DEVELOPMENT OF A PROTOTYPE NANOTECHNOLOGY-BASED CLAY FILTER POT TO PURIFY WATER FOR DRINKING AND COOKING IN RURAL HOMES

Report to the
Water Research Commission

by

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EXECUTIVE SUMMARY

Background of the study and problem statement

At least five million people in South Africa still have no access to treated potable water within reasonable distances from their dwellings. Many thousands more take water from water sources and use it untreated because of problems experienced with provision of adequate and reliable potable water supplies. Further, conventional or package small and rural water treatment plants are often at a disadvantage regarding both their design and operation. In a study of 20 small water treatment plants (Swartz, 2000) it was found that most local (small) water treatment plants were not correctly designed for efficient water treatment or experienced problems in operating on a sustainable basis – thereby compromising final water quality. Surface waters have also steadily become more polluted, especially with regard to microbiological quality, which exacerbates the situation of immune-compromised individuals when drinking inadequately treated or poor quality water. It is an unfortunate fact that the populations still without potable water supply are also the most difficult, expensive and time consuming to service. This leads to people drinking and using water directly from unsuitable water sources, which results in incidences of sickness and even fatalities among young children.

Several clay pot-based, home treatment systems and devices are being used internationally by small, rural communities without bulk potable water services. Although some exploratory work relating to the use of these clay pots in other hygiene based studies has been carried out in South Africa, little has been done to evaluate these units or to improve their functioning in order to empower rural households without water services to ensure that the water they bring into their homes from untreated sources is safe to consume. The Potters for Peace clay pot, for example, has been used in countries such as Nicaragua and Cambodia for some time, but the silver used as the anti-bacterial material is simply painted onto the surface. Incorporating silver throughout the pot may increase water treatment efficiency, but may again increase the cost. A need therefore existed to source and to investigate appropriate nanomaterials-based methods to produce such a ceramic pot, which is ideally both more effective and less expensive than the ceramic units currently in use.

Project objectives

The project aimed to develop a prototype clay pot, incorporating anti-bacterial nanoparticles for the purification of microbially polluted water, for drinking and cooking purposes by rural families currently using water directly from untreated or poorly treated sources. Objectives of the project were the following:

i. Survey the available clay pot units currently being used internationally as home treatment devices and investigate the potentially viable options and their manufacturing processes.
ii. Investigate, through literature review and in practice, which anti-bacterial nanoparticle coatings and/or mixes may be used to efficiently inactivate bacteria and viruses.
iii. Manufacture a range of pots with various porosity values and incorporating various anti-bacterial nanoparticles.
iv. Evaluate their efficiency in bacterial and viral removal compared to that normally achieved by the conventional, silver-coated clay pot.

Methodology

A literature review was undertaken in which options potentially feasible for use in rural homes were investigated. Clay pot units currently being employed internationally as home treatment devices were summarized and the potentially viable options to use, as well as their manufacturing processes, were investigated. The anti-bacterial nanoparticle coatings and/or mixes which may be used to efficiently inactivate bacteria and viruses were identified. Following indications from the literature survey, a local ceramic pot was developed. However, rather than painting colloidal silver on the inside and outside of the pot as done in the well-known "Potters for Peace" ceramic pot, the inclusion of nanosilver into the clay by the incorporation of the silver in the firing process of the pot was investigated. A successful prototype ceramic pot was produced in conjunction with a commercial ceramic production plant (Cermalab cc) and evaluated in terms of efficiency of microorganism removal in laboratory tests.

Summary of the major findings and conclusions reached

Literature review
The following results emanated from the literature search during the study period:

Ceramic filters, whether produced commercially by companies in the developed world or by local potters in developing countries, have been shown to be effective in removing bacteria, in particular, *Escherichia coli,* and larger organisms such as protozoa and helminths, and in decreasing the incidence of diarrhoea among users. However, they are not very effective for virus removal.

The mechanisms of removal/inactivation of pathogens in silver-treated ceramic pots are not well understood. Physical straining, sorption and inactivation by silver all appear to play a role. Removal efficiency by sorption mechanisms appears to decline over time as sorption sites are exhausted. Routine cleaning will not regenerate sites within the filter walls. Testing limited volumes of water in new filters may therefore give an unrealistic impression of removal efficiencies, especially for viruses. Filters must be regularly scrubbed to remove surface clogging to restore the flow rate. Filters appear to remain effective for seven or more years if properly used and maintained. Plastic filtered water receptacles are easier to clean and disinfect than ceramic ones.

Clean filter discharge of typical Potters for Peace filter pots ranges from 1-3 ℓ/h. The flow rate is assumed to be related to the porosity, pore size and structure as well as the dimensions of the filter element, which in turn depend on the manufacturing process. However, the relationship between pore characteristics, discharge and removal efficiency has yet to be successfully quantified. The use of porous grog in the fabrication of filter elements is reported to improve flow characteristics.

Water treatment efficiencies in the field are often lower than those obtained in laboratory studies. Typical removal efficiencies in the field are expected to be up to 2 log bacteria, 0.5 log viruses and 4 log protozoa. Education about water and sanitation issues and training in the proper use and maintenance of the filters is critical to their successful implementation. Filter effectiveness has also been found to correlate with frequent follow up visits to households by community or health workers. Both treated and stored raw water can easily be contaminated by improper handling so training should include safe collection, handling and storage of water.

Ceramic filter elements are fragile and easily broken if dropped. Broken filter elements are a major reason for disuse of the filters in field studies, as is a damaged spigot on the filter receptacle. It is therefore important that communities have access to replacement parts.

Experimental study

The mechanisms by which silver amendments to filters act to improve bacterial removal in ceramic filters are not well understood. Silver ions that leach from the filter may play a role but silver is not usually detected in the filtrate after the first six months of use. Silver coated onto inert surfaces has been shown to generate active oxygen species through a catalytic reaction with oxygen. This can kill viruses and bacteria on contact with the surface. The same phenomenon has been observed with other metals and metal oxides including CaO and MgO. The advantage of silver is that it does not alter the pH of the water. Combinations of silver with other metals such as copper and zinc may improve removal efficiencies through synergistic effects; however, this has never been tested in this application.

The use of nanoparticles offers the possibility of enhanced reactivity compared to conventional coatings due to very high active surface densities. The biocidal activities of various types of nanoparticles have been tested, often in suspension with bacteria, which allows the particles to penetrate into the cells, but also when immobilised in inert matrices. Biocidal activity appears to correlate with smaller particle sizes (<10 nm), prevalence of {111} crystal facets and even dispersion of the nanoparticles.

Nanoparticles with demonstrated antimicrobial activity include silver, copper, magnesium and calcium oxide and their halogen adducts, titanium dioxide based photocatalysts and carbon nanotubes (in suspension). Except in the case of silver, the conditions under which these particles have been tested usually do not reflect the conditions expected in ceramic filters (pH, concentration, photocatalytic effects, mobility of nanoparticles, contact time).

There are general concerns about the use, environmental fate and impact of nanotechnologies largely due to lack of data. Recent studies have shown that some types of carbon nanotubes have adverse effects in mammals and in beneficial microbial populations in wastewater treatment.

A synthetic Silver Impregnated Porous Pot (SIPP) ceramic unit for household water filtration, incorporating nanosilver and producing approximately 1 ℓ/h of product water flow, has been successfully produced.

Based on the results, it has been effectively demonstrated that the new SIPP-M2 pots, in which nanosilver is impregnated into the clay during the firing process, were just as effective in removing bacterial contamination from influent water as the established Potters for Peace (PFP) pots sourced from Kenya but with unit water treatment cost advantages.

Utilising the SIPP pot, an average *Escherichia coli* removal rate of 1.2 logs (equivalent to 91.8% removal) could be displayed, up to a water production of 32 ℓ. The more efficient bacterial performance of the SIPP-M2 pots as compared to the PFP pots was attributed to the imbedded silver nanoparticles in the micropores. Since the imbedded silver nanoparticles are harder to wash away, the resultant bactericidal activity of the pot is longer than that of PFP pots since they only have painted colloidal silver on the inside and outside surfaces.

The silver leached from the SIPP pot was, however, at a level of between 0.5 and 0.6 mg/ℓ, higher than the WHO recommendation of 0.1 mg/ℓ.

Although the cost of the silver needed per pot is higher for the SIPP pot than the PFP pot, the SIPP pot is more cost-effective in terms of unit water treatment cost.

From these studies, the following recommendations are noted for further research and development of a successful unit for household water purification:

- Further research should be carried out to evaluate the long term efficiency of the SIPP ceramic unit developed under this consultancy.
- Additional tests should be conducted with bacterial loadings of 10^6 CFU, *E. coli, Vibrio cholera* and *Salmonella typhimurium* in order to determine the effect in a mixed microbial solution. The tests should be conducted with synthetic and natural water.
- Future pot designs should incorporate at least 20% conditioned zeolite to target heavy metals or other inorganic contaminants.
- Properly conditioned lime should also be incorporated into the pot mixture in order to target the removal of fluoride.
- Since pots displayed a high silver elution at the beginning of the experiment (<5 ℓ), it is recommended that for future experiments, the pots should first be primed with sterile distilled water before the contaminated water is processed.

Other materials which may serve as the filter and basis for nanomaterials should be investigated. For example, silver nanoparticles deposited in polyurethane foam have been shown to be effective in inactivating bacteria at substantially higher flow rates than are achieved in current ceramic filter models.

Other nanomaterials as disinfection agents should be investigated for possible incorporation into home filtration units.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

1. INTRODUCTION

At least five million people in South Africa still have no access to treated potable water within reasonable distances from their dwellings and many thousands more take water from water sources and use it untreated because of problems experienced with adequate and reliable potable water supply. Further, small and rural water treatment plants are often at a disadvantage regarding both their design and operation. In a study of 20 small water treatment plants (Swartz, 2000) it was found that most local (small) water treatment plants were not correctly designed for efficient water treatment or experienced problems in operating on a sustainable basis, thereby compromising final water quality. Surface waters have also steadily become more polluted – especially with regard to microbiological quality, which exacerbates the situation of the immune compromised when drinking inadequately treated and poor quality water. It is also an unfortunate fact that the people still without potable water supply are the most difficult, expensive and time consuming to service. This leads to people drinking and using water directly from unsuitable water sources, which in turn leads to frequent incidences of sickness, morbidity and even fatalities among young children.

A number of clay pot based home treatment systems and devices are being used internationally by small, rural communities without potable water services (decentralised systems – see Chapter 2). Although some exploratory work has been performed in South Africa, relating to use of these clay pots in other hygiene based studies, little has been done to evaluate these units in South Africa or to improve their functioning in order to empower rural households without water services to ensure that the water they bring into their homes from untreated sources is safe to drink and use for cooking. The Potters for Peace clay pot, for example, has been in use in countries such as Nicaragua and Cambodia for some time, but the silver used as the anti-bacterial material is simply painted onto the surface. Incorporating silver throughout the pot will increase efficiency, but may also increase the cost. A need therefore exists to source and investigate appropriate nanomaterials-based methods to produce such a ceramic pot, which is both effective and less expensive than the current ceramic units, where colloidal silver is simply painted onto the surface.

This project therefore aimed to develop a prototype clay pot, incorporating anti-bacterial nanoparticles, for the purification of microorganism polluted water for drinking and cooking purposes by rural families currently using water directly from untreated or poorly treated sources, with objectives being the following:

i. Survey the available clay pot units currently being used internationally as home treatment devices and investigate the potentially viable options and their manufacturing processes.
ii. Investigate, through literature search and in practice, which anti-bacterial nanoparticle coatings and/or mixes may be used to efficiently inactivate bacteria and viruses.
iii. Manufacture a range of pots with various porosity values and incorporating various anti-bacterial nanoparticles.
iv. Evaluate their efficiency in bacterial and viral removal compared to what is normally achieved by the conventional, silver-coated clay pot.

2. LITERATURE REVIEW

Clay pot units currently being employed internationally as home treatment devices are summarised below and the potentially viable options to use, as well as their manufacturing processes, were investigated. The anti-bacterial nanoparticle coatings and/or mixes may be used to efficiently inactivate bacteria and viruses were assessed.

2.1 Porous ceramic filters

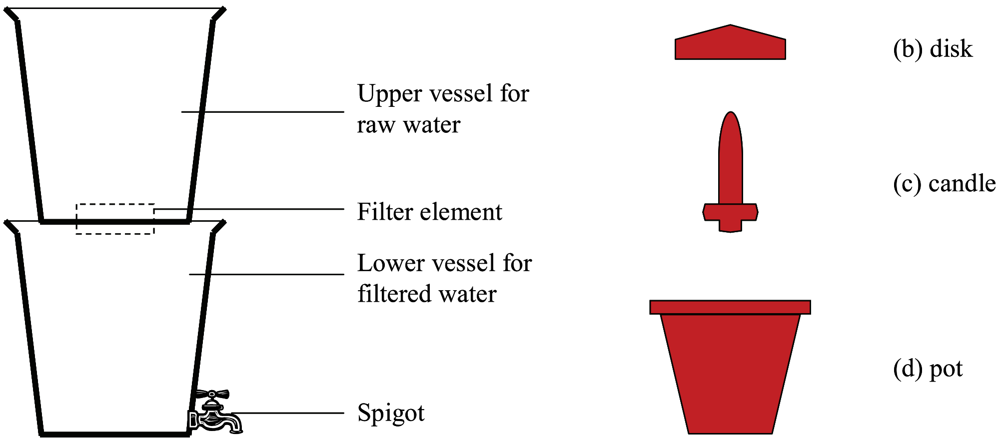
Porous ceramic filters made of clay, carved porous stone and other materials have been used to purify water since ancient times (Sobsey, 2002). Modern ceramic filters are usually in the form of disks, pots or hollow cylindrical “candles” (Mattelet, 2006). Typical filters are illustrated in Figure 1 to 3.

The filter system usually consists of two interlocking vessels such as plastic buckets placed one on top of the other. Raw water is poured into the top vessel and drains under gravity through the filter element into the lower vessel. Flow rates are typically in the range 1-4 ℓ per hour (MIT, 2008). The filtered water receptacle is fitted with a spigot to facilitate safe dispensing of the treated water. In the case of the pot filter, the pot itself serves as the upper vessel.

Ceramic filters and are fabricated from a variety of mineral media including different types of clay (kaolin, red terracotta, black clay), diatomaceous earth, or glass typically mixed with a fine combustible material such as flour, sawdust, rice husk (Sobsey, 2002; MIT, 2008). The pore size and filtration properties of different filters depend on the materials and fabrication methods used.

Different types of ceramic filters are used to remove turbidity and microorganisms, chemical contaminants such as arsenic and iron, and even organic compounds which cause taste and odour (MIT, 2008). Some ceramic filters are manufactured to contain activated carbon for organics removal. Carbonaceous material is incorporated into the filter element and converted to activated carbon by slow heating in the absence of air. This improves the filter performance especially in terms of taste and odour removal (Mattelet, 2006). However, activated carbon can also provide a breeding ground for microorganisms which can negatively impact overall microbial removal.

