Separation and Purification Technology 199 (2018) 161–169

Contents lists available at ScienceDirect

Separation and Purification Technology

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

Efficient separation of oily wastewater using polyethersulfone mixed matrix membrane incorporated with halloysite nanotube-hydrous ferric oxide nanoparticle

Syarifah Nazirah Wan Ikhsan[a,b], Norhaniza Yusof[a,b,*], Farhana Aziz[a,b], Nurasyikin Misdan[c], Ahmad Fauzi Ismail[a,b], Woei-Jye Lau[a,b], Juhana Jaafar[a,b], Wan Norharyati Wan Salleh[a,b], Nur Hanis Hayati Hairom[c]

[a] Advanced Membrane Technology Research Centre (AMTEC), N29A, Universiti Teknologi Malaysia, 81310, Malaysia
[b] Faculty of Chemical and Energy Engineering (FCEE), Universiti Teknologi Malaysia, 81310, Malaysia
[c] Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

ARTICLE INFO

Keywords:
Oily wastewater treatment
Ultrafiltration
Mixed matrix membranes
Hydrous ferric oxide
Halloysite nanotube

ABSTRACT

In this work, self-synthesized halloysite nanotube-hydrous ferric dioxide (HNT-HFO) nanocomposites prepared via chemical precipitation method were incorporated in polyethersulfone (PES) to fabricate novel ultrafiltration (UF) mixed matrix membranes (MMMs) for oil-water separation process. Prior to filtration experiments, the morphologies and physicochemical properties of prepared HNT-HFO nanocomposites and MMMs were characterized using scanning electron microscope with energy-dispersive X-ray, transmission electron microscope, Fourier-transform Infrared spectroscope, atomic force microscope and contact angle goniometer. It was found that the membrane contact angle decreased remarkably from 81.39° to about 50.30° upon addition of 23.08 wt% of HNT-HFO nanocomposite (2.0 loading ratio) in the PES matrix. The improved surface hydrophilicity resulted in the flux enhancement in the MMM, achieving close to 650 L/m^2 h bar of pure water flux. This value was about 10 times higher than the flux shown by the pristine PES membrane. In addition to the excellent water flux, the MMM also exhibited almost complete elimination of oil molecules (99.7% rejection) when tested with 1000 ppm oily solution. The findings indicated the potential use of the newly developed MMMs for efficient purification of oily wastewater in the oil field and refinery processes.

1. Introduction

The growth of the oil and gas industry especially the petroleum refining has alerted concern due to the increasing amount of oily wastewater it produced [1]. The need to purify and treat the oily wastewater has intensified as the three important environmental drivers namely the governments, the public and the industry have sought to minimize the waste generation to protect the environment [2]. Numerous techniques have been adapted to separate oil/water mixture which include air flotation, gravity separation, adsorption, coagulation, and flocculation [3]. However, these strategies are found to be inadequate in treating oil-in-water emulsion particularly for the oil droplets with size as small as 0.1 μm [4].

Over the years, the microporous polymeric-based membrane has been increasingly utilized in a wide range of water treatment processes, owing to the significant improvement in its intrinsic properties (e.g., hydrophilicity and anti-fouling resistance) as well as low energy requirement and ease of operation [5]. In general, ultrafiltration (UF) membranes with pore sizes around 0.01 and 0.1 μm are considered sufficient to treat oil–water emulsions and produce high-quality permeate [6], but its relatively low resistances against the deposition and adsorption of oil molecules are likely to reduce the lifespan of the membrane, particularly when high concentration of oily wastewater is dealt with. In order to address the problem, many works have been carried out to improve the membrane surface hydrophilicity by incorporating with hydrophilic inorganic nanofillers [7–9]. Increasing the quantity of hydrophilic nanofillers in the polymeric matrix could improve membrane surface hydrophilicity as demonstrated in previous works [4,10], but the nanofiller amount needs to be properly controlled in order to avoid the formation of membrane with poor mechanical properties resulted from incompatibility between nanofillers and polymer and/or excessive particles agglomeration.

* Corresponding author at: Advanced Membrane Technology Research Centre (AMTEC), N29A, Universiti Teknologi Malaysia, 81310, Malaysia.
E-mail address: norhaniza@petroleum.utm.my (N. Yusof).

https://doi.org/10.1016/j.seppur.2018.01.028
Received 29 September 2017; Received in revised form 15 January 2018; Accepted 15 January 2018

Many types of nanofillers have been previously tested for the mixed matrix membrane (MMM) fabrication for the oily wastewater treatment. Kumar et al. [11] for instance incorporated bentonite in polysulfone (PSF) membrane and reported that with only adding 8 wt% bentonite, the water flux of the resultant membrane could be improved by 50% while maintaining oil rejection at > 90% in comparison to control membrane.

In another study by Yuliwati et al. [12], the Polyvinylidene fluoride (PVDF) membrane was modified by titanium dioxide (TiO_2) in the presence of lithium chloride monohydrate during dope solution preparation. As reported, the modified membrane was potential to be used in refinery produced water purification. Upon addition of 1.95 wt% TiO_2, the modified PVDF could achieved water flux of 82.50 L/m^2 h with oil rejection recorded at 98.8%. As a comparison, the pristine PVDF membrane only showed 82.5 L/m^2 h water flux and 98.8% oil rejection.

