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Nanofiltration membranes enhanced with TiO_2 nanoparticles: a comprehensive study

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ABSTRACT

TiO_2 nanoparticles are of potential interest for nanofiltration membranes in view of flux increase and improved fouling resistance. Conclusions from published studies, however, cannot be translated to other applications because results depend on specific parameters of which the precise effect is still unknown. In this study, PES flat-sheet membranes were manufactured for wastewater treatment application. The effects of TiO_2 nanoparticles as additive on the preparation of polyethersulfone (PES) blend nanofiltration membranes were investigated in terms of pure water flux, hydraulic membrane resistance (permeability) and solute rejection performance. A polyethersulfone (PES) membrane was modified by dispersing nanoparticles of titanium oxide (TiO_2) in a PES solution. The membranes were prepared with 30 wt.% of polymer PES by phase inversion method. 1-Methyl-2-pyrrolidone and deionized water were employed as solvent and coagulant, respectively. Membrane fouling was explored with humic acids as a model organic foulant. Overall, the permeability was higher for blended membrane while the rejection was almost similar for both types of membranes using a model dye as a reference. Moreover, fouling was more pronounced for the neat PES membranes as compared to the TiO_2 blended membrane. In addition the membranes were characterized using SEM and contact angle measurements.

Keywords: Nanofiltration; Membrane fouling; PES; TiO_2; Nanoparticles

1. Introduction

One of the most important concern of the nanofiltration technology applied to wastewater treatment is the membrane fouling phenomenon, usually attributed to adsorption of organic substances on the membrane surface [1,2]. Adsorbed molecules increase the membrane hydrophobicity or could decrease pore diameters, and thus reduce water transport across the membrane [3–5]. In addition, the formation of the fouling layer could alter other functional properties of the membrane surface such as membrane charge, which affects the rejection performance [1,6].

Some researchers have taken interest in to increase the effectiveness of nanofiltration membranes, using nanoparticles as additives. The general aim is to obtain

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membranes with a better performance, in terms of permeability, antifouling properties, solute rejection, or membrane lifetime. To accomplish this objective, TiO_2 appears as one of the most studied material, but also silica (SiO_2), carbon nanotubes, alumina (Al_2O_3), silver (Ag), zirconia (ZrO_2), gold (Au), zerovalent iron (FeO), and palladium (Pd) are of potential interest [7–9].

In this study, the addition of TiO_2 nanoparticles to the membrane structure was carried out through blending with the membrane casting solution [10–12]. This method involves the addition of TiO_2 nanoparticles during membrane synthesis. A suspension of the dissolved polymer and the nanoparticles is cast on a support layer. In order to minimize the influence of aggregation of nanoparticles that affect the dispersion rate of nanoparticles on the membrane performance results, twenty-four pieces of membranes were tested. Overall membrane characterization was performed to determine some physico-chemical properties of manufactured membranes, such as hydrophilic character, permeability and fouling resistance. In addition, the rejection potential of membranes was explored using methylene blue as a model compound.

2. Materials and methods

2.1. Materials

PES, type Radel, supplied by Solvay (Belgium) was employed as the base polymer. 1-Methyl-2-pyrrolidone (NMP, 99.5%) was used as the polymer solvent. The support layer (Viledon FO2471) used for the PES membrane manufacturing was obtained from Freudenberg (Weinheim, Germany).

In this study, titanium tetraisopropoxide (TTIP) was used as a precursor of TiO_2 nanoparticles. 0.125 mol of TTIP was added dropwise to 100 ml of deionized water under vigorous stirring at room temperature. The sol samples obtained by hydrolysis process were irradiated in ultrasonic cleaning bath for 1 h. To hydrolyze the TTIP samples and obtain monodisperse TiO_2 particles, the samples were then aged in closed beaker at room temperature for 24 h. After aging, these samples were dried at 100°C for 8 h in air to vaporize water and dried gel samples obtained were calcinated further at 500°C for 1 h. The size of TiO_2 nanoparticles synthesized was about 25 nm of diameter.

Sigma–Aldrich humic acid (St. Louis, MO) was selected as a model organic foulant in this study. Humic acids (HA) is a major component of natural organic matter that can be found in wastewater streams and refers to the fraction of humic substances obtained by chemical and biological degradation products from plant and animal residues [13].

Methylene blue is a heterocyclic aromatic chemical compound with the molecular formula $C_{16}H_{18}N_3$ S Cl and molecular weight of 319.85 g mol^{-1}. It was purchased from Acros Organics (Belgium).

