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Performance of a novel ZrO_2/PES membrane for wastewater filtration

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ABSTRACT

The membrane bioreactor (MBR) process has now become an attractive option for the treatment and reuse of industrial and municipal wastewaters. However, the MBR filtration performance inevitably decreases with filtration time due to membrane fouling. Over the past two decades, increased interests in improving the performance of filtration membranes (i.e., reducing membrane fouling) have encouraged the development of new classes of chemically modified membranes. In this study polyethersulfone (PES) membranes and membranes with five different weight ratios of ZrO_2 to PES of 0.01, 0.03, 0.05, 0.07 and 0.1, were prepared by the phase inversion method and applied to activated sludge filtration in order to evaluate their fouling characteristics. The membranes were characterized using field-emission scanning electron microscope (FESEM). The ZrO_2/PES membrane strengths were higher than those of the neat membrane. The membrane molecular weight cut-off (MWCO) and membrane thickness were slightly affected by the ZrO_2 addition. ZrO_2 entrapped membranes showed lower flux decline compared to the neat PES membrane, with fouling mitigation increasing with ZrO_2 particles content. The optimum load of ZrO_2 immobilized membranes for membrane bioreactor (MBR) application in terms of highest membrane permeability and lowest fouling rate was the 5% weight fraction of ZrO_2 with PES.

1. Introduction

The preparation of organo-mineral composite membranes with controlled properties has attracted attention recently. The formation of composite porous membranes by the addition of mineral fillers has been described in the literature for different applications such as gas separation, pervaporation nano- and ultrafiltration [1–4]. The modified membranes have the advantages of excellent separation performances, good thermal and chemical resistance and adaptability to the harsh wastewater environments [5,6]. Molinari et al. [5,6] investigated the use of TiO_2 nanoparticles in water purification. The fouling mitigation effects of immobilized TiO_2 UF membranes during the activated sludge filtration were investigated by Bae and Tak [7]. Recent studies of polyvinylidene fluoride (PVDF)-blending modifications have focused on blending the polymer with inorganic materials such as silica [8], Al_2O_3 [9] and some low molecular weight inorganic salts, such as lithium salts [10]. In our previous work [11], the effect of Al_2O_3 nanoparticles on the membrane fouling characteristics by activated sludge was studied by casting different weight ratios membranes of Al_2O_3 to polyethersulfone (PES) of 0.01, 0.03, 0.05, 0.1, and 0.2. The results showed that Al_2O_3 entrapped membrane had lower flux decline during activated sludge filtration compared to neat polymeric membrane.

Zirconia membranes are known to be chemically more stable than titania and alumina membranes, and therefore are more suitable for liquid phase applications under harsh condition [12]. Zirconia is also one of the common catalysts and hence it is a potential membrane material for high temperature catalytic reactions [13]. Furthermore in a comparative study, the toxicity of ZrO_2, as measured by IC50 concentration was higher than TiO_2 [14]. Guizard et al. [15] prepared ZrO_2 membranes, using a zirconium salt as precursor. The authors reported 85% retention of yellow acid (M = 759 g/mol). Vacassy et al. [16] used a polymeric sol–gel method to develop a ZrO_2 membrane on a commercial multi-channel support with a ZrO_2 ultrafiltration layer (MWCO support of 15 kDa), and observed 54% retention for saccharose (M = 342 g/mol) and 73% for Vitamin B12 (M = 1355 g/mol). Benfer et al. [17] used a polymeric sol–gel method using acetylacetone, diethanolamine or acetic acid as the modifier, to prepare a tubular ZrO_2 membrane, and observed 30% and 99% retention of orange G (M = 452 g/mol) and direct red (M = 991 g/mol), respectively. Dumon and Barmer [18] concluded that the presence of negatively charged phosphate or citrate groups at the surface of the ZrO_2 membrane (M6 Carbosep) prior to the ultrafiltration test favors a low adsorption of ovalbumin protein at pH 6.8–7.8. Zirconia micro-filtration membrane was also used after flocculation to treat oily wastewater [19]. The results showed that the membrane fouling decreased and the permeate flux and permeate quality increased with flocculation as pretreatment. Faibish and Cohen [20] developed a ceramic-supported polymer (CSP) zirconia-based ultrafiltration membrane and evaluated it for the filtration of synthetic anionic decane-in-water micro-emulsions

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with oil droplets in the size range of 18–66 nm. The membrane demonstrated fouling resistance even though it was completely wetted by the micro-emulsion solution and despite significant surface roughness of both the native and CSP membranes. Schaep et al. [21] casted a Zerfon® membrane using high polymer content (ZrO_2/polysulfone ratio of 80/20) in order to get denser membranes, closer to nanofiltration region with MWCO of 3200 Da. The filtration experiments carried out with different salts (Na_2SO_4, $CaCl_2$ and $MgSO_4$) showed that the ion retention in a salt mixture at 0.3 mequiv./l were 82%, 47%, 42% and 18% for SO_4^{2-}, Mg^{2+}, Na^+ and Cl^-, respectively.

Despite the aforementioned work on solute rejection of zirconia membranes [16–21] extensive literature search using SciFinder Scholar for zirconium oxide incorporation in membranes revealed few studies [22–24]. The aforementioned studies [22–24] confirmed the increased membrane permeability of ZrO_2 membranes. Moreover, no studies have been conducted on ZrO_2 immobilized PES membranes for sludge filtration and to fill this gap, this research aimed at preparing ZrO_2/PES membranes by introducing small amounts of ZrO_2 particles into the PES casting solution in order to improve the performance of PES membrane for wastewater filtration. Membrane structure was characterized by FESEM. The membrane strength, molecular weight cut-off (MWCO) and optimum ZrO_2 particles load were determined. The effect of ZrO_2 particles on biofilm attachment to membrane surface as represented by gel/cake layer formation and consequently the fouling mitigation effect of ZrO_2 particles was studied using activated sludge filtration.

