Journal of Water, Sanitation and Hygiene for Development | 04.1 | 2014

Removal of selected microorganisms using silver-impregnated and coated, low-cost, micro-porous, ceramic water filters

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ABSTRACT

There is great need to purify the contaminated water which the poor people in Africa have access to, and make it safe for drinking in a way that is affordable and effective. A particular challenge is the removal of pathogenic bacteria and viruses, which traditionally are eliminated by expensive nano-filtration or reverse osmosis. An added requirement is satisfying the recent recommendation of the WHO for household water-treatment systems to eliminate 99.99% of microbial contamination, which is proving exceptionally difficult to achieve in poor countries at a cost they can afford. We report on the successful testing of a low-cost, locally produced ceramic filter that has the potential to meet the WHO criterion at a cost of US$10 per year. In one version the filter consisted of a silver-impregnated, highly porous ceramic; in another modification silver nano particles were incorporated on the ceramic surface. The silver-impregnated filter was tested on water samples contaminated with selected Gram negative bacteria: *Escherichia coli, Proteus mirabilis* and *Pseudomonas aeruginosa,* for its oligodynamic effect and for its effective reduction of bacteriophages. The ceramic filters reduced the viral count by 94–99% and we believe that, with further development, our prototype is easily capable of achieving the WHO criterion.

Key words | ceramic water filter, drinking water, oligodynamic, virus, water treatment

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INTRODUCTION

Various physical and chemical methods are available for domestic water treatment (WHO 2012). In Africa, however, ceramic filters used in households are seen as a superior, more cost-effective purification method when using raw water and poorly disinfected drinking water when compared with conventional centralised treatment and water reticulation systems (Lantagne 2001; Clasen & Boisson 2006). The small pore size of ceramic filters normally makes them effective in removing bacteria and protozoa but not viruses, which are much smaller and pass through the filters. Furthermore, the WHO (2011) is applying increasing pressure on the manufacturers of ceramic filters to comply with their recommended level of microbial reduction of 99.99% based on representative monitoring data from local, regional or national surveys. Such data should highlight the temporal and spatial variability with respect to protozoa, bacteria and viruses distribution in countries where the filters are produced.

The removal of pathogenic viruses from polluted drinking water is technologically challenging. Figure 1 shows the various methods of purifying domestic water, and their effectiveness. The small particle size of viruses (25–200 nm) makes it possible to remove them using expensive nano-filtration and reverse osmosis, which are not suitable or affordable on a domestic scale.

Bacteriophages usually do not travel independently in water, however, but ‘hitch a ride’ on larger host bacteria. These larger hosts, to which the virus is attached, may then be removed together with the viruses, either by filtration or by their inactivation through incorporation of

doi: 10.2166/washdev.2013.027

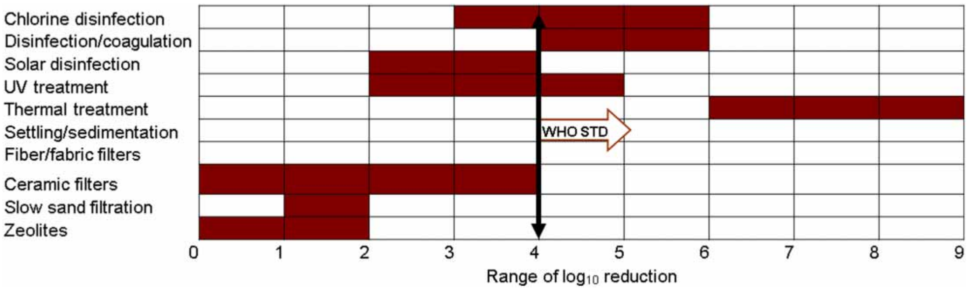

Figure 1 | Effectiveness of different methods to reduce polluted drinking water contaminated with viruses. Effectiveness is defined in terms of log_{10} reduction (LRV), as follows: LRV1 (reduction by 90%); LRV 2 (reduction by 99%); LRV3 (reduction by 99.9%); etc. The WHO now recommends a disinfection standard of LRV ≥ 4 (reduction equal to or greater than 99.99%).

metallic ions into their enzyme system in a chemical reaction, or by a combination of the two methods.

