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Development and performance characteristics of silane crosslinked poly(vinyl alcohol)/chitosan membranes for reverse osmosis

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ABSTRACT

Novel thin film poly(vinyl alcohol)/chitosan (PVA/CS) based reverse osmosis membranes infused with silane crosslinked tetraethylorthosilicate (TEOS) were prepared by dissolution casting methodology. The performance characteristics and the scope of the reverse osmosis membranes were explicated by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analyzer (TGA), differential scanning calorimetery (DSC), scanning electron microscopy (SEM), contact angle, X-ray diffraction (XRD) and reverse osmosis (RO) permeation tests which determined the functional groups and network of covalent crosslinks, thermal properties, morphology, hydrophilicity, structural investigation and RO properties, respectively. It was found that the membrane surface became smoother, more hydrophilic, with improved thermal stability, increased salt rejection and good permeation flux after the appropriate infusion of TEOS. The crosslinked membranes showed more hydrophilicity compared to the uncrosslinked PVCS membrane. The SEM micrographs of membranes revealed dense structure with no mottled surfaces. PVCS-4 showed an optimal flux of 1.84 L/m^{2}h and 80% salt rejection that confirmed the selective interaction of TEOS molecules with PVA/CS polymer backbone compared to the pristine (PVCS) membrane. The antibacterial properties of the membranes showed the inhibition of the growth of *Escherichia coli* successfully.

Introduction

The availability of transportable and sanitized drinking water is constantly lessening in this planet with the growth of human population especially in third world countries. Several proposals are in progress to attain the feasible engineering and scientific solutions for the availability of portable drinking water through various processes including conservation, recycling and desalination [1]. Liquid separation practices impart a major role in chemical and other techniques which make them an appealing field for research and development [2]. Desalination is one of the major and striking separation methods for hygienic water accessibility. The membrane based desalination methods can be classified according to the pore size of membrane and rejection mechanism such as: electrodialysis, membrane distillation, ultrafiltration, microfiltration, nanofiltration and reverse osmosis [3]. In desalination process, RO is a prevailing membrane technology that separates pure water from saline or impure water. The membrane rejects the salt ions from feed solution, allowing only pure water to pass [4]. The water scarceness crises is predicted to become more and more severe in the coming decades [5]. Thus, there is a dire need to sort out the solution for effectual increase in the amount of drinkable water by developing additional water sources. Sea water desalination is one of the most important techniques to relieve this issue. [6,7]. With the increased water requirement and reduced accessibility of conventional water reservoirs, pressure dependent membrane processes such as RO and nanofiltration have become significant substitute for water treatment technologies to enhance water supply from alternate resources [8]. To achieve the goal of water recycling and reuse, RO membranes are used as waste water treatment, for the removal of inorganic ions as well as small neutral molecules [9]. The polymer membranes impart a key role in membrane based water treatment process and find out the economic and technological efficiency of above said processes [10].

PVA is extensively employed for the synthesis of composites and blends with many renewable and natural polymers. It is a

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water soluble synthetic polymer having biodegradability, good mechanical properties, film forming and excellent chemical resistance [11]. Though, PVA needs some modification to control the swelling of membranes in aqueous solutions. Some modification procedures, such as crosslinking, blending, etc. have been employed by many researchers, and water insolubility of PVA membranes has been enhanced significantly and swelling is reduced [12].

Chitosan (CS), a derivative of biopolymer chitin, is one of the mostly used polysaccharide. Its wide technological applications are due to its distinct biological and physical properties like low toxicity, biodegradability, hemostatic potential and relatively facile modification [13–15]. It is a natural hydrophilic biopolymer and has been used as a membrane material for RO membranes [16]. It is preferred due to its natural occurrence, high abundance, chemical resistance, good membrane forming characteristics, adequate mechanical strength and ease of handling [17]. Polymer blending is an effective route to prepare the membranes with a lot of desired properties. Proper blending can enhance the separation performance by reducing the polymer chains mobility through intermolecular bonding [18]. PVA/CS blended membranes hold the inherent characteristics of both PVA and CS. PVA has a semi-crystalline structure while CS has large free volume with less compact structure. Therefore, blending of PVA with CS resulted in decreasing the crystallinity with improvement in flux [12]. PVA membranes are frequently used for dehydration of organics with good flux but poor selectivity due to membrane swelling. To improve the membrane performance, different membrane modification techniques like crosslinking, blending and introducing various chemical agents in main polymer chains are used. Crosslinking is widely used to improve the physicochemical properties of membranes like mechanical and thermal stability, crystallinity, etc. [19].