2. Experimental

2.1. Membrane preparation

PES Radel A-100 (Solvay Advanced Polymers, Alpharetta, GA, USA) was used as the base membrane material. The membranes were prepared by the phase inversion method [25]. Zr(IV) oxide (Alfa-Aesar Canada Ltd.) 99% metals basis excluding Hf particles were used. The certificate of analysis provided by the supplier indicated the following composition (by weight): HfO_2 <3%, Fe_2O_3 of 0.006%, Cl^- of 0.0013%, SiO_2 of 0.004% and TiO_2 of 0.005%. Fig. 1 shows the ZrO_2 particles size distribution using Zeta Plus particle sizers (Brookhaven Instruments Corp, UK). The analysis was run for 5 times and the mean particle diameter was 221 ± 0.154 nm. It should be noted that particle followed a lognormal distribution with a 10th–90th percentile of 148–340 nm. Although the ZrO_2 particles were in the nanometer size range, the term nanoparticles has been avoided as it refers primarily to particles that are sized between 1 and 100 nanometers [26]. The 0.01, 0.03, 0.05, 0.07 and 0.1 ZrO_2/PES ratios (w/w) membranes were prepared by dispersing the ZrO_2 particles in N-methyl pyrrolidone (NMP) solution, after which the solutions were sonicated at 60 °C for 72 h to obtain uniform and homogeneous casting suspensions. Subsequently, 18 wt.% PES polymer was added and the mixture was sonicated again for a week. A 100 μm casting knife was used to cast the membranes onto a glass plate at room temperature. The nascent membrane was evaporated at 25 ± 1 °C for 15 s and then immersed in a deionized water coagulation bath maintained at 18 ± 1 °C for 2 min. To remove the remaining solvent from the membrane structure before testing, all prepared membranes were transferred to a water bath for 15–17 days at room temperature.

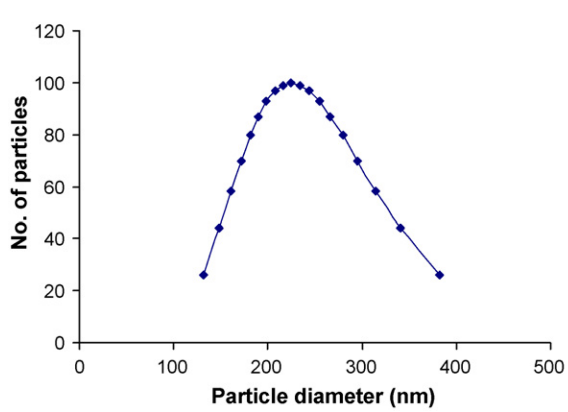

Fig. 1. ZrO2 particles size distribution.

2.2. Membrane characterization

The cross-sectional morphologies of the membranes were characterized using field-emission scanning electron microscopy (FESEM, Leo 1530, LEO Electron Microscopy Ltd.) at 1 kV with no conductive coating. The deionized water (DIW) flux was determined for the PES control membranes and the ZrO_2 entrapped PES at different trans-membrane pressures (TMPs) of 0.345, 0.69, 1.034, 1.38 and 1.724 bar. The maximum TMPs sustained by the membranes were determined by changing the TMP from 0.345 to 3.1 bar in increments of 0.345 bar using DIW. The TMP at which the membrane ruptured was taken as the maximum TMP sustained by the membrane. Molecular weight cut-off (MWCO) of the membrane was determined using 10% aqueous solutions of polyethylene oxide (PEO) (Acros Organics, USA) with Mw of 100, 200, 300 and 600 kDa. The concentrations of PEO were measured using LEICA Auto ABBE refractometer model 100500B (Letica Co., Rochester, MI, USA). Rejection was calculated by Eq. (1):

$$\%R = \left(1 - \frac{C_{per}}{C_{feed}}\right) \times 100 \quad (1)$$

where C_{per} is the concentration of PEO in permeate and C_{feed} is the concentration of PEO in the feed. The smallest molecular weight that is rejected by 90% is taken as the MWCO of the membrane [27].

2.3. Activated sludge

Activated sludge used in this study was cultivated in a submerged laboratory scale MBR (Fig. 2) treating synthetic wastewater for more than 8 months. Starch and casein, $(NH_4)_2SO_4$, and KH_2PO_4 were used as carbon, nitrogen and phosphorus sources, respectively. Additional nutrients and alkalinity ($NaHCO_3$) were also supplied to the reactor. The feed composition and the influent wastewater characteristics are summarized in Table 1 while Table 2 presents the activated sludge and effluent characteristics.

2.4. Membrane fouling analysis

Since the mode of constant TMP is suitable for the study of membrane fouling and is widely used for wastewater treatment [28–30], membrane filtration was carried out using a stirred batch cell operated under constant trans-membrane TMP (Model No. 8050, Amicon) as shown in Fig. 3. In order to alleviate the impact of compaction of the new polymeric membranes on flux, pre-filtration studies with pure deionized water (DIW) were conducted (8–10 filtrations) until a steady-state flux (J_{iw}) was achieved. For sludge filtration, the TMP and stirring speed were kept constant at 0.69 bar (as this is a typical TMP for submerged membranes like Zenon [31]) and 600 rpm, respectively. The permeate flux was determined by monitoring the volume of permeate with time. After the filtration test, the membrane was washed in a cross-flow manner with DIW and the pure DIW flux (J_{fw}) was measured 4 times after this cleaning