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A new outlook on membrane enhancement with nanoparticles: The alternative of ZnO

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ABSTRACT

Although several studies explored the use of nanoparticles as additives in membrane structures, mixed matrix membranes still suffer from difficulties in synthesis and applications. In this paper, a new outlook on enhancement of membranes with nanoparticles is proposed by using ZnO as an alternative to TiO_2. Although ZnO has attractive features that potentially could fill the objectives of mixed matrix membranes with lower cost and better performance, challenges in development remain. This paper investigates the synthesis of ZnO enhanced membranes and evaluates the performance of mixed matrix membranes with ZnO nanoparticles. Polyethersulfone (PES) membranes manufactured by diffusion induced phase inversion in N-methyl-pyrrolidone (NMP) using a range of procedures were blended with ZnO nanoparticles in a wide range of concentrations from ultralow to high (0.035–4 wt%). It was shown that the new membrane materials embedded with ZnO nanoparticles have significantly improved membrane features. The influence of the ZnO nanoparticles on the characteristics of PES/ZnO membranes was investigated with microscopic observations, contact angle measurement, filtration experiments, fouling resistance determination and observation of the rejection of selected dyes. The results showed an overall improvement compared to the neat membranes in terms of permeability as well as dye rejection and fouling resistance by adding ZnO nanoparticles even in small and ultralow concentrations.

1. Introduction

Nanoparticles, having unique physico-chemical properties that differ from bulk materials, are of high interest in the manufacturing of membranes to achieve a high degree of control over membrane fouling and the ability to produce desired structures as well as functionalities [1–5]. Membrane fouling is the main problem that limits the use of membranes in a wide range of applications from an economic or even technical point of view. Nanoparticles may offer a key to resolve this problem. The fouling phenomenon is often attributed to adsorption of organic compounds on the membrane surface, although other types of fouling such as biofouling and scaling may also occur. The main effect of membrane fouling is a dramatic decrease of the flow through the membrane. A diminished membrane performance occurs together with excessive operating costs [6,7] and a decrease in rejection of the target compounds [8–10] and permeation properties [11–13] caused by the higher hydrophobicity of the membrane surface. It depends on the membrane characteristics [14–17] and on the filtration mode (cross-flow or dead-end filtration) [18] but it can be said that the application of membranes is threatened by the critical formation of fouling and the reality shows that their use in industrial applications is extremely restricted if this problem is not solved.

Strong efforts are being done in several membrane applications using nanoparticles, advancing towards a good performance and trying to understand the fouling phenomenon. Two methods are reported in general to prepare composite membranes, one by dispersing the nanoparticles in the casting solution and prepare the membrane via phase inversion [19–25] and a second by dipping the prepared membrane in a suspension with nanoparticles [26,27]. In addition, many types of nanoparticles have been studied to improve the membranes properties, silica (SiO_2), carbon nanotubes, alumina (Al_2O_3), silver (Ag), zirconia (ZrO_2), gold (Au), zerovalent iron (Fe^0), palladium (Pd) and, as most studies focus on, TiO_2 nanoparticles [5]. TiO_2 is a functional nanomaterial, but also has disadvantages in the use, such as the simultaneous filtration and photocatalytic activity that is aimed at, the dispersion in the bulk of the polymer or in the top layer, and the overall cost of the TiO_2 enhanced membranes, which is not only related to the intrinsic cost of the nanoparticles, but also to the synthesis procedure.

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In this work, a new outlook on the use of nanoparticles in membrane structures is explored, through the use of zinc oxide (ZnO) nanoparticles. ZnO is one of the most important multifunctional semiconductor materials and exceptionally important for application in photo-catalysis and anti-bacterial materials, due to its excellent optical, electrical, mechanical and chemical properties [28]. The lower cost of ZnO and the increase of the surface-to-volume ratio obtained when ZnO is used as particles in a nano-sized scale make this alternative a potential system that can meet the demand of an efficient and lower-cost device.

Furthermore, another issue that can limit the application of nanoparticles is their toxicity since it is thought that nanoparticles may persist as small particles in aquatic systems and that their bioavailability could be significantly greater than that of larger particles. For ZnO nanoparticles, positive conclusions have been obtained [29–33]. The use of nanoparticulate ZnO does not produce an increase in toxicity since the size distribution and surface area are not related to toxicity. Already in 2007 Franklin et al. [34] compared the toxicity in algae of nanoparticulate ZnO, bulk ZnO and $ZnCl_2$ and observed that toxicity is attributable solely to dissolved zinc, this is, to simple solubility of the compounds since ZnO nanoparticles aggregate in freshwater systems forming flocs of even several microns with a saturation solubility similar to that of bulk ZnO. Also, since ZnO nanoparticles will be embedded in a solid matrix (the membrane), a stable system can be developed, keeping their physical properties associated to their size and the chemical activity related to their availability in the membrane. Thus, the use of ZnO in the nano-size scale incorporated in membranes is a promising and novel system that may be the solution for the development of low-cost and fouling-prevention membrane technology.

