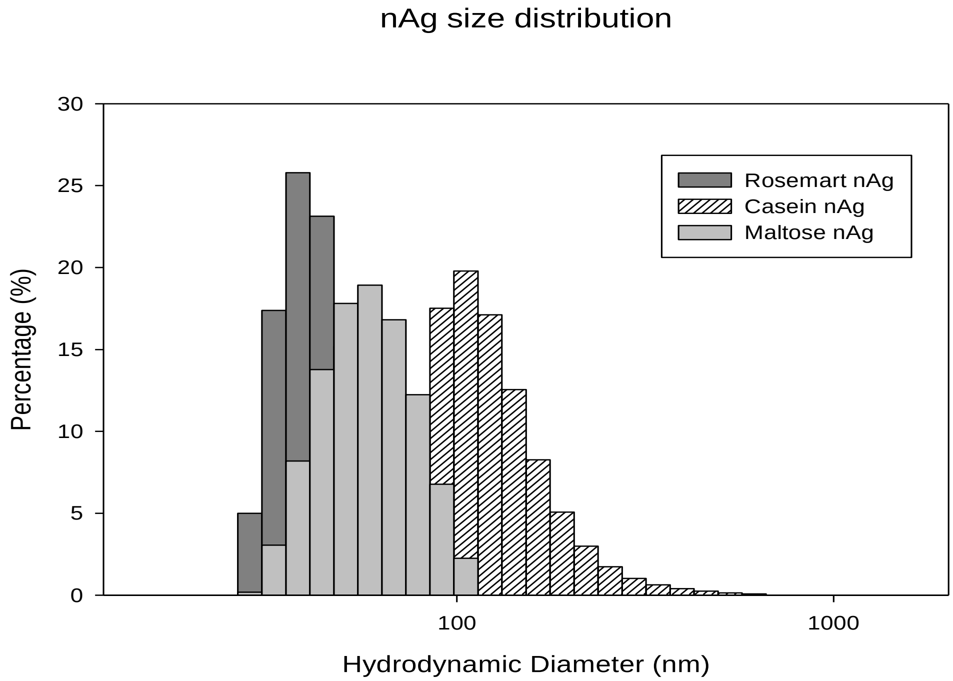


Figure 2.2 TEM images of nAg. Rosemary nAg at 40000X and 200.0 kV, Maltose nAg at 40000X and 200.0 kV (Center), Casein nAg at 12000X and 220.0 kV (Right). All images taken in backscatter mode. Red scale bar is 100 nm.