In the study reported here we combined low-cost, ceramic filtration to trap a host with chemical disinfection technology (silver) to inactivate the viruses in infected drinking water.

EXPERIMENTAL PROCEDURE

Ceramic filter preparation and characterisation

A locally developed, low-cost, micro-porous ceramic water filter (*OUTBAC*; out bacteria), manufactured using a traditional slip casting process, was employed to trap and inactivate the viral host. This filter is more effective and efficient than that of other low-cost producers as a result of using less raw material, lower energy consumption and expenditure (Simonis & Basson 2011, 2012). The ceramic filter production process uses a slip casting process which requires a minimum amount of capital investment for manufacture and is therefore ideally suited for manufacture in rural Africa (Simonis & Basson 2013). The ceramic filter material used in this study was obtained from this production process.

The filters were cut into 25 mm × 25 mm squares for physical characterisation and coating. According to Wistreich (1997), Naegeli in 1893 observed that metallic silver kills green algae in highly diluted aqueous suspension. Various substrate coatings on ceramic filters such as iron and aluminium hydroxide have been used by other authors which also increased the inactivation of viruses in aqueous media from less than 30% without coating, to more than 80% effectiveness with a coating (Farrah *et al.* 1991). None of the coatings have achieved the WHO (2011) disinfection standard of LRV 4 and for this reason we selected metallic silver and silver oxide, with its electropositive properties, as the primary anti-viral agent.

Physical testing

For the physical testing of the samples the pore structure of the ceramic filter, which had been produced by sintering, was determined in three complementary ways: scanning electron microscopy (SEM), hydraulic conductivity and water immersion (Lambe 1951; ASTM C20 - 00 2010). SEM demonstrated the bi-modal nature of the pore former, with larger pores resulting from the pore former after firing and the smaller pores resulting from the necks (contact areas) between the larger pores. The 'necking' traps the bacteria and viruses and therefore becomes the determining factor for viral protection. Water immersion demonstrated the high apparent porosity and water absorption values of the ceramic. A standard testing protocol for porous ceramics was followed (found in the Supplemental Material available online at http://www.iwaponline.com/washdev/004/027.pdf).

Silver coating of ceramic: sputter coating

The sputtering system chamber consisted of platens, which both rotate and are water cooled, and magnetrons that are planar (three off-axis). The filter samples were silver-coated at room temperature in a vacuum enclosure pumped to 1.3×10^{-4} Pa. The distance between the object and magnetron is adjustable for obtaining a homogeneous coating and rate of deposition.

The ceramic surfaces were sputter coated at room temperature using a silver metal target. The procedure used for coating was as follows: The chamber was cleaned with acetone to reduce contamination. A silver target was set into the DC magnetron and two ceramic samples together with one silicone substrate were loaded. Vacuum was applied for a period in excess of 2 hours (pump down). Argon gas was applied to the chamber. The magnetron was powered at 80 W for 60 s at a deposition pressure of 3×10^3 Pa. The chamber was then de-pressurised with air and the magnetron powered off.

Silver and silver oxide impregnation of ceramic: wet chemical impregnation

A second method of introducing silver into the porous filter material involved wet chemistry. The untreated ceramic filter units were immersed in a 1 mg l^{-1} silver nitrate solution for 30 min (Van Halen *et al*. 2009). They were then removed from the solution, air dried and heated to 600 °C in an oxidising or a reducing environment, to produce a superficial deposit of Ag_2O or Ag^+ on the ceramic material, respectively (Wegmann *et al*. 2008).