2.2. Membrane preparation

PES membrane and blend PES membrane with TiO_2 nanoparticles were prepared using phase inversion induced by immersion precipitation technique. Polyethersulfone polymer (at 30 wt.%) was used and dissolved in N-methyl-pyrrolidone solvent to neat PES membrane. TiO_2 blended membrane was manufactured by dissolving 0.125 g of TiO_2 nanoparticules in 78 ml of NMP solvent for three hours by mechanical stirring at 200 rpm and room temperature. Subsequently, was added 30 g of polymer to the nanoparticle/solvent solution and stirred for 24 h at 500 rpm and 40°C of temperature. After formation of homogenous solution, the films were cast with 250 µm thickness by with a filmograph (K4340 Automatic Film Applicator, Elcometer) in an atmosphere with controlled relative humidity (38% of RH) on nonwoven polyester as support layer. The membrane films were immersed in non-solvent bath (distilled water at 20°C) for precipitation. The membrane was afterwards repeatedly washed with distilled water to remove the remaining solvent and wet stored. For each polymer solution composition, eight identical membrane sheets were made and tested to obtain an average value of flux and solute rejection.

2.3. Membrane characterization

The top surface of membranes was observed by means of Scanning Electron Microscope (Philips- FEI. QUANTA 200). All membrane samples were dried at room temperature and coated with a thin layer of gold before observation.

The hydrophilicity of membrane top surface was characterized on the basis of a water contact angle system (DSA 10 Mk2 Krüss, Germany) equipped with video capture at room temperature. A water droplet was placed on a dry flat homogeneous membrane surface and the contact angle between the water and membrane was measured until no change was observed. The average contact angle for distilled water was determined for six measurements on the different membrane surfaces.

Membrane compaction was carried out at a transmembrane pressure of 20 bar and a constant temperature of 25°C in dead-end mode (Sterlitech HP4750 Stirred Cell) prior to the filtration experiments. Pure water permeability and dye rejection were determined for a wide range of membranes; the obtained results are the average of 24 experimental values. The active membrane area was 14.6 cm^2. The volume of the appropriate solution was 250 ml. The initial water flux was measured 30 s after the pressurizing. Permeate was collected in a graduated cylinder for a time interval until steady-state condition [13].

After compaction, the pure water permeability was calculated by measuring the pure water flux (J_w) at different transmembrane pressures (ΔP) from 2 to 20 bar; the slope of the linear regression of the water flux as a function of transmembrane pressure was determined as the permeability. Rejection performance of membranes was studied at a transmembrane pressure of 10 bar. Concentration polarization at the membrane surface is minimized by stirring Teflon coated magnetic stirring on top of the membrane.

2.4. Study of membrane fouling

Fouling was explored by cross-flow filtration of 5 mg l^{-1} humic acid solution at 15 bar and for about 36 h filtration time. In order to evaluate the fouling resistance of membranes was compared the relative flux of neat and TiO_2-blended membranes. The relative fluxes (RF) were defined as the ratio of the organic solution flux (J_v) to the pure water flux (J_w):

$$RF = \frac{J_v}{J_w} \tag{1}$$

2.5. Analytical methods

The concentrations of methylene blue in the permeate and feed were determined by a double beam spectrophotometer (Shimazu UV-1601). Regression factor (R^2) obtained for calibration within the experimental concentration range were above 0.99.

3. Results

3.1. Membrane characterization

The SEM micrographs (Fig. 1) of the neat and blended-TiO_2 membranes exhibit a higher porosity for the modified membrane. Addition of TiO_2 increases the number and length of microvoids and also decreases the thickness of the thin top layer. Formation and grow of microvoid could be related to the kinetics of immersion-precipitation process. The presence of TiO_2 nanoparticles increases the water diffusion into the growing membrane, during the phase inversion process, due to its higher hydrophilic nature, and hence, acts like a pore former agent [14,15]. The increase of the number of pores of membrane surface could be explained from the enhancement of water affinity for the blended membranes as consequence of TiO_2 addition.

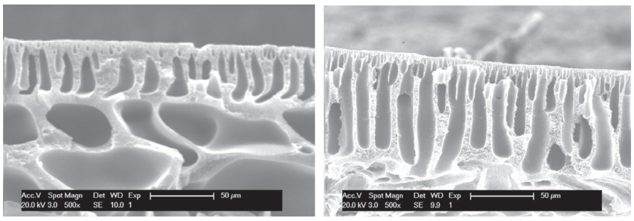

Fig. 1. SEM pictures of cross-sectional area of neat (A) and blended-TiO_2 composite (B) membranes.

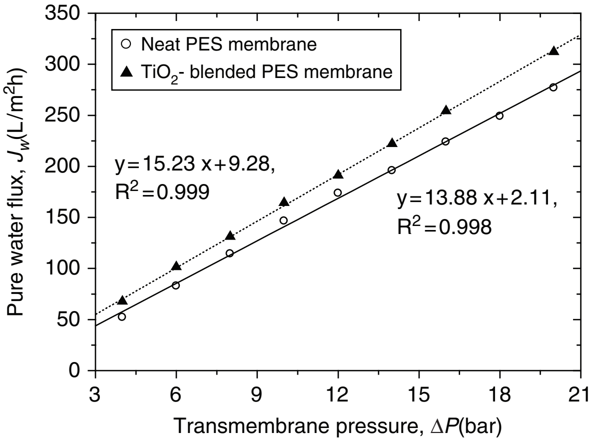

Fig. 2. Pure water permeabilities of neat and TiO_2-blended composite membranes.

