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Treatment of paper mill effluent using Polyethersulfone/functionalised multiwalled carbon nanotubes based nanocomposite membranes

R. Saranya [a], G. Arthanareeswaran [a,*], Dionysios D. Dionysiou [b]

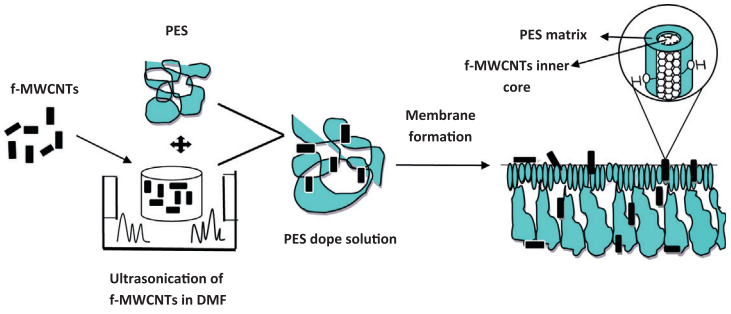
[a] Membrane Research Laboratory, Department of Chemical Engineering, National Institute of Technology, Tiruchirappalli 620015, India
[b] Environmental Engineering and Science Program, Department of Biomedical, Chemical and Environmental Engineering (DBCEE), 705 Engineering Research Center, University of Cincinnati,Cincinnati, OH 45221-0012

HIGHLIGHTS

- CNTs have offered higher hydrophilicity to PES/f-MWCNTs nanocomposite membranes.
- PES/f-MWCNTs membranes showed good rejection capability.
- Rejection efficiency has improved without compromising the permeability.

GRAPHICAL ABSTRACT

Nanocomposite membrane formed from Polyethersulfone and functionalised multi walled carbon nanotubes.



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ABSTRACT

Functionalised multi-walled carbon nanotubes (f-MWCNTs) in different concentrations were incorporated into polyethersulfone (PES) to fabricate PES/f-MWCNTs nanocomposite membranes for ultrafiltration studies. MWCNTs were synthesized by chemical vapour deposition method that were later functionalised using concentrated acids (H_2SO_4/HNO_3) to impart hydroxyl and carboxyl functional groups on its side walls. Hydrophilic property of PES-f-MWCNTs, identified by the contact angle measurement, was improved by 18.7% more than that of neat PES membrane. The pure water flux increased from 24.28 L m^{-2} h^{-1} to 53.91 L m^{-2} h^{-1} on addition of 0.5 wt.% of f-MWCNTs to PES. The increase in flux is attributed to the surface hydrophilicity of PES-f-MWCNTs and it also clearly signifies the impact of functionalised MWCNTs on PES. Solute separation studies were performed wherein 27–30% rejection, much higher than that of neat PES membrane, was observed. Treatment of Kraft paper mill effluent with and without lignin recovery was also investigated by analysing the performance of PES-f-MWCNTs nanocomposite membranes on colour, chemical oxygen demand (COD) and total dissolved solids (TDS) reduction.

1. Introduction

The development of polymer nanocomposites and rapid advances in the field of nanotechnology has created great opportunities for major progress in the field of membrane science. Polymer nanocomposite membranes composed of inorganic nanomaterials are developing due to their higher durability and performance in many separation applications [1,2]. Composite membranes containing nano-sized inorganic materials, blended or architecturally position in the membrane matrix, are attractive because of their enhanced properties, such as high perm-selectivity, higher hydrophilicity, and enhanced fouling resistance [3]. These advances have

* Corresponding author. Tel.: +91 431 2503118; fax: +91 431 2500133.
E-mail addresses: arthanaree10@yahoo.com (G. Arthanareeswaran), dionysios.d.dionysiou@uc.edu (D.D. Dionysiou).

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motivated many researchers and propelled a large number of studies to explore novel inorganic nanomaterials in the fabrication of tailor-designed polymer nanocomposite membranes.

The discovery of carbon nanotubes (CNTs) by Lijima [4] has opened up new directions for many applications. CNTs have the ability to interact and alter the physico-chemical properties of the membrane [5]. This property along with their nanoscale dimensions makes CNTs to emerge as a promising candidate for synthesizing next generation polymer nanocomposites. Polymer/CNT composites are expected to have good processability characteristics of the polymer and excellent functional properties of the CNTs [6]. In the context of application in polymer composites, multi-walled carbon nanotubes (MWCNTs) are of particular interest over single-walled carbon nanotubes (SWCNTs) in view of their relatively low cost and availability in larger quantities as a result of their more advanced stage in commercial production.

CNTs synthesis by chemical vapour deposition (CVD) is the most popular method because of its low cost, simple configuration and high flexibility in adjustable parameters for controlling the CNTs structures [7,8]. The homogeneous dispersion of CNTs in polymer matrix highly ensures the compatibility and effective utilisation of CNTs for composite membrane applications. Hence, CNT functionalization helps to prevent aggregation, by dispersing and stabilizing the CNTs inside the polymer matrix. The functional groups must be introduced in such a way between the polymer and the CNTs without blocking or affecting the pore structure of CNTs [9]. Several research studies related to functionalisation of CNTs for incorporation into polymers have been reported. Acidified-MWCNTs/polysulfone (PSF) membranes have been prepared by Choi et al. [10,11] by dissolving in N-methyl-2-ketopyrrolidine followed by immersed phase inversion process. Qui et al. studied different types of MWCNTs functionalisation using 5-isocyanato-isophthaloyl chloride (ICIC) for imparting isocyanate and isophthaloyl chloride groups thereby to improve the properties of PSF [12].

