



ELSEVIER

Contents lists available at ScienceDirect

Journal of Membrane Science

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

Composite polyvinylidene fluoride (PVDF) membrane impregnated with Fe₂O₃ nanoparticles and multiwalled carbon nanotubes for catalytic degradation of organic contaminants



Alla Alpatova, Mohamed Meshref, Kerry N. McPhedran, Mohamed Gamal El-Din*

Department of Civil and Environmental Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2W2

ARTICLE INFO

Article history:

Received 13 December 2014

Received in revised form

28 April 2015

Accepted 2 May 2015

Available online 11 May 2015

Keywords:

Catalytic polymeric membrane

PVDF

Fe₂O₃

Fenton process

Membrane fouling

ABSTRACT

Porous polyvinylidene fluoride (PVDF) polymeric membranes with inclusion of Fe₂O₃ nanoparticles and multi-walled carbon nanotubes (MWCNTs) were developed for the Fenton-like catalytic degradation of organic contaminants at neutral pH. The PVDF was modified by *in situ* polymerization with methyl methacrylate to improve its hydrophilicity, and a range of membranes with different Fe₂O₃ and MWCNTs loadings were casted. The effect of these compositions on membrane morphology, surface functionality and hydrophilicity was investigated by microscopic, spectroscopic and surface characterization techniques. Contact angle measurements showed that MWCNTs did not change the membrane hydrophilicity, while the Fe₂O₃ was effective in increasing hydrophilicity. The optimum combination of 0.2% MWCNTs and 1% Fe₂O₃ induced pore formation and improved membrane permeability. The removal efficiency of cyclohexanoic acid (CHA) and humic acids (HAs) were evaluated. Batch studies revealed that 48% of CHA was degraded after 24 h of membrane exposure with H₂O₂. For HAs, removal with H₂O₂ addition was significantly higher than without at 53.1 ± 4.4% and 28.1 ± 4.1%, respectively. These membranes also showed a significant reduction in membrane fouling. Overall, the permeate flux achieved with H₂O₂ was four times higher as compared to without H₂O₂ addition which is ascribed to the catalytic oxidation of organic molecules which accumulated at the membrane surface.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

A recent trend in the field of advanced separation processes is the development of polymeric composite membranes with additional properties that can provide better removal of refractory organic contaminants in various treatment processes [1–3]. Membrane filtration is a popular treatment method for the production of high quality water for different municipal and industrial needs; however, uses remain limited due to membrane fouling and high energy consumption [4]. One way to overcome these shortcomings is to degrade organic contaminants at the membrane surface and within membrane pores in a catalytic microporous membrane reaction utilizing the oxidation power of generated hydroxyl radicals ($\cdot\text{OH}$) [2,5]. In addition to reduced membrane fouling, this process is expected to improve removal of organic molecules

with molecular sizes below the average membrane pore size that would otherwise freely pass through the membrane [2].

The polyvinylidene fluoride (PVDF) is widely used in membrane manufacturing due to its high chemical resistance, ability to sustain oxidative treatment and film-forming properties [1,6,7]. PVDF-based microfiltration and ultrafiltration membranes can be easily fabricated through the phase inversion method given PVDF readily dissolves in organic solvents [8]. Although PVDF membranes are extensively used for various water treatment applications, their high hydrophobicity as compared to other membrane materials remains a challenge due to reduced filtration efficiency. The critical surface tension of PVDF polymer is 25 dyn/cm, which is almost half that of other common membrane materials including polysulfone (41 dyn/cm) and polyacrylonitrile (44 dyn/cm) [9,10]. This low surface energy for PVDF results in increased surface fouling, and subsequently decreased permeate flux and shortened membrane life span. It has been shown that modification of PVDF polymer membranes with hydrophilic monomers can reduce its hydrophobicity [11,12] and improve anti-fouling properties towards proteins, hydrocarbons and other organic contaminants [13,14]. For example, one way to improve PVDF wetting capacity is through the *in situ* polymerization with hydrophilic macromolecules. Physico-chemical and mechanical properties of

* Correspondence to: NSERC Senior Industrial Research Chair in Oil Sands Tailings Water Treatment Helmholtz – Alberta Initiative Lead (Theme 5), 3-093 Markin/CNRL Natural Resources Engineering Facility, Department of Civil and Environmental Engineering University of Alberta Edmonton, Alberta, Canada T6G 2W2. Tel.: +1 780 492 5124; fax: +1 780 492 0249.

