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Acrylonitrile butadiene styrene/chitosan blend membranes: Preparation, characterization and performance for the separation of heavy metals

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ABSTRACT

In the present work, an attempt has been made to prepare new blend membranes with different compositions of acrylonitrile butadiene styrene (ABS) and chitosan (CHS) on polyethersulfone (PES) substrate membrane. The new membranes are characterized using, FTIR–ATR, XRD, SEM, EDXA, TGA and swelling behavior. These membranes are used to separate mercury and sodium ions from aqueous solutions at different operating conditions. The results showed that the maximum rejections of mercury and sodium ions are 96.25% and 89.74% for ABS membrane, respectively, for 5 ppm feed concentration and 16 L/min feed flow rate. CS membrane (CHS:ABS = 100:0) gave highest permeate volume flux among all the blended membranes.

1. Introduction

Mercury and its compounds have harmful effects on human physiology and other biological systems when they are found above the tolerance level. Mercury, being a very toxic heavy metal, affects the environment adversely and due to this reason it is very important from environmental pollution and management point of view. The CPCB limit for mercury is 1 $\mu g\,L^{-1}$ for drinking water and 5 $\mu g\,L^{-1}$ for wastewater discharge [1].

Due to the excellent chemical and mechanical properties of polyethersulfone (PES), it is widely used for the preparation of the membranes, especially ultrafiltration and reverse osmosis membranes. But because of its hydrophobic nature, the application of PES membrane was limited. Therefore, there is a need to introduce hydrophilic group to increase the water permeation rate when aqueous solutions are used.

By using blending, one may get the advantage of candidate polymer into a new high performance blend polymer product [2,3]. Polymer blends are investigated because of their simplicity and their efficiency in developing new materials. Many nanofiltration membranes, prepared by blending/crosslinking, are reported in literature [4–7]. Modification of PES membrane surface can be achieved by physical adsorption (i.e., coating) of blended polymer onto its surface.

Chitosan (CHS), which is the deacetylated form of biopolymer chitin, the second most abundantly available polymer in nature after cellulose, is an extremely hydrophilic material. Presence of reactive amino and hydroxyl groups in the chitosan is responsible for the hydrophilicity. Hence, coating of CHS to the PES membrane enhances the hydrophilicity and permeation rate of PES membrane [2]. But separation/rejection capability of a solute may be decreased with the use of hydrophilic group.

Therefore, to increase the separation/rejection of metal ions another polymer acrylonitrile butadiene styrene (ABS) is introduced to the PES membrane. ABS is a commercial material with relatively low cost and good mechanical properties. ABS is a mixture of styrene, butadiene and acrylonitrile. Among them styrene, and butadiene have a hydrophobic nature and acrylonitrile has a hydrophilic nature. ABS also provides strength, rigidity and toughness. Hence, ABS is chosen as a polymer for modification of the properties of PES membrane [3].

The main aim of the present work is to prepare new blend membranes by using polymer blend (CHS and ABS) with glutaraldehyde as a crosslinking agent on a PES ultrafiltration substrate membrane. The characterization of the resulting membranes is investigated with the help of Fourier transform infrared spectroscopy–attenuated total reflectance (FTIR–ATR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA), thermogravimetric analysis (TGA) and swelling behavior. Experiments are performed with these

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newly prepared membranes to investigate membrane permeability, effect of applied pressure and feed concentration on permeate flux and observed rejection of mercury and sodium ions from synthetic aqueous solution sodium sulfate–water, sodium chloride–water, mercury sulfate–water and mercury chloride–water systems.

2. Materials and methods

2.1. Materials

The main materials used are PES–UF 30 kD (Permionics, Vadodara, India), chitosan in the powder form (M/S. Marine Chemicals, Cochin, Kerala, India), with mean molecular mass of 1.25×10^5 and degree of acetylation 85%, acrylonitrile butadiene styrene (National Chemicals, Vadodara, India), glutaraldehyde solution 25% (Merck, India). Distilled water of pH 5.9 ± 0.2, conductivity 1.0 μS/cm (Millipore, Elix, Bangalore, India) is used throughout the experiments.

2.2. Membrane preparation

CHS solution is prepared by dissolving 15 g CHS in 85 g (2 wt.%) acetic acid. The solution is stirred at 1000 rpm (REMI model-R 24, India) for 12 h to get the homogeneous polymer mixture. The resultant homogeneous mixture is transferred to an air tight conical flask and kept for 24 h in a refrigerator for the removal of entrapped air bubbles. The same procedure is repeated for the preparation of ABS solution in tetrahydrofuran.