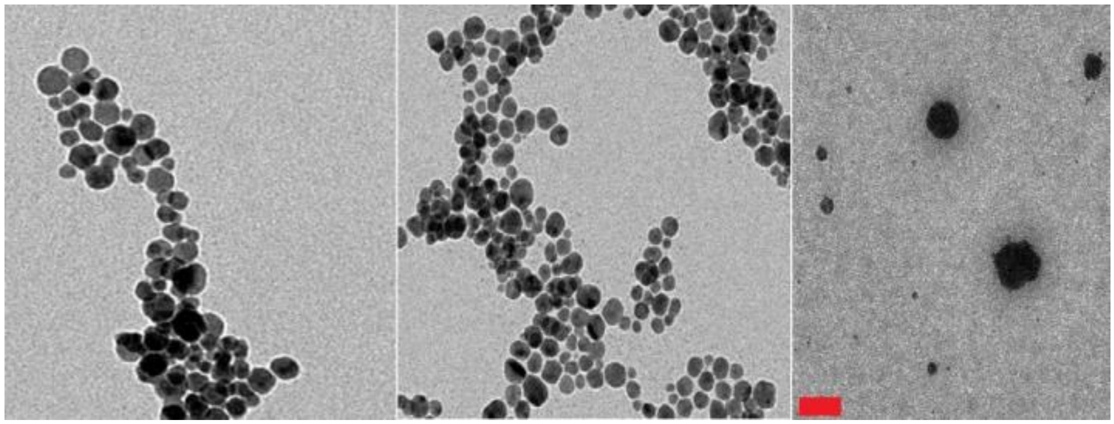


Figure 2.3 Nanoparticle antimicrobial properties in challenge water

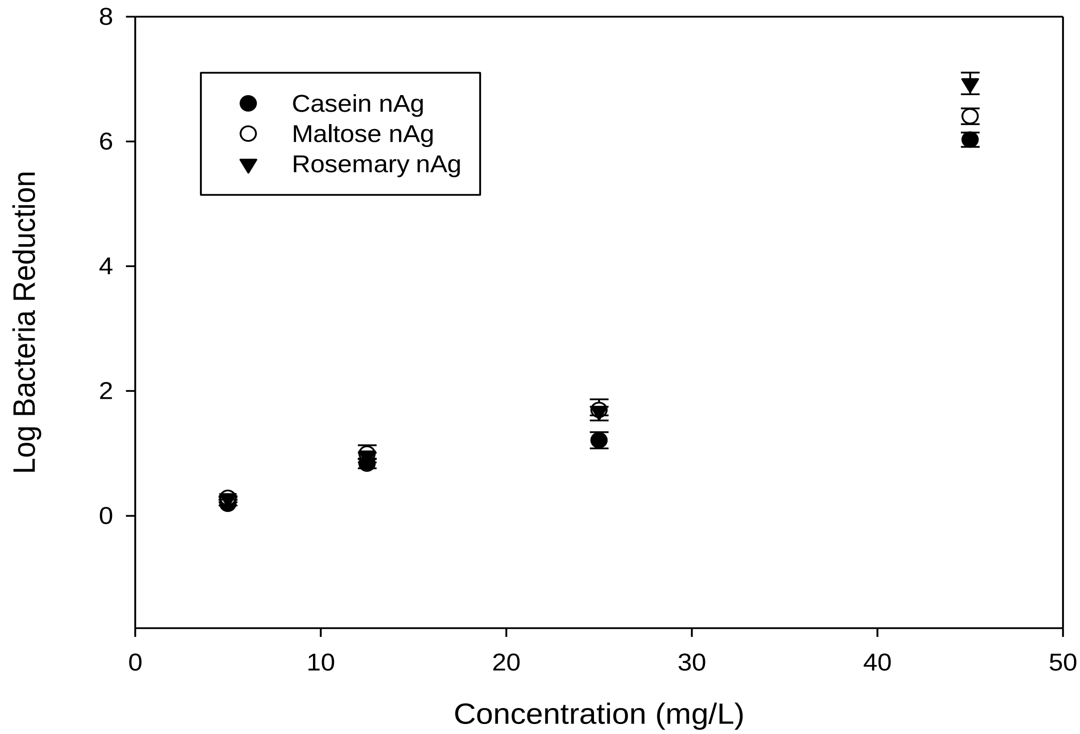


Figure 2.4 Results of bacterial removal experiments for Red Art clay filters over the experimental period.

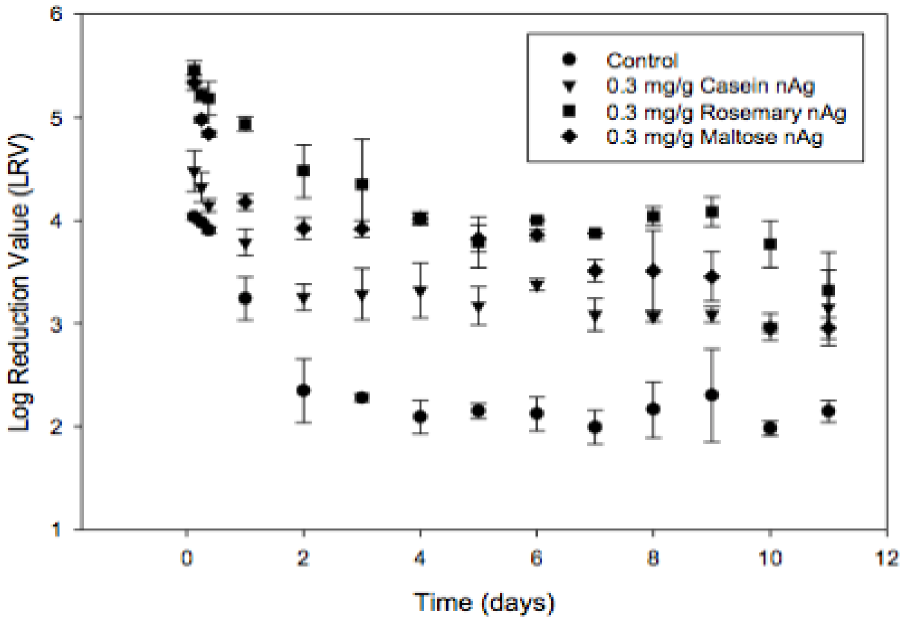


Figure 2. 5 Superficial and internal concentration of bacteria in control and amended disks.

