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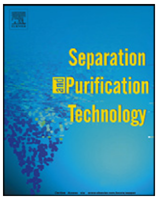

Comparison of ceramic and polymeric membrane permeability and fouling using surface water

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ABSTRACT

The trans membrane pressure (TMP) increase at a constant flux of 150 L m^{-2} h^{-1} due to membrane fouling by direct filtration with lake water is investigated for four ceramic (Al_2O_3, ZrO_2, TiO_2, SiC) and a PES/PVP polymeric microfiltration membrane(s). The membrane structures and compositions are characterised with permporometry (pore size, porosity) and XPS. The TiO_2 and SiC membrane have a 5 and 24 times larger average pore size than expected based on supplier information.

The TMP increase rate due to fouling inversely follows the measured pore size. Reversible fouling decreases in the order of polymeric $\approx Al_2O_3 \approx ZrO_2 > TiO_2 >$ SiC, and for irreversible fouling polymeric $> ZrO_2 > Al_2O_3 > TiO_2 >$ SiC.

Removal of non purgeable organic carbon (NPOC) is around 30% for the ceramic membranes, and 13–25% for the polymeric membrane. The reversible NPOC load decreases in the following order $(Al_2O_3 > (ZrO_2 \approx TiO_2)) \approx$ SiC > polymeric. The higher degree of fouling on the polymeric membrane is partly due to its lower volume/area ratio, compared to ceramic membranes. Mass balance analysis shows that 85 ± 8% of the NPOC is accounted for. Thus, the used soaking method (pH 12 NaOH, >1 h) does not fully remove the NPOC, suggesting that a more aggressive cleaning solution should be used.

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1. Introduction

Ceramic membranes have been hailed for their advantageous properties when compared to polymeric membranes. The advantages of ceramic membranes compared to polymeric membranes are often stated to be: (i) a relatively narrow pore size distribution and higher porosity, resulting in better separation characteristics and a higher flux, (ii) a higher mechanical stability (allowing higher pressures), (iii) a higher chemical stability resulting in longer membrane lifetimes, and (iv) higher hydrophilicity resulting in high fluxes at low pressures [1–7]. Higher hydrophilicity is also associated with lower fouling [6]. Evidence to support all of these advantages of ceramic membranes is, however, not so easily found. A study in which the pore size distributions (usually measured by fractional rejection of molecules) of a thin film composite and a TiO_2 membrane are compared, shows that they are very similar [8]. Unfortunately, no further studies in which pore size distributions are measured for both polymeric and ceramic membranes within a single article could be found. The pore size distribution of ceramic membranes can be narrow [9], but the same is true for polymeric membranes [10]. The higher mechanical stability of ceramic membranes is evident from applied high backwash pressures [11–13], although ceramic membranes are more prone to breakage than polymeric membranes. The chemical stability of ceramic membranes is higher than that of polymeric membranes, and decreases in the order of TiO_2, ZrO_2, Al_2O_3, SiO_2 and their hydrothermal stability decreases in the order of ZrO_2, Al_2O_3, TiO_2, SiO_2 [14,15]. The stability also depends on the membrane structure, with finer structures being less stable. The hydrophilicity of polymeric membranes depends on the used polymers and can be high; some polymeric membranes have a contact angle with water of 10° [16]. For ceramic membranes the hydrophilicity depends on the used materials. The contact angle of water for ceramic membranes covers a broad range, and the same can be said of polymeric membranes [9,10,17], making it hard to determine whether ceramic membranes are indeed more hydrophilic than polymeric ones.

Differences in fouling behavior of polymeric and ceramic membranes can be expected, as the surface groups of ceramic and polymeric membranes are different. In the scientific literature, studies comparing the fouling of ceramic and polymeric membranes for direct water filtration could not be found. However, some work has been done within the Techneau framework [18]. Mueller et al. [19,20] compared the fouling of a ceramic membrane (TiO_2 top layer, Al_2O_3 support) with that of a polymeric (polyethersulfone) membrane, both operated under the same conditions, by analysing the cleaning in place (CIP, at pH 11) waste from natural organic

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matter (NOM) loaded membranes by liquid chromatography organic carbon detection (LC-OCD) and fluorescence excitation-emission matrices (FEEM). LC-OCD showed that the CIP-waste of the polymeric membrane showed a higher polysaccharide content than the ceramic membrane [20]. FEEM showed that the CIP-waste of the polymeric membrane had higher fluorescence for protein-like organic compounds, and the CIP-waste from the ceramic membrane showed higher fluorescence for humic substances [19]. As polysaccharides are thought to be a major foulant for microfiltration/ultrafiltration (MF/UF) [21,22], ceramic membranes may have a lower potential for organic fouling [20]. However, more research into fouling mechanisms of polymeric and ceramic membranes is needed to prove whether polysaccharides lead to irreversible fouling.

In general, pretreatment is often employed when low pressure membranes are selected. Studies show that 30–40% of the low pressure membranes operate without pretreatment, and that especially coagulation and powdered activated carbon are commonly applied as pretreatment for MF/UF [23,24]. Coagulation is the most successful pretreatment for fouling control, but may increase fouling and thus requires an optimized dosing of the used chemicals [24]. For these reasons we decided to study the performance of the membranes without coagulation, or any other form of pretreatment – although in a future study we intend to incorporate this aspect as well.

