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Modification of ceramic microfilters with colloidal zirconia to promote the adsorption of viruses from water

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ABSTRACT

The purpose of this study was to test the feasibility of modifying commercial microporous ceramic bacteria filters to promote adsorption of viruses. The internal surface of the filter medium was coated with ZrO_2 nanopowder via dip-coating and heat-treatment in order to impart a filter surface charge opposite to that of the target viruses. Streaming potential measurements revealed a shift in the isoelectric point from pH <3 to between pH 5.5 and 9, respectively. While the base filter elements generally exhibited only 75% retention with respect to MS2 bacteriophages, the modified elements achieved a 7 log removal (99.99999%) of these virus-like particles. The coating process also increased the specific surface area of the filters from $\approx 2\,m^2/g$ to between 12.5 and $25.5\,m^2/g$, thereby also potentially increasing their adsorption capacity. The results demonstrate that, given more development effort, the chosen manufacturing process has the potential to yield effective virus filters with throughputs superior to those of current virus filtration techniques.

1. Introduction

Potable water is becoming an increasingly scarce resource in the face of increasing populations and industrialization worldwide, and this is a driver for the development of effective, yet simple and economical methods with which to purify wastewater, contaminated ground- and surface water, etc. One of the main issues here is the potential presence of human enteric viruses which have been the source of various serious outbreaks of viral infections worldwide in the past decades (Maier et al., 2000; Carter, 2005; Friedman-Huffman and Rose, 1998). Several technologies representing a range of removal efficiencies and of varying cost and complexity are available with which to eliminate viruses from water, and it is generally only in complex multistage treatments combining several of these technologies that viruses can be removed with an efficiency in excess of 99.9% (Carter, 2005; Leong, 1983). As far as single-stage filtration processes are concerned, only reverse osmosis membranes provide this level of retention; however, this technology is hampered by its high cost, high pressure drops and low flowrates, and extreme susceptibility to fouling (Leong, 1983; Madaeni, 1999; Zularisam et al., 2006).

A technology with the potential to combine high virus retention with high flowrates and low cost which has drawn some attention in the past is adsorption depth filtration based on diatomaceous earth (DE; also known as kieselguhr) (Neefe et al., 1947; Brown et al., 1974a,b; Chaudhuri et al., 1974; Farrah et al., 1991). These and other adsorption filters (i.e. microporous membranes) (Sobsey and Jones, 1979; Toranzos

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et al., 1986; Lee et al., 1993) rely on attraction of the viruses to the filter surface under the influence of van der Waals and electrostatic forces and hydrophobic interactions (Gerba, 1984), with the literature showing that the dominating mechanism is electrostatic attraction. While the van der Waals forces are always attractive, the electrostatic forces may be attractive or repulsive, depending on whether the signs of the surface charges (or so-called zeta potentials, as defined in the DLVO theory (Verwey and Overbeek, 1948)) of the virus particle and the filter medium surface are opposite or similar, respectively. Since DE and many common viruses can both possess a net negative surface charge across a wide pH range (Gerba, 1984; Oulman and Baumann, 1964), DE will electrostatically repel viruses in many cases and as such is not a natural choice as a material for a virus adsorption filter.

However, kieselguhr remains an interesting material for the application because of its good availability, proven bacterial retention performance, and potential for high flowrates. In order to promote the electrostatic adsorption of viruses on DE, the material can be modified with coatings which impart a positive surface potential between pH 5 and 9, the pH range generally found in potentially potable surface water. This has been achieved both with the application of organic polyelectrolytes (Brown et al., 1974a,b; Chaudhuri et al., 1974) and of metallic hydroxides of aluminum, calcium, iron, and magnesium (Farrah et al., 1991) and virus removal efficiencies on the order of 99% have been demonstrated. Despite these positive results and the other beneficial characteristics of DE mentioned above, no further effort appears to have been made in the direction of a practical DE-based virus filter.

The goal of the current study was to test the practicality of modifying commercial kieselguhr-based water filters optimized for the removal of bacteria with electropositive zirconium (hydr)oxide nanoparticle coatings to promote the removal of viruses. Zirconium oxide was chosen on the basis of tabulated surface potential data for the material (Kosmulski, 2001) and initial zeta potential measurements by the authors, which indicated that it could exhibit a positive surface charge across a wide pH range. The metallic (hydr)oxide route, rather than the organic polyelectrolyte route, was chosen with a view to being able to regenerate the filters at temperatures where organic coatings would be destroyed. The aim of introducing the nanostructured coatings was to increase the specific surface area of the DE filter medium and thereby increase the number of adsorption sites in the filter, and therefore presumably the capacity.

2. Materials and methods

2.1. Filter modification

The base filter medium chosen was the tubular ceramic element used in the "Katadyn Pocket" portable water filter (Katadyn Products Inc., Switzerland). The elements consist of a proprietary mixture of DE and layered silicates and are manufactured using an extrusion process followed by firing at temperatures over 1000 °C. The characteristics of these filter elements are summarized in Table 1. In operation, water is forced through the tube wall from the outside and the filtrate flows out from the bore of the element.

Table 1 – Characteristics of the base filter element type "Pocket"

Filter type	Depth
Pore size[a]	0.2–2 μm
Specific surface area[b]	2.2 m^2/g
Geometrical density	0.85 g/cm^3
Length	12.15 cm
Outer diameter	4.0 cm
Inner diameter	2.55 cm
Throughput[c]	60 l/h
0.5–2 mm bacteria reduction[d]	0.99999%

[a] Mercury intrusion porosimetry.
[b] BET.
[c] Deionized water at 3 bar and 25 °C.
[d] *Klebsiella terrigena* (ATCC333-257) (USEPA, 1987) and *Pseudomonas aeruginosa* (BAG, 2005).

The nanometric material chosen with which to coat the filters was a colloidal dispersion of "zirconia" particles stabilized with acetate at pH 3.5 (NYACOL® ZrO_2 Acetate Stabilized, Nyacol Nano Technologies Inc., USA). According to the manufacturer, the particles are 5–10 nm in size and possess a positive surface charge at the specified pH of 3.5.[1] Despite the allusion to crystalline ZrO_2 in the product name, it could be shown that the particles in the colloid are amorphous and only become crystalline when heat-treatments are applied (data presented below). A calculation of the particle density in the as-delivered colloid based on the density of the dispersion and the mass lost after drying at 150 °C shows that the particles have a density of approx. 3.3 g/cm^3 (compared with 5.6 g/cm^3 for crystalline monoclinic ZrO_2). In accordance with the manufacturer's specifications, the colloid yielded 20 wt% crystalline solid ZrO_2 after drying and calcining at 1000 °C in air. Due to the undefined physical nature of the nanoparticles in the colloid, these are referred to simply as hydrated zirconium oxide, or "$Zr(OH)_x$" particles in this text.

The filter elements were immersed (dip-coated) for 2 h in the pristine $Zr(OH)_x$ colloid which was allowed to permeate the porous medium by capillary forces alone. Calculations showed that, on average, 90% of the pore volume was filled during this stage of the process (see also Fig. 8). After dip-coating, the filters were dried for 12 h at 150 °C in air. Finally, the elements were calcined 1 h in static air at 250, 300, or 400 °C to fix the $Zr(OH)_x$ coating in place on the filter medium surface.

2.2. Physical characterization

At the various stages of processing described above, samples were characterized using scanning electron microscopy in

[1] Between 2 and 4 nm measured by laser non-invasive back scattering and surface charge confirmed as positive by electrophoresis (Zetasizer Nano ZS, Malvern Instruments, UK).