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Synthesis, characterization, permeation and antibacterial properties of cellulose acetate/polyethylene glycol membranes modified with chitosan

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HIGHLIGHTS

- 2-stage phase inversion protocol is devised for synthesis of asymmetric membranes.
- A biopolymer (chitosan) is used as an additive.
- Salt rejection, membrane hydraulic resistance and bacterial tolerance are improved.
- Nodules and interstices spaces are observed in AFM images.
- Environmentally benign membranes are fabricated successfully.

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ABSTRACT

In this work, a number of cellulose acetate/polyethylene glycol-600 membranes, with different ratios were prepared by 2-stage phase inversion protocol. The permeation properties were studied by subjecting membranes in indigenously fabricated reverse osmosis plant. The flux and salt rejection of membranes were determined. The membrane with highest salt rejection was selected for modification with chitosan. The modified membranes were characterized for their compositional analysis, surface roughness, surface morphology, permeation properties, membrane hydraulic resistance and antibacterial activity. The presence of functional group was determined by FTIR spectra. Chitosan was found to significantly enhance the salt rejection and membrane hydraulic resistance. All modified membranes exhibited remarkable antibacterial properties. The varying nature of nodules and interstices spaces was observed in the images obtained by the atomic forced microscopy. The asymmetric surface morphology of membranes was elucidated from the scanning electron microscope. The synthesis of cellulose acetate membrane, doped with polyethylene glycol and modified with chitosan, provides a convenient access towards the development of sustainable chemistry.

1. Introduction

Since the inception of life on earth, freshwater has been considered as an elixir of life [1–3]. Unfortunately, the reservoirs of freshwater are continuously beetling off due to economic expansion and climatic changes. Growing global water scarcity proves to be the Achilles' heel for the economy of a country [4–6]. Therefore, there is an urgent need to overcome the demand of fresh water by developing additional water sources [7]. Solutions like water conservation, construction of new dams or water transport are insufficient to cope with increasing demand. There is no silver bullet for resolving water scarcity issue, however, in order to tap this seemingly boundless problem, desalination, has been formulated as a significant solution to overcome the shortage of fresh water [8–10]. This process enables to access the unlimited water resources of the oceans, which can be converted into drinking water [11–13].

Desalination processes can be further split into two primary categories: (i) membrane processes and (ii) thermal processes [14]. Membrane processes are gaining more fame as they are energy efficient and environment friendly [15,16]. A number of membrane based desalination techniques have been developed including capacitive deionization, membrane distillation, electro-dialysis, reverse osmosis and forward osmosis. Among all of these techniques, reverse osmosis (RO) is a most frequently used one and is believed to play a leading role in

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the years to come [17]. The multiple advantages offered by RO plants involve low energy consumption, cost reduction, expedient operation, eco-friendly process and elevated recovery rate.

Polymeric membranes are used in a large scale in RO plants. These membranes are synthesized by a phase inversion protocol. This versatile technique is used to obtain membranes with a variety of morphologies, ranging from enormously very porous structures to dense membranes [18]. The process of phase inversion involves several conceptually different methods such as diffusion-induced phase separation, vapor-phase precipitation, phase inversion by controlled evaporation and thermal-induced phase separation (TIPS). These methods involve complex multi-component mass transfer except thermal-induced phase separation which primarily depends on heat transfer [19–21].

The performance of a membrane is notably influenced by its constituents, which affect many properties, in particular hydrophilicity, surface charge, permissible pH range and chlorine tolerance limit [22]. Several polymers have been known for a long time to prepare membranes, nevertheless cellulose acetate (CA) membranes are well-liked due to their superior transport characteristics, low protein adsorption, excellent water affinity, apt mechanical strength, excellent film-forming property, high hydrophilicity with desalting nature and easy availability [23].

Despite all these advantages, cellulosic membranes are highly susceptible to microbial attack and self-sterilized membrane surface approach is currently seeing increasing research interest. Readily available antimicrobial agents like silver oxide (AgO), zinc oxide (ZnO), titanium oxide (TiO_2), fullerenes and carbon nanotubes have been incorporated in the membranes to prevent microbial attack [24]. The application of a biocide within polymeric matrix has opened new frontiers in the development of self-sterilized surface. Recently, attempts have been made to render membrane surfaces as an antimicrobial by graft co-polymerization and interfacial polycondensation of amine-containing polymers, which are considered as potentially antimicrobial agents [25, 26].