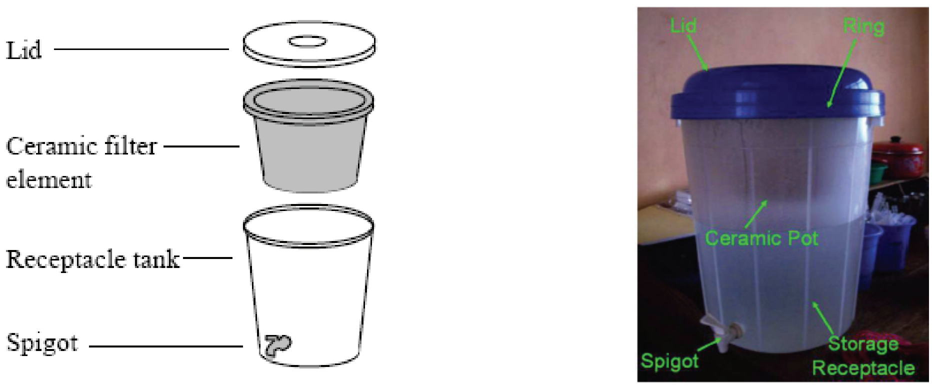
The focus of this study is filters which improve the microbial quality of the water. Removal of turbidity and microbes occurs by straining or adsorption depending on the filter material, pore size and characteristics of the particles being removed. These filters are often also coated or impregnated with silver to provide them with antibacterial properties. This enhances bacterial removal/inactivation and also prevents biofilm growth on the element. Filters must be periodically cleaned to remove accumulated solids and restore flow rate. It is also imperative that filters are structurally sound as even small cracks will result in bypassing and contamination of the filtered water.



(a) Filter system

Filter elements

Figure 1: Typical ceramic filter system and elements



(a) Potters for Peace Filtron system (Roberts, 2003)

(b) Kosim filter system, Ghana (Swanton, 2008)

Figure 2: Clay pot filter systems Filtron (a) and Kosim (b)

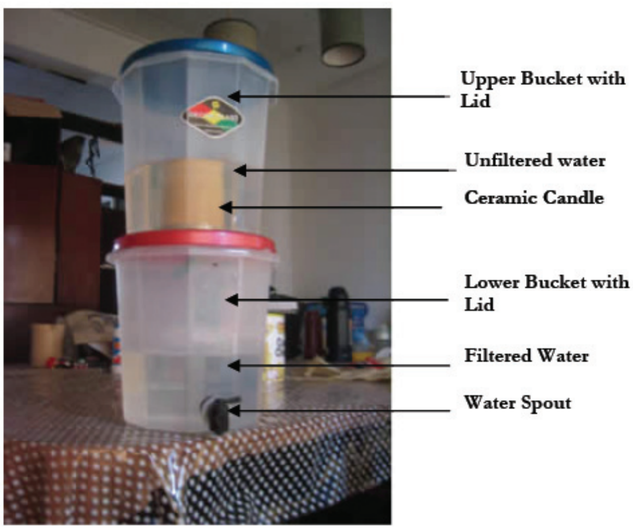


Figure 3: Typical candle filter arrangement, Ghana (Hwang, 2003)

Filters manufactured commercially in developed countries such as the USA are often rated for microbiological removal. For example, the USEPA requires Point-of-Use Microbiological Water Purifiers such as ceramic filters to provide at least 6 log bacteria, 4 log viruses and 3 log Cryptosporidium and Giardia cysts (USEPA, 1987). These filters are costly to produce and to test and the ceramic filters used in the developing world are unlikely to provide the same performance. Nonetheless, they are easy to use and should provide some improvement in water quality (Sobsey, 2002).

Porous ceramic filters are therefore considered an appropriate technology for developing countries. The basic raw materials are clay and a fine combustible material such as flour which is available almost anywhere in the world. The main barriers to their manufacture and distribution are the availability of trained workers, fabrication and distribution facilities and cost (Sobsey, 2002). Nevertheless, local manufacturing of the filters represents a potential sustainable development initiative in itself. The establishment of adequate quality control methods is a very important part of the production process and the development of simple and affordable methods for testing the quality and integrity of the filters should be a priority (Sobsey, 2002). The advantages and disadvantages of ceramic filters for developing countries are summarised in Table 1.

Table 1: Advantages and disadvantages of ceramic filters for home water treatment in developing countries (adapted from MIT, 2008)

Advantages	Disadvantages
• Simple to use • Relatively cheap to manufacture and produce. Filter system typically costs US$ 5-30. • Ceramics manufacture well established in many countries and locally available materials can be used. • If properly designed and used, can remove up to >99% indicator organisms and meet WHO turbidity standards.	• Low filtration rates so cannot treat large volumes of water. • Requires regular cleaning. • Reliability and maintenance depend on user. • Filters can be fragile so breakage during transport or use is a problem. • Rate of production has slow in some countries where it has been introduced. • Difficult to maintain consistency in local production in developing countries. • Ineffective for virus removal • No disinfectant residual in the filtered water

2.1.1 Low cost filters produced in developing countries

One of the major advantages of ceramic filters is that, with some start-up support, they can easily be produced by local potters using cheap local materials, providing both economic and health benefits to the communities which adopt them. This section describes two different models which are produced in several different countries: the Potters for Peace filter pot, or Filtron, and the Ceramique d'Afrique candle filter.

2.1.1.1 Potters for Peace Filtron

The Potters for Peace (PFP) clay pot, or Filtron, is the most widely used model and is currently produced in more than ten countries around the world (http://www.pottersforpeace.org). It was originally developed by the Central American Research Institute of Industrial Technology (ICAITI), an industrial research institute in Guatemala, as part of a 1981 InterAmerican Bank funded study into low cost options for domestic drinking water filtration (ICAITI, 1984). The design was subsequently adopted and promoted by PFP, an international network of potters which aims to promote and support socially responsible ceramics production and fair trade in the developing world. The PFP Filtron resembles a terracotta flowerpot and has a capacity of ~6-8 ℓ and wall thickness of approximately 1 cm. The filter is made by combining equal volumes of moist terracotta clay and fine sawdust or other combustible material and then forming either by wheel throwing or hand building. More recently, hand operated jacks have also been used to provide a more uniform thickness. After firing, a solution of colloidal silver or silver salts, usually $AgNO_3$ is applied. The advantage of the PFP is that it is very simple to make and the production can easily be undertaken by traditional potters. Its disadvantage is it that the filter element occupies a large volume for a relatively small filter area which limits the flow rate.

A detailed description of the production of PFP filters at the Filtron workshop in Managua, Nicaragua is available in a production manual downloadable from the PFP website (PFP, 2001). Filters produced at this facility have been purchased by a large number of local and international aid organisations (Lantagne, 2001a). Filter production in different parts of the world has been adapted to use readily available local materials. The Managua facility uses unfired clay cast-offs from a local brick factory. The clay has been pressed and aged for several weeks which gives it better properties than freshly dug clay. The clay is crushed, pulverized in a hammer mill and then combined with sawdust. Since every clay source is different, the general PFP recommendation is to start with a 50/50 by volume mixture and then adjust the ratio to obtain the desired properties (PFP, 2001). Water is slowly added to the mix to achieve the desired consistency. The Mantagua facility uses 9.5 ℓ of water to 27 kg dry clay powder and 10 kg of sawdust, and mixes it in a concrete mixer slowed down to 60 rpm using a reduction box (PFP, 2001). The filters are then formed by hand, thrown on a wheel or press moulded (Lantagne, 2001a). The Mantagua facility uses a 12 ton hydraulic jack for press moulding. Once removed from the mould, filters must be allowed to dry completely before firing at 887°C for 8-9 h (Lantagne, 2001a; PFP, 2001).The filters are allowed to cool completely then soaked in water overnight prior to flow testing. The original flow specifications were 1-2 ℓ/h and filters outside this range were discarded. This was based on a minimum estimated contact time of 1 hour with the silver coating at 2 ℓ/h (Lantagne, 2001a). However, Lantagne subsequently found that flow rates of up to 3 ℓ/h did not negatively impact microbial removal and the PFP website now gives the acceptable flow range as 1-3 ℓ/h.

Colloidal silver solution is then applied to all the filters which meet the flow specifications. The stock solution used at Mantagua is a 3.2% silver solution stabilised by proteins obtained from Microdyn in Mexico. Prior to 2002, for each filter, 2 mℓ of stock were diluted in 300 mℓ filtered water and then painted onto the filter with a clean brush. Two thirds of the diluted solution was applied to the inside of the filter and the remaining one third to the outside (Lantagne, 2001a). From 2002 onwards, each filter was soaked in approximately 200 mℓ of 0.32% colloidal silver solution for 30 s (Campbell, 2005).

The materials and manufacturing procedure vary between facilities and countries. For example, ceramic filter pots produced by Resource Development International at a factory in Kandal

Province, Cambodia use raw milled clay mixed with ground rice husks which is press moulded and fired at 870 °C. After flow testing (1-3 ℓ/h required), 300 mℓ of 230 mg/ℓ reagent grade $AgNO_3$ solution is applied to the filter, with $^2/_3$ applied to the inside and $^1/_3$ applied to the outside (Brown, 2007).

2.1.1.2 Ceramiques d'Afrique candle filter

The Ceramiques d'Afrique candle filter element is a small 5-8 cm diameter by 10-14 cm high ceramic cylinder (Harvey, 2000). Its development was spurred in part by the difficulties in transporting the much bulkier PFP filters on badly damaged roads in Nicaragua following Hurricane Mitch. In addition, the relatively large surface area to volume ratio allows for higher flow rates by using more than one element in each bucket system. The disadvantage of the candle compared to the pot is that it is much more difficult to make. The filter element is made from a mixture consisting of 45% red plastic clay, 45% porous grog and 10% combustible such as flour sieved to 30 mesh. Porous grog is itself a mixture of clay and flour which is pressed, dried, fired and then crushed with a mortar and screened to 30 mesh before being mixed with more clay and flour. This mixture is pressed in a mould to form the candle and then a solution of colloidal silver or silver nitrate is brushed on before firing. If nitrate is used, a further firing is required to burn off the nitrate under reducing conditions. More complete descriptions of the process can be found at http://www.potters.org/subject32525.htm and http://www.geocities.com/ceramafrique/. The use of porous grog makes the filter fabrication process more complicated but is the key to the higher flow rates that can be achieved.

Potters for Peace are also currently working on an extruded candle filter model (PFP, 2008), presumably also with the goal of increasing the flow rate of the system.

2.1.2 Waterborne Pathogens and Removal Mechanisms

Waterborne pathogens can be divided into four categories: viruses (Enteroviruses including polio, Hepatitis A and E, etc), bacteria (*Escheria coli, Campylobacteria, Legionella pneumophila, Salmonella, Shigella, Vibrio cholerae*, etc.), protozoa (*Cryptosporidium parvum, Giardia lamblia*, etc.) and helminths (roundworms, pinworms, flatworms, tapeworms, etc).

Ceramic filter pore sizes are generally in the range 0.1-10 μm. In the PFP filter design, the goal is to achieve a pore size of approximately 1 μm and (Lantagne, 2001a) and a flow rate of 1-3 ℓ/h (http://www.pottersforpeace.org).

By comparison, microbial contaminants range in size from 0.02 to 0.2 μm for viruses, 0.3 to 100 μm for bacteria of various shapes, and 8 to 100 μm for protozoa. Helminths are invertebrate animals and are much larger. Therefore, a filter with a characteristic pore size of 1 μm should remove all helminths, protozoa and a substantial portion of bacteria by size exclusion but viruses will be able to pass through.

Most ceramic filters remove a large proportion of solids and silt and many will also remove parasites including cysts, ova and guinea worm, and some bacteria based on size exclusion (Kauser, 2004). Filters also have some capacity to remove smaller particles including viruses and bacteria and other contaminants through sorption processes but this capacity will diminish as available sites are exhausted unless the filter can be regenerated. Brown (2007) also found that removal rates of both bacteria and viruses were significantly higher in new filters (for approximately the first 100 ℓ filtered) but decreased significantly thereafter. In the case of viruses, the average removal rate dropped by nearly three orders of magnitude in spite of the filters being regularly cleaned according to the manufacturer's instructions.

Silver amendments to filters can improve bacterial removal but do not appear to be effective against viruses. Van Halem (2006) found that virus removal was actually better in filters without silver addition and assumed that this was due to more available sorption sites. Basu et al.(1982) reported producing bacteria free water using candle filters with pore size 6-31 µm which had been soaked in silver salts. Lantagne (2001a) found that applying silver to both the inside and outside of filter pots is critical for effective bacteria removal. Van Halem (2006) reported that the presence of silver improved the removal of *E. coli* but not of total coliforms. However, Brown (2007) found that there was no significant difference in average *E. coli* removal rates in filters with and without silver. Apart from Lantagne's finding that that both the inside and the outside of the pot should be coated with silver, there is currently no concensus on the effect of type of silver and application method on bacterial removal nor on the relative contribution of silver compared to other removal mechanisms including straining and absorption.

2.1.3 Filter Effectiveness

2.1.3.1 Turbidity Removal

Lantagne (2001b) found that turbidity reduction of filters tested in the field ranged from 30 to 100% with a few filters actually increasing the turbidity of the filtered water. An increase in turbidity was taken as an indication that the filters had not been cleaned. Most of the filters were able to reduce the turbidity below the WHO standard of 5 NTU. Brown (2007) found that ceramic filters reduced turbidity from a mean of 8.9 NTU to a mean of 2.6 NTU.

2.1.3.2 Microbial Removal and Inactivation

Escherichia coli is the most commonly used indicator of faecal contamination of drinking water. It is a rod shaped bacterium, 1-2 µm in length and 0.1-0.5 µm in diameter, similar in size and morphology to *Salmonella*, *Shigella*, *Campylobacter* and *Vibrio* spp. (Brown, 2007). Thermotolerant coliforms may be used as an alternative indicator organism in many cases (WHO, 2006). Total coliforms include a wide range of organisms, not all of which are indicators of faecal contamination. However, they can be used as indicator of overall treatment effectiveness (WHO, 2006). Hydrogen sulphide producing bacteria are present in high concentrations in human waste and are therefore also useful as indicators of faecal contamination (Lantagne, 2001b). The goal of treatment should be to reduce *E. coli* and total coliforms to undetectable levels (0 CFU/100 mℓ) although it must be noted that pathogenic organisms which are more resistant to treatment may still be present. Other more resistant indicators include intestinal enterococci, *Clostridium perfringens* spores and bacteriophages (viruses). *Clostridium* spores are also used as surrogates for protozoan cyst removal (van Halem, 2006). Bacteriophages are viruses which only impact bacteria but share many other properties with human viruses and may therefore be used as surrogates to determine virus removal efficiency (WHO, 2006). MS2 bacteriophage is a useful surrogate for enteric viruses. Similar to poliovirus and Hepatitis A in size, shape and nucleic acid content (~25 nm, icosahedral shape and RNA nucleic acid), it has been shown to be a conservative estimator of mammalian virus removal in a number of different water treatment processes (Brown, 2007).