Testing treated filters against selected microorganisms

Subsequent to the coating and impregnation, prototypes of the ceramic filters were first tested for their oligodynamic action in susceptibility tests with selected microorganisms, *Escherichia coli* as fecal indicator and selected Gram-negative bacteria (Muller 1985), *Proteus mirabilis* and *Pseudomonas aeruginosa* (Test 1). This was then followed with Test 2 filtration test using pre- (assay challenge water) and post-filtrate (filtered through the silver coated and impregnated ceramic filters) testing using bacteriophages from hosts *Escherichia coli* and *Salmonella typhimurium* (Clokie & Kropinski 2009).

Test 1: Susceptibility of bacteria to silver-impregnated and coated filters

The pour plate technique was used to distribute three bacterial cultures throughout the agar trapped in position as the medium hardened. The procedure followed for pouring the preparation over the silver-coated ceramic was as follows:

1. The silver coated 25 mm × 25 mm square ceramic samples were placed aseptically into sterile Petri dishes.
2. 10 ml sterile melted nutrient agar (Merck Cat. No. 1.05450.0500) was prepared and cooled to 50 °C.
3. Inoculate the cooled, sterile nutrient agar with 200 μl of *E. coli* culture.
4. The silver-coated ceramic was aseptically placed in a sterile Petri dish and the inoculated nutrient agar was gently poured into the Petri dish.
5. The agar was left to solidify, and then incubated at 37 °C for 24 h.
6. Steps 1 to 4 were repeated for *Proteus mirabilis* and *Pseudomonas aeruginosa*.
7. After incubation the zones of inhibition were measured in mm and recorded.
8. The silver coated ceramic's layer thickness and particle size were inspected using an atomic force microscope (AFM).

Test 2: The plaque assay method for bacteriophages

Phage suspensions were prepared for the filtration tests with the uncoated, silver-coated and silver impregnated filters.

1. Somatic phages (host *Salmonella typhimurium*) and F^- specific phages (host *Escherichia coli*) were used for pre- and post-filtration with the uncoated, silver-coated and silver impregnated filters.
2. After growth, the phages were centrifuged and stored in McCartney bottles at 5 °C.
3. The phage suspensions were filtered through the sputter-coated ceramic filter and the filtrate collected.
4. The plaque concentration before and after filtration was determined using the double-agar method.

RESULTS

Physical testing

From a previous study (Simonis & Basson 2011) on the same filter it was demonstrated that the ceramic filters had a bi-modal pore size. The smaller pores had a pore size of 0.3 micron and the larger pores a size of approximately 5 micron. The bi-modal pore size distribution suggests why these filters act as such an effective micro-sieve in filtering out microbes and other suspended material from polluted drinking water. The two pore sizes are clearly visible in the SEM images in Figure 2 where the larger pores predominate but with the smaller pores still visible within the matrix.

Hydraulic conductivity

Table 1 summarises the flow properties (K values) for the porous filter previously tested (Lambe 1951; Simonis & Basson 2011) using different pore former concentrations for increased porosity. The nano coated filters gave slightly lower K values. The medium K was selected for the filtration testing as it produced a filtration rate of 2–4 litres per hour, double the volume of water compared with the PfP filter (Potters for Peace water filter: Van Halen *et al.* 2009). This makes the filter suitable for supplying sufficient quantity of purified water for the daily needs of a family of five.

The high apparent porosity and water absorption capacity of the OUTBAC filter is indicated in Table 2. The results complement those for the hydraulic conductivity and can be understood in relation to the SEM images.

Microbial testing

Oligodynamic action by treated filters

An image of the homogeneous silver coating using the AFM method is shown in Figure 3. Table 3 shows the results of the inhibitory actions of the silver nano coating using the pour plate technique. Both the Ag^+ and Ag_2O are shown to be effective in relation to the magnitude of the zones of inhibition for the microbes tested.

