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Preparation and characterization study of PPEES/chitosan composite membrane crosslinked with tripolyphosphate

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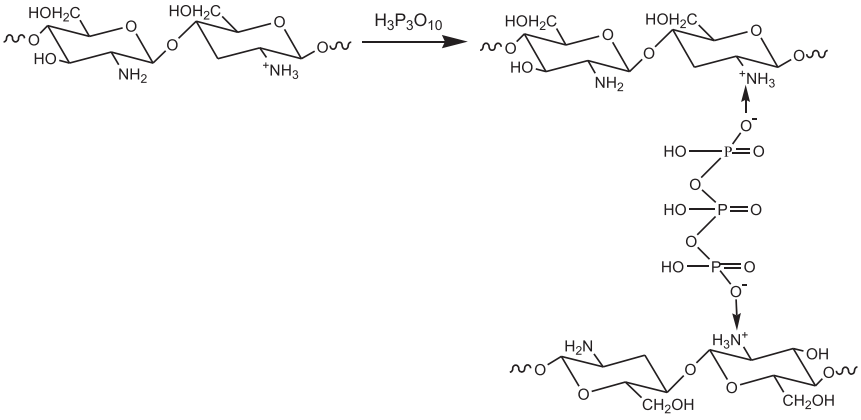
HIGHLIGHTS

- Chitosan supported on PPEES was prepared.
- Chitosan layer was ionically crosslinked with TPP.
- Higher crosslinking density was observed in acidic media.
- Membranes showed rejection of 55% and 21% towards $MgSO_4$ and NaCl respectively.
- Flux recovery ratio of 73% was observed.

GRAPHICAL ABSTRACT

A novel composite membrane was prepared using chitosan (CH) as the active layer supported on Poly (1,4-phenylene ether ether sulfone) PPEES. The CH layer was ionically crosslinked with sodium tripolyphosphate (TPP). The membranes showed rejection up to 55% and 21% towards $MgSO_4$ and NaCl respectively at pH = 5 and exhibited a flux recovery ratio of 73%.



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ABSTRACT

A novel composite membrane was prepared using chitosan (CH) as the active layer supported on a Poly(1,4-phenylene ether ether sulfone) (PPEES) membrane. The chitosan layer was ionically cross linked with sodium tripolyphosphate (TPP). The composite nature of PPEES/CH membranes was confirmed by Scanning Electron Microscopy (SEM). Infrared (IR) spectroscopy results and SEM–EDX analysis confirmed the crosslinking of chitosan surface with TPP. The membranes exhibited higher crosslinking density in acidic media than in basic media. The changes in the hydrophobic nature of PPEES membrane surface due to deposition of chitosan active layer followed by crosslinking were studied by their contact angle measurement, water flux and water uptake studies. The membranes showed rejection up to 55% and 21% towards $MgSO_4$ and NaCl respectively at pH = 5 and a flux recovery ratio of 73%.

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1. Introduction

Incessant efforts are in progress in the membrane technology field to make water treatment an environmentally benign process. In this direction, use of biodegradable and biocompatible materials as membrane material serves as an important criterion to be fulfilled. Chitosan is

Abbreviations: BSA, bovine serum albumin; CH, chitosan; DD, degree of deacetylation; EDX, energy dispersive X-ray spectroscopy; IR, infrared radiation; $MgSO_4$, magnesium sulfate; M_w, average molecular weight; NaCl, sodium chloride; NMP, N-methyl pyrrolidone; PPEES, poly (1,4-phenylene ether ether sulfone); PWF, pure water flux; SEM, scanning electron microscopy; TPP, sodium tripolyphosphate.

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one such candidate which has been a matter of growing interest in past years due to its non-toxicity, biodegradability, antimicrobial activity and biocompatibility [1–4]. Chitosan is a heteropolysaccharide obtained by deacetylation of chitin which is the second most natural polymer after cellulose. So far the use of chitosan has been widely explored in the preparation of adsorbent membranes, and pervaporation membranes and for drug delivery applications [5,6]. However the potential of chitosan in the preparation of thin film composite membrane hasn't been tested much since traditionally polyamides have dominated this area.

Chitosan with reactive functional groups in its backbone can be used in the preparation of composite membranes, provided their chemical stability is improved by crosslinking. In acidic media, the protonation of amine groups results in partial dissolution of the polymer, thus causing deterioration of the membrane material. Thus crosslinking becomes an important post-treatment process of chitosan membranes for it is known to improve their chemical stability and pore size distribution [7,8]. Data on the use of a number of crosslinking agents for chitosan are available in literature. Miao et al. prepared a nanofiltration composite membrane using sulfated chitosan which was subsequently crosslinked by glutaraldehyde [9]. The same group worked on the preparation of an N,O-carboxymethylchitosan composite membrane crosslinked with epichlorohydrin [10]. Musale and Kumar studied the sieving properties of chitosan/polyacrylonitrile membranes using glutaraldehyde as the crosslinking agent [11]. A positively charged nanofiltration membrane was prepared from quaternized chitosan by toluene diisocyanate crosslinking [12].