E-mail address: mgamalel-din@ualberta.ca (M. Gamal El-Din).

the membrane blends prepared by this technique were shown to be significantly improved as compared to other blending methods [11,15,16].

The inclusion of nanoparticles (e.g., carbon nanotubes, Fe₂O₃, TiO₂, Al₂O₃, etc.) into the polymer matrix can significantly improve membrane separation properties [1,7,10,17–19]. Previously, we found that the addition of multi-walled carbon nanotubes (MWCNTs) into a polysulfone matrix enhanced the membrane permeability and decreased contact angles [17]. Zhao et al. [18] found that permeate flux and rejection of bovine serum albumin for PVDF/MWCNTs membranes were improved by 114% and 31.8%, respectively. In addition, the inclusion of metal oxide fillers into the polymeric matrix has positively impacted membrane characteristics. For example, the fouling resistance of PVDF membranes was enhanced upon Al₂O₃ addition [10]. Gojny et al. [20] concluded that carbon nanotubes have a combination of a high aspect ratio, with low density and high strength and stiffness, making them an effective reinforcing additive in polymeric materials. As well, Mago et al. [21] found that carbon nanotubes added to a PVDF matrix assisted formation of interconnected continuous and open structures promoting its mechanical strength. As well, a significant improvement in PVDF membrane permeability was achieved with ZrO₂ particles due to enhanced pore formation [19].

Another benefit of metal oxides are their ability to catalyse the degradation of refractory organic pollutants by producing ·OH radicals in advanced oxidation processes (AOP) [1,22–24]. An example of an AOP is the heterogeneous Fenton-like reaction that utilises a combination of hydrogen peroxide (H₂O₂) and immobilized Fe (III) species at near neutral pH [23]. As a result of this pH, the catalyst can maintain its ability to decompose H₂O₂ without iron hydroxide precipitation [24]. Iron oxide minerals have demonstrated high efficiency in catalysing Fenton-like oxidation reactions during water remediation [23–25]. Moreover, PVDF membranes with immobilized Fe₂O₃ nanoparticles have been recently synthesised for dechlorination of trichloroethylene (TCE) at a near neutral pH [1]. The authors have reported that depending on iron and H₂O₂ ratio, TCE conversion as high as 100% was achieved. Moreover, when these membranes were tested with real groundwater, the TCE conversion remained high, reaching 53.5% after 33 h of operation.

Clearly the addition of nanoparticles and metal oxides into polymeric membranes is a promising advanced treatment process for the reduction of membrane fouling with subsequent cost savings, with the added benefit of degradation of organic compounds. Thus, the objectives of the present study were: (1) to develop porous PVDF polymeric membrane with inclusion of Fe₂O₃ and MWCNTs for the degradation of organic contaminants on the membrane surface and within its pores; (2) to evaluate morphology, physico-chemical characteristics and permeability of fabricated membranes; and (3) to test membrane performance with respect to oxidation of cyclohexanoic (CHA) acid and humic acids (HAs) in a Fenton-like reaction at pH 7.

In these membranes, various combinations of MWCNTs and Fe₂O₃ are expected to improve permeate flux, while the Fe₂O₃ will promote oxidation of organic molecules by decomposition of H₂O₂ to hydroxyl (·OH) radicals and subsequent oxidation of organic molecules. The immobilization of Fe₂O₃ within the polymeric matrix is will reduce costs associated with conventional heterogeneous catalysis where nanoparticles are directly dispersed in a liquid phase where they need to be recovered after reaction completion. For membrane optimization purposes, two model organics (CHA and HAs) were chosen to test the membrane performance. CHA is a toxic low molecular weight (~200–300 kDa) naphthenic acids (NAs) contaminant found in oil sands process-affected water (OSPW) [26]. HAs is a well-known contaminant of surface waters which causes severe membrane fouling [27].

