Fabrication of catalytic ceramic membranes for water filtration
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ABSTRACT
The paper describes the use of the layer-by-layer technique to coat ceramic membranes with iron and manganese oxide nanoparticles. The coatings are thin (<50 nm) and relatively uniform. These coatings enhance the performance of the hybrid ozonation-filtration process.
With the coated membranes it is possible to significantly reduce fouling, improve the removal of DBP precursors and more effectively kill Escherichia coli bacteria.

Key words | ceramic membranes, fouling, membrane filtration, ozone, ultrafiltration

INTRODUCTION
The implementation of sand filtration and disinfection for drinking water treatment in the early twentieth century greatly reduced the number of outbreaks of waterborne diseases. However, incidents such as the 1993 Milwaukee Cryptosporidium outbreak, which resulted in over 100 deaths, highlighted the need for further improvements in drinking water treatment. Improved water treatment systems are also needed to address the problems created as increased population and the effects of global warming place strains on water resources. The limited availability of high quality water sources will force water utilities to use poorer quality water sources or reuse wastewater. This will also necessitate improved treatment methods to ensure the safe drinking water.

As a result of the failure of conventional water treatment systems to adequately remove microbial contaminants, under certain circumstances the water utility industry has increasingly turned to membrane filtration to provide a more reliable means of protecting human health (US Environmental Protection Agency 2001). One of the major challenges associated with the operation of membrane filtration, particularly, UF plants is the energy (and therefore, cost) required for their operation as a result of the decrease in the permeate flux due to membrane fouling (Seidel & Elimelech 2002; Taniguchi et al. 2003; Lee et al. 2004; Li & Elimelech 2004). Membrane fouling lowers the economic efficiency of membrane systems by reducing the quantity of treated water, shortening the life of the membranes and increasing the frequency of membrane cleaning. Fouling rates are influenced by the concentration and nature of the particulates and solutes present, hydrodynamics, the pore size of the membrane, and the surface characteristics of the membrane. The fouling of membranes in drinking water systems has been attributed primarily to natural organic matter (NOM) (Seidel & Elimelech 2002; Taniguchi et al. 2003; Lee et al. 2004; Li & Elimelech 2004).
It appears that in many cases this is true; however, some researchers have attributed fouling to both organic and inorganic species (Howe & Clark 2002). This apparent contradiction may arise due to the variability in the fouling behavior of natural waters (Howe & Clark 2002).

One approach to mitigating fouling problems is to combine membrane filtration with chemical oxidation using ozone for the destruction of organic foulants (Karnik et al. 2005c). Ozone is a powerful oxidant that is widely used as a disinfectant in water treatment systems. In this application, ozone is of particular interest because of its demonstrated reactivity with NOM (Karnik et al. 2005c).

Organic polymeric membranes are used in the majority of membrane applications for drinking water treatment systems. In our work we have chosen to use ceramic membranes because of their resistance to ozone. The use of ceramic membranes in water treatment is relatively new. Compared with polymeric membranes, ceramic membranes are more resistant to chemical oxidation and temperature extremes (Burgraff & Cot 1996), more durable (Burgraff & Cot 1996) and less prone to fouling (Kim et al. 1999). Another advantage of ceramic membranes is that, because of their durability, they are less prone to rupture. A further advantage is that by coating the ceramic membrane with substances that catalyze the decomposition of ozone to OH radicals, the mitigation of fouling can be enhanced (Karnik et al. 2006).

Numerous methods exist for the fabrication of ceramic membranes (Burgraff & Cot 1996). Ceramic ultrafiltration (UF) and nanofiltration (NF) membranes typically consist of several layers. As illustrated in Figure 1, the separation (or filtration) layer is supported by a substrate. It is important to membrane performance to achieve a thin separation layer that is free of defects. One or more intermediate layers may be placed between the support and the separation layer. The purpose of these intermediate layer(s) is to reduce the roughness of the layer underlying the separation layer. Thus, the thickness of the separation layer can be kept small, which minimizes the resistance of the filter.

The separation layer is usually prepared by sol-gel processing techniques (Kim et al. 1999; Tsuru 2008). This process can produce membranes with pore sizes from less than 1 nm to approximately 50 nm. In this paper we describe a novel method to coat ceramic membranes with nanoparticles using the layer-by-layer method (Karnik et al. 2005b).

**METHODS**

**Membrane fabrication**

A 7-channel Inside Ceram ceramic membrane (TAMI North America), with a nominal molecular weight cut-off of 5 kDa, was coated with iron or manganese oxides using the layer-by-layer technique. The membrane was 250 mm long and its outside diameter was 10 mm. The manufacturer states that the membrane has a TiO₂ filtration layer.

A schematic representation of the layering process for coating the membrane with iron oxide is shown in Figure 2. Alternating applications of the Fe₂O₃ nanoparticles and 40 mM phytic acid were used to build up the coating on membrane (Karnik et al. 2005b). The phytic acid serves as a binder to hold the layers of Fe₂O₃ particles together. The thickness of the coating was controlled by the number of times that the layers of Fe₂O₃ nanoparticles and phytic
acid were applied. After the desired number of layers was applied, the coated membrane was sintered in air at 900°C.

