Microporous and Mesoporous Materials 173 (2013) 121–128

Contents lists available at SciVerse ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Embedding TiO_2 nanoparticles versus surface coating by layer-by-layer deposition on nanoporous polymeric films

Jeonghwan Kim [a], Arcadio Sotto [b], Jungwoo Chang [a], Dowoo Nam [a], Arman Boromand [c], Bart Van der Bruggen [c,*]

[a] *Department of Environmental Engineering, INHA University, Namgu, Yonghyundong 253, Incheon, Republic of Korea*
[b] *Department of Chemical and Energy Technology, Rey Juan Carlos University, Tulipán s/n, 28933 Móstoles, Madrid, Spain*
[c] *Department of Chemical Engineering, KU Leuven, W. de Croylaan 46, B-3001, Leuven, Belgium*

ARTICLE INFO

Article history:
Received 11 September 2012
Received in revised form 21 January 2013
Accepted 6 February 2013
Available online 16 February 2013

Keywords:
TiO_2 nanoparticles
TiO_2 embedded membranes
Surface coating
Layer-by-layer deposition

ABSTRACT

Hybrid polymeric films based on titania (TiO_2) nanoparticles on a polyethersulfone (PES) support were obtained by embedding nanoparticles, by dipping in a single layer and by layer-by-layer assembly. First, TiO_2 nanoparticles were doped into a polymeric film during phase-inversion. The permeate flux of TiO_2-embedded membranes in (nano)filtration was higher than for the bare PES membrane in the ultralow concentration range of TiO_2 nanoparticles (0.035–0.125 wt.%). At the highest concentration of TiO_2 nanoparticles tested (0.375 wt.%), however, the permeate flux decreased significantly. Compared to the TiO_2-embedded membrane, the permeate flux of TiO_2-deposited membranes prepared by dipping in one single layer was relatively low. After applying layer-by-layer coating, the permeate flux increased considerably as the number of coating layers was increased to >10. SEM images showed that addition of TiO_2 nanoparticles during phase inversion resulted in larger finger-like pores in the membrane structure, without changing the surface structure. TiO_2-deposited PES membranes prepared by the layer-by-layer coating proved to have a porous coating layer of TiO_2 nanoparticles, covering the surface completely. The surface of TiO_2-deposited films proved to be less rough than that of the bare PES membranes. Release of TiO_2 nanoparticles from the membrane surface was not observed during cross-flow filtration, indicative of strong binding of TiO_2 nanoparticles on the membrane surface. Similar rejections of humic acid were observed for bare PES membranes and TiO_2-multilayer coated PES membranes, confirming that the membrane structure was not damaged by increasing the number of coating layers of TiO_2 nanoparticles on the membrane surface.

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1. Introduction

Developing new materials for advanced separations is at the core of material science for water and wastewater treatment [1–3]. The fabrication of ‘mixed matrix’ membranes, in which inorganic additives are used in a polymeric membrane structure, has received much attention recently [4–5]. The goals in improving membrane materials with inorganic additives are increased permeability, reduced fouling, good chemical and mechanical stability [1]. In addition, it allows membrane structures to be tailored for the rejection of specific chemical species [6].

The use of metal oxide nanoparticles in the fabrication of polymeric membranes provides a high degree of fouling control and the ability to produce desired structures as well as functionalities due to their unique characteristics [7]. Many kinds of nanoparticles have been used, but most applications can be found for titania (TiO_2) nanoparticles as inorganic additives to various polymers [8–10]. This originates in the wide use of TiO_2 nanoparticle as a photocatalyst; several studies report the use of titania mostly with UV irradiation to reduce membrane fouling or increase permeate flux [7]. However, combining polymeric membranes with UV irradiation may be problematic because a polymeric membrane is likely to be damaged by oxidation reactions on a timescale longer than used in lab studies. Nevertheless, many researchers showed positive results in the use of TiO_2 nanoparticles to improve membrane functionalities [9]. Without UV irradiation, the use of TiO_2 nanoparticles may also be interesting particularly for hydrophobic membranes made of e.g., polyethersulfone (PES), because of the hydrophilic characteristics provided by the TiO_2 nanoparticles [10–13].

Combining polymeric membranes with TiO_2 nanoparticles can be achieved by either deposition of nanoparticles on membrane surface [11,14] or embedding into the membrane structure [9,15]. For the TiO_2-embedded membrane, nanoparticles are added to the casting solution used for membrane synthesis by phase

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* Corresponding author. Tel.: +32 16322340; fax: +32 16322991.
E-mail address: bart.vanderbruggen@cit.kuleuven.be (B. Van der Bruggen).

1387-1811/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2013.02.011

inversion. Alternatively, prepared polymeric membranes can be dipped into a colloidal solution containing metal oxide nanoparticles to induce self-assembly surface coating. Rahimpour et al. [9] compared the performance of TiO_2-embedded PES membranes and self-assembly TiO_2-deposited PES membranes under UV irradiation. They found that the surface coating procedure was more beneficial than the entrapment procedure in terms of improving the membrane's permeability. Similar results were observed by Kwak et al., but a negative effect was also reported: TiO_2 nanoparticles deposited on the membrane can be removed from the surface during filtration, thus mitigating hydrophilicity of polymeric membranes [14].

