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Chemical Engineering Research and Design

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

# Titanium dioxide nanotubes embedded mixed matrix PES membranes characterization and membrane performance

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ARTICLE INFO

*Article history:*
Received 29 March 2014
Received in revised form 9 November 2014
Accepted 15 November 2014
Available online 21 November 2014

*Keywords:*
Titanium dioxide nanotubes
Blend membrane
Membrane performance
Mathematical model

ABSTRACT

This study describes the preparation, characterization, and evaluation of performance of blend polyethersulfone/titanium dioxide nanotubes (PES/$TiO_2$NTs) membranes. $TiO_2$NTs were synthesized via hydrothermal process and used in preparation of blend PES/$TiO_2$NTs membranes by phase inversion process. The effects of embedding $TiO_2$ nanotubes on membrane morphology, mechanical properties and performance were presented. The scanning electron microscopy (SEM) images displayed a typical asymmetric membrane structure with a dense top layer, a porous sub-layer, and fully developed macropores at the bottom of PES/$TiO_2$NTs membranes due to the migration of $TiO_2$NTs to membrane surface during the phase inversion process. Contact angle measurements indicated that the hydrophilicity of the membrane was improved by adding $TiO_2$NTs. Using vacuum membrane distillation (VMD) application, the results indicated that the membrane performance was improved, particularly, permeate flux and salt rejection %. The mathematical model of VMD was applied to determine the highest performance of the membrane at the optimum conditions. The experimental results indicated that using 0.53% $TiO_2$NTs in membrane preparation solution; it was possible to obtain NF/RO blend membrane with high performance, where the salt rejection % increased to 97% with permeate flux 18.2 kg/$m^2$ h. These results agree well the results of the VMD model.


## 1. Introduction

Nanomaterials have been used in membrane fabrication to produce membranes with desirable structure due to their large specific surface area (Kim et al., 2008; Brunet et al., 2008). Using nanomaterials, the membrane performance can be improved and lead to high selectivity and permeability. In addition, the hydrophilicity, strength, stiffness, water permeability and antifouling properties of the membrane can be enhanced by introducing inorganic nanomaterials into membrane matrix (Vatanpour et al., 2012a; Kim and Van der Bruggen, 2010; Li et al., 2007; Xu et al., 2009; Razmjou et al., 2011). Titanium dioxide ($TiO_2$) is one of the most important semiconductors in our daily life for its unique properties including superior photo-reactivity, superhydrophilicity, nontoxicity, long-term stability, and low cost (Mansourpanah et al., 2009; Madaeni

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http://dx.doi.org/10.1016/j.cherd.2014.11.008
0263-8762/

**Nomenclature**

| | |
|---|---|
| A | effective area of the membrane ($m^2$) |
| $C_f$ | concentration at feed bulk (mg/L) |
| $C_p$ | concentration at permeate (mg/L) |
| J | mass vapor flux ($kg/m^2$ h) |
| $M_w$ | molecular weight of water (kg/kmol) |
| P | total pressure (Pa) |
| $P_{fm}$ | water vapor pressure at the feed membrane surface (Pa) |
| $P_{pm}$ | water vapor pressure at the permeate surface (Pa) |
| $\Delta P_v$ | vapor pressure difference at membrane sides (Pa) |
| $P_v$ | vapor pressure at feed side (Pa) |
| R | universal gas constant ($m^3$ Pa/mol K) |
| r | membrane pore radius (m) |
| $T_m$ | mean temperature (K) |
| $T_f$ | water feed temperature (K) |
| $T_{fb}$ | temperature at the feed bulk side (K) |
| $T_{pb}$ | temperature at the permeate bulk side (K) |
| $T_{fm}$ | temperature at the feed membrane surface (K) |
| $T_{pm}$ | temperature at the bulk membrane surface (K) |
| $T_{im}$ | interfacial temperature at the membrane surface (k) |
| t | permeation time (h) |
| V | volume of the pure water permeate ($m^3$) |

*Dimensionless numbers*

| | |
|---|---|
| $\theta$ | temperature polarization coefficient (TPC) |
| $\tau$ | tortuosity factor |

*Greek letters*

| | |
|---|---|
| $\delta$ | membrane thickness (m) |
| $\varepsilon$ | membrane porosity |
| $\eta$ | water vapor viscosity (Pa s) |
| $\rho$ | water density ($kg/m^3$) |

*Subscripts*

| | |
|---|---|
| b | bulk |
| f | feed |
| m | membrane |
| VMD | vacuum membrane distillation |

et al., 2011a). In the recent years, many researchers focused on the preparation of $TiO_2$ nano-inorganic mixed matrix membranes to improve membrane performance by reducing fouling and increasing hydrophilicity (Khataee et al., 2009; Teow et al., 2012; Li et al., 2009a,b; Abdallah et al., 2014; Cong et al., 2007; Chung et al., 2007; Kwak and Kim, 2001; Kim et al., 2003; Luo et al., 2005; Bae and Tak, 2005a,b; Bae et al., 2006; Mo et al., 2007; Madaeni and Ghaemi, 2007).

