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AFM, SEM and EDS characterization of manganese oxide coated ceramic water filtration membranes

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ABSTRACT

Tubular ceramic membranes (molecular weight cut-off, 5 kDa) were coated with manganese oxide nanoparticles. Atomic force microscopy imaging of the coated membranes showed no statistically significant change in the surface roughness or maximum height of the surface features compared with the uncoated membrane. However, scanning electron microscopy imaging showed an increase in grain size with increasing number of coating layers. Energy dispersive X-ray spectroscopy mapping and line scanning showed manganese present throughout the membrane, indicating that either manganese oxide nanoparticles penetrated into the filter or residual Mn^{2+} ions present in the suspension were sorbed onto the filter and oxidized, forming manganese oxide. The coated membranes were used to treat water containing natural organic matter (NOM) in a hybrid ozonation–membrane water filtration system. Treatment reduced the total organic carbon (TOC) in the water samples by 56%.

1. Introduction

Nanofiltration and fine ultrafiltration membranes, traditionally fabricated from polymers, have been used to remove natural organic matter (NOM) from water [1–7]. However, one problem with the use of these membranes is that NOM fouling results in a decrease in the water flux through the membranes [3–7]. Ozone has been used to resolve the fouling issue [8–13], however, it degrades commonly used polymeric membranes [14,15]. Ceramic membranes can be used in combination with ozone, as they are resistant to ozone [10–13,16–24]. Coating the ceramic membranes with catalytic materials has been shown to enhance their performance when used in combination with ozone [13,21–25]. Karnik et al. [13,22–25] demonstrated that coating a commercially available ceramic membrane with Fe_2O_3 nanoparticles improved the performance of a hybrid ozonation–filtration system. The enhanced performance was linked to the catalytic decomposition of ozone by the iron oxide to produce hydroxyl and other radicals [23]. The radicals produced at the Fe_2O_3 surface degraded organic foulants, resulting in a decrease in membrane fouling and a concomitant decrease in the dissolved organic carbon in the permeate [23]. The grain size of the Fe_2O_3 coating layer (as evaluated using SEM) increased with increasing number of coating layers, up to a maximum of 40 layers, which corresponded to the largest improvement in water quality, in terms of the reduced concentration of ozonation and chlorination disinfection by-products in the product water [22].

Manganese-containing catalysts have been shown to increase the rate of decomposition of ozone [26–29]. Manganese oxide is also known to catalyze the oxidation of organic compounds by ozone [30–42]. Ma and Graham [43,44] showed that manganese oxide catalysts enhanced the oxidation of atrazine by promoting ozone decomposition and hydroxyl radical formation. Thus, coating a membrane with manganese oxide is expected to produce a catalytic surface, which in the presence of ozone will reduce fouling by the oxidation of the natural organic matter (NOM) that deposits on the membrane surface. However, the optimum choice of the MnO_2 preparation method, the number of coating layers, and sintering conditions must still be determined. In this paper we have studied the effect of particle preparation method, the number of coating layers, the sintering temperature and the sintering time on the structure of the resulting catalytic coatings and the quality of water treated using the coated membranes.

Surface modification affects the surface morphology of ceramic membranes [22,45–49]. The deposition of nanoparticle layers on membranes has been characterized by various techniques includ-

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ing atomic force microscopy (AFM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and transmission electron microscopy (TEM) to study morphological features including pore size [22,45–49], roughness [22,45–48], grain size [22,48,49] and in addition, the diffusion of the coating material into the membrane [22,48,50]. In the work described in this paper, AFM, SEM and EDS have been used to characterize the surface of manganese oxide coated ceramic membranes.

2. Experimental

2.1. Preparation of nanoparticles

Two methods were used to prepare the manganese oxide nanoparticles. The first method involves the ozonation of $MnCl_2$ (>99%, Sigma–Aldrich Co., St. Louis, MO) in water. A detailed description of the first method is provided elsewhere [48]. Briefly, 1000 mL of deionized (DI) water was ozonated for 20 min at a flow rate of 50 mL/min in a covered glass reactor, then 100 mL of a 2 mM $MnCl_2$ (99+%, Sigma–Aldrich Co., St. Louis, MO) solution was injected. The ozone flow was stopped immediately after the $MnCl_2$ was added. The resulting colloidal suspension had a pH of 3.7.

The second approach to the preparation of manganese oxide nanoparticles was based on the method described by Luo [51]. Briefly, 100 mL of a 20 mM $KMnO_4$ (>99.0%, Sigma–Aldrich Co., St. Louis, MO) aqueous solution was mixed with an equal amount of an aqueous solution of 80 mM poly(allylamine hydrochloride) (PAH, average molecular weight: 15,000, ≥95.0%, Sigma–Aldrich Co., St. Louis, MO) and stirred vigorously for 5 min at room temperature.