2. Materials and methods

2.1. Chemicals

PVDF ($M_w \sim 275,000$), N,N-dimethylformamide (DMF), methyl methacrylate (MMA), dibenzoyl peroxide (BPO), HAs, sodium hydroxide (NaOH), sulfuric acid (H₂SO₄), nitric acid (HNO₃), sodium thiosulphate (Na₂S₂O₃), H₂O₂, titanium (IV) oxysulfate solution, paraffin oil and Fe₂O₃ nanopowder (average particle size < 50 nm) (all chemicals were ACS grade) were purchased from the Sigma-Aldrich (St. Louis, MO, USA). MWCNTs (average diameter: 5–10 nm, length: 10–30 μm, and specific surface area > 200 m²/g) were obtained from Sun Innovations Inc. (Faremont, CA, USA). The CHA (> 99% purity) was purchased from TCI America (Portland, OR, USA). ACS grade ammonium acetate (C₂H₃O₂NH₄), acetic acid (C₂H₄O₂), and methanol (CH₃OH) were purchased from Fisher Scientific (Fair Lawn, NJ, USA). The Milli-Q water was produced by a Milli-Q Ultrapure Water System (Millipore Corp., Bedford, MA, USA).

2.2. Modification of PVDF polymer

The modification of the PVDF polymer was conducted following the method described in [16]. Briefly, 48 g of PVDF beads were dissolved in DMF to create a 10 wt% solution, followed by addition of 3.0 g MAA (monomer), 0.03 g BPO (initiator), and the resulting solution was degassed by purging nitrogen gas for 15 min. The reaction flask was submerged into a beaker filled with paraffin oil to help maintain a constant reaction temperature; the beaker was then immersed in a water bath (Boekel Scientific Inc., Feasterville, PA, USA) at 75 °C for 5 h to allow the polymerization reaction to occur.

2.3. Membrane fabrication procedure

We prepared eight membranes with different MWCNTs and Fe₂O₃ loadings (Table 1). The membranes were assigned as M (UM)–“X”–F“Y”, where M or UM define if the membrane was casted from a modified or unmodified PVDF, respectively, F denotes Fe₂O₃, and X and Y corresponds to MWCNTs and Fe₂O₃ wt% content, respectively. Membranes were fabricated by immersion precipitation following the method described in [28]. Corresponding masses of MWCNTs or Fe₂O₃ were added to 10 g of the polymerised solution or 10 g of 10 wt% unmodified PVDF solution in DMF. The flasks were sonicated for 10 min (Bransonic[®], Branson Ultrasonics, Danbury, CT, USA) to evenly disperse nanoparticles. The solutions were left open for 10 min to allow the release of air bubbles. The polymeric films were casted using a stainless steel Doctor-Blade knife (Microme II, Paul N. Gardner Company Inc., Pompano Beach, FL, USA) on a glass plate, and after 30 s of exposure to air, the glass plate was poured into Milli-Q water at

Table 1
Composition of casting mixtures.

Membrane code	Concentration of nanoparticles, wt%	
	MWCNTs	Fe ₂ O ₃
M-0-F0	0	0
M-0.2-F0	0.2	0
M-0.5-F0	0.5	0
M-1-F0	1	0
M-0.2-F0.2	0.2	0.2
M-0.2-F0.5	0.2	0.5
M-0.2-F1	0.2	1.0
M-0.2-F2	0.2	2.0
UM-0-F0	0	0

Download English Version:

<https://daneshyari.com/en/article/633039>

Download Persian Version:

<https://daneshyari.com/article/633039>

[Daneshyari.com](https://daneshyari.com)