Lantagne (2001a) reported that filters produced at the PFP factory with flow rates ranging 1.0-2.5 ℓ/h removed *E. coli* but not total coliforms or hydrogen producing bacteria as determined by presence/absence tests. In another set of tests, Lantagne (2001a) reported that PFP filters removed 100% of total coliforms in laboratory studies but two genera, *Aeromonas* and *Pleisomonas*, which include species which are considered minor pathogens, were detected in the filtrate. Various studies conducted by PFP and the Centre for the Investigation of Water Resources at the Autonomous University of Nicaragua (CIRA-UNAN) have found that filters with colloidal silver applied to both the inside and the outside of the filter remove 100% of four indicator organisms, total and faecal coliforms, faecal streptococcus and *E. coli*, from a variety of raw water sources including river and well water, effluent from a contaminated sand filter and a contaminated piped urban supply (Lantagne, 2001a). Filters without silver remove the bulk of these indicators but generally do not achieve 100% removal. Filters were still effective after up to seven years (Lantagne, 2001a; Campbell, 2005).

Tests conducted at a commercial laboratory in the USA found that a PFP filter removed greater than 4 log of *Giardia* cysts and *Cryptosporidium* oocysts. However, only one filter and one influent concentration of each pathogen was tested so there was no data on the expected range of performance (Lantagne, 2001a). The same preliminary study also looked at virus removal using MS2 coliphage as a model. Removal efficiency declined from 68% to 19% between 30 minutes and six hours, confirming that the filter is not effective for virus removal. Brown (2007) reported that filters removed 90-98% of MS2 in laboratory tests using spiked samples.

Furthermore, Brown also found that microbial removal rates were significantly higher in new filters (for approximately the first 100 ℓ filtered). *E. coli* removal dropped from a mean of 2.9 log removal in the first 100 ℓ to 2.1 log removal thereafter. The reduction in viral removal was even more dramatic. This dropped from 4.1 log removal to 1.2 log removal over the same test period. This is consistent with the exhaustion of potential absorption sites in new clay filters. During this time, the filters were cleaned several times following the manufacturer's instructions. This is important because laboratory testing often only involves relatively small volumes of water and new filters which may bias the results. In a 12 week laboratory study comparing filter pots produced in Ghana, Cambodia and Nicaragua using spiked Dutch canal water, van Halem (2006) reported complete removal of total coliforms in 93% of samples, 4-7 log reduction of *E. coli*, 2-6 log removal of *Clostridium* spores and 0.3-0.5 log removal of MS2 bacteriophage. Filters treated with silver improved the removal of *E. coli* compared to filters without silver but the absence of silver did not significantly impact total coliform or *Clostridium* removal. However, filters without silver actually showed better virus removal. This was assumed to be due to a reduction in absorptive surface where the filters had a silver coating.

Microbial removal rates in the field are often lower than those obtained in the laboratory by researchers and technicians. One possible reason is that in laboratory studies, the filter receptacle is usually washed prior to use (Lantagne, 2001b), whereas researchers in the field use the filters as they find them to simulate actual operating conditions.

In field sampling at 24 homes in Nicaragua, Lantagne (2001b) reported that 96% of filtrate samples tested positive for total coliforms, 73% of filtrate samples tested positive for H_2S-producing bacteria and 53% of samples with *E. coli* in the raw water also had *E. coli* in the filtrate. All raw water samples tested positive for total coliforms and H_2S-producing bacteria. Brown (2007), however, found that locally produced Cambodian filters removed approximately 99% of *E. coli* in both laboratory and field tests even with filters that were not treated with silver (laboratory trials only). However, removals of *E. coli* in the field ranged from 6 log reduction to negative removals in 5% of samples (higher *E. coli* in the filtered water than the source water). The strong performance of the filters in the field may have been due to the fact that the non-government organisation (NGO) which distributed the filters in the study area also provided training and health and sanitation education. Filter effectiveness was maintained over an 18 week field study with filters producing an average of 20 ℓ per day.

Actual removal rates during routine operation may be even lower than those found by field researchers due to the way the filters are used and mistakes made by the users (Baumgartner et al., 2007). This would also be true of the high performance filters produced in developed countries. Expected baseline performance of ceramic filters (actual performance in the field when used by relatively unskilled people) is 2 log removal of bacteria, 0.5 log removal of viruses and 4 log removal of protozoa (Brown, 2007). Clasen et al. (2004) found that households using commercially produced ceramic candle filters (Katadyn Ceradyn™, Katadyn Produkte AG, Zurich, Switzerland) in a pilot study in Columbia had an average of 75% less thermotolerant coliforms in their drinking water compared to households in a control group. In four rounds of sampling, 96% of drinking water samples from households using the filters had no thermotolerant coliforms compared to 16% of samples from control households. In this study, participants were trained to use the filters but received no other health and sanitation education from the project team. In a similar study conducted in Columbia, households using the filter had an average of 75% less thermotolerant coliforms in their drinking water compared to households in a control group. 48% of households using the filters had no thermotolerant coliforms detected in their drinking water compared to less than 1% of control households (Clasen et al., 2005). The Katadyn® filter has been shown to be capable of 6 log removal of bacteria and 3 log removal protozoa in laboratory trials (Clasen et al., 2004) however, it is unlikely that they would be consistently able to achieve this level of performance in the field. There are no data directly comparing the performance of commercial filters from the industrialised world with locally produced filters from the developing world, but it is likely that they would be limited by the same external factors when implemented in the field so that in practice their performance may not be significantly different.

2.1.4 Effectiveness in reducing waterborne diseases

Peletz (2006) studied the use of Kosim filters in Northern Ghana and found that the filters reduced the risk of diarrhoea by 42% in children under five. In a subsequent study in the same region, Johnson (2007) found that households using the filter were 69% less likely to have diarrhoea compared to households without the filter. In pilot study to introduce PFP filters to Cambodia, Roberts (2003) found that 17% more households using the filter reported no cases of diarrhoea in the previous month compared to households which neither boiled nor filtered their water. Use of the filter reduced diarrhoea incidence per person by half, diarrhoea costs per person by a third and missed days of school/work per person by a factor of four. Households which had previously boiled their water did not report definitive health benefits but saved time and expense. Brown (2007) found that the use of locally produced ceramic filter pots in Cambodia reduced diarrhoea by 46% in users compared to non-users. Lantagne (2001b) found that no child in homes where filtrate samples tested negative for *E. coli* and H_2S-producing bacteria had diarrhoea in the previous month. Clasen et al. (2004) found that diarrhoea risk was 70% less for individuals in households using the filters compared to controls in a Bolivian study while Clasen et al. (2005) reported an average of 60% lower incidence of diarrhoea in members of households using filters compared to control households in a Columbian field study.

2.1.5 Flow Reduction

Two of the original ICAITI prototype designs were tested for flow rate reduction with use over a period of 365 days. Flow decline ranged from 39 to 64% (ICAITI, 1984). Lantagne (2001b) observed similar declines in a field study of communities using filter pots. The higher the turbidity of the raw water, the more rapid the flow decline. Van Halem (2006) found that filter discharges dropped from 1-2 ℓ/h to <0.5 ℓ/h within a few weeks. However, the flow rate can be restored by scrubbing both the inside and outside of the filter with, for example, a toothbrush. This removes particles which are larger than the filter pores from the external surfaces. It also supposedly removes a micro-layer of silver coated ceramic but the filter is sufficiently thick to sustain multiple scrubbings over its lifetime and the silver penetrates several millimetres into the filter material even when it is applied to the outside only (Lantagne, 2001a).

2.1.6 Filter lifespan

There is no consensus on the maximum period a silver coated ceramic filter can be expected to perform satisfactorily in the field. Lantagne (2001a) and Campbell (2005) reported that filters up to seven years old still removed 100% of *E. coli* and 94 to 100% of total coliforms. The seven year old filters performed less well than 2-5 year old filters, however, it must be noted that the seven year old filters were produced before 1999 when half the amount of silver subsequently used was applied to each filter (Lantagne, 2001a). Brown (2007) found that locally produced filters in Cambodia maintained their effectiveness after 44 months of use in the field. Filter manufacturers usually recommend reapplication of silver solution to the filters after some period of time, for example, PFP recommended reapplication once a year. Lantagne (2001a) concluded that there was no evidence that the silver coating became less effective over time but cautioned that periodically reapplying the silver periodically should provide an additional margin of safety and therefore should be continued until comprehensive testing showed that it was unnecessary.

What is clear is that proper maintenance and handling of the filter is required to avoid breakages maintain the flow rate and prevent contamination of the filtered water. Roberts (2003) reported a 0.6% rate of accidental breakage per month in a pilot study in Cambodia conducted by International Development Enterprises (IDE). This corresponded to a recommendation that the filter element and plastic receptacle be cleaned every two weeks. IDE subsequently decided that the cleaning rate was excessive and recommendation was revised to cleaning the element and receptacle once a month or when there is a significant drop in flow rate. Cleaning procedures are discussed in Section 2.1.10. Lantagne (2001b) reported that one community visited in the Nicaraguan field trials tied the filter receptacles to the wall with wire to reduce the risk of breakages.

2.1.7 Community acceptance and usage rates

In the Cambodian pilot study, Roberts (2003) found that 20% of households given filters had stopped using them after one year. In about half the cases, this was due to the filter element being broken. It was thought that reducing the recommended cleaning rate from twice to once a month would reduce the rate of breakage and that households which had paid for the filters instead of receiving them for free would be more committed to continue using them. This was confirmed in a follow up study which showed that continued filter use was associated with cash investment in the filter (Brown, 2007). Brown found a disuse rate of approximately 2% per month, also largely due to breakages.

In Roberts' study, 98% of households reported a high degree of satisfaction with the filter due to the taste of the water, ease of maintenance, health benefits and the fact they no longer needed to boil their water. A University of Tulane study quoted by Lantagne (2001b) found that women in three communities in Nicaragua who used the PFP filter in their homes liked the fact that it was easy to use compared to other POU devices supplied by NGOs, easy for their children to use, it is a closed system and keeps the water cool. The main reasons given for discontinuing use included insufficient flow (indicating that the filter was not being cleaned), the filter or spigot was broken or leaked, and that the men took all the water when they went to work in the morning leaving nothing for the rest of the family. The study concluded that it was important that communities had access to spare parts. In another PFP sponsored study quoted by Lantagne (2001b), a Nicaraguan social worker found that filter usage ranged from ten to 94% in eight communities visited and was positively correlated with education about the importance of clean water, training in the use of the filter and health capacity in the community (not explained). Continued follow up (monthly visits by NGO personnel or community leaders) with communities was critical to the filter success. Many users did not know how to clean their filters properly and were using contaminated water to clean them. The common problems reported were low flow rates, broken spigots and filter elements.

In a follow up study which involved visiting 33 homes in seven communities in which filters had been distributed six to 18 months previously, Lantagne (2001b) found that usage rate varied from 33 to100% and was correlated with follow up visits by community leaders. The most common reason for discontinued use was again breakages.

2.1.8 Factors affecting ceramic filter performance

2.1.8.1 Filter hydraulics

Flow rate and removal by size exclusion in ceramic filters is determined by the porosity and the pore size of the filter. Porosity is defined as the fractional volume of voids within the filter material. The higher the porosity, the greater the flow rate that can be achieved but the lower the expected microbial removal efficiency (Mattelet, 2006) in part due to reduced contact time with the silver disinfectant although there is little data in this regard. Porosity and pore size are determine by the amount and size of the fine combustible material used in the filter fabrication process.

In the PFP model, the design goal is to have an average pore size of ~1 µm. Scanning electron microscopy (SEM) on a ceramic sample taken from the lip of a PFP filter pot has shown that actual pore sizes vary from 0.6-3.0 µm (Lantagne, 2001a). In addition, SEM revealed much larger cracks (<150 µm) and spaces (<500 µm) throughout the filter material. If these cracks are interconnected, they will lead to substantially higher flow rates and potentially lower removal efficiencies whereas isolated flaws do not affect the flow once they have become saturated with water. Van Halem (2006) used mercury intrusion porosimetry to determine the pore size and total pore area of ceramic filters produce in Ghana, Cambodia and Nicaragua. The average pore size was 14-19 µm while the porosity was 37-43%. While the average pore size appeared to be much larger than 1 µm, it is not clear how much the large pores contributed to the conductivity of the filter, i.e. the channels which allow fluid to pass through the filter may be significantly smaller. Basu et al. (1982) reported flow rates of 3-4 ℓ/h in filters with pore size 6-31 µm.

Other factors which affect flow rate include wall thickness, filter area and water head (Mattelet, 2006). The driving force for filtration is the head of water above the filter. It is therefore important to keep the level above the filter topped up to maintain the flow rate The thinner the filter wall, the lower the hydraulic resistance and hence the higher the flow. However, thinner walls potentially result in lower removal efficiencies for both turbidity and microorganisms, as well as in a more fragile filter. The wall thickness of a PFP is typically around 10 mm. The flow rate through the filter under any given set of conditions is proportional to the filter area. Laboratory studies have shown that more of the flow through the filter goes through the side walls than the bottom of the filter (Lantagne, 2001a). This is presumably due to the larger flow area presented by the sides compared to the bottom.

A hydraulic model of the flow in a PFP filter was developed by Ericksen (2001) for Red Cross International. The model objective is to determine the maximum hydraulic conductivity which allows an adequate contact time for disinfection. The conductivity depends on filter thickness, porosity and pore size. A revised version of the model is presented in Lantagne (2001a) and includes the effect of tortuosity. The tortuosity of the pores may increase microbial removal efficiency by increasing the number of collisions with the ceramic surface as microbes travel through the pores. A University of Colorado study attempted to characterize both the porosity and tortuosity factors of the PFP filter but the results were inconclusive (Fahlin, 2003). Filter hydraulics are also discussed in some detail by van Halem (2006).

2.1.8.2 Raw water quality

High suspended solids and organic loads result in rapid clogging of the filter which reduces the flow rate and the volume of water than can be filtered between cleanings (Mattelet, 2006). Filters may become rapidly clogged with iron precipitate when deep well water is used as the source (Brown, 2007).

2.1.8.3 Handling and safe storage practices

Improper handling can easily contaminate the filter system. Users should be trained not to touch the outside of the filter pot, inside of the filtered water receptacle, mouth of the spigot or to set the filter element down on a dirty surface (Roberts, 2003). In addition it is very important that users are trained not to use contaminated water to clean the filter element and receptacle (Lantagne, 2001b). Water used to wash the filter and receptacle should be filtered, boiled or disinfected in some other way. The type of receptacle used to collect and store the filtered water also appears to be important. In field sampling in Nicaragua, Lantagne (2001b) found that all filtrate samples collected from ceramic receptacles contained hydrogen sulphide producing bacteria whereas all samples which were free of this indicator were collected from plastic receptacles. This may be because ceramic is harder to clean and disinfect than plastic.