2.2. Coating of membranes

A layer-by-layer technique based on that developed by Lvov et al. [52] and Espinal et al. [53] was used to coat the ceramic membranes with manganese oxide nanoparticles. The procedure used to wash and disperse the particles prepared by ozonation was as follows: first, centrifugation (ThermoForma General Purpose Centrifuge, Thermo Scientific, Waltham, MA, 30 min at 2500 rpm) was used to settle the manganese oxide particles and the supernatant was subsequently decanted and discarded. The solids were then mixed with 10^{-4} N KNO_3 (≥99.0%, J.T. Baker Co., Phillipsburg, NJ), and sonicated (58 W, Branson Ultrasonics Corporation Model 250 Sonifier, Danbury, CT) for 30 min in an ice bath to disperse the nanoparticles. The final pH of the resulting suspension was 6.3. The ceramic membrane (INSIDE CéRAM, TAMI North America, St. Laurent, Québec, Canada) had a tubular design with 7 channels. The outside diameter of the membrane was 1 cm and the length was 25 cm. The nominal molecular weight cut-off was 5 kDa. The manufacturer's literature indicated that the membrane has a titanium oxide ceramic support and a titanium oxide and zirconium oxide filtration layer.

The coating procedure was as follows: the channels of the ceramic membrane were filled with a 0.2 wt% poly(diallyldimethylammonium chloride) (PDDA) solution (Aldrich, average MW < 100,000). The PDDA solution was allowed to stand for 15 min and then the membrane was rinsed for 15 s with 0.01 M NaOH (≥98.0%, J.T. Baker Co., pH 12). After rinsing, the membrane channels were filled with the manganese oxide suspension. The suspension was allowed to stand for 15 min and then the membrane was rinsed for 15 s with 0.01 M NaOH. This sequence produced one layer. The sequence was then repeated to obtain the desired number of layers of nanoparticles. After coating, the membrane was sintered in air at either 550 °C for 30 min or 500 °C for 45 min (the temperature of the furnace was increased at a rate of approximately 10 °C/min and the membranes were allowed to cool in the furnace for 8 h).

2.3. Microscopy sample preparation and analysis

A schematic representation of the AFM sample preparation technique is given in Fig. 1a. AFM sample preparation started with cutting a 1 mm thick cross-section from the coated membrane using a diamond-wafering saw. An arc-shaped specimen taken from this section was mounted on a stainless steel disc (12 mm in diameter) using double-sided adhesive tabs, so that the manganese oxide coated surface was pointing upward.

AFM images were obtained using a Nanoscope III Multimode Atomic Force Microscope (Digital Instruments Inc.) in air, using the contact mode. A triangular Si_3N_4 NP probe (Veeco Instruments, CA), with a nominal cantilever spring constant of 0.12 N/m and nominal frequency of 20 kHz, was used. The tip height was 2.5–3.5 μm, with a nominal radius of 20 nm and a side angle of 35°. On each sample five different areas, of dimension 20 μm × 20 μm, were scanned at a rate of 0.5 Hz. Average values were determined from this data for the roughness and height of each sample.

AFM roughness and height data were obtained using the Nanoscope program (Nanoscope 5.30 r3 sr3, Veeco Instruments, CA). The average roughness (R_a) for the image is defined as the arithmetic average of the absolute values of the surface height deviations measured from the mean plane, rather than the frequency or spacing of the features. The height comparisons were performed using the maximum roughness (R_{max}), defined as the maximum vertical distance between the highest and lowest data points in the image.

Fourier transform analysis (MATLAB R2008b, The MathWorks, Natick, MA) was also used to analyze AFM data. To look for possible changes in the amplitude or frequency of the surface features, 30 AFM line scans were analyzed per sample using the fast Fourier transform (FFT) function. The Fourier transforms were plotted and the amplitude and frequencies of the surface features were compared.

In a similar method as for the AFM samples, SEM samples were prepared by cutting a 1 mm thick cross-section from the coated membrane using a diamond-wafering saw. This section was then cut into a small arc-shaped specimen of approximately 3 mm in length. The arc-shaped specimen was then placed on an aluminum SEM stub with carbon tape, so that the coated surface of the membrane was pointing upward. A schematic representation of the SEM sample preparation is given in Fig. 1b.

A schematic representation of the EDS sample preparation is given in Fig. 1c. Samples were prepared by placing a small arc-shaped portion of the membrane on the aluminum stub such that the cross-sectional surface of the membrane was pointing upward. In this manner, a map of the spatial distribution of manganese within the membrane can be recorded, so that the depth of penetration of the manganese into the membrane could be observed.

As the samples were non-conductive, they were coated with a conductive material. For the SEM samples, a thin layer of gold was applied using a gold sputter coater (Emscope SC 500, Ashford, Kent, Great Britain) at a rate of 7 nm/min with a current of 20 mA for a total thickness of approximately 21 nm. Since the gold coating interferes with the detection, the EDS samples were coated with carbon using a carbon string evaporator (EFFA Mk II carbon coater, Ernest Fullam Inc., Latham, NY).

SEM micrographs were obtained using a JEOL 6400 V SEM (Japan Electron Optics Laboratories, Tokyo, Japan) with a LaB_6 emitter (Noran EDS, Noran Instruments Inc., Middleton, WI) at an accelerating voltage of 15 kV and magnification of 25,000×. Grain size measurements were made from the SEM micrographs using the intercept method (ASTM Standard E 112-96 (2004)). Two hundred (200) grains were measured to compute the average grain size. The average grain size from five micrographs of each sample is reported. A Noran EDS analyzer (Noran Instruments Inc., Middle-