In spite of high research activity in the area of CNTs, their application in membrane science is only slowly developing. The facile and inexpensive fabrication of composite membranes containing properly aligned f-MWCNTs is highly demanding. CNTs in membrane fabrication was reported by Hinds et al. [14] on preparing an organic–inorganic membrane using polymer/CNT blend that exhibited high flux. Merkel et al. [13] also synthesized CNTs aligned nanoporous polymeric membranes. However, CNT incorporated polymeric membranes were mostly utilised for the gas separation [15–17] and pervaporation applications. Peng et al. used CNTs filled polyvinyl alcohol (PVA) membranes [18] for the separation of solvent mixtures. Shirazi et al. performed similar studies to investigate the dehydration of isopropanol using (PVA)/CNT nanocomposite membranes and observed an increase in water selectivity at an optimum loading of CNTs [19].

PES is the material of choice for numerous membrane applications due to its outstanding mechanical strength, thermal stability, and formability [20]. The main disadvantage is its low hydrophilicity and permeability leading to increased membrane fouling. Hence, blending of f-MWCNTs was investigated to fabricate better membranes by increasing the permeability and diffusivity by increasing the weight fraction of carbon nanotubes [21]. According to Barth et al. [22], PES is more suitable for liquid state separations. However, CNT blended PES membranes have not yet been used for waste water treatment. In order to improve permeability and anti-fouling efficiency of such composite membranes for water filtration was reported by Choi et al. [23] using f-MWCNTs based PES blend membrane. In particular, these evidences imply that CNT blended PES membranes were reported only for water filtration and water treatment.

In the current study, MWCNTs have been functionalised by refluxing with concentrated nitric and sulphuric acid thereby rendering hydroxyl and carboxyl groups on their side walls. PES/f-MWCNTs nanocomposite membranes were prepared by varying PES and f-MWCNTs ratio in membrane casting solution followed by phase inversion method. The addition of f-MWCNTs is limited to 0.5 wt.% because there was an incompatibility between PES and f-MWCNTs leading to steric hindrance beyond 0.5 wt.%. f-MWCNTs in higher amounts would also result in agglomeration in casting solution that eventually affects membrane formation and permeability properties. The increase in hydrophilic f-MWCNTs content also leads to higher viscosity of doped casting solution which would delay the phase separation resulting in denser sub-layer and smoother surface of the nanocomposite membranes [23]. Roy et al. also had reported that substantial amount of MWCNTs would not help to achieve a percolation threshold [24].

Characterisation studies of the prepared membranes in terms of contact angle, thermal properties, chemical structure, and morphology have been performed. The properties of nanocomposite membranes were also assessed by means of pure water flux studies, hydraulic resistance, and performance in rejection and permeation of salt solutions. The ability of PES/f-MWCNTs nanocomposite membrane in the treatment of Kraft paper mill effluent was evaluated based on reduction of colour, COD and TDS from the secondary effluent of paper mill industry. Moreover, in order to intensify the membrane ultrafiltration (UF) performance, lignin recovery process was carried out. The pH minimisation during lignin recovery was also examined to evaluate the effect of pH on the membrane UF performance and also concerning the improvement in COD and TDS reduction, thereby emphasizing the stability and rejection efficiency of PES/f-MWCNTs nanocomposite membranes.

2. Experimental section

2.1. Materials

PES (Veradale 3000) was supplied by Solvay Solexis (India) limited. *N,N′*-dimethylformamide was purchased from Qualigens fine chemicals, Glaxo India limited. MWCNTs were synthesised by catalytic chemical vapour deposition (CVD) method. Magnesium sulphate and sodium chloride were obtained from CDH chemicals limited, India. Polyethyleneglycol (PEG) of different molecular weights (6 kDa, 10 kDa and 20 kDa) was purchased from Merck (India) limited. Concentrated sulphuric acid (98%), nitric acid (69%), formalin (98%) and ethanol (99%) were procured from Fischer Scientific Company, India. Acetylene gas cylinder was supplied by BOC India limited. All chemicals used were of analytical grade. Ultrapure water was produced in the laboratory using Millipore pilot plant. The effluent was obtained from Seshasayee paper mills, Erode, India.

2.2. Synthesis of f-MWCNTs by chemical vapour deposition method

MWCNTs were synthesized by means of chemical vapour deposition over a rare alloy, mischmetal (approximately 50% cerium and 25% lanthanum, with small amounts of neodymium and praseodymium) – based AB_3 alloy hydride catalyst at ~700 °C [25,26]. Acetylene gas was supplied as the carbon precursor in this technique. The as-formed pristine MWCNTs contain impurities such as amorphous carbon, fullerenes, and other metal catalysts. Hence, they were purified by means of air oxidation at 350 °C for 4 h followed by acid treatment using concentrated HNO_3 reflux for 24 h. Further functionalization was carried out by ultrasonicating purified MWCNTs in the mixture of H_2SO_4 and HNO_3 (ratio 3:1) at 60 °C for 6 h. This step helps in rendering hydroxyl and carboxyl functional groups over the side walls of MWCNTs and is illustrated in Fig. 1. Finally, fine powder of f-MWCNTs was obtained by