Elimination of test phages by treated filters

Both coated and uncoated filters reduced somatic phage in the test filtrate by 94–99% (Table 4). F^- phage was relatively poorly eliminated by silver-impregnated filters (22–46%), whereas the sputter-coated filter reduced the F^-phage test sample by a satisfactory 97%.

Water passing through the ultra-porous, ultra-fine ceramic pores slowed the bacteriophages down for inactivation by incorporation of metallic ions into their

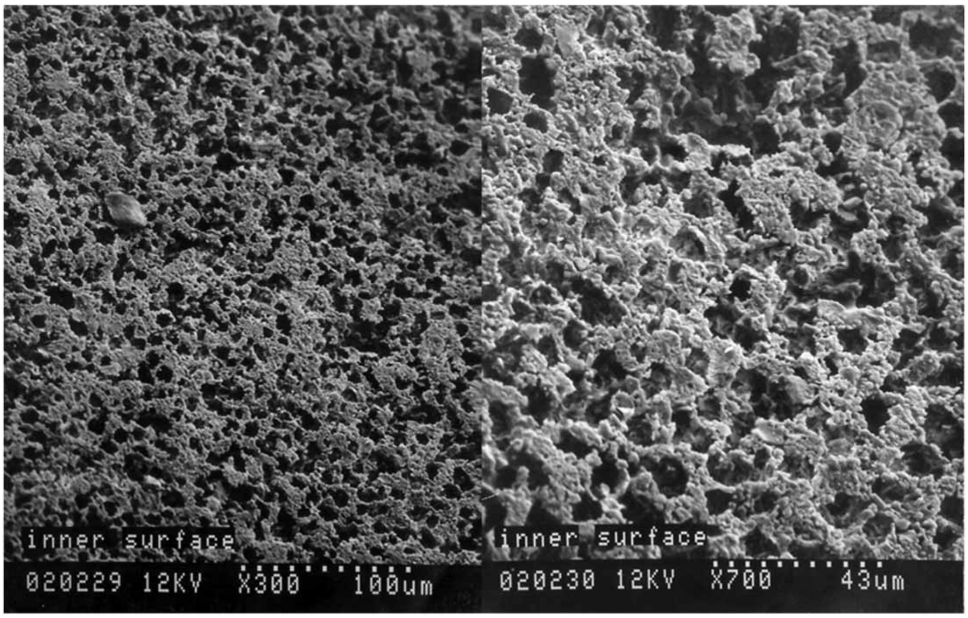

Figure 2 | SEM images of the OUTBAC filter surface showing the homogeneous pore size distributions of the larger and smaller pores with d50 (average pore size) of 5 and 0.3 micron, respectively.

Table 1 | Hydraulic conductivity (K) values for the porous uncoated and coated filters (Simonis & Basson 2011, 2012)

Relative conductivity	K (cm s^{-1})	Coating
High	$> 10^{-1}$	
Medium	10^{-1} to 10^{-3}	Uncoated
Low	10^{-3} to 10^{-5}	Coated
Very low	10^{-5} to 10^{-7}	
Practically impermeable	$< 10^{-7}$	

Table 2 | Porosity and water absorption of the OUTBAC filter (Simonis & Basson 2011, 2012)

Coating	AP (%)*	WA (%)	ASG (g cm^{-3})
Uncoated	67	85	2.42 (± 0.01)
Coated	73	109	2.44 (± 0.05)

* Sample size (n = 10).