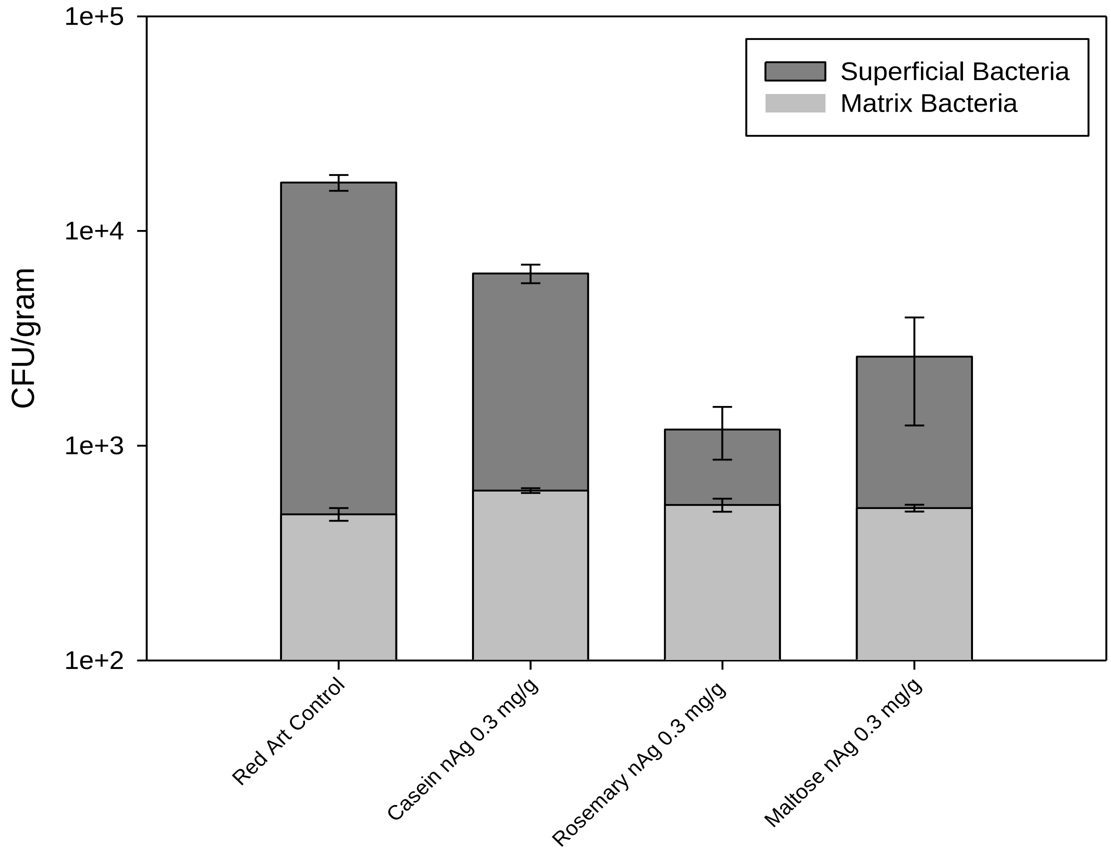


Figure 2.6 Lead concentration in the effluent of control and amended disks. Red line represents the influent concentration.

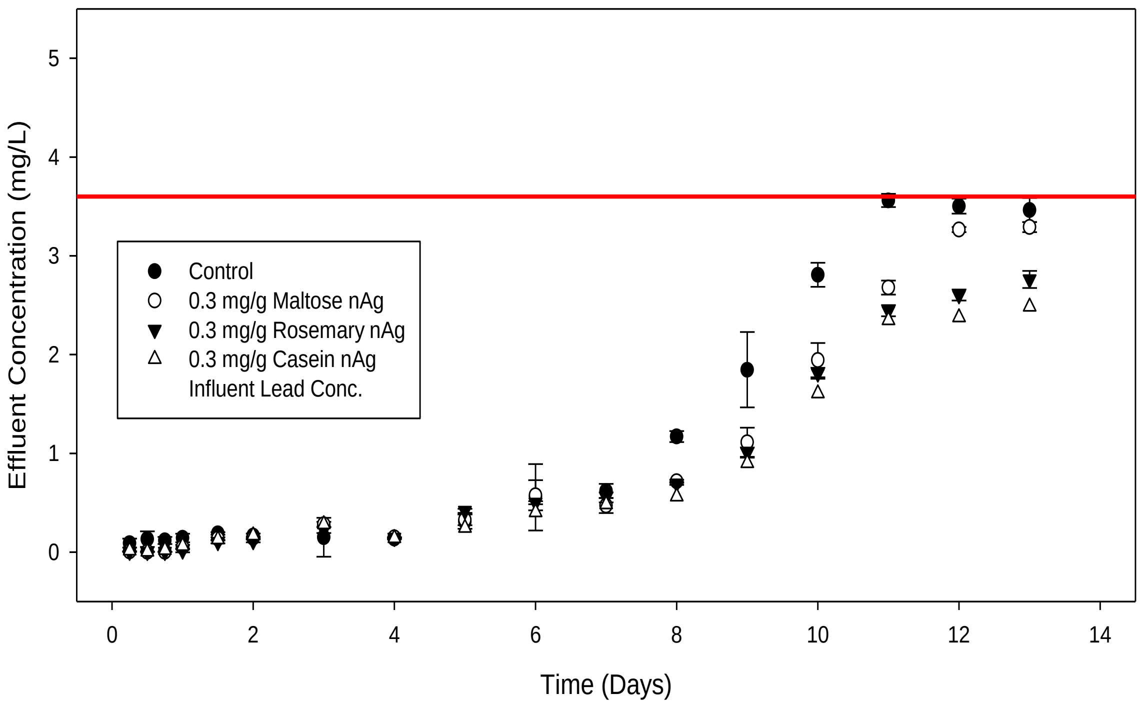
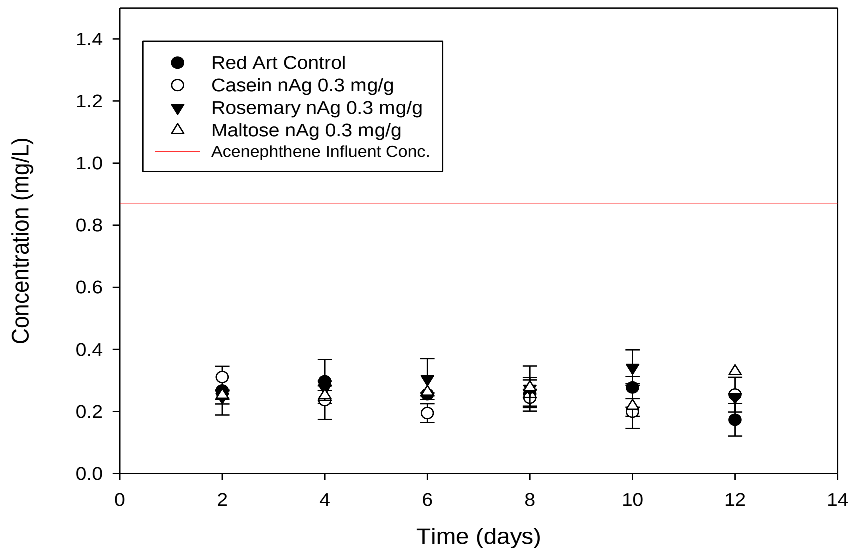
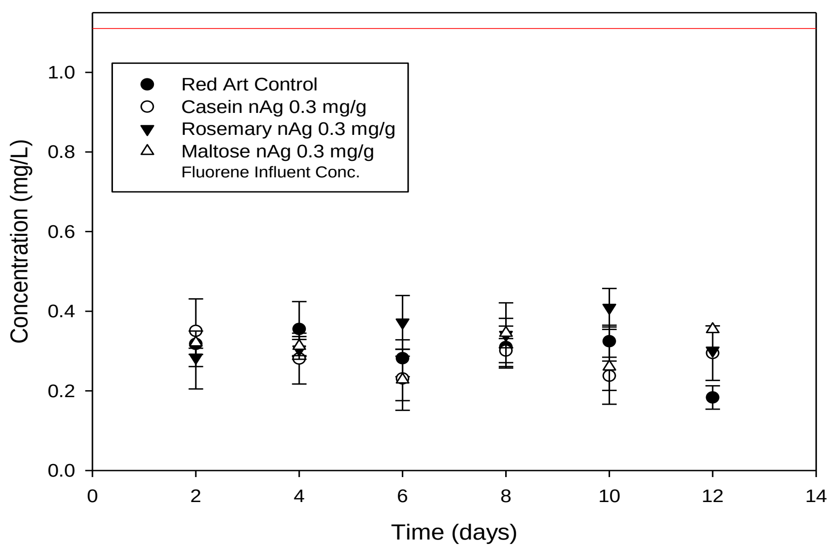