Similarly, manganese oxide coated membranes were fabricated using a MnO$_2$ nanoparticles and poly (diallyldimethyl ammonium chloride) (PDDA) as a binder. Once the desired number of layers was achieved, these membranes were sintered at 500°C for 45 min. The MnO$_2$ nanoparticles were synthesized by ozonating 1,000 mL of DI water for 20 min, then injecting 100 mL of a 2 mM manganese (II) chloride (Aldrich, 99 + %) solution. The resulting particles were gel-like flakes with an average size of 92 nm ± 14 nm (Corneal et al. 2009).

Membrane characterization

Samples were prepared for surface characterization using scanning electron microscopy (SEM) and transmission electron microscopy (TEM) by cutting a cross section of the sample using a diamond-wafering saw. Cross sections of approximately 1 mm thick were then sliced into arcs approximately 3 mm long. TEM samples were prepared by affixing the arcs to slotted copper grids so that the cross section was facing up. The samples were thinned and polished until they were sufficiently thin, then they were dimpled and ion milled. TEM images were obtained using a JEOL 2200FS transmission electron microscope (200 kV accelerating voltage, Japan Electron Optics Laboratories, Tokyo, Japan).

SEM samples were prepared by affixing the arcs to aluminum stubs using carbon tape so that the coated surface of the membrane was facing up. The samples were then coated with gold. SEM images were obtained using a JEOL 6400V scanning electron microscope (Japan Electron Optics Laboratories, Tokyo, Japan) equipped with a LaB$_6$ emitter (Noran EDS, Noran Instruments Inc., Middleton, WI).

Membrane filtration

A bench scale crossflow filtration system was used to investigate fouling during the ozonation-membrane filtration process (Kim et al. 2009). In this system gaseous ozone was injected into the recirculation loop in the system, so that ozone directly contacted the membrane. In full-scale membrane ultrafiltration applications, it is a common practice to use some form of pretreatment, such as microfiltration or coagulation-sedimentation, to remove the bulk of the solids. This prevents rapid fouling of the membrane. Pretreatment in our system was accomplished by filtering samples through a 0.2 micron Sterastyl filter (Doulton USA, Southfield, MI). The dissolved ozone concentration was measured using an ozone microsensor (AMT, Rostock, Germany).

RESULTS AND DISCUSSION

TEM imaging

TEM micrographs of a cross section of the ceramic membrane coated with iron oxide particles show the layered structure of the supporting membrane with a titania filtration layer and the Fe$_2$O$_3$ coating layer (Karnik et al. 2008). A thin, uniform coating on the ceramic membrane was achieved using the layer-by-layer technique. The average thickness of the iron oxide coating on a membrane coated with 40 layers of Fe$_2$O$_3$ nanoparticles was approximately 46 nm (Karnik et al. 2008).

As shown in Figure 3, for the membrane coated with 40 layers of MnO$_2$ nanoparticles, the thickness of the manganese oxide coating appears to be about 20–25 nm. The exact thickness of the coating is unknown, since the coating may have been damaged during the sample preparation process.

Figure 3 | TEM image of a membrane coated with 40 layers of MnO$_2$ nanoparticles.
SEM imaging

Figure 4 shows the SEM micrographs for the uncoated sintered membrane (Figure 4a, c), Fe$_2$O$_3$ coated membrane (Figure 4b) and the Mn oxide coated membrane (Figure 4d). Figure 4b reveals the coarsening of the grains on the membrane surface coated with iron oxide surface compared to the uncoated membrane (Figure 4a). With the Mn oxide coated membrane, there was a small increase in the grain size on the membrane surface after coating. The average size of the grains in the underlying uncoated sintered TiO$_2$ membrane was approximately 76 (± 6) nm. The average grain size for the membranes coated with 40 layers of the Mn oxide particles was approximately 87 (± 8) nm.