2.2.1. Preparation of polymer blend

CHS and ABS polymer solutions in varying proportions are mixed by continuous agitation in order to obtain homogeneous polymer blend solutions. An appropriate amount (0.25 wt.%) of glutaraldehyde (GA) solution, as a crosslinking agent, is also added in polymer blend solution during agitation. Then the prepared resultant homogeneous solution is kept in a refrigerator for overnight for the removal of any entrapped air bubbles. Varying proportions of blended membranes (CHS and ABS polymers) are given new notation (see Table 1).

2.2.2. Casting of blend polymer on PES membrane

PES–UF membranes are used as substrate membranes for the preparation of new blend membranes. PES–UF membrane has a MWCO of 30 kDa, and withstands pressure up to 2 MPa, and also capable of withstanding pH in the range of 2–13. PES membrane has three layers; the first layer is a 5–20 μm polyethersulfone polymer layer that does the actual rejection. The second layer is made of polysulfone of about 50 μm thickness. The third layer, used to bear resistance and strength, is made of polyester with a thickness of about 150 μm. PES membranes (substrate membranes) are kept in distilled water overnight and before casting the polymer blend solution on substrate membranes distilled water is wiped with filter paper. After that, the homogeneous polymer blend solution of ABS and CHS is casted on substrate membrane by using a doctor blade with approximately equal thickness and allowed it for natural solvent evaporation at room temperature. The resultant membranes are kept in the vacuum oven for about 4–5 h to remove the residual traces of solvent. All the newly prepared blend membranes are stored in air tight polyethylene bags with 0.1% sodium metabisulfate solution and characterized within 2–3 days of preparation.

Table 1
Notations of different blend membrane along with composition.

Blending (CHS:ABS)	Membrane
100:0	CS
75:25	CA25
25:75	CA75
0:100	ABS

2.3. Characterization of membranes

2.3.1. FTIR–ATR

The FTIR–ATR spectra are obtained for substrate and blend membranes using GX 2000 FTIR spectrometer (PerkinElmer).

2.3.2. XRD

In order to observe the molecular packing of the blend membranes, X-ray diffraction (Xpert MPD, Philips, Holland) method is used. XRD curves of the membranes are obtained by using an Iso-Debyeflex X-ray powder diffractometer having monochromatic radiation of α-rays emitted by Cu at a wave length of 1.54 Å.

2.3.3. SEM and EDXA

Top surface and cross-section views of the substrate membrane (PES–UF) and the new blend membranes are characterized by using SEM analysis and chemical composition of the substrate and blended membranes are analyzed by EDXA method (ESTM TMP + EDXA, Philips, Holland). For both the analysis, substrate and blend membranes are cut into pieces of various sizes and wiped with filter paper. These pieces are dipped into liquid nitrogen for 20–30 s and frozen. The frozen pieces of the substrate and blended membranes are broken and kept in a desiccator till they are used for SEM and EDXA analysis.

2.3.4. TGA

TGA analysis (TGA-7, PerkinElmer, Norwalk, CT) is used to investigate the loss of water from membrane material and degradation of membrane material during heating. The temperature range used is from 30 to 500 °C, and heating rate employed is at 10 °C/min. For flushing purpose nitrogen gas is used at the rate of 20 mL/min.

2.3.5. Measurement of swelling behavior

The dry blend membranes are weighed periodically after carefully wiping their surfaces with a filter paper. Measurements are carried out in water at 28 °C. The swelling ratio (SR) to these samples were calculated by using the Eq. (1)

$$\%\,\text{swelling ratio} = ([W_s - W_d]/W_d) \times 100 \quad (1)$$

where, W_d is the weight of the dry membrane and W_s is the weight of the membrane swollen in the solution at time t.

2.4. Experimental procedure

Appropriate amounts of sodium and mercury salts are added to distilled water to prepare different feed concentration solutions. Filtration experiments are carried out using a Perma®-pilot scale membrane system (Permionics, Vadodara, India). The experimental set-up and the details of the same are available elsewhere [8,9]. Experiments are performed with different blend membranes prepared from CHS and ABS. The effective membrane surface area is 150 cm^2 (length 15 cm and width 10 cm). It is assumed that the 1 mm thin channel passage in the membrane test cell and the high cross-flow feed rates used in the experimentation will enable the system in controlling the concentration polarization up to some extent. Before performing the experiments for the rejection