The novelty of this paper is in the synthesis of ZnO enhanced membranes in view to significantly enhance the performance of nanofiltration technology in terms of permeation, rejection and fouling resistance. The eventual membrane structure was also studied in this work.

2. Experimental

2.1. Materials

Polyethersulfone (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). ZnO nanoparticle and humic acid (HA) were purchased from Sigma–Aldrich (St. Louis, MO). HA is known as a foulant in natural waters being fraction of humic substances obtained from chemical and biological degradation products from plant and animal residues [35].

Six different dyes were used to explore the size interaction in the interface solute-membrane pore. Organic compounds purchased from Acros Organics (Belgium) were selected in order to cover a large range of molecular mass. The selected dyes were methyl red (269.21 Da), neutral red (288.77 Da), methylene blue (319.85 Da), Sudan black (456.54 Da), Victoria blue (506.10 Da), Congo red (696.67 Da).

2.2. Preparation of membrane

Neat PES membranes and ZnO-entrapped PES membranes were prepared using phase inversion induced by immersion precipitation. PES cast from four different concentrations in N-methyl-pyrrolidone (NMP) (25, 27, 30 and 32 wt%) was used as the polymer matrix. The ZnO-entrapped membranes were prepared by dissolving different amounts of nanoparticles in the corresponding volume of NMP for 3 h by mechanical stirring at 200 rpm and room temperature. Eleven different concentrations of ZnO nanoparticles were used: 0.035, 0.07, 0.085, 0.125, 0.250, 0375, 0.500, 0.750, 1, 2 and 4 wt%. Subsequently, the polymer was added to the solution, which was stirred for 24 h at 500 rpm and 40 °C. After formation of a homogenous solution, the films were cast with 250 μm thickness using a filmograph (K4340 Automatic Film Applicator, Elcometer) in an atmosphere with controlled relative humidity on nonwoven polyester as support layer. Prior to the casting, the support layer was wetted with NMP to prevent the polymer solution of intruding in the pores of the support layer. The prepared films were immersed in a 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 stored wet. For each polymer solution composition, five identical membrane sheets were made and tested to obtain an average value of flux and solute rejection.

2.3. Characterization of the membrane surface

A contact angle measuring system DSA 10 Mk2 (Krüss, Germany) was used to measure the water contact angle of the synthesized membranes. 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 further change was observed. The average contact angle for distilled water was determined in a series of 8 measurements for each of the different membrane surfaces. To visualize membrane surface characteristics, scanning electron microscopy (SEM) measurements were performed. SEM images were made with a Philips XL30 FEG instrument with an accelerating voltage of 20 keV. Cross-sections were prepared by fracturing the membranes in liquid nitrogen.

2.4. Filtration experiments

The prepared membranes were characterized for water flux, pure water permeability (membrane hydraulic resistance) and dye rejection studies using dead end filtration experiments. Comparison of the fouling-resistant ability of the manufactured neat and blended membranes was explored by cross-flow experiments.

Pure water permeability and dye rejection were determined for a wide range of membranes. Four membrane coupons of the same membrane sheet for eight membranes of each type were tested. Therefore, the obtained results are the average of 32 experimental values. The maximum experimental errors were less than 5% and 8% for PES and PES/ZnO membranes, respectively.

The pure water flux was determined from a compaction experiment at a transmembrane pressure of 10 bar and a constant temperature of 25 °C in dead-end mode with a Sterlitech HP4750 Stirred Cell. A nitrogen cylinder coupled with the pressure regulator was connected to the top of vessel to pressurize the cell. The active membrane area was 14.6 cm^2. The thoroughly washed membrane was cut into the desired shape and fitted in the dead end device. The volume of the appropriate solution was 250 mL. The initial water flux was measured 30 s after the pressurization. Permeate was collected in a graduated cylinder for a time interval until steady state [36].

After compaction, the pure water permeability (PWP) was determined by measuring the pure water flux (J_w) at different transmembrane pressures (ΔP) from 2 to 14 bar; the slope of the linear regression of the water flux as a function of transmembrane pressure was determined as the permeability. The PWP was calculated by the following equation:

$$\mathrm{PWP} = \frac{J_w}{\Delta P} \tag{1}$$