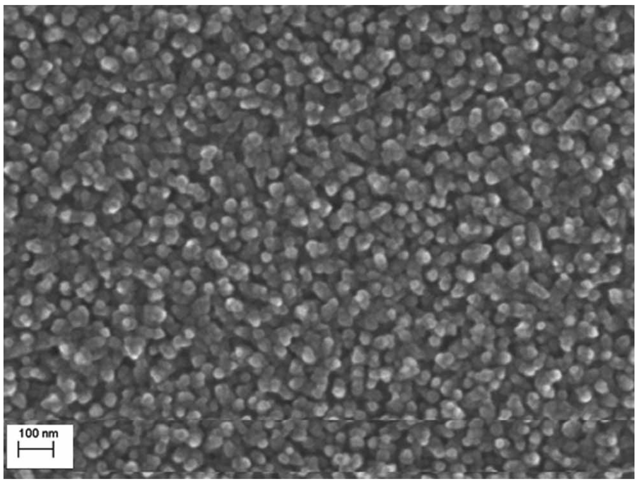

Figure 3 | AFM image of the silver-coated ceramic surface where the diameters of the nano-particles vary between 40 and 50 nm.

Table 3 | Oligodynamic action of silver-coated ceramic

Organism	Diameter of zones developed (mm)		
	Sputter coated Ag^+	Wet chemical impregnated Ag^+	Wet chemical impregnated Ag_2O
E. coli	11	11	21
P. mirabilis	5	14	15
P. aeruginosa	10	11	18

enzyme system. The uncoated ceramic was not effective in eliminating viruses and therefore needs the combined effectiveness of the silver ions.

CONCLUSIONS

The viral load of contaminated water was greatly reduced using silver-coated (97–98%) and slightly to significantly reduced for silver-impregnated ceramic filters (22–95%). The oligodynamic effects of silver-coated ceramic filters have shown significant zones of inhibition for *Escherichia coli, Proteus mirabilis* and *Pseudomonas aeruginosa*.

The efficiency of the Ag^+ sputter-coated filters was dramatically increased in the F^- and somatic phage filtration tests, showing 97% and 99% improvement, respectively.

The efficiency of incorporating Ag^+ as active surfaces in the porous ceramic using a wet chemical impregnated process proved to be less effective for Ag^+, with the somatic phage, showing 94% reduction in viral load and the F^- phage demonstrating only a 46% reduction.

The incorporation of Ag_2O as active surfaces in the porous ceramic resulted in the lowest reduction of the F^- phage but much improved somatic phage reduction of 95%.

Both the sputter coated and impregnated silver (Ag^+), with the additional requirement of being fired under a reducing environment, proved to be more effective than silver oxide as an active surface coating agent in the porous ceramic. The tested phage filtration results compared well with other low-cost filter products but in comparison are closer to meeting the WHO (2011) recommendations.

RECOMMENDATIONS

We believe that changing the nano-particle diameter and increasing the thickness of the silver coating could further increase the effectiveness, bringing it in line with the WHO (2011) recommendations for viral protection.

Due to the high surface area of the ceramic filter (5 $m^2 g^{-1}$) it is believed that increasing the silver impregnation concentration from 1 to 2 mg l^{-1} could further improve the effectiveness, bringing it in line with the WHO (2011) recommendations for viral protection (Mpenyana-Monyatsi

Table 4 | Reduction in bacteriophages for the coated and impregnated ceramic filter

		Plaque concentration (per ml of filtrate) and reduction (%)							
				Sputter coated		Wet chemical impregnated			
Host	Phage	Initial	Uncoated	Ag^+	%	Ag^+	%	Ag_2O	%
E. coli	F^-	2.5×10^5	2.3×10^5	6.8×10^4	97	1.4×10^5	46	2.0×10^5	22
S. typhimurium	Somatic	2.1×10^3	2.0×10^3	30	99	100	94	130	95

et al. 2012). Wet impregnation is a much easier and less expensive way of incorporating Ag^+ as active surfaces in the porous ceramic compared with sputter coating the outside surface only, which requires expensive and sophisticated equipment.

The results suggest that nano-silver coated ceramic filters could potentially be used as a low-cost, household-type water filter, for microbial removal. They also have the advantage of avoiding harmful chemical by-products resulting from the use of chemicals to disinfect water.

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First received 31 January 2013; accepted in revised form 21 August 2013. Available online 21 October 2013