The vessels used to collect water from the source can be an additional source of contamination. Lantagne (2001b) found that filtrate samples collected from three homes in the field contained higher total coliform counts than the original source water. Since many coliform species can reproduce outside a human host, it was concluded that this was likely due to bacterial growth in the plastic buckets used to collect water from the source. These were typically stored under the sink creating another possible route for contamination. Brown (2007) also found that treated water could be re-contaminated by unsafe handling and storage and recommended that this should be addressed in all training programmes.

2.1.9 Importance of community education, training and follow up

An AFA Guatemala study (1995) found that the incidence of diarrhoea in children under 5 was lowest in households which received ceramic filters and general health hygiene education (0.33-3.0%), followed by households which received only filters (0.38-3.7%), followed by households receiving only education (2.29-4.78%) compared to a control group which received neither (2.34-6.57%). Brown (2007) found that households with some knowledge of safe water, sanitation and hygiene practices were more likely to continue using the filter over the long term.

Lantagne (2001b) found that some users did not understand the relationship between head and filter flow rate and would only refill the filter once it was completely empty. However, the main reason for low filtration rates in this study was failure to clean the filter once it clogged up. Lantagne concluded that training in filter use must include the following:

- The filter should only be cleaned with filtered water.
- The filter should be vigorously scrubbed to restore flow rate.
- The filter system should be secured to the wall to prevent breakages.
- The filter should be allowed to empty to before lifting it to reduce the risk of dropping and damaging it.
- The filter should be refilled frequently to maintain head and flow rate.
- Training must include health and sanitation education so users understand why filtering water is important.

2.1.10 Cleaning procedures

Recommendations for cleaning the filters vary between manufacturers and distributors and significantly impact filter performance. Lantagne (2001b) found that vigorous scrubbing of a used filter with a tooth brush to remove a fine layer of clay restored the flow rate from 0.28 ℓ/h to 2 ℓ/h. This was in line with recommendations by Katadyn, a commercial distributor of ceramic filters. Katadyn claimed that the filter is thick enough to sustain up to 300 such cleanings. Lantagne noted that while there is some concern about losing the bacteriostatic silver layer, the silver actually penetrates at least several millimetres into the filter material, even when only brushed onto the surface. It is also very important that filters and receptacles are cleaned with filtered water to avoid contamination. Lantagne recommended the development of a cleaning kit to be sold along with the filters. This should include:

- Scrubbing brush.
- Cloth and disinfectant to clean the receptacle.
- Instructions on proper cleaning methods.

Lantagne (2001a) found that filters cleaned with chlorine or solid detergent removed 100% of total, and faecal coliforms along with streptococcus whereas a filter cleaned with liquid detergent had slight total and faecal coliform contamination.

2.1.11 Antimicrobial materials and surfaces

Silver

Ceramic filters are often coated or impregnated with silver to improve microbial removal and prevent biofilm development on the filters. Silver has a long history of use as an antimicrobial agent in water treatment and in other application such as an environmental biocide and ingredient in medications (Gupta et al., 1998; Lantagne, 2001a; Morones et al., 2005) however, the mechanisms involved are still not well understood. Lantagne (2001a) identifies four groups of mechanisms which have been proposed in the literature:

i. Silver reacts with thiol (-SH) groups in structural groups and inactivates vital functional enzymes (Gupta et al., 1998; Matsumura et al., 2003). Berger at al. (1976) found that electrically generated colloidal silver inhibited 16 bacterial species including *E. coli* at 1.25 µg/mℓ colloidal silver and killed them at 10.5 µg/mℓ. Mammalian cells were not affected.

ii. Silver produces structural changes in bacterial membranes. Feng et al. (2000) observed structural changes in cell membrane involving silver reacting with sulphur containing groups. This was thought to interfere with cell respiration and permeability.

iii. Silver interacts with nucleic acids to disrupt cell function. Feng et al (2000) found that DNA loses replication ability after microbes have been treated with silver and suggested that this may be due to the tendency of silver to react with phosphorous groups.

iv. Silver deposited on inert surfaces exhibits a strong catalytic reaction with oxygen which results in bacteria and viruses being killed on contact (Heinig, 1993). This mechanism is thought to be of particular relevance to silver impregnated filter. Heinig (1993) found that the rate of the catalytic reaction depended on the size and dispersion of the silver on the surface and the oxygen concentration.

Other inorganic materials with antimicrobial properties

Other metals with demonstrated antimicrobial activity are copper and zinc (Feied, 2004). Silver is, however, less cytotoxic and generally more potent against bacteria than either copper or zinc. Silver is approximately 10 times more effective against bacteria than copper and three orders of magnitude more effective against microbes in general compared to zinc (Feied, 2004). Copper is however effective against fungi and combining copper with silver may have synergistic effects. Lin et al.

(1996) found that at Cu^{2+}/silver^{+}concentrations of 0.04/0.02 mg/ℓ and higher, the rate of inactivation of *Legionella pneumophila* is greater than an additive effect of each ion alone. At lower ion concentrations, the combined effect was only additive. At these concentrations, *L. pneumophila* was completely deactivated (>6 log reduction) in 3.6 hours (~3 log reduction in 30 minutes). These authors found that copper ions bound rapidly with cells in suspension and suggested that the disruption of the cell membranes by copper may facilitate the penetration of silver ions. The same concentrations of silver and copper were much less effective against *Mycobacterium avium* which have unusually impermeable cell walls (Lin et al., 1998). Zinc is also generally combined with silver (Feied, 2004).

There is currently a growing interest in the use of antimicrobial surfaces (surfaces on which pathogenic microbes show rapid degradation) to minimise the spread of infection in medical facilities, public places and in the food industry (Lopez et al., 2004; Jia et al., 2005) and the development of 'destructive absorbents' for decontaminating surfaces and facilities, for example, after a biological or chemical weapons attack (Koper et al., 2002). It must be noted that the bulk of the studies on these antimicrobial materials are focused on the potential development of antimicrobial surface treatments and materials and not on water treatment. In addition, the contact times are generally 24 hours or more whereas the contact time in PFP filters is approximately one hour. Nonetheless, silver itself is considered slow acting compared to common disinfectants such as chlorine (WHO, 2006) and yet is still effective in the filter. Therefore materials which perform comparably with silver in these other applications may potentially also be effective in water treatment applications.

Various metal containing surfaces and powders provide broad-spectrum antimicrobial effects through the slow release of metal ions. For example zeolite crystals can be manufactured with metal ions in their pores which are released over many years (for intermittently or frequently moist surfaces). A commercial formulation of silver-zinc zeolite provided by AgION Technologies, Inc (Wakefield, Massachusetts, USA) has been shown to be effective against a range of pathogens (Feied, 2004).

Calcium oxide powder slurries have been shown to exert antimicrobial effects which are separate from the effects of increased alkalinity (Sawai et al., 2001). It is thought that this is due to the generation of active oxygen species such as superoxide anion (O_2^-). Sawai and Yoshikiwa (2004) reported antifungal activities for MgO and CaO powders. Zinc oxide (ZnO) powder also showed some antifungal activity but the doses required were much higher. The disadvantage of the using of MgO and CaO in the context of the clay filter is that they would tend result in high pH (possibly >10) which would exceed guidelines for drinking water quality. The pH in filtered water from the filter pot would presumably depend on the rate of dissolution of Ca/Mg and might or might not result in excessively high pH levels. However, while the biocidal effects of these materials have been shown to not be only due to pH effects, there is no data on biocidal activity at lower pH levels.

Most of the work on antimicrobial materials has focused on bacteria. However, iron and iron oxides have been shown to be effective in removing viruses in some situations. Zhang (2009) found that magnetite (the dominant iron corrosion product under anaerobic conditions) was effective in removing two bacteriophages MS2 and [straight phi]X174. In addition, aqueous Fe(II) inactivated [straight phi]X174 but not MS2. Zero-valent iron Fe(0) itself did not appear to absorb or inactivate either phage. These authors suggested that different viruses might be removed or inactivated by iron to different extents and via different mechanisms and proposed that elemental iron could be used a granular filter media to remove viruses. However, currently available data relate to the simulation of groundwater i.e. anoxic conditions, which are not applicable to the ceramic filter. Brown (2007) found that adding iron oxides (FeOOH) to filter clay during manufacturing did not significantly impact either virus or bacterial removal.

2.2 Nanomaterials in POU water treatment

Nanoparticles and nanostructures have characteristic dimensions in the range 1-100 nm. At this scale, materials often exhibit significantly different physical, chemical and biological properties, very large specific surface area and quantum effects which occur at the nanoscale. There is increasing interest in the potential use of nanotechnology in point of use (POU) water treatment devices particularly for use in the developing world with proponents suggesting that nanotechnology-based materials can be used to create cheaper, more durable and more efficient POU devices (Theron et al., 2008). Several devices and treatment methods incorporating nanomaterials are already commercially available and others are currently being developed. These include filters, filtration membranes, catalysts and nanoparticles for groundwater remediation. Since these technologies are very new, most of the information available on currently available devices comes from the manufacturers and there is little independent verification of their performance (Meridian Institute, 2006). Various concerns have been raised about the potential risks of using nanoparticles and materials in general, including potential environmental and human health effects as well as socio-economic and ownership issues and again, due to the newness of these technologies, there are little or no data addressing these topics (Meridian Institute, 2006). This section reviews current nanomaterials which could potentially be incorporated into ceramic filter design.

A comprehensive review of the scientific literature on potential and emerging applications of nanotechnology in water treatment is provided in Theron et al. (2008). Nanotechnology applications include the use of nanoparticles and nanomaterials in separation technology (membranes and absorbents), catalytic destruction of various organic pollutants and the use of bioactive nanoparticles for disinfection.

Extensive work on the use of carbon nanotubes in low pressure membranes and as absorbents has been performed (Theron et al., 2008). Carbon nanotube membranes look like a promising alternative to conventional reverse osmosis membranes for desalination at much lower pressures due to almost frictionless flow of water molecules (Theron et al., 2008). Carbon nanotube membranes remove contaminants down to seven water molecule diameters which includes all microbes but with almost frictionless flow, therefore requiring low operating pressures for high water recoveries. It is not clear that this technology could be combined with ceramic filters unless an intact nanotube layer could be deposited on the surface or inside the filter element. For example, Nanomesh, a material produced by Seldon Laboratories, a small US company, consists of carbon nanotubes bound together on a porous flexible substrate. It can be used for filters that operate under gravity. It can be wrapped around any support structure to create a filter. In theory, it could be inserted into a clay pot as the support (like a coffee filter) but this may not be an optimal use of either technology. A nanomesh POU device known as the ‘water stick’ is currently being used by doctors in Africa (Meridian Institute, 2006).

The most promising nanoparticles with proven antimicrobial activity are metallic and metallic oxide nanoparticles especially silver and titanium dioxide catalysts used in photocatalytic disinfection. Nanosized metallic particles exhibit properties which are different from both ions and bulk material, including increased catalytic activity due to due to their large surface area and morphologies with highly active facets (Theron et al., 2008). Metallic nanoparticles stabilised and immobilised in various matrices have also been shown to have antimicrobial properties. There is considerable interest in the use of these particles in materials such as paint, plaster and other coatings to create surfaces which rapidly disinfect themselves. Their advantages over organic antibacterial agents such as Triclosan include high antibacterial activity with low toxicity, chemical stability, long lasting action and thermal stability (Esteban-Cubillo et al., 2006). These properties also make them potentially attractive for use in ceramic filters.

In general, technologies which impart antimicrobial properties to surfaces and filters can either release an active ingredient which inactivates microbes or the active ingredient can be permanently bound to the surface and kill only as a result of direct contact between surface and microbe. The same is true for nanotechnologies. The advantage of the latter strategy is that there are fewer concerns about the ultimate fate and environmental/health impact of released active ingredient. The disadvantage, however, is antimicrobial effectiveness will decrease as the surface becomes coated with non-biological matter and dead cells (Feied, 2004), which is certainly expected to occur in the case of filtration.

2.2.1 Silver nanoparticles

Silver, which has a long history of use as a disinfectant, is a natural starting point. Several researchers have looked at the disinfectant properties of silver nanoparticles with varying characteristics and effectiveness against various microorganisms. Disinfection efficiency appears to depend on the dose, size and shape of the nanoparticles, and on the target organism (Theron et al., 2008). In general, Gram-negative bacteria such as *E. coli* are more susceptible than Gram-positive species such as *Staphylococcus aureus*, possibly as a result in differences in the structure of their cell membranes. Gram-negative bacteria have a 2-3 nm layer of peptidoglycan between the cytoplasmic membrane and outer membrane whereas Gram-positive bacteria have a 30 nm thick peptidoglycan layer and no outer membrane (Theron et al., 2008).

Morones et al. (2005) examined both the exteriors and interiors of four different species of Gram-negative bacteria (*E. coli*, *S. typhus*, *P. aeruginosa* and *V. cholerae*) after treatment with suspensions of silver nanoparticles using Scanning Transmission Electron Microscopy (STEM). Nanoparticles were observed to have both attached to the cell membranes and to have penetrated into the cytoplasm. The mean size of nanoparticles both attached to and inside the cells was 5 ± 2 nm compared to mean size of 16 ± 8 nm of free nanoparticles in the suspension used to treat the cells. The authors concluded that interaction between cells and nanoparticles primarily involved particles in the 1-10 nm range. Metal particles sized ~5 nm exhibit size-dependent changes in local electronic structure which are reported to increase the reactivity of the particle surfaces (Raimonci et al., 2005). In addition, Morones et al. (2005) found that ~98% of the nanoparticles smaller than 10 nm exhibited octahedral and multiple twinned icasohedral and decahedral morphologies, all of which present mainly {111} surfaces which have high atom density facets which have been shown to favour silver reactivity. Morones et al. (2005) suggested that these effect as well as the high specific area of the particles allowed nanoparticles in the 1-10 nm to bind with the cell membranes. Once attached, the nanoparticles caused structural changes to the membrane, making them more permeable and allowing the particles to enter into the cells.

The nanoparticles caused dose dependent inhibition of subsequent cell growth. *Escherichia coli* and *S. typhus* were more susceptible than *P. aeruginosa* and *V. cholerae* but no significant growth of any of the species was observed at nanoparticle concentrations, which the authors calculated to correspond to approximately two thousand 1-10 nm particles per cell. Nanoparticles in solution will release silver ions which may also contribute to antimicrobial effects. The authors found that nanoparticles freshly dissolved in 0.2 M $NaNO_3$ immediately released $silver^+$ at concentrations of ~108 µg/ℓ but after 24 hours the concentration had dropped to ~20 µg/ℓ. These concentrations are similar to those found in the filtrate from the first few runs of newly silver coated ceramic filters (Lantagne, 2001a) and may contribute to biocidal effects. However, the response of cells to silver nanoparticles appears to be different to that of silver ions. Cells treated with silver nitrate show a low molecular weight region which is believed to be the cell conglomerating its DNA as a defence mechanism against toxic compounds when the cell detects a disturbance at the cell membrane (Feng et al., 2000; Morones et al., 2005) This phenomenon is absent from cells which have been penetrated by nanoparticles (Morones et al., 2005).