Crosslinking can be achieved by two mechanisms, either by chemical method or by ionic method. Ionic crosslinking is known to be the simpler method amongst the two which proceeds faster under mild conditions [13]. Crosslinking by glutaraldehyde, as reported in our earlier work [14] and epichlorohydrin [2] proceeds via covalent bond formation. However, these chemical crosslinking agents pose the prospect of inducing undesirable effects on human health. For example, glutaraldehyde is known to primarily affect the mucosal membranes of the eyes, nose and respiratory tract because of its toxicity [15]. Physical crosslinking by electrostatic interaction instead of chemical interaction thereby has an advantage, which avoids the possible toxicity of reagents. In this scenario, tripolyphosphate emerges as a very promising reagent.

Sodium tripolyphosphate (TPP) is a polyanion and can interact with cationic chitosan by electrostatic forces [16]. In acidic solutions, $-NH_2$ of chitosan molecule gets protonated to form NH_3^+ ion which interacts with the anionic tripolyphosphate by ionic interaction and is transformed into gel [17]. The ionotropic gelation is a very simple, mild and commonly used technique for the preparation of crosslinked chitosan beads, gels or films [18,19]. To our knowledge, chitosan composite membrane using TPP as crosslinking agent has not been reported so far.

In the current work, the use of sodium tripolyphosphate as crosslinking agent for the preparation of a chitosan thin film composite membrane was explored for the first time using PPEES as support membrane material. The properties of PPEES is known to be comparable to the most widely used polysulfone having good film forming ability, high glass transition temperature and chemical stability. The stability of the crosslinked PPEES/CH composite membranes in different pH solutions was analysed along with their hydrophilicity and rejection property.

2. Experimental

2.1. Materials

Chitosan (CH: Degree of deacetylation (DD) = 85%, M_w = 450,000 Da) was procured from Seafresh Industries, Bangkok-Thailand. PPEES and sodium tripolyphosphate (TPP) were obtained from Sigma Aldrich Co., N-methyl pyrrolidone (NMP) was obtained from Merck India, Ltd., and Bovine Serum Albumin (BSA) was procured from CDH Ltd. All the reagents were of analytical grade and were used without further purification.

2.2. Membrane preparation

2.2.1. Preparation of PPEES membrane

PPEES membrane was prepared as mentioned in our previous work [14]. Briefly, 20% (w/v) of PPEES solution was prepared in NMP. The homogeneous solution was first filtered and degassed before casting on a glass plate with the help of a finely polished glass rod. The membrane thus cast was immersed in a coagulation bath containing water as non-solvent. It was kept in distilled water for 24 h to ensure complete phase inversion.

2.2.2. Preparation of PPEES/CH membrane and its crosslinking

The casting solution of chitosan was prepared by dissolving 1 g of chitosan in 1% aqueous solution of acetic acid. The filtered chitosan solution was over-coated on a surface dried PPEES membrane and allowed to dry at room temperature. The dried membrane was further immersed in 1 M NaOH solution for 24 h in order to convert chitosan acetate into chitosan. The excess of solvents and NaOH was removed by washing the base treated membrane several times with distilled water. The active layer of chitosan supported on PPEES membrane was crosslinked using TPP as reported by Mayer and Kaplan [20]. Briefly, the PPEES/CH composite film was immersed in aqueous 1.3% (w/v) phosphate solution for 2 h at 4 °C. The pH of crosslinking bath was maintained at 5 by the addition of 1 M HCl. The crosslinked membranes were washed thoroughly with distilled water to ensure removal of surplus TPP solution. The membranes were then dried at room temperature and stored until further characterization. The structure of crossslinked chitosan molecule is represented in Fig. 1.

Another set of membrane was prepared without the addition of hydrochloric acid in TPP solution to study the effect of pH of crosslinking bath on the prepared membranes. The initial pH of TPP solution was found to be 9.2.

3. Characterization of PPEES/CH/TPP membranes

3.1. Morphology of the membrane and IR analysis

The crosslinking of chitosan layer by TPP and its chemical constitution were confirmed by the FTIR spectroscopic technique. The operating range of FTIR was from 4000 to 400 cm^{-1}. The morphology of the membrane was studied using SEM images recorded on the JEOL-6380LA Analytical SEM instrument. Prior to the surface observation, samples were mounted on a metallic base using double-sided carbon tape. SEM imaging was done by sputtering the sample with gold for conductivity. For cross-section images, the sample was first fractured in liquid nitrogen to achieve a clean cut.

3.2. Hydrophilic properties of the membrane

The hydrophilicity of the membrane was analysed in terms of its wettability and water uptake capacity. The wettability of the membrane was studied by measuring the contact angle of the water droplet with membrane surface using an FT-200 Dynamic contact angle analyser. Contact angle measurement is a direct indication of the membrane surface hydrophilicity.

The water uptake capacity of the membrane was studied to understand the bulk hydrophilicity of the membrane. The procedure for water uptake study has been mentioned elsewhere [21]. Since chitosan contained amine functionality, it was decided to study the water uptake capacity of crosslinked and uncrosslinked membranes in acidic and basic conditions. In this study, membranes were cut into size of 1 cm^2 and their dry weight was recorded following which they were

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