In this work, we have fabricated the crosslinked hydrophilic PVA/CS membranes. The use of chitosan/PVA/TEOS membranes as a potential source for RO applications has not been studied before which was the novelty of this work. FTIR, thermal analysis, SEM, XRD and antibacterial tests were performed. The RO tests were executed on dead end filtration system and evaluated the desalination performance of a salt solution using these membranes.

Experimental

Materials

Chitosan with average molecular weight 1–3 × 10^5 g/mol was obtained from ACROS Organics. PVA (M_w = 1.3 × 10^5 g/mol) and tetraethylorthosilicate (TEOS) were bought from Sigma Aldrich. Acetic acid, (CH_3COOH), was provided by Merck Co. (Darmstadt, Germany). Ethanol was procured from BDH chemicals Ltd. All the chemicals were of analytical grade and used without any treatment.

Method

Chitosan (1 g) was dissolved in 30 mL of 2% aqueous solution of acetic acid under constant stirring at 65 °C for 2 h. PVA (4 g) was dissolved in 50 mL distilled water at 90 °C. The two solutions were blended under constant stirring at 65 °C for 2 h so that a clear solution was obtained. To study the effect of crosslinker, different concentrations (Table 1) of TEOS (in 5 mL ethanol to get silanol) was added drop wise in each solution. After 4 h blending, the blended solution was placed in vacuum to remove bubbles and finally poured on petri dishes. After drying, the films were dried under vacuum. The proposed interactions in the developed PVA/CS/TEOS membrane are given in Scheme 1.

Table 1
Codes for membrane samples with their compositions. Q8

Sample code	Poly (vinyl alcohol) (wt%)	Chitosan (wt%)	TEOS (μL)
PVCS	80	20	0
PVCS-1	80	20	100
PVCS-2	80	20	200
PVCS-3	80	20	300
PVCS-4	80	20	400
PVCS-5	80	20	500

Fourier transform infrared spectroscopy

The FTIR spectra of membranes were recorded using Fourier transform infrared spectrophotometer (Shimadzu Scientific Instruments, IRPrestige-21, Japan), in the range of 4000–400 cm^{-1} using attenuated total reflectance (ATR) with ZnSe crystal. The resolution was 4 cm^{-1}. The air background of the instrument was run before each sample of membrane at 200 scans per spectrum.

Thermal analysis

Differential scanning calorimetry/thermal degradation measurements of the PVA/CS blended membrane samples were investigated using TA instruments SDTQ600 thermogravimetric analyzer at a temperature ramp of 20 °C/min from 30 to 600 °C. Nitrogen flow was set at 100 mL/min to provide inert atmosphere during the analysis. The moisture content of the membranes was determined from the weight loss corresponding to the first step from the curves.

Scanning electron microscopy

The cross-sectional and surface morphologies of the PVA/CS blended membranes were studied by scanning electron microscopy JEOL JSM-6480. The small pieces of membranes were placed in vacuum chamber and the electron beams were sputtered on membranes and images were examined on different magnifications.

Water content

For the swelling experiments, the crosslinked PVCS membranes were dried at 40 °C under vacuum for 6 h and weighed. The samples were immersed in distilled water for 72 h at 25 °C. The constant weight experiments were used to ensure that the swollen membranes reached the equilibrium state. To remove any excess surface water the swollen membranes were blotted carefully with tissue paper, and the weight of the swollen membranes was determined using mass balance. The water content of the membrane was calculated using the Eq. (1): Q4

$$X(\%) = \frac{W_S - W_d}{W_d} \times 100 \quad (1)$$

where W_s is the weight of swelled membrane (g) and W_d is the weight of the dried membrane (g).

Degradation studies

In order to assess the degradation profile of PVA-CS membranes, the samples were soaked in buffer solutions of different pH (3, 7.4 and 9) for seven days. The membranes were removed and

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