In Fig. 2 the experimental data of pure water flux for different transmembrane pressure values are shown. From the linear regression of the flux as a function of pressure, it is possible to determine the permeability of membranes. In agreement with the surface analysis discussed previously, the addition of nanoparticles to the membrane structure has a positive effect on the water transport across the membrane. The permeability also increases due to water-affinity considerations, comparing the hydrophilic character of nanoparticles with the polymeric material used (polyethersulfone).

The presence of nanoparticles could have an additional effect which takes place during the phase inversion process. Nanoparticle addition also could upset the interaction between polymer and solvent molecules by the hindrance effect of nanoparticles, encouraging easier diffusion of solvent molecules from the polymer matrix, resulting in the formation of a membrane with a more porous structure [16]. Meanwhile nanoparticles stayed in the polymer matrix during the process of phase inversion. Consequently, enhancement in the membrane porosity (Fig. 1) results in increasing of the membrane permeability (Fig. 2).

In Fig. 3(a) comparison between both types of membrane in terms of surface hydrophilicity (contact angle),

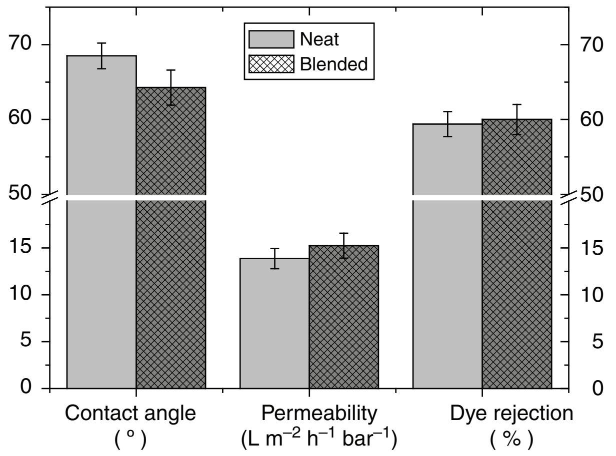

Fig. 3. Comparison between neat and blended membranes taking into account the following characteristics: contact angle measurement, permeability and methylene blue rejection.

permeability and the dye rejection is displayed in the same graph. The error bars regarding to analyzed properties have been included in the graph. Considering the similarity of obtained values (errors are relatively low) it is possible to affirm that the dispersion rate of nanoparticles through the membrane is relatively uniform.

The contact angle measurements and the water permeabilities obtained for both types of membranes are coherent each other; as a result of the TiO_2 addition, the membrane surface is more hydrophilic, enhancing both the degree of membrane surface wetting and the water permeation rate.

To improve the porosity of membranes some researchers have used different additives as pore former, such as polyvinylpyrrolidone and polyethyleneglycol [17,18]. In these cases the used additives are soluble in water and hence are removed from the membrane structure at the end of the phase inversion. Contrary, the added TiO_2 nanoparticles are still entrapped into the membrane. So, the possible plugging of the membrane pores by nanoparticles during immersion precipitation is another issue that should be considered for the understanding of TiO_2 entrapped membrane performance [14]. From the size interaction analysis point of view, the dye rejection observed for blended membrane was similar to the rejection for the neat membrane, so steric hindrance (pore size) of both types of membranes is, on average, comparable. Water molecules are small and they pass through the membranes more easily; the permeability is not affected by steric hindrance effect associated to nanoparticles, rather is improved.

3.2. Fouling resistance

Cross-flow filtration experiments were carried out for humic acids solution at fixed concentration of 5 mg l^{-1} during 36 h at 25°C and 15 bar transmembrane pressure. The flux decline was explored in terms of relative fluxes (Eq. 1) in order to take into account the possible disparities between the different membrane pieces. To determine the relative flux corresponding to every membrane, the pure water flux was measured before studying the fouling resistance of membranes in contact with HAc solution. The relative fluxes of neat and blended membranes are shown in Fig. 4. The results clearly show that the fouling resistance of TiO_2-blended membrane is significantly improved. The extent of membrane fouling decreased considerably by around 22%.