Figure 2. 8 Acenaphthene (top) and fluorene (bottom) concentrations in disk effluent. Red line marks influent concentration


Red Art Control
Casein nAg 0.3 mg/g
Rosemary nAg 0.3 mg/g
Maltose nAg 0.3 mg/g
Acenephthene Influent Conc.
Concentration (mg/L)
Time (days)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
2
4
6
8
10
12
14


Red Art Control
Casein nAg 0.3 mg/g
Rosemary nAg 0.3 mg/g
Maltose nAg 0.3 mg/g
Fluorene Influent Conc.
Concentration (mg/L)
Time (days)
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
10
12
14

CHAPTER 3:

FIELD TRIAL OF CERAMIC WATER FILTERS FOR USE IN CLEANSIP WATER BOTTLE IN SOWETO, SOUTH AFRICA

ABSTRACT

In this chapter, the performance of Red Art Clay ceramic disks functionalized with two types of silver nanoparticles (nAg) was assessed when used along with the CleanSip water bottle. The CleanSip bottle was developed by researchers at the University of Johannesburg (South Africa) and is an inexpensive portable water treatment. The system was tested with a synthetic challenge water, proposed by the National Sanitation Foundation as a standard for testing point-of-use water treatment to ensure acceptable performance. Additionally, two natural water samples from the Klip River, and the Emmarentia Dam were used in this study as well. These water bodies commonly used as drinking water sources by local communities.

Natural water samples exhibited up to a 3.81 and 3.92 LRV of bacteria in samples from Emmarentia Dam and the Klip River, respectively, when filtered through a ceramic disk treated with Rosemary-nAg. Maltose-nAg also proved effective at reducing bacterial concentrations in both waters, exhibiting an LRV of 3.76 from Emmarentia Dam and 3.64 from the Klip river. Untreated Red Art disks exhibited LRVs of 2.87 for Klip River water and 1.95 for Emmarentia dam. LRVs followed a similar trend than in Chapter 2, where Rosemary-nAg removed more bacteria than both the control and the maltose nAg disks. As in previous studies [20, 35] results suggest that variation in performance of the system are due to that variance in influent water composition, in which the turbidity of the natural waters effects the filtration efficiency, possibly clogging larger pores, allowing fewer bacteria to pass through the filter.

CHAPTER 3.1

INTRODUCTION

The Soweto Region of South Africa faces many water quality and supply challenges. Improved drinking water sources are available, but municipalities do not always meet the safe drinking water standards for the country[1]. Lack of access to improved sanitation facilities, and portable toilets are common in many communities, contributing to the bacterial contamination of surface water (Figure 3.1).

Furthermore, many residents of this area work in mines and agricultural areas do not have access to improved water sources and are forced to consume untreated surface water. The University of Johannesburg in South Africa developed the CleanSip water bottle as a solution to this problem, aiming to provide workers with a portable means of water filtration. The bottle is designed in three pieces an influent water reservoir, a filter cartridge with a one-way valve, and a receptacle reservoir to hold water after it has passed through the filter cartridge. Operation of this water bottle is diagramed in Figure 3.2.

During preliminary testing of the CleanSip bottle by the University of Johannesburg, a flocculant-disinfectant agent (Moringa seeds) was used to settle particulate matter and pathogenic organisms. However, after use of the flocculent the water appeared cloudy and with small flocs that did not look attractive to the consumer. A solution to this issue was to replace the flocculant-disinfectant agent with a membrane filter such as the ceramic disks.

Ceramic water filters are a sustainable, locally produced, and low-cost water treatment option, making them a viable option for use in the CleanSip system. In addition, CWFs have already proven to be an effective and socially accepted means of water filtration in rural communities in South Africa [2]. In the resource-limited settings present in many provinces in South Africa, ceramic filter cartridges are a low cost solution made from locally available materials and labor.

The objectives of this chapter were to; a) confirm performance of CWF in CleanSip bottle with Challenge water; b) assess bacterial removal performance of CleanSip bottle when natural samples are filtered.

CHAPTER 3.2

METHODOLOGY

CERAMIC DISK MANUFACTURING AND CHARACTERIZATION

Ceramic disks were manufactured as described in the corresponding section in Chapter 2. The size of the disk was modified to of 6.5 cm in diameter and a thickness of 1.5 cmto fit the CleanSip water bottle.