Other researchers have shown that shape as well as size affects the antibacterial effectiveness of silver nanoparticles. Pal et al. (2007) found that truncated triangular silver nanoplates with a {111} lattice plane were more effective against *E. coli* compared to spherical and rod shaped nanoparticles and silver ions.

Several researchers have also experimented with imbedding silver nanoparticles in various solid matrices. Son et al. (2004) prepared ultrafine cellulose acetate particles containing imbedded silver nanoparticles with average diameter 15.4 nm. These were reported to have high antibacterial activity against Gram –positive *S. aureus* and Gram-negative *E. coli*, *Klebsiella pneumoniae* and *P aureginosa*.

Jain and Pradeep (2005) coated silver nanoparticles onto polyurethane foam which they then tested for use as antimicrobial filter. Polyurethane was chosen because it is cheap, non-toxic and contains carbamate groups (–N(H)COO-) which were expected to bond with the nanoparticles. The silver nanoparticles were prepared by boiling silver nitrate solution with sodium citrate and cooling to precipitate the nanoparticles. Foam sheets were soaked overnight in the nanoparticle suspension, thoroughly rinsed to remove adsorbed ions and then air dried. There was no loss of nanoparticles after four to seven washing and drying cycles, indicating the nanoparticles were securely bonded to the foam. The microbial removal efficiency was tested by wrapping a 6 mm thick piece of foam twice around a 157 mm diameter 20 cm long ceramic candle filter and passing a suspension of *E. coli* through it at a rate of 0.5 ℓ/min. Influent concentrations of 10^3 CFU/mℓ and 10^5 CFU/mℓ were used. Samples were collected at hourly intervals over a period of four hours. No *E. coli* were detected in any of the effluent samples. The authors did not report bacterial removal for the ceramic filter alone.

2.2.2 Copper nanoparticles

Esteban-Cubillo et al. (2006) reported that 2-5 nm copper nanoparticles imbedded in sepiolite ($Mg_8Si_{12}O_{30}(OH)_4(H_2O)_4.8H_2O$) achieved 3 log reduction of *E. coli* and *S. aurelius* after 24 hours of incubation. This was in contrast to a study by Top and Ulku (2004) which found that copper (II) in zeolite had negligible bactericidal activity. The former authors (Esteban-Cubillo et al., 2006) attributed their favourable results to the fact that sepiolate matrix ensured a narrow size distribution and uniform spacing of the nanoparticles, maximising the reactive surface. The presence of the inert matrix also appeared to stabilise the nanoparticles in air.

2.2.3 Magnesium oxide and calcium oxide nanoscale powders

Magnesium and calcium oxide (MgO and CaO) nanoscale powders have been investigated by several authors for their potential use as destructive absorbents for chemical and biological agents including spore-forming *Bacillus* such as anthrax. Koper et al (2002) investigated the biocidal activity of aerogel prepared nanoscale powders of MgO and CaO both with and without halogen adducts (MgO-Cl_2, MgO-Br_2 and CaO-I_2) compared to larger sized crystals of the same materials . These authors reported that ZnO was found to be biocidal on its own but results were not presented. In an earlier study by the same group (Richards et al., 2000), it was shown that when vegetative cells or bacterial spores came into contact with MgO-Cl_2 nanoparticles, they opened up allowing the nanoparticles to enter the cells and adhere to the protein and DNA within resulting in rapid deactivation.

The halogen adducts also slowly release halogen gas over several days when exposed to air which would have an additional biocidal effect on cells not in direct contact with the material (Koper et al., 2002). Within a few days of exposure to open air, the powders convert to harmless common minerals such as limestone and dolomite. The latter two properties are desirable in an absorbent powder used for decontaminating facilities but in the case of the ceramic filter would mean a rapid reduction in microbial removal efficiency.

Koper et al. (2002) found that dry contact with halogenated metal oxides resulted in up to 3.7 log deactivation of *Bacillus cereus* spores within two minutes, depending on crystal size (nano versus micro and larger) and halogen content. Deactivation of *E. coli* was even greater (up to 4.68 log reduction). Non-halogenated oxide powders were not effective against *Bacillus* spores but nanoscale MgO produced >3.68 log reduction of *E. coli*. Halogenated metal oxides in suspension were also shown to completely eliminate MS2 bacteriophage with 5 minutes contact time at concentrations of 1 mg/mℓ. Concentrations of 1 to100 μg/mℓ resulted in 0.5 to 3.7 log reduction. Non-halogenated powders were not tested for antiviral activity in this study.

Makhluf et al. (2005) investigated the effectiveness of nanocrystalline MgO without halogenation against *E. coli* (Gram-negative) and *Staphylococcus aureus* (Gram-positive). They found that antibacterial activity was related to particle size with the smallest particles at ~8 nm having the highest activity (83% reduction of both bacteria after one hour of incubation at 1 mg/mℓ and the largest particles at ~23 nm having the lowest activity (33% and 20% reduction of *S. aureus* and *E. coli* respectively). MgO and $Mg(CH_3COO)_2$, the precursors of the nanoparticles showed no activity against either bacteria. The pH of the nanoparticle suspension in contact with the cells was found to be ~10.6 which could have contributed to the antimicrobial effect. However, incubating the cells in saline solution of pH 10.6 in the absence of nanoparticles did not result in any loss of cell viability. The authors instead proposed that the activity of the nanoparticles was due to the formation of active oxygen species which attack both the cell membranes and cell contacts. This effect should increase with increasing surface area, hence the greater activity of the smaller particles.

2.2.4 Titanium dioxide based photocatalytic nanoparticles

Among the most promising bioactive nanoparticles for water disinfection are TiO_2 based photocatalysts (Theron et al., 2008). However, these particles generally have to be illuminated with an ultraviolet source to achieve the photocatalytic effect. A limited amount of research has been conducted on disinfection in the visible range; nevertheless this technology is unlikely to be compatible with the ceramic filter pot concept. The photocatalytic effect would only occur on the outside surfaces of the filter and the amount of light available would be limited since the filter element is enclosed in a covered container which would reduce transmittance even if it was transparent. However, TiO_2 nanoparticles modified with platinum (Pt(IV) chloride complexes have been reported to be effective against *E. coli*, even in the absence of light (Mitoraj et al., 2007). This was thought to be due to the toxicity of platinum to bacteria.

2.2.5 Carbon nanotubes

Recently published research has shown that carbon nanotubes can physically damage bacterial cells leading to their inactivation. Kang et al. (2007) found that *E. coli* cells incubated with narrow size range (0.75-1.2 nm, mean diameter 0.9 nm) single walled carbon nanotubes (SWNT) exhibited a substantial loss in activity (73%, 80% and 89% for 30, 60 and 120 min contact time respectively). The nanotubes tended to form aggregates to which the cells showed preferential attachment. Direct contact between cells and nanotubes was required for inactivation as free swimming cells (not attached to nanotube aggregates) were not affected. Inactivation of *E. coli* filtered onto a SWNT coated filter and incubated for 60 minutes was not significantly different to results for the suspended SWNT. Scanning electron microscopy showed that cells incubated with SWNT lost their cellular integrity whereas control cells remained intact. A five-fold increase in plasmid DNA and a two-fold increase in RNA in solution in the presence of SWNTs confirmed the loss of cytoplasmic material from the damaged cells.

It is important to note that commercial preparations of nanotubes typically contain high levels of contaminants including metals from their fabrication, separation and cleaning processes which can contribute to toxic effects. Khang et al. (2007), however, subjected their SWNTs to further purification to remove traces of cobalt catalyst in order to eliminate such effects. They concluded that the primary killing mechanism was physical contact and piercing of the cells. Other studies have also indicated that nanotubes of various types can pierce and enter cells leading to death due to their cylindrical shape and high aspect ratio. Small diameter nanotubes are more effective than larger nanotubes (Lee et al., 2004; Chipot and Tarek, 2006; Kostarelos et al., 2007).

These results suggest that depositing narrow size range SWNT with diameters ~1nm in a ceramic filter could potentially be effective for bacterial inactivation. However, it is not clear what the effect would be if the nanotubes were bound to the clay and unable to enter the cells (although they might still be able to damage the membranes). There would also be concerns about the potential release and ingestion of the nanotubes in the filtered water and their ultimate environmental fate once the filters are disposed of since the nanotubes can also damage other types of cells including human tissues.

2.2.6 Other potentially anti microbial nanomaterials

Since nanotechnology is a new and emerging field, there have been relatively few studies of antimicrobial nanoparticles and only a limited number of available nanomaterials have been tested for antimicrobial activity. However, conventional materials which have proven antimicrobial properties are likely also to exhibit antimicrobial activity in nanoparticle form. In many cases, nanoparticles of these materials are already available although their antimicrobial potential has yet to be assessed. For example, use of zero valent iron (ZVI) and bimetallic iron containing nanoparticles for degradation of chemical contaminants, in particular chlorinated organic, is extensively covered in the literature on nanotechnology water treatment applications. It has been reported that bimetallic particles containing iron and another metal such as platinum or nickel are more stable in air than iron alone (Theron et al., 2008), however, the use of nano-iron in any of its forms for microbial removal does not appear to have been investigated as yet. Furthermore, as discussed in Section 2.1.11, preliminary data on the addition of iron to the filter to improve virus removal have not been promising.

Nanofibrous alumina filters are made from positively charged aluminium nanofibres on a glass filter substrate. Argonide (http://www.argonide.com), a Florida based company, produces a material called Nan°Ceram® which they claim is capable of greater than 6 log virus removal. The material is available as cartridge filters and as filter media. Due to their positive charge, the alumina nanofibres can absorb negatively charged particles including virus, bacteria, salt, heavy metals etc. The filter media can produce 1.0-1.5 $\ell/h.cm^2$ without the application of pressure. The addition of activated alumina nanofibres could potentially increase absorption of viruses. However, the filters eventually have to be regenerated. Conventional activated alumina filters need to be regenerated after several months of operation using a solution of alum or caustic (Meridian Institute, 2006). Argonide has found that viruses can be eluted using 0.02 M sodium carbonate (Na_2CO_3) solution (pH ~9.7), EDTA and 1.5% beef serum extract with 0.25% glycine solution at pH 9.3. In practice, the need to chemically regenerate the media would limit its effectiveness in the field. It may also be difficult to include both alumina and antibacterial particles such as silver in the same filter element without them interfering with each other.

2.2.7 Health and environmental concerns

2.2.7.1 Silver, copper and zinc

The only currently known health consequence of excessive silver intake is a condition known as argyria in which skin and hair become discoloured by silver accumulation. However, the only known cases have been due to excessive consumption of silver containing medications and not to the use of silver for disinfecting drinking water (Lantagne, 2001a). The World Health Organisation does not at present have a health based guideline for silver, citing inadequate data (WHO, 2006). However, it has estimated that 0.1 mg/ℓ silver ion in drinking water should have no adverse effects over a lifetime of consumption based on half the NOAEL (no-observed-adverse-effect-level) intake shown to cause argyria.

Lantagne (2001a) reported that PFP filters painted with colloidal silver solution showed elevated silver concentrations in the filtrate from the first run after silver application but that the values obtained (29-61 μg/ℓ) were well below the WHO guideline. The filtrate concentration dropped to 20 μg/ℓ or less in the next two runs and silver was detected in the filtrate of only two out of 24 filters in use for six months. Potters For Peace recommends discarding the water from the first run due to the metallic taste, although this does not appear to pose a health threat to consumers.

The current WHO health based guideline for copper is 2 mg/ℓ. There is no current guideline for zinc although concentrations in excess of 4 mg/ℓ as zinc sulphate impart an undesirable astringent taste to water (WHO, 2006).

2.2.7.2 Leaching of metals from clay

Van Halem (2006) found that filters produced in Cambodia leached arsenic into the filtrate in excess of WHO guidelines. The arsenic was naturally present in clay used in the filter production. Filters produced in Ghana and Nicaragua did not have the same problem. It was therefore recommended that filters always be tested for leaching of toxic metals present in the clay source from which they are produced.

2.2.7.3 Toxic potential of nanoparticles

General concerns about the rapid increase in the production and use of nanoparticles arise from the current lack of specific technologies for removing them as well as the lack of data on human health effects, environmental impact and fate. Most studies on toxicological effects have focused on carbon based nanoparticles and metal oxides; in particular TiO_2 based materials. The results of these studies are summarised in Tables 3 and 4 of Theron et al. (2008). Adverse effects have been observed in both *in vivo* studies using laboratory mammals and *in vitro* studies using human cell cultures; however, these have been at much higher doses than are likely to occur in practice. It has recently been reported that carbon nanotubes with similar morphology to asbestos fibres can have the same adverse health effects (Poland et al., 2008).

A general concern relating to any microbiocidal agent that persists in the environment is that it may negatively impact beneficial as well as harmful microbes both in natural ecosystems and wastewater treatment plants with potentially devastating consequences. For example, recent research has shown that silver nanoparticles, colloidal silver and silver ions all have inhibitory effects in autotrophic nitrifying bacteria in biological wastewater treatment with nanoparticles having the greatest effect of the three at the same total silver concentration (Choi et al., 2007). Ghafari et al. (2008) have also found that ingestion of carbon nanotubes inhibits the ability of ciliated protozoa to ingest and digest prey bacteria. These protozoa play an important role in the regulation of bacteria populations in natural ecosystems and in wastewater treatment. These results also show a potential mechanism whereby nanotubes can move up the food chain.