In this study, we investigate the performance of four different ceramic membranes (TiO_2, ZrO_2, Al_2O_3, and SiC) and one polymeric membrane (polyethersulfone–polyvinylpyridine, PES–PVP). The performance and fouling of the membranes by surface water are compared under the same flux and backwash procedure. In practice, in full scale application, the membranes would be used under different operational conditions than here. The ceramic membranes are usually operated at a higher flux than the polymeric, and the backwash and cleaning procedures would also be very different for the ceramic and polymeric membranes. However, since we want to compare the membrane properties on the level of the membranes rather than different operational conditions, we decided to fix the flux and backwash procedure.

Thus, this paper is on the comparison of the membrane properties with respect to trans membrane pressure increase (TMP) and characterisation of fouling by surface water. Therefore we characterise the membranes in order to verify the membrane properties as supplied by the suppliers. We characterise the water type and follow the TMP due to both reversible and irreversible fouling in filtration experiments at a constant flux. The reversible fouling is the TMP increase within one filtration cycle, and the irreversible fouling is determined from the increase in the TMP directly after the backwash. The following membrane properties were obtained: pore size distribution, porosity, zeta-potential, and elemental composition of top and support layer. The composition (Ca^{2+} concentration, conductivity, LC-OCD, turbidity, etc.) of the feed water type was measured, as well as the non-purgeable organic compound (NPOC) content of the backwash water, permeate and the CIP-waste. This allows us to make a mass balance of the NPOC and to determine the separation characteristics of the membranes.

2. Materials and methods

2.1. Membranes and characterisation

The Al_2O_3, TiO_2 and ZrO_2 single channel tubular membranes were obtained from Atech innovations GmbH (Gladbeck, Germany) and had a support layer of Al_2O_3. The SiC membranes (a flat disc type for the pore size, porosity, X-ray photoelectron spectroscopy (XPS) and zeta-potential measurements, and a single channel tubular membrane for the fouling experiments) were obtained from Cometas (Bagsvaerd, Denmark). The polymeric filter pen membrane, composed of a PES/PVP blend, was obtained from Norit Filtrix (Amersfoort, The Netherlands). Pore sizes and the materials as provided by the suppliers (for the top layer) of the membranes are given in Tables 1 and 2. Note that due to the varying requirements of the characterisation devices we used different membrane dimensions for each test. The pore size of the membranes as given by the supplier was similar for the individual membranes. Details about the membranes used in the filtration test are given in Table 1, and for characterisation by porometry, XPS and zeta-potential measurements are given in Table 2.

The pore size and pore size distribution of the ceramic membranes was measured with a Porolux 1000 capillary flow porometer (IB-FT GmbH, Wildau, Germany). The membranes were cut into samples with a length of approximately 7 cm and were fitted on one end with a PVC collar of 12 mm outer diameter and a Swagelok ferrule set. The other end was closed by potting with a two component resin. Porofil (Benelux Scientific, Tiel, The Netherlands) wetting fluid was used to wet the membrane prior to the measurements, which were carried out in duplicate. The mean pore diameter is calculated from the mean flow pressure, which corresponds to the intersection of the wet curve with the calculated half-dry curve (calculated from a dry and a wet run).

The porosity was measured on an Accupyc 1330 pycnometer from Micromeritics instruments Corporation (Norcross, U.S.A.). For these measurements the membranes were cut into small pieces of about 7 mm length. A sample was sealed in a sample compartment of known volume. Helium was added, and then expanded into another calibrated volume. The pressure before and after the cell expansion was measured to compute the sample volume. The porosity was subsequently calculated from the density.

The elemental composition of the membranes was measured on a Quantera SXM (scanning XPS microprobe) from Physical Electronics (Chanhassen, U.S.A.). The XPS measurements were done with an Al Kα monochromatic (at 1486.6 eV) X-ray beam, with a beam size of 100 μm (power 25 W, I_e 2.6 mA). The Quantera SXM was controlled with Compass software and the data reduction was done with Multipak v8.0. Samples of the membranes of approximately 7 mm length were used for the XPS measurements. Elemental spectrum scans of the both top and support layer (3 locations) were measured (at two points per location), averaged and interpreted with the help of standard books.

All the above measurements were carried out at the European Membrane Institute (EMI) at the University of Twente (The Netherlands).

Zeta-potential measurements were performed using the zeta meter SurPass (Anton Paar GmbH, Austria). These measurements were performed on a flat sheet membrane of SiC and on seven channels tubular membranes of Al_2O_3, TiO_2 and ZrO_2. A special adapter was used to force the measuring electrolyte solutions (pH 6–10, 10^{-3} M KCl) through the porous wall that separate two individual channels. The zeta potential was calculated from the streaming potential measurements as described elsewhere [25].

2.2. Water type and characterisation

The first set of membrane filtration tests at fixed backwash pressure was performed with surface water from Noord-Bergum lake (The Netherlands). A batch of 400 L was sampled (on the 20th of November 2009 and subsequently homogenised and filtered through a 1 μm cartridge filter. The water was stored at 4 °C and the water composition is given in Table 3 (1st batch). The amount of NPOC found is nearly the same as the amount of DOC, due to pre-filtering though a 1 μm cartridge filter. The second set of experiments at comparable backwash flux was performed with surface

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