Recently, Lai et al. [4] incorporated dual-nanofiller composed of hydrous manganese oxide (HMO) and TiO_2 at different weight ratio, aiming to optimize the properties of polyethersulfone (PES) MMM for oil-water separation process. It was found that the weight composition of HMO and TiO_2 needs to be properly controlled in order to achieve good balance of water flux and oil removal rate. Overall, the newly developed MMMs could achieve 26.4–31.7% higher water flux compared to the pristine PES membrane without compromising oil removal rate. Most importantly, these presence of nanofillers played key role in reducing flux decline as a result of improved surface resistance against oil fouling and are of potential to extend membrane lifespan.

All of the relevant works have shown the impactful enhancement of membrane efficiency upon incorporation of nanofillers. It was reported that the nanofillers could improve not only the membrane structural morphology and surface chemistry but also enhance filtration properties by achieving higher water flux without compromising separation efficiency. Furthermore, the improved surface antifouling resistances against oil molecules make the developed membranes more practical to be used for industrial process.

However, to ensure the fabricated MMMs have the maximum efficiency, few attributes need to be considered. Good combination between membrane matrix and nanofillers will lead to good separation properties, excellent stabilities as well as improved permeability and selectivity. Of the nanofillers available, hydrous ferric oxide (HFO) and halloysite nanotube (HNT) have the potential to become the nanofillers for the MMMs owing to their unique characteristics. Both types of nanofillers are of hydrophilic in nature due to the presence of hydroxyl functional groups (−OH) and exhibit high specific surface area [13,14]. The presence of a large amount of −OH groups on the membrane surface is the important factors determining both membrane hydrophilicity and water permeability and thus anti-fouling properties during oily wastewater treatment process. Therefore, in this study, we have tested 4 different loadings of HNT-HFO nanocomposite to evaluate the optimum combination of membrane matrix and nanofillers that can increase the hydrophilicity of the MMMs.

This work aimed to study the potential of a new type of nanocomposites - HFO-HNT for PES MMM fabrication and evaluate the impacts of HNT-HFO loading (0.5, 1.0, 1.5 and 2.0 ratio) on the intrinsic properties and filtration performance of PES-based membranes for oily wastewater treatment process. All of the fabricated membranes were characterized by SEM-EDX, FTIR, AFM and contact angle goniometer and the results were correlated with membrane water flux and oil rejection.

2. Materials and method

2.1. Chemicals

Commercial PES pellets (Ultrason®E) purchased from BASF SE Germany is the main component in membrane formation. N-Methyl-2-pyrrolidone (NMP) and polyvinylpyrolidone (PVP) (MW = 24,000 g/mol) supplied by Merck are utilized as solvent and pore forming agent, respectively. Ferric chloride hexahydrate ($FeCl{\cdot}6H_2O$), hydrochloric acid (HCl) and ammonia solution (NH_3) and HNTs obtained from Merck are used to synthesize HNT-HFO nanocomposite.

2.2. Synthesis of HNT-HFO

The HNT-HFO nanocomposite was synthesized based on chemical precipitation method as described in the work of Xie et al. [15] with some modification. At first, 67.75 g of $FeCl{\cdot}6H_2O$ was added into 0.205 L HCl aqueous solution (0.01 M). Prior to precipitation phase, 0.5 g of HNT was added into the mixture under constant magnetic stirring at 150 rpm. Subsequently, 3.0 M of NH_3 solution was added dropwise until the solution pH reached 10. The mixture was then kept in ultrasonic bath for 2 h to allow the nanoparticles to disperse homogenously. It was followed by washing the resulting precipitate with distilled water till it reached neutral condition. The precipitate was left for 2 weeks for ageing purpose. After completing aging, the obtained nanocomposite was dried at oven at 70 °C for 3 days before being grinded and sieved.

2.3. Preparation of dope solution

To prepare the dope solution for membrane fabrication, a predetermined amount of PVP was first dissolved in NMP solvent. Different loading of HNT-HFO were added to the solution followed by PES pellets. The mixture was continuously stirred at 500 rpm for 24 h until it became homogenous. The dope solution for the pristine PES membrane was prepared exactly as the MMMs, except no nanofillers were added. Table 1 summarize the composition of dope solutions prepared in this work.

2.4. Preparation of flat sheet membrane

To prepare a flat sheet membrane, small quantity of dope solution (20 mL) was first poured onto a smooth and clean glass plate. The solution was then casted by a casting blade at a speed of 5 cm/s to form a film of 250-mm thickness. The cast film together with the glass plate was then immersed into a deionized water bath to allow phase inversion to take place. Once the film was peeled off naturally from the glass plate, it was transferred to another water bath and kept for another 3 days to remove residual solvent and PVP. At last, the film (membrane) was dried at room temperature (with 60–70% humidity) prior to use.

2.5. Membrane characterization

Transmission electron microscope (TEM) (HT 7700, Hitachi) was used to examine the morphology of the synthesized HNT-HFO nanocomposites. The membrane surface and cross-section morphology were inspected using a field emission scanning electron microscope (FESEM) (SUPRA 35VP, ZEISS). Elemental analysis on each membrane was performed with an energy-dispersive X-ray (EDX) spectrometer. The surface wetting characteristics of membranes were determined by conducting static measurements with a contact angle goniometer (OCA

Table 1
Composition of dope solution.

Membrane	HNT-HFO/PES ratio	PES (wt %)	PVP (wt %)	NMP (% wt)	HNT-HFO (% wt)
PES	0	15.00	1.5	83.5	–
HH1	0.5	13.95	1.40	77.67	6.98
HH2	1.0	13.04	1.30	72.61	13.04
HH3	1.5	12.24	1.22	68.16	18.36
HH4	2.0	11.54	1.15	64.23	23.08