2.3 Conclusions

i. Ceramic filters, whether produced commercially by companies in the developed world or by local potters in developing countries, have been shown to be effective in removing bacteria, in particular, *E. coli,* and larger organisms such as protozoa and helminths, and in reducing the incidence of diarrhoea among users. However, they are not very effective for virus removal.

ii. The mechanisms of removal/inactivation of pathogens are not well understood. Physical straining, sorption and inactivation by silver all appear to play a role. Removal efficiency by sorption mechanisms appears to decline over time as sites are exhausted. Routine cleaning will not regenerate sites within the filter walls. Testing limited volumes of water in new filters may therefore give an unrealistic impression of removal efficiencies, especially viruses. It is recommended that at least 100 ℓ of water should be filtered through any given filter before determining removal efficiencies.

iii. Filters must be scrubbed regularly to remove surface clogging to restore the flow rate. Filters appear to remain effective for seven or more years if properly used and maintained. Plastic filtered water receptacles are easier to clean and disinfect than ceramic ones.

iv. Clean filter discharge of typical filter pots ranges from 1 to 3 ℓ/h. The flow rate is assumed to be related to the porosity, pore size and structure as well as the dimensions of the filter element, which in turn depend on the manufacturing process. However, the relationship between pore characteristics, discharge and removal efficiency has yet to be successfully quantified. The use of porous grog in the fabrication of filter elements is reported to improve flow characteristics. Using multiple candle filters instead of a single pot is another way to increase the flow of a filter unit.

v. Removal efficiencies in the field are often lower than those obtained in laboratory studies. Typical removal efficiencies in the field are expected to be 2 log bacteria, 0.5 log viruses and 4 log protozoa. Education about water and sanitation issues and training in the proper use and maintenance of the filters is critical to their successful implementation. Filter effectiveness has also been found to correlate with frequent follow up visits to households by community or health workers. Both treated and stored raw water can easily be contaminated by improper handling so training must include safe collection, handling and storage of water.

vi. Ceramic filter elements are fragile and easily broken if dropped. Damaged spigots on the filter receptacle and broken filter elements are a major reason for disuse of the filters in field studies. It is therefore important that communities have access to replacement parts.

vii. The mechanisms by which silver amendments to filters to improve bacterial removal in ceramic filters are not well understood. Silver ions which leach from the filter may play a role but silver is not usually detected in the filtrate after the first six months of use. Silver coated onto inert surfaces has been shown to generate active oxygen species through a catalytic reaction with oxygen. This can kill viruses and bacteria on contact with the surface. The same phenomenon has been observed with other metals and metal oxides including CaO and MgO. The advantage of silver is that it does not alter the pH of the water. Combinations of silver with other metals such as copper and zinc may improve removal efficiencies through synergistic effects; however, this has never been tested in this application.

viii. The use of nanoparticles offers the possibility of enhanced reactivity compared to conventional coatings due to very high active surface densities. The biocidal activities of various types of nanoparticles have been tested, often in suspension with bacteria, which allows the particles to penetrate into the cells, but also when immobilised in inert matrices. Biocidal activity appears to correlate with smaller particles sizes (<10 nm), prevalence of {111} crystal facets and even dispersion of the nanoparticles. Nanoparticles with demonstrated antimicrobial activity include silver, copper, magnesium and calcium oxide and their halogen adducts, titanium dioxide based photocatalysts and carbon nanotubes (in suspension). The conditions under which these particles have been tested usually do not reflect the conditions expected in ceramic filters (pH, concentration, photocatalytic effects, mobility of nanoparticles, contact time). However, silver nanoparticles deposited in polyurethane foam have been shown to be effective in inactivating bacteria at substantially higher flow rates than are achieved in current ceramic filter models.

There are general concerns about the use, environmental fate and impact of nanotechnologies largely due to a lack of data. Recent studies have shown that some types of carbon nanotubes have adverse effects in mammals and in beneficial microbial populations in wastewater treatment.

3. DEVELOPMENT OF A PROTOTYPE NANOTECHNOLOGY CERAMIC POT

From the literature review it may be seen that ceramic filters, whether produced commercially by companies in the developed world or by local potters in developing countries, are effective in removing bacteria (in particular *E. coli* and larger organisms such as protozoa and helminths), and in reducing the incidence of diarrhoea among users. From the review it also became clear that the more advanced and recently-developed nanomaterials, such as zero valent iron, various nano-metal oxides, carbon nanotubes etc., were not yet suitable to incorporate into ceramic pots. Therefore, it was decided to concentrate on the further refinement of nano silver addition to clay pots in order to produce a practical unit for use by rural people for home water purification. The pot developed would be compared to the ceramic pot in general current use, the PFP ceramic pot.

The goal behind this further development was to determine whether a new approach towards the synthesis and fabrication of silver imbued porous pots could yield improvement in performance and/or cost savings. The form of silver decided on was $AgNO_3$, since this was a relatively inexpensive form of silver – and much less expensive than the colloidal silver used in the PFP pot (see Cost Analysis in section 3.3).

3.1 Materials and methods

Below is a description of the synthetic fabrication of silver nanoparticle impregnated porous pots (Synthetically Impregnated Porous Pots or SIPP) and its characteristics and performance compared to PFP pots sourced from a licensed vendor in Kenya.

3.1.1 Synthetically Impregnated Porous Pots fabrication method 1

A fabrication method based on the PFP procedure was developed in conjunction with Cerma Labs, although further investigations were carried out and the method developed to suit local conditions. Various mixes were evaluated by Cerma Labs in the process. The optimal mix for the pot used a total of 2 kg of dry ingredients listed in Table 2. The ingredients were mixed with 800 mℓ of tap water per kg.

Table 2: Composition of standard SIPP

Ingredient	%
Ball Clay	65
Sawdust	30
Paper fibre (<2 mm)	5

Pots were fired to 600°C in air to burn off sawdust and then heated to 1000°C in air followed by soaking in water for 0.5 h. The water flow rates were subsequently measured and selected pots were chosen for further $AgNO_3$ treatment.

[1] *Note: The fabrication of all pots presented in this report was conducted by Mr Bruce Berger and his team at Cermalab Materials Testing Laboratory, Pretoria using the instructions given by the TUT research team.*

Post fire silver impregnation

The $AgNO_3$ treatment involved saturating the heat treated pots for 24 h in 0.1 M $AgNO_3$ solution and then drying and firing (to decompose the nitrate) to 600°C (Stem, 1972). The pots were then heated for an additional 0.5 h at 600°C in either air or argon. Lastly, the pots were weighed to determine the residual amount of silver.

Process variations:

- After undergoing the original heat treatment process and soaking in 0.1M $AgNO_3$ for 24 h, **Pot #5** was dried and then fired to **950°C and held for 0.5 h in N_2**. The final pot yielded a flow rate of 0.74 ℓ/h with an unverified amount of silver.
- After undergoing the original heat treatment process and soaking in 0.1M $AgNO_3$ for 24 h, **Pot #J5** was dried and then fired to **600°C and held for 0.5 h in air.** The water flow rates measured displayed an increase from 0.562 ℓ/h prior to the final heat treatment step to 0.923 ℓ/h (64.2%) post heat treatment was noted. The process yielded a final silver loading of 1.27 wt% silver, i.e., 1.27 g of silver per 100 g clay pot mass.
- After undergoing the original heat treatment process and soaking in 0.1M $AgNO_3$ for 24 h, **Pot #J6** was dried and then fired to **600°C and held for 0.5 h in argon.** Water flow rate measurements displayed an increase from 0.517 ℓ/h to 0.6 ℓ/h (16.1%) after the final heat treatment step. The process yielded a final silver loading of 0.87%.

Table 3: Summary of pots fabricated with method 1 (SIPP-M1).

Pot ID #	Process	Pot weight (kg)	Flow rate (ℓ/h)	Ag (wt%)
5	• Original fire: 1000°C in air • Post fire silver impregnation • 950°C and held for 0.5 h in N_2	1.4	0.735	Not determined
J5	• Original fire: 1000°C in air • Post fire silver impregnation • 600°C and held for 0.5 h in air	1.6	0.923	1.27
J6	• Original fire: 1000°C in air • Post fire silver impregnation • 600°C and held for 0.5 h in argon	1.5	0.600	0.87

After the final heat treatment step, each pot appeared orange in colour and displayed a granular texture. Though there were variations among the final weight and size of the pots, on average the pots displayed the following approximate measurements:

- Height = 45 cm
- Base outer diameter = 27 cm
- Top inner diameter = 35 cm

3.1.2 Synthetically Impregnated Porous Pots fabrication method 2

Using the optimal mix of ingredients given in Table 2, the fabrication process was modified to include $AgNO_3$ in the clay mixture prior to initial firing. In addition to the ingredients listed in

Table 2, 23.5 g of $AgNO_3$ per 1.6 ℓ of water (molar concentration = 0.14 M) was included in the mixture prior to heat treatment. The mixture was placed into a ceramic mould, formed, dried and underwent the following heating schedule:

Table 4: Heating schedule for fabrication method 2 (SIPP-M2).

Step	Process
1	950°C for 0.5 h in air
2	600°C for 2.5 h in air with full extraction of smoke generated
3	600°C for 3 h with 30 mℓ/min N_2 flow and half extraction
4	950°C for 2 h in N_2
5	950°C for 0.5 h with 30 mℓ/min N_2 flow and half extraction
6	Cool down with 30 mℓ/min N_2 flow and half extraction

The pots fabricated with method 2 were nearly identical in size and appearance; however, they were designed with a thicker rim, approximately 3.8 cm. Pots that underwent the same heating schedule but did not contain the $AgNO_3$ were treated as the experimental control. See Table 5 for a list of pots fabricated with method 2.

Table 5: Summary of pots fabricated with method 2 (SIPP-M2)

Pot ID #	Process	Pot weight (kg)	Flow rate (ℓ/h)	Ag (wt%)
N1A	Std method with heating in schedule in Table 4.	1.1	0.85	0.013
N2A	Std method with heating in schedule in Table 4.	1.1	3.3	0.013
NO	Std method with heating in schedule in Table 4 but *without* $AgNO_3$.	1.1	- - -	- - -

3.1.3 Potters for Peace

For comparative purposes, pots from the certified PFP plant[2] in Lumuru, Kenya were sourced and tested. The pots appeared burned orange and brown in colour and displayed a smoother texture than that of the SIPP pots described above. On average, the sizes of the pots were just a little larger than the SIPP pots listed above:

- Weight = 2 kg
- Height = 46 cm
- Base outer diameter = 27 cm
- Top inner diameter = 35 cm

3.1.4 Bactericidal efficiency

The bactericidal properties of the SIPP and PFP pots were assessed against bacterial suspensions composed of a mixed population of *E. coli*, ATCC 43895 and ATCC 2592. The bacteria were

[2] Chujio Ceramics, www.chujioceramics.com, tel: +254-722-393-816

harvested in nutrient broth (M1.0 g/ℓ meat extract, 2.0 g/ℓ yeast extract, 5.0 g/ℓ peptone, 8.0 g/ℓ NaCl) which was autoclaved at 121°C for 0.25 h and adjusted to pH 7.1 ± 0.2. The bacterial loading was varied between 10^6 and 10^3 CFU/mℓ in saline buffered distilled water (SBW, 8.5 g/ℓ NaCl).

Prior to the start of each experiment, an overnight *E. coli* culture, incubated at 37 °C, was re-suspended in nutrient broth to yield an optical density of 0.1 OD (Hach, DR/3000 Spectrophotometer) at 600 nm, which was confirmed at approximately 10^7 CFU/mℓ by a growth curve. Large quantities of SBW were sterilized by autoclave or storage under UV for 24 hours or prior to the preparation of the stock suspension. Stock bacterial suspension was prepared by diluting the overnight subculture of *E. coli* to reach the desired *E. coli* concentration in 20 ℓ of sterile SBW. For each experiment, 5 ℓ of the bacterial suspension was transferred from the stock into the target pot and 200 mℓ in two separate bottles of 100 mℓ from the effluent of the pot were collected at hourly intervals. One bottle was analyzed for pH, turbidity and silver concentration while the other (sterile) bottle was analyzed for bactericidal efficiency. Immediately after the 100 mℓ of effluent was added to the bottle designated for the bactericidal study, sodium thiosulphate ($Na_2O_3S_2$) was also added to result in a 15% $Na_2O_3S_2$ solution. The $Na_2O_3S_2$ solution effectively chelated the silver and prevented further bactericidal action before the bacteria were plated and enumerated (Reasoner and Geldreich 1985).

To effectively evaluate the bactericidal efficiency of the pots, each sterile bottle with 100 mℓ and 15% $Na_2O_3S_2$ were serially diluted by 10^{-2}, 10^{-3} and 10^{-4}. Each dilution was subsequently sterile filtered onto a 0.45 µm cellulose filter membrane and the membrane filter was plated onto solid nutrient agar (1.0 g/ℓ meat extract, 5.0 g/ℓ peptone, 2.0 g/ℓ yeast extract, 8.0 g/ℓ NaCl, 15.0 g/ℓ agar). The agar plate was then incubated at 37°C for 24 h and the CFU were determined with a heterotrophic plate counter.

3.1.5 Analytical & mechanical characterization

The silver content of each pot fabricated with method 1 was measured by calculating the increase in weight percent divided by the original weight of the pot. Since the $AgNO_3$ was mixed with the clay in fabrication method 2, silver content was calculated as a percentage of silver in the pot per gram of the weight of the pot.

The silver content was confirmed with X-ray Fluorescence Spectroscopy (XRF) which was performed at the University of Pretoria. Each sample was crushed and transferred to a plastic bag, to which approximately 6 mℓ of PVA was added. The bag contents were thoroughly mixed and poured into a metal specimen holder where they were subsequently hydraulically pressed into round pellets for AA analysis.

Determination of the silver elution at each successive time point was performed on a Spectra AA-20 Spectrometer with a graphite tube atomizer (Varian Inc., Hanson, California, USA). First, soluble silver+ was achieved from the 100 mℓ effluent by adding a 1% HNO_3 solution into 100 mℓ of the filtrate from the pot, shaking at 150 RPM for 24 h. Second, standard solutions of 1-5 mg/ℓ were prepared to calibrate the Spectra AA. Both standard and experimental solutions were run with a silver electrode lamp with a current at 3.5 mA and wavelength of 328.1 nm.

Mechanical strength tests were conducted to evaluate the durability of the pots. An Instro 1195 (Norwood, MA, USA) was used to perform 3-point bending tests on all samples and the modulus of rupture was calculated. Staff at CermaLab conducted all tests.

Porosity and density measurements for the SIPP-M2 and PFP pots were performed by staff at Cermalab. Each pot was first dried overnight, weighed and then placed into water under vacuum. After thorough saturation, the wet weight was measured along with the suspended weight. From these values, the apparent density, porosity and specific gravity were collected. Additionally, the pore size distribution of the pots was determined with mercury intrusion tests performed at Northwest University.

3.2 Results and discussion

3.2.1 X-ray fluorescence

X-ray fluorescence (XRF) analysis performed at the University of Pretoria confirmed the presence of AgO in both PFP and SIPP pots. It was observed that the PFP displayed approximately 10% the silver loading of the SIPP pots (Table 6). The data also agreed with the values from weight% calculations.

Table 6: X-ray Fluorescence results of PFP and SIPP clay pots

	Standard PFP pot (wt%)	Standard error	SIPP pot M2A (wt%)	Standard error
SiO_2	62.08	4.79	55.77	1.82
TiO_2	0.79	0.02	1.55	0.00
Al_2O_3	21.48	1.44	34.86	1.15
Fe_2O_3	6.10	0.02	1.82	0.01
MnO	0.09	0.00	0.01	0.00
CaO	0.39	0.04	0.29	0.01
Na_2O	4.11	2.93	1.41	1.47
K_2O	1.78	0.06	1.26	0.01
P_2O_5	0.07	0.01	0.06	0.01
ZrO_2	0.20	0.00	0.03	0.02
SO_3	0.09	0.10	0.01	0.01
WO_3	0.02	0.00	0.01	0.01
BaO	0.01	0.00	0.02	0.02
Cl	2.53	3.22	1.25	1.52
ZnO	0.02	0.00	0.01	0.00
Y_2O_3	0.02	0.00	0.01	0.00
CeO_2	0.06	0.00	0.02	0.01
Ag_2O	**0.01**	**0.00**	**1.42**	**0.01**
La_2O_3	0.04	0.00	0.01	0.00

3.2.2 Break strength

The SIPP-M2 clay pot was compared to the PFP pot sourced from Kenya in terms of break strength (Figure 4). After averaging the break strength values from the base and sides of the pot, the PFP pot displayed values approximately 1.5 times greater than the SIPP-M2 clay pot. The higher break strength of the PFP pot over the SIPP pot was probably attributable its greater bulk density.