The flux rapidly declined at the beginning of filtration experiment, especially for the neat membrane. The membranes show a stationary state for the flux, reached in around 6 h for the neat PES membrane. However, the TiO_2-blended membrane was observed to have a nearly constant flux after ca. 18 h. One of the most important phenomena concerning to membrane fouling is the solute adsorption on the membrane surface. Organic adsorption is strongly dependent of the physico-chemical properties of membranes and foulants, especially the affinity of solute towards the membrane material. It has been found that organic substances have a higher tendency to adsorb and deposit on hydrophobic surfaces and hence, adsorption occurs relatively quickly for hydrophobic compounds resulting in a stable normalized flux [4]. More hydrophobic character of the polymeric material in comparison with the improved (more hydrophilic) TiO_2-blended membranes could be an important reason to explain the slower adsorption of humic acids on the surface of neat membrane. This behavior has been confirmed previously by modeling of flux decline based on the adsorption thermodynamics of organic compounds on the nanofiltration membrane surface [5].

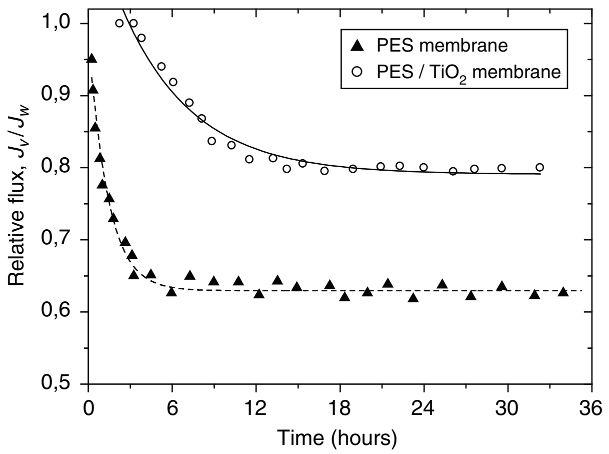

Fig. 4. Temporal evolution of membrane fouling for neat and TiO_2-blended membranes.

4. Conclusions

The analysis of the hydrophilic character and permeability for neat and TiO_2-blended membranes showed that the presence of TiO_2 nanoparticles provided a higher affinity of blended membranes as consequence of water affinity and pore formation properties due to the addition of TiO_2 nanoparticles. The dye rejection potential of neat and TiO_2-entrapped membranes was similar, just slightly higher for TiO_2-blended membranes as consequence of hindrance effect of nanoparticles entrapped in the membrane structure.

The membrane fouling resistance was significantly improved with the addition of TiO_2 nanoparticles as result of increase of hydrophilic character of membrane surface that mitigates the organic adsorption of humic acids on the membrane surface.

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References

[1] B. Van der Bruggen, M. Manttari and M. Nystrom, Sep. Purif. Technol., 63 (2008) 251–263.
[2] P. Xu, J.E. Drewes, T.-U. Kim, C. Bellona and G. Amy, J. Membr. Sci., 279 (2006) 165–175.
[3] Y. Zhao, L. Song and S.L. Ong, J. Membr. Sci., 349 (2010) 75–82.
[4] J.M. Arsuaga, M.J. López-Muñoz and A. Sotto, Desalination, 250 (2010) 829–832.
[5] L. Braeken, K. Boussu, B. Van der Bruggen and C. Vandecasteele, Chem. phys. chem., 6 (2005) 1606–1612.
[6] L.D. Nghiem, P.J. Coleman and C. Espendiller, Desalination, 250 (2010) 682–687.
[7] J. Kim and B. Van der Bruggen, Environmental Pollution, 158 (2010) 2335–2349.
[8] S. Yu, X. Zuo, R. Bao, X. Xu, J. Wang and J. Xu, Polymer, 50 (2009) 553–559.
[9] L. Yana, S.L. Yu and C.B. Xiangb, Polymer, 46 (2005) 7701–7706.
[10] I. Soroko and A. Livingston, J. Membr. Sci., 343 (2009) 189–198.
[11] G. Wu, S. Gan, L. Cui and Y. Xu, Applied Surface Science, 254 (2008) 7080–7086.
[12] X. Cao, J. Ma, X. Shi and Z. Ren, Appl. Surf. Sci., 253 (2006) 2003–2010.
[13] K. Boussu, C. Vandecasteele and B. Van der Bruggen, Polymer 47 (2006) 3464–3476.
[14] T.-H. Bae, I.-C. Kim and T.-M. Tak, J. Membr. Sci., 275 (2006) 1–5.
[15] A. Rahimpour, S.S. Madaeni, A.H. Taheri and Y. Mansourpanah, J. Membr. Sci., 313 (2008) 158–169.
[16] I.C. Kim, K.H. Lee and T.M. Tak, J. Membr. Sci., 183 (2001) 235–247.
[17] A. Rahimpour and S.S. Madaeni, J. Membr. Sci., 305 (2007) 299–312.
[18] K. Jianfeng and K. Li, J. Appl. Poly. Sci., 81 (2000) 1643–1653.