SYNTHESIS AND CHARACTERIZATION OF SILVER NANOPARTICLES

Silver nanoparticles were synthesized and prepared as described in the corresponding section in Chapter 2. Casein-nAgs were not considered in this study due to the fact that they did not perform as well as both the Maltose and Rosemary-nAg, exhibiting only an initial 4.5 LRV compared to LRVs close to 5.5 in Rosemary and maltose-nAg amended filters.

BACTERIAL CULTURES

Bacterial Cultures were grown and prepared according to the process described in Chapter 2.

IMPREGNATION AND RETENTION OF SILVER NANOPARTICLES IN THE CERAMIC DISKS

Ceramic disks were treated with nAg and assessed for silver retention according to the process described in Chapter 2.

COLLECTION OF ENVIRONMENTAL SAMPLES

Two locations in the Soweto Province of South Africa were used as baseline environmental samples (Figure 3.1). The locations consisted of a local reservoir (urban), and a large river (rural). These locations were routinely used as a drinking water source for the local communities. Samples were taken in sterile containers in accordance with EPA Method 1604 [3] for *E.coli* from surface water bodies. Samples were kept at ten degrees Celsius. Fecal coliforms were quantified via membrane filtration in a laboratory setting. Turbidity and conductivity of the environmental samples were measured. Turbidity of environmental samples was measured using an Oakton t-100 turbidity meter. Conductivity was measured using an Oakton CON+ handheld conductivity meter.

EXPERIMENTAL SETUP

The ceramic water filters were fitted in the filter cartridge of the CleanSip water bottle with silicone to prevent short flow and ensure the proper function of the system (Figure 3.2). Three filters were used in this experiment; unmodified Red Art Clay filter, and Red Art Clay filters impregnated with 0.3 mg/g Rosemary-nAg, and 0.3mg/g Maltose-nAg. Experiments were run in duplicate.

Filter performance in the CleanSip bottle was assessed by testing with the modified challenge water as described in Chapter 2, however, metals and hydrocarbons were not added as the equipment necessary to analyze for those constituents was not available at the University of Johannesburg. Due to the size of the CleanSip bottle, 1 Liter of samples were run through each filter in two 500 mL volumes. A treated water sample was taken after a batch of 500 mL of water had passed through the filter under fluctuating-head conditions. Samples were taken in triplicate. Once the performance of the filters was verified with challenge water, new filters were sealed into the CleanSip bottles and the procedure above was repeated with natural water samples.

CHAPTER 3.3

RESULTS AND DISCUSSION

CERAMIC DISK MANUFACTURING AND CHARACTERIZATION

Table 3.1 shows that the ceramic disks exhibited similar hydraulic characteristics to those manufactured and tested in Chapter 2. Values such as hydraulic conductivity, linear velocity, porosity and dispersions coefficients vary slightly from those reported for the smaller disks in Chapter 2. This is likely due to a variation in the manufacturing process due to the slight up-scaling of the disks (5.5 to 6.5 cm in diameter). However, KBr tracer tests yielded >95% tracer recovery, and values obtained from analysis are nearly the same as those exhibited by the smaller ceramic disks in Chapter 2.

SYNTHESIS AND CHARACTERISATION OF SILVER NANOPARTICLES

This study utilized the same Maltose and Rosemary-nAg as were used in Chapter 2. Figure 1.4 shows nanoparticle toxicity in challenge water conditions. The LD_{50} of bacteria when exposed to Rosemary-nAg, Maltose-nAg and Casein-nAg was 13.98mg/L, 13.87 mg/L, and 14.50 mg/L respectively.

IMPREGNATION AND RETENTION OF SILVER NANOPARTICLES IN THE CERAMIC DISKS

When compared to silver retention of the ceramic disks in Chapter 2, all treated disks exhibited about identical (±1%) silver retentions (Tab. 3.1). Similar to Chapter 2, the variance in mass retention can be attributed to the average size and size distribution of the nAg in which the smaller more monodisperse particles are preferentially retained within the matrix of the CWF.

WATER QUALITY AND BACTERIAL QUANTIFICATION OF NATURAL WATER SAMPLES

Natural water samples taken from the Klip River and Emmarentia Dam were found to have concentrations of fecal coliforms: $5.1*10^5$ CFU/100 mL in water from Emmarentia Dam, and $7.1*10^5$ CFU/100 mL in water from the Klip River. The challenge water solution has $7.26*10^6$ CFU/100 mL as described in Chapter 2 (Table 2.1). All experiments were conducted in a laboratory setting at the University of Johannesburg.

Turbidity and Conductivity measurement for all water tested are shown in Table 3.2, which shows that the Challenge water influent the filters exhibited an order of magnitude higher concentration of bacteria, but was much less turbid and had a lower conductivity than the natural waters it was being compared to.

BACTERIAL REMOVAL EVALUATION

Results from the bacterial removal experiment are shown in Figure 3.5. It should be noted that fecal coliform concentration among the three water samples vary by slightly more than one order of magnitude in the three samples.

When the challenge water was used, unmodified Red Art Clay filters exhibit a LRV of 2.90 while Maltose-nAg impregnated disks exhibit an LRV of 4.72, and Rosemary-nAg disks exhibit an LRV of 4.87. These results are similar than those found in the previous study (Chapter 2).