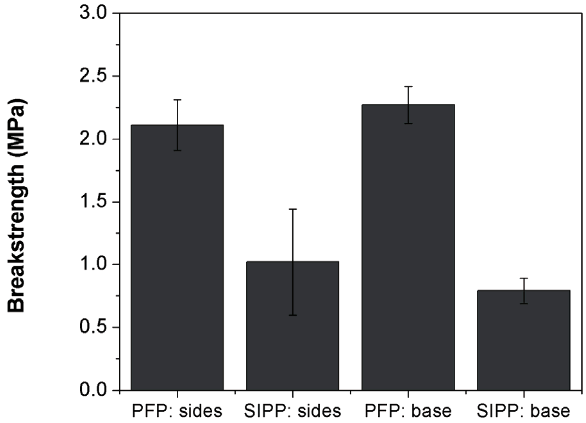


Figure 4: Break strength comparison between PFP & SIPP-M2 pots

3.2.3 Porosity

On average the PFP pot displayed approximately 30% greater bulk density when compared to the SIPP-M2 pot. Bulk density and apparent porosity comparisons between the two are shown in Figures 5 and 6.

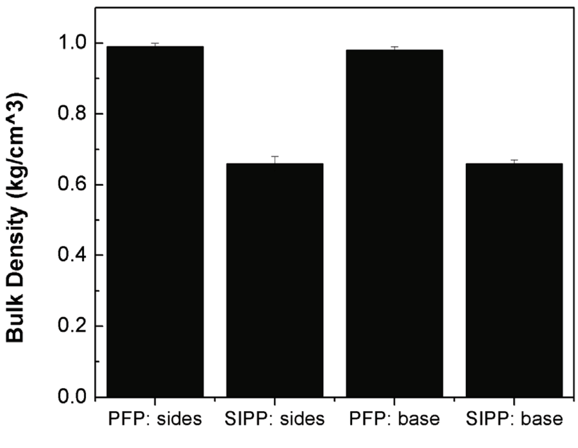


Figure 5: Bulk density comparison

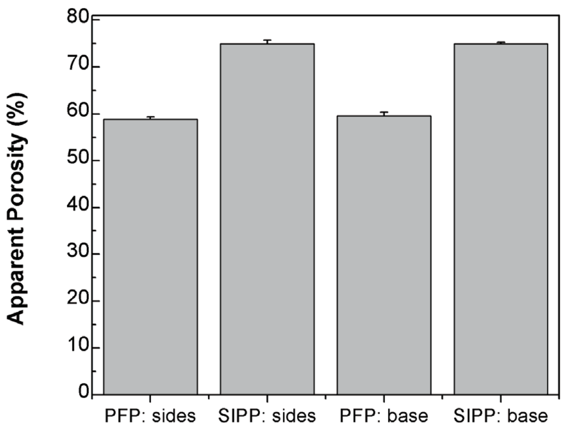


Figure 6: Apparent porosity comparison

The bulk density is directly related to the porosity of the pot which influences the flow rate and consequently the bactericidal effect. On average, the SIPP pot was 26.5% more porous than the PFP pot. Faster flow rates from the SIPP confirmed the higher porosity of the SIPP.

The pore size distribution of the pots was in agreement with the porosity and bulk density data. Through the range of pore sizes, SIPP-M2 pots displayed a greater degree intrusion volume than the PFP pots in most areas. Moreover, a more prominent bi-modal distribution in pore sizes was observed among the SIPP-M2 pots at the sides and base of the pot. Peak values were noted at approximately 50 nm and 30 µm as can be seen in Figure 7.

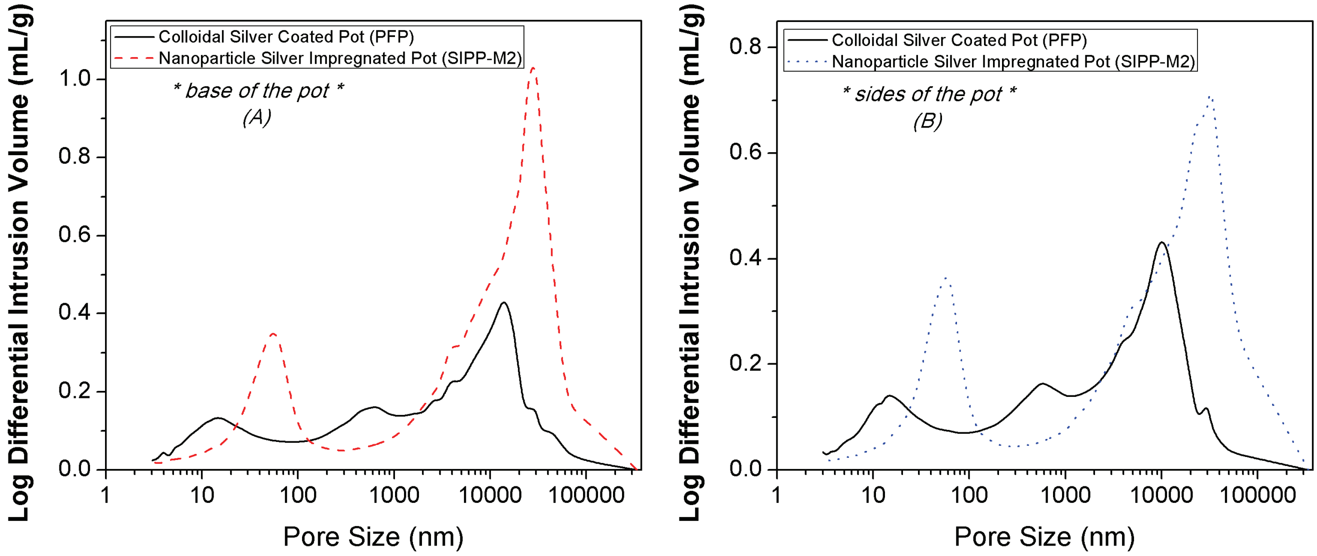


Figure 7: Pore size distribution comparison, (A) bases and (B) sides of SIPP-M2 vs. PFP pots.

3.2.4 Bactericidal performance - comparison contaminated water with 10^6 *E. coli*/mℓ, SIPP vs. PFP

The silver impregnated porous pots fabricated by methods 1 and 2 were compared with the PFP pot from Kenya. The bacterial stock suspension consisted of 20 ℓ of 10^6 CFU *E. coli*/mℓ. Prior to the start of the experiment, each pot was soaked overnight in distilled water to de-gas. Each pot was then filled with 5 ℓ from the stock solution. As previously described, 200 mℓ in two separate bottles were taken for analysis at hourly intervals from the filtrate effluent of each pot and the flow rate was measured. As time progressed, more stock bacterial suspension was prepared and each pot was filled with additional contaminated water. Each pot processed between 11 ℓ and 15 ℓ of water at the end of the experiment. The average measured flow rate for each pot is displayed in Table 7.

Table 7: Flow rate table for the comparative performance test

Pots	Flow rate (ℓ/h)
Porous Pot – No Treatment (control)	1.52
Nanoparticle silver Impregnated Pot (SIPP-M1)	0.89
Nanoparticle silver Impregnated Pot (SIPP-M2)	0.85
Colloidal silver Coated Pot (PFP)	0.67

The results of the bactericidal performance display significant differences between the porous pot with no silver and all other pots which contained silver (Figure 8). Among the pots which contained silver, SIPP fabricated by method 1 displayed the poorest performance while the PFP pot produced the greatest bactericidal efficiency. A strong inverse correlation between the bactericidal performance and the flow rate for each pot was observed; the slower the flow rate, the greater the bactericidal efficiency. Though there was only a 1 log reduction (~90%) in the amount of bacteria that were eliminated, the results suggest that the silver impregnated pots were just as effective in removing the bacteria as the colloidal coated pots. Further analysis of the two systems is presented later on the basis of cost (section 3.3).

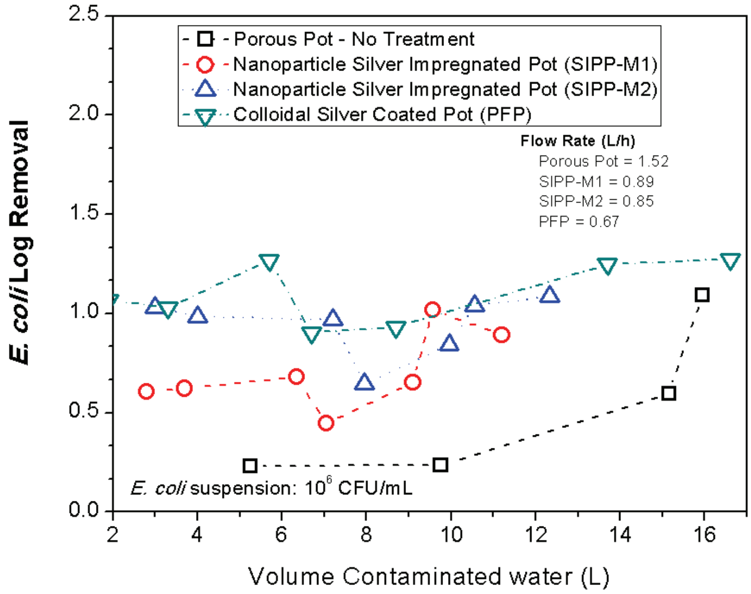


Figure 8: Bactericidal efficiency of SIPP and PFP pots.

All pots which contained silver produced an elution of silver above the WHO recommended limited of 100 ppb. The silver elution was greatest in the early stages (within the first 5 ℓ) but appeared to begin to stabilize by 10 ℓ (Figure 9).

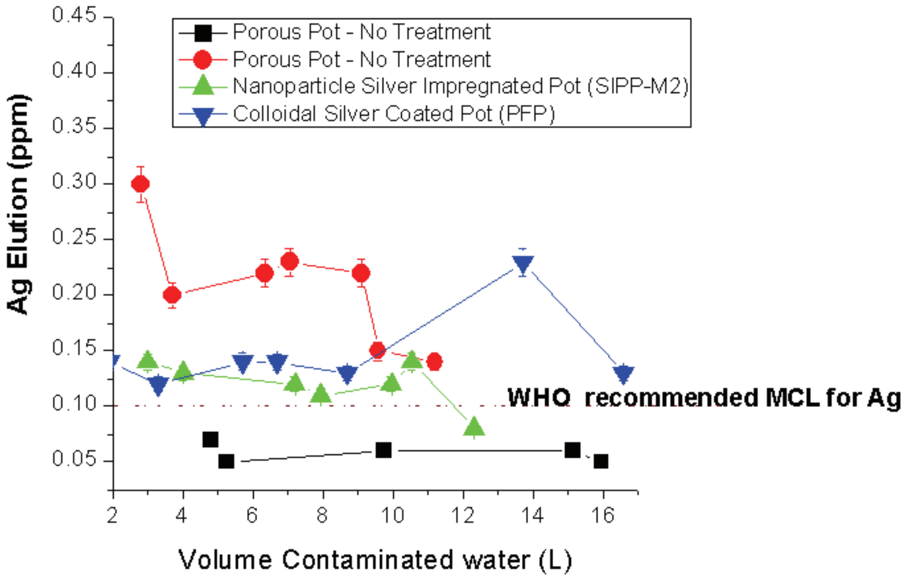


Figure 9: Silver elution from SIPP and PFP pots.

Turbidity was dramatically reduced in the pots which contained silver after the first 5 ℓ of contaminated water were processed (Figure 10). However, no statistical differences in turbidity were seen among the pots which contained silver. Variations in pH were related to the pot in which the water was processed. In general, the pots which did not contain silver tended to produce water with increasing pH through the experimental period. Among the silver impregnated pots, the PFP pot produced water which displayed measured variation of 8.6% with a slight increase in the pH at the end of the experimental time period. In contrast, the SIPP-M2 pot displayed measured variation of 3.5% with a slight decrease in the pH at the end of the experimental time period (Figure 11).

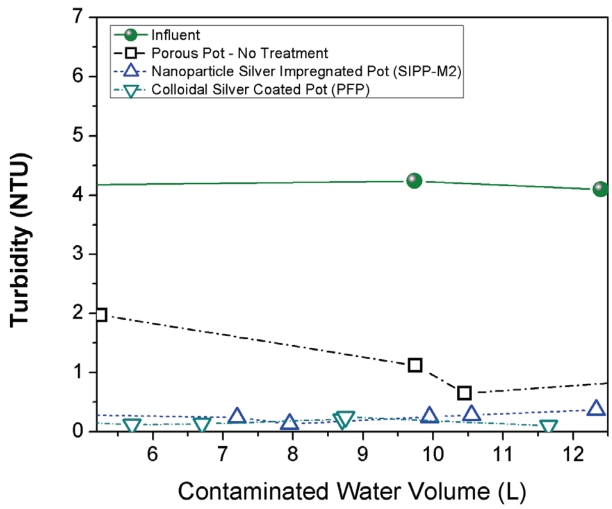


Figure 10: Measured turbidity after processing contaminated water with 10^6 *E. coli* / mℓ

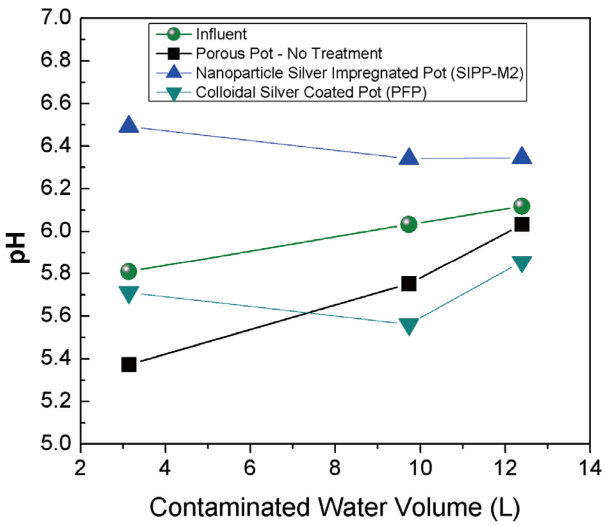


Figure 11: Measured pH after processing contaminated water with 10^6 *E. coli* / mℓ

3.2.5 Bactericidal performance - comparison contaminated water with mixed microbial solution, SIPP vs. PFP

To further validate the efficacy of the nanoparticle silver impregnated pots, a new set of pots was tested with a mixed microbial suspension composed of *E. coli*, *V. cholerae* and *S. typhimurium*, each at 10^3 CFU/mℓ in sterilized saline buffered water. The protocol (Table 8) was identical to that described in DOE-PP3, except that the SIPP-M1 pots were neglected in the study due to their lower performance.

Table 8: Flow rate table for DOE-PP4

Pots	Flow rate (ℓ/hr)
Porous Pot – No Treatment	1.8
Nanoparticle silver Impregnated Pot (SIPP-M2)	3.3
Colloidal silver Coated Pot (PFP)	1.0

DOE-PP4 is the designation for the experiments performed with 10^3 *E. coli, V. Cholerae* and *S. typhimurium* per mℓ. The full definition = Design of Experiment – Porous Pot 4.