Membrane fouling

We have shown previously that stable membrane fluxes can be achieved using ozonation in combination with ceramic membrane filtration (Karnik et al. 2005c). Figure 5 illustrates the normalized permeate flux as function of time in four filtration experiments using (i) no ozone, i.e., conventional membrane filtration, (ii) ozone with an uncoated membrane, (iii) ozone with a manganese oxide coated membrane, and (iv) ozone with an iron oxide coated membrane. In the experiment with no ozone a steady decrease in the permeate flux was observed. The final flux was about 42% of the clean water flux ($J_0$). In the experiment with ozone and the uncoated membrane the permeate flux decreases for the first two hours then it slowly increases. At the end of the experiment the flux is about 60% of the clean water flux. With the experiment with the iron oxide coated membrane the flux initially drops more rapidly than it does in the experiment with the uncoated membrane. For the iron oxide coated membrane the flux reaches a minimum value after about 100 min, it then increases. The increase is more rapid than was the case for
the uncoated membrane. With the manganese oxide coated membrane the flux decreases for about 30 min, then recovers and it is over 90% of the clean water flux at the end of the experiment. In the experiments with ozone the initial dissolved ozone concentration is zero. The dissolved ozone concentration increases until a steady state concentration is obtained after about 1–2 h. The initial decline in flux shown in Figure 5 occurs this period. It appears that the dissolved ozone concentration is too low and ozone does not react with the foulants at a rate fast enough to prevent their accumulation on the membrane surface. As the ozone concentration builds up it is possible to reverse the fouling process. The steady state dissolved ozone concentrations found in the three experiments with ozone are similar (see Table 1). The ozone concentration for the experiment with the uncoated membrane is slightly higher, which may reflect the fact that TiO₂ is a less effective catalyst for the decomposition of ozone than is iron or manganese oxide. As the iron and manganese oxides are more effective catalysts for the decomposition of ozone, the flux recovers more rapidly when the membrane is coated with these metal oxides (even though the dissolved ozone concentration is slightly lower than in the experiment with uncoated membrane).

**Removal of total organic carbon (TOC) and disinfection by-product (DBP) precursors**

The hybrid ozonation filtration system has been shown to remove TOC and disinfection by-product precursors from water from Lake Lansing (Karnik et al. 2005a,b). An uncoated membrane removed up to 50% of the TOC and with the uncoated membrane the formation of simulated distribution system (SDS) haloacetic acids (HAAs) and total trihalomethanes (TTHMs) was reduced by up to 80% and 65%, respectively. An iron coated membrane removed >85% of the TOC and SDS HAAs and SDS TTHMs were reduced by up to 90% and 85%, respectively (Karnik et al. 2005b).

**Removal of E. coli**

The effectiveness of the hybrid-ozonation system for the inactivation of the bacterium, *Escherichia coli* has been evaluated using the iron oxide coated membranes (Karnik et al. 2007). These studies were conducted using a 5 kD MWCO ceramic membrane. As is shown in Table 2, excellent removals (>7 log) of *E. coli* were achieved using this membrane. This result is not surprising given the tightness of the membrane used. However, a very interesting result of this study is that the mortality of the bacteria is significantly higher for the hybrid treatment systems. It appears that the bacteria are concentrated at the

**Table 1 | Steady-state ozone concentration in the retentate**

<table>
<thead>
<tr>
<th>Membranes (5 kD)</th>
<th>Ozone conc. † (mg O₃/L)</th>
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<tbody>
<tr>
<td>Uncoated (Al₂O₃-TiO₂)</td>
<td>0.39 ± 0.03</td>
</tr>
<tr>
<td>Mn oxide coated with 20 layer</td>
<td>0.34 ± 0.02</td>
</tr>
<tr>
<td>Iron oxide coated with 40 layer</td>
<td>0.34 ± 0.01</td>
</tr>
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</table>

*Measured during the last five hours of the filtration experiment.

**Table 2 | Removal of bacteria and % of live bacteria in the product water (from Karnik et al. 2007)**

<table>
<thead>
<tr>
<th>Treatment process</th>
<th>Log removal</th>
<th>% live*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozonation†</td>
<td>4.04</td>
<td>50</td>
</tr>
<tr>
<td>Membrane filtration</td>
<td>6.97</td>
<td>85</td>
</tr>
<tr>
<td>O₃ membrane filt. Uncoated†</td>
<td>7.04</td>
<td>14</td>
</tr>
<tr>
<td>O₃ membrane filt. Fe oxide coated†</td>
<td>7.45</td>
<td>&lt;1</td>
</tr>
</tbody>
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*Results obtained using the BacLight Bacterial Viability Kit, Molecular Probes, Eugene, OR.
†The same ozone dose and contact time was used in all the ozonation experiments.
membrane surface and the secondary radicals produced by the decomposition of ozone at the membrane surface inactivate the bacteria. In the experiment with the iron oxide coated membrane, the survival of the bacteria is less than 1%, which is significantly lower than that with the uncoated membrane. This could be because the iron oxide coating is a more effective catalyst for ozone decomposition and the radicals generated at the surface kill the bacteria. Adhesion of bacteria to the iron oxide surface may also result in the more effective inactivation of the bacteria using the coated membrane.

CONCLUSIONS

We have demonstrated that the layer-by-layer technique can be used to coat ceramic membranes with iron and manganese oxide nanoparticles. The coatings are thin (<50 nm) and relatively uniform. We have also demonstrated that these coatings can enhance the performance of the hybrid ozonation-filtration process. With the coated membranes it is possible to significantly reduce membrane fouling, improve the removal of DBP precursors and more effectively kill *Escherichia coli* bacteria.

REFERENCES


US Environmental Protection Agency 2001 Low-Pressure Membrane Filtration for Pathogen Removal, 815-C-01-001.