When results from the filtration of the natural samples are examined, the unmodified Red Art Clay disks exhibit LRVs of 1.92 from Emmarentia Dam and 2.81 from Klip River water, Maltose-nAg exhibited LRVs of 3.72 from Emmarentia Dam and 3.32 and Klip River, and Rosemary-nAg disks exhibit LRVs of 3.87 from Emmarentia Dam and 3.99 and Klip River respectively. When the results are observed, little variation between the LRVs of the two natural water samples in both the Maltose and the Rosemary-nAg disks was observed.

The National Sanitation Foundation dictates that an effective point-of-use water treatment system meets the threshold of >99.95% of influent bacterial concentration removed in the filtration process [4], which correspond to a LRV of 3.3. When compared to this performance standard, Rosemary-nAg disks perform above this benchmark when tested with all three test waters. Maltose-nAg was above this standard only when challenge water were applied, however, despite exhibiting an average LRV of the trials of Emmarentia Dam water and Klip River water, the range of error fell below the threshold of 3.3 LRV. Unmodified Red Art Clay disks failed to meet this standard across all three tested waters.

The results from the challenge water trial in the CleanSip bottle were compared to the results presented in Chapter 2. The performance of the CleanSip bottle after the filtration of 1 L of water can be compared to Figure 2.5, in which Rosemary-nAg exhibit an LRV of 5.31, Maltose-nAg and LRV of 5.18, and Unmodified Red Art Clay disks a LRV of 4.05.

A large difference was observed in the performance of the unmodified disks when tested with the challenge water when results obtained in both chapters were compared, disks tested in the CleanSip system exhibited a much lower LRV than when tested with the scaled-down version presented in Chapter 2, LRV of 2.81 versus 4.05, respectively.

The influence of water chemistry conditions on the performance of silver nanoparticles is a well studied phenomenon. Previous studies have concluded that more complex water chemistry conditions, such as the presence of divalent cations and high turbidity, often lead to the reduction in toxicity of nanoparticles when exposed to bacteria, especially in the presence of divalent cations [5-7]. When compared to the challenge water chemistry, one notable difference in the natural water chemistry is the high turbidity that it contains. This may contribute to the increased filtration performance exhibited by natural samples from the Klip River, in that the precise water chemistry of the natural waters could not be analyzed.

CHAPTER 3.4

CONCLUSION

The results demonstrate that the CleanSip water treatment system, when used in conjunction with ceramic disks functionalized with silver nanoparticles, has the potential to work as a means of biological filtration despite the failure of many of the filters to meet the standards set by the National Sanitation Foundation. As described in Chapter 2, bacterial removal performance of the system was significantly increased by the amendment of silver nanoparticles. However, not all ceramic disks performed to the standard as set by the National Sanitation Foundation. The system was successfully demonstrated to perform up to the NSF standard for bacterial reduction when used with both Rosemary-nAg impregnated ceramic filters, as well as with Maltose-nAg disks in only one water chemistry condition (Challenge water). The most important factor in the variation of bacterial removal rates appears to be the influent water chemistry conditions, in which the complex water chemistry of the environmental samples significantly decreased the bacterial removal rates of the ceramic disks when compared to the challenge water across all three filters conditions tested. This is due to the negative effect that highly turbid surface waters with have on the bacterial inactivation kinetics of nanoparticles [5].

In the interest of improving the performance of the CleanSip system, recommendations for future experiments include the in-depth evaluation of surface water chemistry conditions such as conductivity, pH, and turbidity of the performance of the CleanSip water bottle. Furthermore, the life effective lifespan of a ceramic water filter cartridge in the CleanSip bottle needs to be assessed for to determine the expected lifespan of the filters. This will likely be highly dependent on the concentration of bacteria in the surface water, as well as the turbidity of the water, which will cause fouling and decreased filter life. Furthermore, the combination of the ceramic filter cartridge and a compound that could act as a flocculant or disinfectant could serve to increase the bacterial removal effectiveness of the system, and warrants further investigation. Advancement in the understanding of the effects of the chemical and physical characteristics of surface water on the performance and longevity of the CleanSip system will contribute to the effective usage of the CleanSip bottle.

CHAPTER 3.5

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6. K. K. Bielefeldt AR, Summers RS. , *Water Research*, 2009, **43**, 3559-3565.

7. S. J. Oyanedel-Craver VA, *Journal of Environmental Engineering-ASCE* 2008, **42**, 927-933.

TABLES

Table 3.1 Characterization of ceramic disks used in CleanSip bottle.

	Control	0.3mg/g Rosemary	0.3 mg/g Maltose
hydraulic conductivity (cm/s)	4.99E-05	4.99E-05	4.99E-05
porosity (%)	43.1	43.1	43.1
linear velocity (cm/min)	0.019	0.019	0.019
coefficient of hydrodynamic dispersion, D (cm^2/min)	0.0050	0.0050	0.0050
Silver retention	NA	96%	92%

Table 3.2 Fecal coliform concentrations from Challenge water and Environmental samples.

	Challenge Water	Klip River	Emmarentia Dam
Fecal Coliform Count (CFU/100 mL)	$7.26*10^6$	$7.1*10^5$	$5.1*10^5$
Turbidity (NTU)	< 5	55	16
Conductivity (µS/cm)	950	1430	1260

FIGURES

Figure 3.1 Map of Johannesburg region of South Africa. Red dot depicts the Emmarentia Dam sampling location, while the green dot depicts the sampling location on the Klip River.