Though the initial mixed microbial suspension contained *E. coli*, *V. cholerae* and *S. typhimurium*, no *V. cholera* or *S. typhimurium* were found after plating at each time point. Thus, it is reasonable to conclude that the original mixed microbial solution did not contain live strains of *V. cholera* or *S. typhimurium* so they were neglected in the analysis of the bactericidal efficiency of the pots.

As can be seen in Figure 12, the nanoparticle silver impregnated pot (SIPP-M2) outperformed the PFP pot. The break seen each data set in Figure 12 and Figure 13 indicates an overnight stop in the continuous running of the pot. Up to the first 15ℓ, no statistical differences were calculated between the *E. coli* log removal of the SIPP-M2 and PFP pot. Moreover, no differences were calculated with the control porous pot that did not receive any silver treatment and SIPP-M2 or PFP.

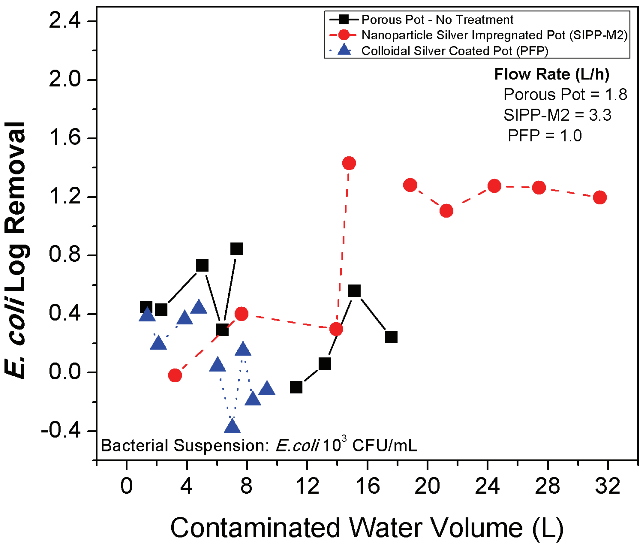


Figure 12: *E. coli* log removal in mixed microbial solution

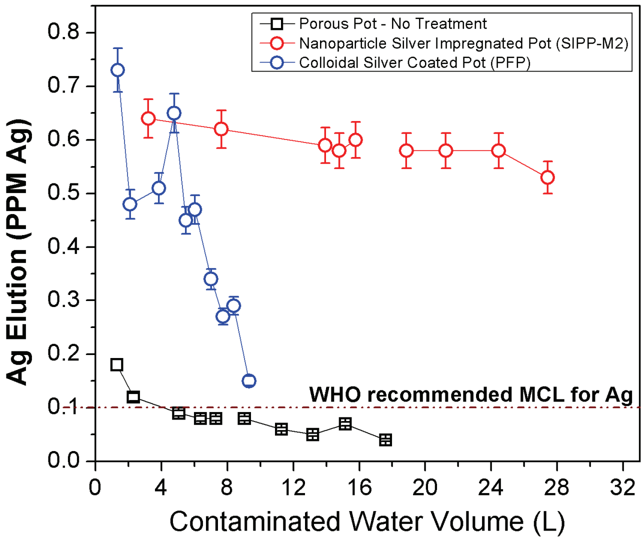


Figure 13: Silver elution in mixed microbial solution

The negative values for the PFP pot after 5 ℓ may be suggestive of bacterial breakthrough. The extremely poor performance of the PFP pot may be due to oxidation of the silver since the pot was stored at room temperature for approximately two months and was not heated prior to use (heating above 280°C would have removed any surface oxidation on the silver) (Shima and Tominaga 2003).

The SIPP-M2 pot, however displayed an average *E. coli* removal rate of 1.2 log (equivalent to 91.8% removal) up to 32 ℓ. The last two data points are trending downward but it is uncertain whether breakthrough has occurred. The longer disinfection capacity of the SIPP-2 pots compared to the PFP pots is attributed to the imbedded silver nanoparticles (Ag_2O and AgO) within the micropores of the pot. Since the silver nanoparticles were within the micropores of the pot, they were less likely to wash away as with the PFP pot which relied on a surface coating of approximately 100 µM colloidal silver on the inside and outside of the pot.

The above conclusion is also supported by the measured values of silver eluted from the pots (Figure 13). As can be seen in this Figure, there was a precipitous decline in the amount of the Ag^+ released from the PFP pot. The SIPP-M2 pot, however, displayed a more gradual decrease in the amount of silver released into the water. It is reasonable to conclude that the longer disinfection capacity of the SIPP-M2 is due to the presence of the silver since independent studies have corroborated the effect of silver in a water purification application, irrespective of substrate (Prashant Jain, 2005; Wang et al., 1998; Li et al., 1998; Inoue et al., 2002; Nangmenyi et al., 2009). Though both pots displayed high levels of silver elution above the 100 ppb level recommended by the WHO, independent studies have indicated the relative non-toxicity of silver and its health benefits (Simonetti et al. 1992).

Lastly, the results show that both SIPP-M2 and PFP displayed equivalent reduction of turbidity and changes in pH values as those seen in the study with contaminated water which contained 10^6 *E. coli*/mℓ.

3.3 Cost analysis

In order to produce a complete analysis of the new SIPP-M2 system versus the established PFP pot, a cost analysis was performed (Table 9). The calculations were based on the current market price of bulk colloidal silver (Bio-Sil SA cc) and $AgNO_3$ (Sigma-Aldrich (Pty) Ltd.).

Table 9: Market price of bulk colloidal silver and $AgNO_3$

	Price
Colloidal silver (500 mℓ)[3]	R55 / 500 mℓ
$AgNO_3$ (>99%)[4]	R2.25 / g

Assumptions for the calculation include the use of 200 mℓ of colloidal silver coating per PFP pot as indicated by Lantagne in the Potters for Peace summary report (Lantagne, 2001a) and that colloidal silver can be re-coated on the same pot for replenished bactericidal effect. Additionally, as demonstrated by the outcome in study with mixed microbial solution, a fresh PFP pot with 200 mℓ of colloidal silver coating yielded approximately 10 ℓ of water before full bacterial breakthrough. Thus, since one 500 mℓ bottle of colloidal silver, which costs R55, would produce 25 ℓ of water the net costs would be R55 /25ℓ or R2.20 /ℓ.

Conversely, different results are achieved with $AgNO_3$. For each SIPP-M2 pot, approximately 0.1 M $AgNO_3$ is used in 1600 mℓ to make the pot. This translates to approximately R161.13 over the amount of water that is produced before bacterial breakthrough. Compared directly, the PFP pot uses 200 mℓ per silver treatment, or R22, and the SIPP-M2 consumes approximately R161 worth of silver. However, given that up to 32 ℓ of water was processed by the SIPP-M2 pot without significant breakthrough, it can be reasonably concluded that the net costs of the SIPP-M2 pots would be less than R1.91 / ℓ. It is important to note that even though the full breakthrough event has not been identified in this study, further use of the pot could be achieved by firing the pot above 600°C to burn off bacterial debris, decompose any oxides and consequently replenish the bactericidal effect of the pot.

3.4 Conclusions from the SIPP study

Based on the results of the experiments described herein, it has been demonstrated that the new SIPP-M2 pots were just as effective in removing bacterial contamination from influent water as the established Potters for Peace pots sourced from Kenya but with advantages over unit water treatment cost attributable to silver addition. Overall, the more efficient bacterial performance of the SIPP-M2 pots may be attributed to the imbedded silver nanoparticles in the micropores. Since the

[3] Bio-Sil South Africa CC, PO Box 75913, Gardenview, 2047, Tel: (011) 615-5504, e-mail: biosil@worldonline.co.za
[4] Sigma-Aldrich (Pty) Ltd., PO Box 10434, Aston Manor 1630, South Africa, Tel: (011) 979-1188 Email: rsa@sial.com

imbedded silver nanoparticles are harder to wash away, the resultant bactericidal activity period of the pot is longer than that of PFP pots since they only have painted colloidal silver on the inside and outside surface.

Thus, the main advantages of the new SIPP-M2 pots include:

i. Lower unit water treatment cost related to silver addition
ii. Longer lasting bactericidal effect
iii. Regenerable with re-firing or recoating with colloidal silver

Overall, the new SIPP-M2 pots, which incorporate the silver in the manufacturing stage, offer a novel approach to produce potable water at low cost in disadvantaged communities. Given the performance of the new SIPP-M2 pots, it may be concluded that the system would be viable in the market place due to their cost and performance. Though a preliminary survey of the patent literature in the area of silver impregnated substrates yielded many sources of information for similar technology, no group reported the same synthetic approach as the one described in this report. Additional work, however, is necessary to complete the full evaluation of the new SIPP-M2 system.

A study with high microbial loading (10^6 *E. coli*/mℓ) must be carried out until breakthrough of bacteria is seen. The information that would be yielded from the completion of the study would further support the cost advantages of SIPP-M2 system.

4. OVERALL CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

- Ceramic filters, whether produced commercially by companies in the developed world or by local potters in developing countries, have been shown to be effective in removing bacteria, in particular, *E. coli,* and larger organisms such as protozoa and helminths, and in reducing the incidence of diarrhoea among users. However, they are not very effective for virus removal.
- The mechanisms of removal/inactivation of pathogens in silver treated ceramic pots are not well understood. Physical straining, sorption and inactivation by silver all appear to play a role. Removal efficiency by sorption mechanisms appears to decline over time as sorption sites are exhausted. Routine cleaning will not regenerate sites within the filter walls. Testing limited volumes of water in new filters may therefore give an unrealistic impression of removal efficiencies, especially viruses.
- Filters must be regularly scrubbed to remove surface clogging to restore the flow rate. Filters appear to remain effective for seven or more years if properly used and maintained. Plastic filtered water receptacles are easier to clean and disinfect than ceramic ones.
- Clean filter discharge of typical Potters for Peace filter pots is in the range 1-3 ℓ/h. The flow rate is assumed to be related to the porosity, pore size and structure as well as the dimensions of the filter element which in turn depend on the manufacturing process. However, the relationship between pore characteristics, discharge and removal efficiency has yet to be successfully quantified. The use of porous grog in the fabrication of filter elements is reported to improve flow characteristics.
- Removal efficiencies in the field are often lower than those obtained in laboratory studies. Typical removal efficiencies in the field are expected to be up to 2 log bacteria, 0.5 log viruses and 4 log protozoa. Education about water and sanitation issues and training in the proper use and maintenance of the filters is critical to their successful implementation. Filter effectiveness has also been found to correlate with frequent follow up visits to households by community or health workers. Both treated and stored raw water can easily be contaminated by improper handling so training should include safe collection, handling and storage of water.
- Ceramic filter elements are fragile and easily broken if dropped. A damaged spigot on the filter receptacle and broken filter elements are a major reason for disuse of the filters in field studies. It is therefore important that communities have access to replacement parts.
- The mechanisms by which silver amendments to filters act to improve bacterial removal in ceramic filters is not well understood. Silver ions which leach from the filter may play a role but silver is not usually detected in the filtrate after the first six months of use. Silver coated onto inert surfaces has been shown to generate active oxygen species through a catalytic reaction with oxygen. This can kill viruses and bacteria on contact with the surface. The same phenomenon has been observed with other metals and metal oxides including CaO and MgO. The advantage of silver is that it does not alter the pH of the water. Combinations of silver with other metals such as copper and zinc may improve removal efficiencies through synergistic effects; however, this has never been tested in this application.
- The use of nanoparticles offers the possibility of enhanced reactivity compared to conventional coatings due to very high active surface densities. The biocidal activities of various types of nanoparticles have been tested, often in suspension with bacteria, which allows the particles to penetrate into the cells, but also when immobilised in inert matrices. Biocidal activity appears

to correlate with smaller particles sizes (<10 nm), prevalence of {111} crystal facets and even dispersion of the nanoparticles.

- Nanoparticles with demonstrated antimicrobial activity include silver, copper, magnesium and calcium oxide and their halogen adducts, titanium dioxide based photocatalysts and carbon nanotubes (in suspension). Except in the case of silver, the conditions under which these particles have been tested usually do not reflect the conditions expected in ceramic filters (pH, concentration, photocatalytic effects, mobility of nanoparticles, contact time).
- There are general concerns about the use, environmental fate and impact of nanotechnologies largely due to lack of data. Recent studies have shown that some types of carbon nanotubes have adverse effects in mammals and in beneficial microbial populations in wastewater treatment.
- A synthetic SIPP ceramic unit for household water filtration, incorporating nanosilver and producing approximately 1 ℓ/h of product water flow, has been successfully produced.
- Based on the results of the experiments described herein, it has been effectively demonstrated that the new SIPP-M2 pots, in which nanosilver is impregnated into the clay during the firing process, were just as effective in removing bacterial contamination from influent water as the established Potters for Peace pots sourced from Kenya but with unit water treatment cost advantages.
- Utilising the SIPP pot, a mean *E. coli* removal rate of 1.2 logs (equivalent to 91.8% removal) could be displayed, up to a water production of 32 ℓ.
- The more efficient bacterial performance of the SIPP-M2 pots as compared to the PFP pots were attributed to the imbedded silver nanoparticles in the micropores. Since the imbedded silver nanoparticles are harder to elute, the resultant bactericidal activity of the pot is longer than that of PFP pots since they only have painted colloidal silver on the inside and outside surface.
- The silver leached from the SIPP pot was, however, at a level of 0.5-0.6 mg/ℓ, higher than the WHO recommendation of 0.1 mg/ℓ.
- Although the cost of the silver needed per pot is higher for the SIPP pot than the PFP pot, the SIPP pot is more cost-effective in terms of unit water treatment cost.

4.2 Recommendations for further work

- The long-term efficiency of the SIPP ceramic unit developed should be evaluated.
- Additional tests should be conducted with bacterial loadings of 10^3 CFU, *E. coli, V. cholera* and *S. typhimurium* in order to determine the effect in a mixed microbial suspension. The tests should be conducted with synthetic and natural water.
- Future pot designs should incorporate at least 20% conditioned zeolites to target heavy metals or other inorganic contaminants.
- Properly conditioned lime should also be incorporated into the pot mixture in order to target the removal of fluoride.
- Since pots displayed a high silver elution at the beginning of the experiment <5 ℓ, it is recommended that for future experiments, the pots should first be primed with sterile distilled water before the contaminated water is processed.
- Other materials which may serve as the filter and basis for nanomaterials should be investigated. For example, silver nanoparticles deposited in polyurethane foam have been

shown to be effective in inactivating bacteria at substantially higher flow rates than are achieved in current ceramic filter models.

- Other nanomaterials as disinfection agents should be investigated for incorporation into home filtration units.

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Appendix

Prototype Clay Filter Pots Developed to Purify Water for Drinking and Cooking in Rural Homes

Porous clay pot control (J7)

Clay pot fired without silver (No silver)

Nanoparticle silver impregnated pots (SIPP-M1) (J5 and J6)

Nanoparticle silver impregnated pot (SIPP-M2)

Colloidal silver coated pot (PFP)