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Polyamide thin film composite membranes containing ZIF-8 for the separation of pharmaceutical compounds from aqueous streams

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ABSTRACT

Pharmaceutical compounds which are hydrophilic and biologically persistent are being recognized as new unregulated contaminants in water. The hydrophilic characteristic deters their removal through biological processes and adsorption. However, electrostatic repulsion and size sieving in nanofiltration (NF) can be used for the removal of these compounds. Although both NF and reverse osmosis (RO) are options for removal of pharmaceutical compounds from aqueous feeds, the high pressure (and therefore high energy consumption) and membrane fouling remain serious concerns. Therefore development of improved membranes continues to be a key research area. Metal organic frameworks (MOF) are a class of porous crystalline compounds which offer advantages of large surface area and controlled porosity. MOFs have been used as adsorbents. More recently, MOF membranes and MOF incorporated polymeric membranes have gained importance. In this work, MOF incorporated polymeric membrane was prepared and tested for removal of the common analgesic acetaminophen (or paracetamol, MW 151 g/mol). Thin film polyamide composite membranes were synthesized by interfacial polymerization with zeolitic imidazolate framework-8 (ZIF-8). Two different structures were prepared and characterized (i) polysulfone (PSF) support membranes with ZIF-8 and polyamide (PA) separation layer, and (ii) layer-by layer (LBL) polyamide/ZIF-8 nanocomposite membrane on top of PSF support. The latter synthesis protocol produced defect free TFC membrane with 55% acetaminophen retention and permeance equivalent to conventional PSF/PA membrane.

1. Introduction

Nanofiltration (NF) and reverse osmosis (RO) are widely recognized as the best technology for the production of drinking water and removal of micro-pollutants. RO membrane systems can produce high quality water, but their installation and running cost is very high, also water produced from RO is demineralised water. NF is a pressure driven membrane process with separation characteristics between RO and ultrafiltration (UF). NF is characterized by high permeation flux and high retention of multivalent ions along with lower operation pressure and lower operation cost compared to RO. NF systems are used in various industries for water treatment, pharmaceuticals concentration, biochemical processing, etc. [1,2].

In integrally skinned asymmetric NF membranes, it is difficult to control the structure of the top layer (which controls selectivity and flux). One way to solve this problem is to make the top layer in a separate step (e.g. by interfacial polymerization) using alternative chemistries, resulting in thin film composite (TFC) membranes. The key advantage of TFCs compared to integrally skinned asymmetric membranes is the top selective layer and porous support layer can be independently controlled and optimized to achieve high selectivity and high permeability. This makes them competitive and attractive commercially as well. TFC membranes have emerged as excellent candidates in a wide variety of applications, particularly in water and wastewater treatment processes. Many microporous/mesoporous materials have gained considerable importance for having great potential to fabricate high performance membranes. Such materials are carbon nanotubes, graphenes, metal organic frameworks (MOFs), covalent-organic materials, microporous organic polymers, zeolites, and double layered hydroxide. Such materials are used to improve the performance of polymeric membranes, which usually have the inherent drawback in terms of the trade-off between permeability and selectivity. Metal organic frameworks (MOFs) are a new kind of porous materials, composed of metal ions/clusters and organic ligands. They are highly attractive for their applications in membrane separation because of the improvement in membrane performance based on the identical pore sizes and highly porous

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structures. It has been experimentally proven that MOF based membranes can exhibit significantly improved performance in gas separation [3–7], pervaporation [8], NF [9–11] and RO [12] processes. MOF membranes are reported to form on different supporting materials, ranging from inorganic substrates, such as silica, alumina, to organic substrates, such as porous polymeric membranes [13,14]. In situ growth of zeolitic imidazolate framework-8 (ZIF-8) and $Cu_3(BTC)_2$ [BTC = benzene-1,3,5-tricarboxylic acid] on polysulfone (PSF) porous UF membranes were prepared for gas separations [15]. $Cu_3(BTC)_2$ membranes prepared by thermal spray seeding and secondary growth method on polyvinylidene fluoride (PVDF) membranes were used for gas (e.g. H_2, CO_2, CH_4 and N_2) separations [16,17]. ZIF-8 on PSF support and polyamide/ZIF-8 nanocomposite membrane were studied for rejection of salt, phenol, dye dissolved in water and alcohol [11,18,19].

Pharmaceutical compounds are not completely assimilated by humans and animals during treatment. These compounds and their degradation products are continuously discharged in the aquatic environment mostly via domestic wastewater effluents. Most water treatment plants are not fully designed to eliminate such trace organic contaminants [20]. Intake of such compounds has adverse effects on human and animal health, as these are biologically persistent compounds [21]. NF/RO has been found to be effective in removing most of the organic and inorganic compounds and microorganisms in raw water [20–26]. However, retention of many pharmaceutical products by NF is much lower than predicted by size exclusion mechanism [27]. So, tighter NF is required for higher retention of pharmaceutical compounds [28].