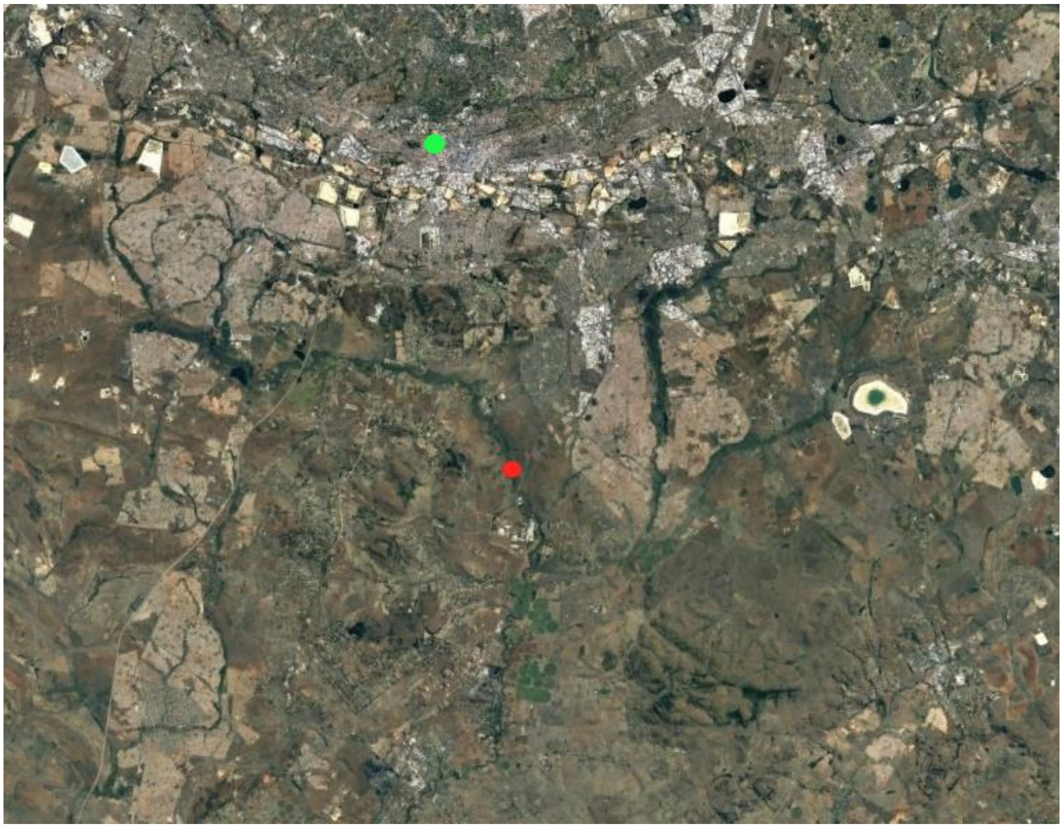

Figure 3.2 Ceramic disk sealed in CleanSip water bottle cartridge

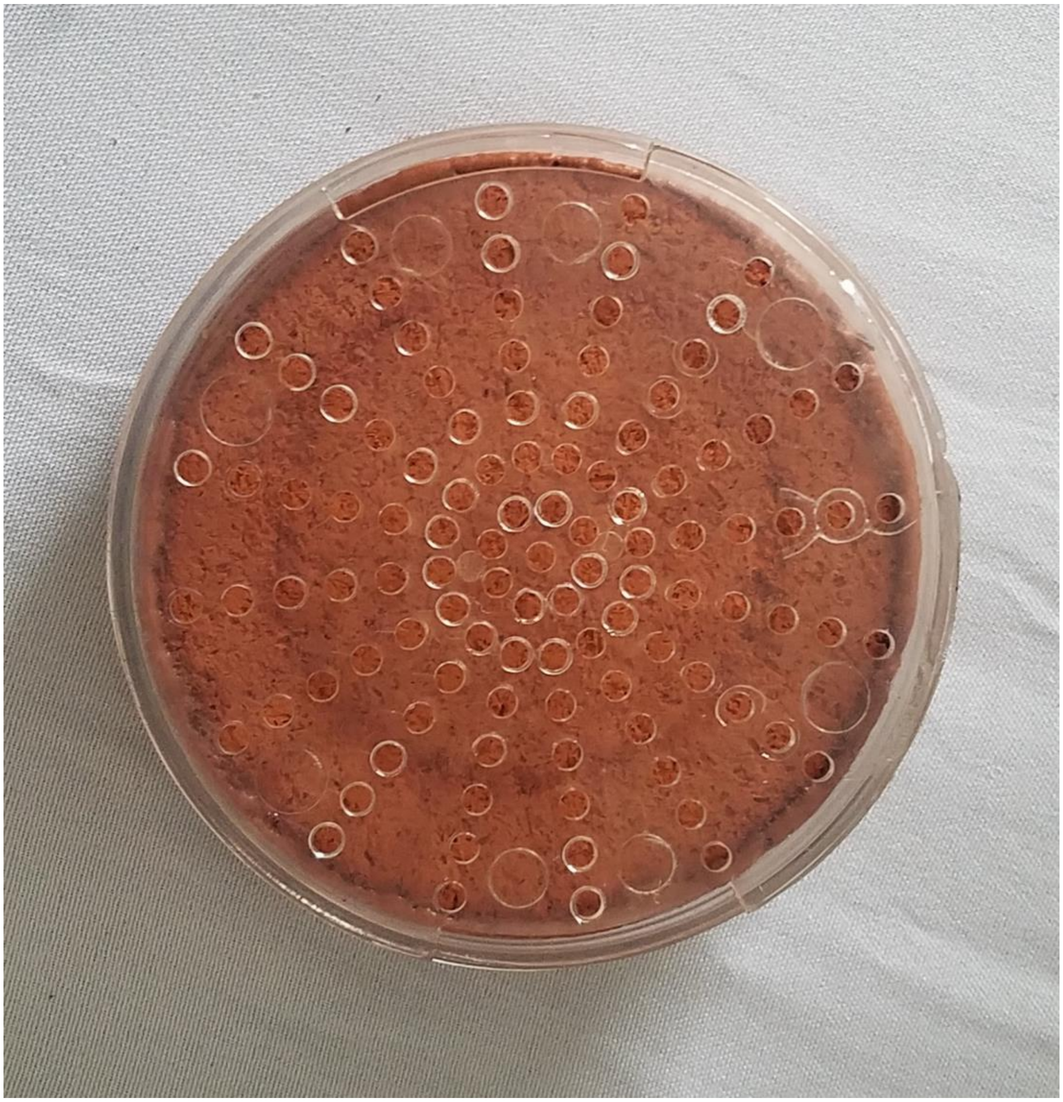

Figure 3.3 Water tap located in informal settlement in Soweto, South Africa. The blue building in the background of the picture is an outhouse which leaks into the small ditch that is seen running directly around the tap. This tap serves approximately 1700 people. The tap is located directly to the left of the building in the foreground, surrounded by the cement blocks.

Figure 3.4 The CleanSip water bottle and the operating procedure. The CWF is placed in the filter holder in the middle of the bottle. The red piece is a one-way valve. 