Although many efforts have been made in the use of TiO_2 nanoparticles as additives for polymeric membranes, most studies are focusing on the photocatalytic activity of TiO_2 nanoparticles, and its effect on the performance of the membranes. The intrinsic effect of TiO_2 nanoparticles on hydrophobic membranes, however, is still unclear. Although a stable structure is obtained by embedding nanoparticles, this procedure shields the intrinsic effects of the nanoparticles, so that their functionalities cannot be used efficiently [7]. The deposition method, on the other hand, yields unstable membranes in the sense that nanoparticles are gradually released to the solution in contact with the membrane [7]. These undesired effects make the use of TiO_2 nanoparticles in polymeric membranes less straightforward. One potential alternative is in the concept of thin film nanocomposite (TFN) membranes [16], which involves the application of nanoparticles in an ultrathin polymeric top layer, usually made of a polyamide by interfacial polymerization. Nanoparticles are less shielded in this concept, because they may act as a bridge between the feed solution and the supporting layer. The anchoring in the polymeric top layer enhances the stability of the eventual membrane. However, this can be applied only for materials which can be used in the interfacial polymerization procedure, excluding robust materials such as poly(ether)sulfones (PES).

Deposition procedure using nanoparticles with polymeric membrane is still in order. Karnik et al. (2005) applied successfully layer-by-layer technique using organic binder to develop ceramic membrane with Fe_2O_3 nanoparticles [17]. Development of multilayer of nanoparticles on membrane surface can be achieved by inducing covalent and electrostatic binding between functional groups of membrane (e.g., sulfone group) or organic binder such as phytic acid (e.g., PO_4^{-3}) and Ti^{+4}. By building up several coating layers, they improved the catalytic properties of a TiO_2/Al_2O_3 ceramic membrane when combined with chemical oxidation process such as ozonation. A layer-by-layer approach to induce a film of nanoparticles on a polymeric membrane may provide surface functionality, however, still requires further study on the intrinsic effects of nanoparticle addition on membrane. The aim of this paper is to investigate the advances that can be made with these novel materials as a functional filtration barrier. The stability of these membranes in terms of erosion of TiO_2 nanoparticles is assessed, as well as their intrinsic performance in comparison with classical bare PES membrane, TiO_2-embedded and TiO_2-coated poly (ether) sulfone (PES) membranes for water treatment applications.

2. Materials and methods

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). 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 subsequently aged in a 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. Dried gel samples obtained were calcinated further at 500 °C for 1 h.

Surface analysis and microscopic observations of prepared TiO_2 nanoparticles were performed by using XRD (X-ray diffractometer system, DMAX-2500, Rigaku) and transmission electron microscope (TEM; CM 200, Philips Inc.). Electrophoretic mobility of TiO_2 nanoparticles was measured by phase analysis light-scattering (ZetaPALS, Brookhaven Instrument Corp., NY) and converted into Smoluchowski equation. To evaluate the rejection of the prepared membranes, humic acids (HA) were used in this study. These constitute a major component of natural organic matter that can be found in natural waters and refer to humic substances obtained by chemical and biological degradation products from plant and animal residues. Sigma–Aldrich humic acid (St. Louis, MO) was selected as a model organic foulant in this study. Polyethylene glycols (PEGs) with increasing molecular weights (400, 600, 800, 1500, 4000, 6000 and 8000 Da) were also used to estimate the molecular weight cut-off (MWCO) of manufactured membranes. The solute concentration was fixed at 2000 mg L^{-1} in all cases. The concentration of PEG solutions was measured with a total organic carbon (TOC) analyzer (model TOC-V CSN from Shimadzu Scientific Instruments, Japan).

2.1. Membrane preparation

Control polyethersulfone (PES) membranes and TiO_2-embedded PES membranes were prepared using phase inversion induced by immersion precipitation. PES cast from a solution containing 27 wt.% of polymer in N-methyl-pyrrolidone (NMP) was used as the polymer matrix. The TiO_2-embedded 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. The following concentrations of TiO_2 were used: 0.035, 0.085, 0.125, and 0.375 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. TiO_2-coated PES membranes were first prepared by a single layer dipping method. A PES membrane prepared by phase-inversion as described above was dipped into a colloidal solution containing TiO_2 nanoparticles of 0.125 wt.% for 24 h and rinsed with deionized water to induce a self-assembled coating layer on the membrane surface.

2.2. Membrane preparation with layer-by-layer coating

In order to form more well-defined TiO_2 coating on membrane surface, the layer-by-layer deposition on polymeric surfaces was performed in this study. The layer-by-layer deposition is known from application on diatomite and is based primarily on the

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