The present study will thus report the preparation of ZIF-8 based TFC-NF mixed-matrix membranes and examine its first application for separation of pharmaceutical compounds from aqueous streams. TFC polyamide composite membranes were synthesized by interfacial polymerization with ZIF-8. Two different structures were prepared and characterized (i) PSF support membranes with ZIF-8 and polyamide (PA) separation layer, and (ii) layer-by layer (LBL) polyamide/ZIF-8 nanocomposite membrane on top of PSF support. The membranes were studied for the rejection of $MgSO_4$ and acetaminophen solution in water. The morphology of the membranes and their solute retention capacity were investigated.

2. Materials and methodology

2.1. Materials

Zinc nitrate hexahydrate [$Zn(NO_3)_2{\cdot}6H_2O$], 2-methylimidazole (H-MeIM), Acetaminophen, N-Methyl-2-Pyrrolidone (NMP), Trimesoyl chloride (TMC), M-phenylene diamine (MPD), Triethylamine (TEA), Sodium dodecyl sulfate (SDS) were purchased from Sigma Aldrich, Mumbai, India. Polysulfone (PSF) 1700 was purchased from Udel Solvay, India. Potassium ferricyanide, Ferric chloride and Magnesium sulphate ($MgSO_4$) were obtained from Qualigens, Mumbai, India. Methanol was procured from Fisher Scientific, India, and n-Hexane from Loba Chemie, Mumbai, India. All the chemicals were of analytical grade and were used as received. Non-woven polypropylene/polyethylene fabric was purchased from Novatexx 2471 from Freudenberg, Germany.

2.2. ZIF-8 synthesis

$Zn(NO_3)_2{\cdot}6H_2O$ (1.17 g) was dissolved in 8 g deionized (DI) water as solution A. Solution B was prepared by dissolving 22.70 g of H-MeIM in 80 g of DI water. Solution A was then added in solution B under stirring. The operation was carried out at room temperature (25 ± 2 °C). The synthesis mixture turned milky almost instantly after the two solutions were mixed. After stirring for 24 h, the product was collected by centrifugation at 7000 rpm for 20 min. The supernatant was discarded and the residue was washed with DI water several times. The product was dried at 100 °C overnight followed by vacuum oven drying for 8 h at 100 °C.

2.3. Membrane synthesis

PSF support membranes were prepared by phase inversion technique. PSF was dried in air oven overnight at 110 °C. Different compositions of PSF (14, 16, 18, 20, 22, and 24 wt%) were dissolved in NMP (as solvent) for 24 h at room temperature. The solution was cast on a non-woven polypropylene support using automatic film applicator and immediately the ensemble was immersed in the coagulation bath (for solvent and non-solvent exchange). The bath contained tap water (as non-solvent) at room temperature. After 10 min the membrane was dipped in another bath of tap water for 2 h and stored in distilled water in a refrigerator for further use. Films were cast at constant speed of 77 mm/s at 200 μm wet thickness.

A thin PA layer was synthesized on top of the PSF support via interfacial polymerization (IP). It involves the chemical reaction between the monomers MPD in aqueous solution and TMC in n-hexane. A PSF support layer was impregnated for 5 min in a solution of 2% (w/v) MPD, 2% (w/v) TEA and 0.1% (w/v) SDS in water. Then the excess solution was removed from the PSF membrane using a rubbery roller. After 1 min, a solution of 0.1% (w/v) TMC in n-hexane was poured gently on the impregnated support layer. The hexane solution was drained off after 1 min of polymerization and the synthesized TFC membranes were dried at room temperature for 5 min. Post treatment was done by placing the membranes for 10 min in an oven at 50 °C. Finally the membranes were stored in distilled water in the dark. The membranes were named as TFC-PSF 14% or TFC-PSF 20% i.e. thin film composite membrane prepared on 14 wt% or 20 wt% polysulfone support membrane respectively.

PSF support with ZIF-8 containing PA membranes were prepared via IP method. PSF support was coated with MPD/TEA/SDS aqueous solution. The excess solution was removed using rubber roller. The membrane was immersed in ZIF-8 TMC/hexane solutions of different content of ZIF-8 (0.02, 0.04, 0.06, 0.08, 0.1 g/100 mL) for 1 min. The membrane was rinsed with hexane and dried at room temperature (27 ± 2 °C), followed by drying in air oven and storage in DI water. The experiments were done within 24 h.

ZIF-8 suspension was prepared by mixing $Zn(NO_3)_2{\cdot}6H_2O$ solution (10 g) in 200 mL of methanol and 100 mL of DI water. H-MeIM (30 g) solution was prepared in 200 mL of methanol. The solutions were mixed for 30 min. A PSF UF membrane stuck on a polytetrafluoroethylene plate was immersed in the ZIF-8 suspension for 16 h. Then, the wet membrane was extensively washed with water and methanol to remove unreacted reagents. This was followed by drying the obtained membranes at 60 °C for 2 h to produce a modified supported membrane through in situ growth procedure; this process was repeated 4 times. PA selective layer was fabricated on a UF membrane through IP as discussed above. The wet membrane was dried at room temperature and then cured at 60 °C for 2 min to obtain PA/ZIF-8 layer by layer (LBL) membrane. The membrane was washed several times with water and then stored in DI water for further use.

2.4. Analytical method

Acetaminophen (0.01 g) was first dissolved in methanol (15 mL) and then the volume was made-up with distilled water (100 mL) to prepare a stock solution of 0.1 g/L. The stock solution was stored in