1) Unscrew top from bottle. 2) Fill bottom reservoir with source water. 3) Screw top of bottle back on to bottom reservoir. 4) Ensure a connection is made an no leaks are present. 5) Invert water bottle at ~45 degrees. Filtration can take up to 30 minutes. 6) Filtered water is held in upper reservoir. One way valve prevents back flow. 7) Water is ready for consumption.

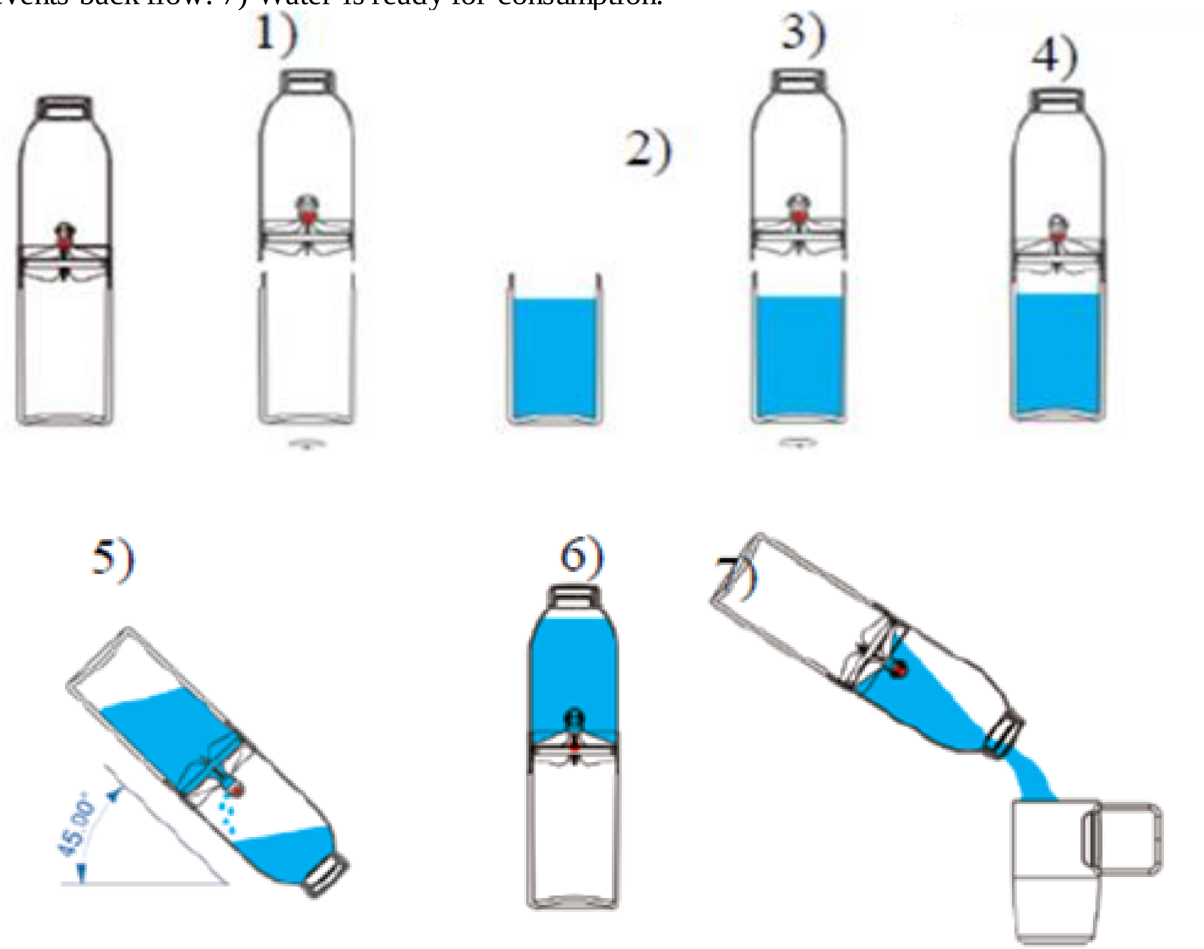

Figure 3.5 Log bacterial removal of CWFs used in conjunction with the CleanSip water bottle tested with three conditions; challenge water, Emmarentia Dam, and the Klip River