In this paper, a detailed study towards the synthesis of environmentally benign membranes is reported. These membranes were prepared by using different ratios of cellulose acetate, polyethylene glycol and chitosan, an antimicrobial biopolymer. A 2-stage phase-inversion protocol was devised involving thermal-induced phase inversion followed by a controlled evaporation procedure. The prepared membranes were characterized for their permeation activity, compositional analysis, antimicrobial properties, surface morphologies and their efficacy was evaluated using reverse osmosis process.

2. Materials

Cellulose acetate (CA, M_w 30,000 and acetyl content 39%), polyethylene glycol-600 (PEG) and acetone were supplied by BDH laboratories supplies Poole, England and formic acid was purchased from Merck (England). Chitosan (CS, extracted from crab shell with M_w 85,000–90,000 and the degree of deacetylation 75%) was provided by the Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, Islamabad, Pakistan [27]. All chemicals and solvents were used as received.

2.1. Preparation of doped solutions

10 g of CA was dissolved in 80 mL of acetone with constant stirring at 80 °C for 2 h. To this homogenous solution, 10 g of PEG was added with regular stirring at 80 °C for 6 h. The viscous and clear solution was obtained which was termed as a blended doped Solution, CA/PEG-1 [28]. Different amounts of CA (12, 14 and 16 g) and PEG (8, 6 and 4 g) were used to prepare three additional doped solutions which were labeled as CA/PEG-2, CA/PEG-3 and CA/PEG-4 respectively. The casting solutions were allowed to cool down to room temperature (25 °C) and kept for 24 h in a sealed flask to remove micro bubbles formed in the solution.

2.2. Casting of membranes

The doped solutions were spread slowly on a glass plate ensuring uniform thickness by a micrometer adjustable film applicator (Ref: 1117/300 Sheen instruments). The temperature of the casted membranes was lowered to 0 °C to induce thermally induce phase separation (TIPS) which caused the formation of dense asymmetric structure. It was followed by precipitation under controlled evaporation by increasing temperature up to 60 °C [29]. The skinned membranes were obtained [30–32] which were carefully removed from the glass plates by using a sharp knife. The thickness of the resulting membranes was measured to be in the range of 0.05–0.2 mm. These membranes were evaluated for the permeation performance and CA/PEG-4 membrane was selected for further modification by incorporating antimicrobial biopolymer, chitosan (CS) and termed as CPC1–CPC5.

2.3. Modification of doped solutions

Chitosan (0.5–2.5%, w/v) was dissolved in formic acid (10 mL) and added to the CA/PEG-4 blended dope solution with constant stirring for 2 h at 80 °C. The membranes (CPC–CPC5) were casted and dried as mentioned previously (Section 2.2).

2.4. Experimental set up of reverse osmosis plant

The permeation experiments were carried out in the RO experimental rig using a plate and frame membrane module. The process flow diagram for plate and frame membrane module is shown in Fig. 1. It consists of feed tank of 10 L capacity. The temperature of the feed solution was indicated and controlled by a thermocouple and controller setup. The feed was circulated using a circulation pump of 1 kW with feed flow of 2500 L/min. The effective membrane area in contact with the feed was 0.018 m^2. The permeate was collected from the sample points, provided after the membrane module. The feed tank was filled with saline solution with conductance of 20 mS. The pressure during the process was increased from 10,000 to 150,000 Pa. Feed temperature was kept at 30 °C during the process. The permeation process was continued till it attained a steady state.

3. Characterization

The prepared membranes were subjected to various characterization techniques which are described as below.

3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of membranes were recorded by using Shimadzu IR Prestige-21 equipped with Horizontal Attenuated Total Reflectance (HATR) kit and in the transmission mode at wave number range 4000–400 cm^{-1}. The experiments were run with air as the background. For each spectrum 100 scans were accumulated with a resolution of 4 cm^{-1}.

3.2. Scanning electron microscopy (SEM)

The morphologies and structures of the membranes were characterized by a JSM-6480, Jeol field emission scanning electron microscope. The membranes were cut into small pieces and placed on stub and kept in a specific chamber in a vacuum. The electron beams were sputtered on sample and images of membranes on varying resolutions were observed.