Blending of polymers is a technical way for providing polymers with set of desired properties at the lowest price such as a combination of strength and toughness, impact strength or solvent resistance. Blending also benefits the industrialist by offering improved process ability, rapid formulation changes, deposit flexibility, product uniformity, and high yield (Wang et al., 2008).

Phase inversion method is one of the most important and popular techniques for manufacturing many functional polymeric materials that are widely used in engineering applications (Wa et al., 2004; Abdallah and Ali, 2012). In addition, the antifouling properties for the membrane can be modified by blending with inorganic nanoparticles such as $Al_2O_3$, $SiO_2$, $TiO_2$, $Fe_3O_4$, and carbon nanotubes (Huang et al., 2008; Choi et al., 2006; Celik et al., 2011; Vatanpour et al., 2011). In recent years, $TiO_2$ nanoparticles blend membranes have been fabricated by precipitating the nanoparticles on the surface of the porous membranes (Vatanpour et al., 2012a; Madaeni et al., 2011b) or blending them with polymeric casting solution (Cong et al., 2007; Ebert et al., 2004).

The addition of nanotubes such as carbon (CNTs) or titanium dioxide ($TiO_2$) in preparation of polymeric membrane can provide high hydrophilicity, good chemical stability, innocuity, and high-surface area (Bae and Tak, 2005a). Because of nanotube materials can reinforce the polymeric membrane as a result of their high-aspect ratio and high in axis strength. In addition, titanium dioxide nanotubes ($TiO_2$NTs) can be synthesized by a solution chemical method to form unique open-end nanotubular morphology with typically 3–5 nm and 10–13 nm in inner and outer diameters, respectively (Shaban et al., 2013). As a consequence of the physical–chemical characteristics, mutual and synergy combination of it slow-dimensional nanostructure, membrane performances can be enhanced by the addition of optimized ratio of $TiO_2$NTs during the preparation process (Shaban et al., 2013).

However, there are no detailed studies for utilizing titanium dioxide nanotubes $TiO_2$NTs to modify the membrane properties and performances, which could solve the problems of fouling and increase the lifetime of the membrane (Razmjou et al., 2011; Mansourpanah et al., 2009; Madaeni et al., 2011a; Khataee et al., 2009; Teow et al., 2012; Li et al., 2009a; Abdallah et al., 2014). In addition, $TiO_2$NTs could be used to produce the next generation of membranes with high selectivity, reasonable flux, low fouling, and enhanced mechanical properties due to remarkable physical and chemical properties. So $TiO_2$NTs could play a great role for improving the membrane performance due to the excellent properties such as porosity, thermal stability, high mechanical strength and high-surface area (Razmjou et al., 2011; Li et al., 2009a; Abdallah et al., 2014; Bae and Tak, 2005b).

The hydrophobic porous membranes are preferable in membrane distillation systems, which will resist wetting and oppose liquid water from entering the membrane pores. Then the hydraulic pressure of the bulk water on either sides of the membrane can overcome the inherent surface tension and allow feed water to pass through the membrane. Also, the salt rejection increases by increasing the hydrophobicity of the membrane (El-Bourawi et al., 2006). But, the fouling by proteins and other organic matter is commonly attributed to the hydrophobic nature of membrane materials that leads to a high interfacial energy with water-rich media, which is decreased upon biomolecules adsorption. So, the suggested structure of the membrane that used in this research is different; it is not hydrophobic porous membrane, but it is asymmetric dense membrane with adopted hydrophilic properties. The hydrophilic properties of suggested membrane will be adopted to improve the membrane antifouling properties by introducing the titanium dioxide ($TiO_2$) nanotubes at different percentage into the membrane matrix. This is highly expected to improve the strength and stiffness, the water permeability, and the antifouling properties of membrane. Also, the salt rejection % is expected to increase due to the dense layer which is the separation layer (Li et al., 2009a; Abdallah et al., 2014).