Surface and pore modification of tripolyphosphate-crosslinked chitosan/polyethersulfone composite nanofiltration membrane; characterization and performance evaluation

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Abstract—A PES-based composite nanofiltration membrane was prepared by spreading a thin layer of sodium tripolyphosphate (STPP)-modified chitosan (CS) on a PES membrane. Two approaches of modification were employed: coating, and injecting the chitosan solution into PES membrane by applying pressure. Physicochemical properties of the prepared membranes were characterized by FTIR-ATR, zeta potential, contact angle, AFM and FE-SEM methods. AFM images showed a denser and more compact surface for STPP-modified membranes compared to the unmodified one. The membranes prepared by the second approach illustrated favorable properties: the increase of both flux and rejection. Engaging of -NH2 groups in CS with polyanionic phosphate groups of STTP resulted in less availability of functional groups. Furthermore, denser and relatively higher positively charged surface could be the main reasons for higher rejection of membrane composed of 0.05 wt% STTP towards copper ions in comparison with other membranes. Furthermore, the presence of SO42- ions in the CuSO4 solution slightly changed the positive charge of the membrane surface, resulting in tangible variations in rejection. According to the Donnan exclusion theory, relative increase of the negative charge of the surface in the presence of the highest concentration of STTP caused less NaCl and CuSO4 rejection compared to the other STPP modified membranes.

Keywords: Polyethersulfone Membrane, Thin Film Composite, Chitosan, Sodium Tripolyphosphate, Metal Ions Removal

INTRODUCTION

As a remarkable and impressive separation technology, membrane processes have gained new importance in the separation and purification of water as well as recovery and pollution control in recent years [1-3]. Nanofiltration (NF) is fairly new pressure-driven membrane separation technology that has significantly grown in the world in the past few decades [4,5]. The membrane process based on NF technology has been widely employed in industrial water production, water softening, pharmaceuticals, chemicals, paper production, and wastewater treatment as well as seawater desalination [6,7].

With rapid industrial development such as mining operations, fertilizer industries and metallurg, a large amount of wastewater comprising heavy metals is evacuated into bodies of water [8]. Unlike some organic pollutants, heavy metals are not biodegradable, cannot be decomposed and tend to accumulate in living organisms. Heavy metal toxicity has detrimental effects on human physiology and ecological systems even at very low concentration [9]. So, choosing a suitable and efficient method for the removal of toxic heavy metals has become one of the major concerns in water treatment. Chemical precipitation, ion exchange, solvent extraction, adsorption, membrane filtration and electrochemical treatment are confi-
brane materials, pharmaceuticals and nutraceuticals. These properties allow the formation of stable ionic complexes by multivalent aqueous soluble poly-anions under gentle physiological conditions. Chitosan is a polycationic polymer which can interact with negatively charged species with low molecular weight such as triply-phosphate (TPP) through electrostatic forces creating ionic cross-linked networks. Sodium Tripolyphosphate (STPP) is a non-toxic poly-anion, usually recognized as pentasodium triphosphate (Na₅P₃O₁₀), which is a straight chain derivative of phosphoric acid [21].

The amine (-NH₂) and hydroxyl (-OH) groups in the polymer chain of chitosan act as coordination sites for heavy metal ions. Metal ions can attach to amino groups in chitosan with chelation mechanism or electrostatic attraction [22].

Several studies have been carried out on fabrication of chitosan nanofiltration membranes with various reagents. Boributh et al. fabricated a chitosan membrane using PVDF as substrate for reducing protein fouling [15]. The results confirmed good antifouling properties. Miao et al. created a novel kind of thin film composite (TFC) membrane based on sulfated chitosan (SCS) via the coating and cross-linking with epichlorohydrin (ECH) [4]. Shen et al. synthesized a composite membrane having chitosan as the active layer supported on poly(1,4-phenylene ether-ether-sulfone) (PPEES) membrane and glutaraldehyde as cross-linking agent [1]. In another work, the same authors prepared nanoporous chitosan membranes by PPEES as support membrane and sodium tripolyphosphate (TPP) as cross-linking agent in different pHs. The membranes showed higher crosslinking density in acidic media [21].

In this paper, we fabricated a type of modified chitosan-coated TFC nanofiltration membrane using a PES membrane as substrate membrane. To achieve the desired performance, CS-modified membranes were cross-linked by STPP. Nonporous chitosan membranes were prepared using two different approaches: coating and chitosan solution flowing through the surface and body of PES membrane [15]. The effect of STPP as cross-linking agent on the membrane properties such as water flux, rejection, membrane fouling resistance, hydrophilicity and pore size was examined and the results were discussed. SEM, AFM, zeta potential, contact angle and FTIR measurements were carried out to characterize the membranes. The effects of NF membrane operating conditions on the removal of heavy metal (copper) from aqueous solutions were also investigated in detail. Batch adsorption experiments were performed to study thermodynamics and kinetics of the adsorption.

**EXPERIMENTAL**

1. Materials

Polyethersulfone (PES, 58 kg/mol) in powder form was purchased from BASF Company (Germany) and was used for the formation of PES porous supports. Polyvinylpyrrolidone (PVP, 25 kg/mol) as pore former, poly (ethylene glycol) 600 (PEG, 600 g/mol), acrylic acid (AA), acetic acid, NaOH, sodium tripolyphosphate (STPP), ethanol and N, N-dimethylformamide (DMF) from Merck were utilized. Chitosan and Congo red and Safranin dyes for the evaluation of pore size of the membrane were purchased from Sigma-Aldrich Company. NaCl and CuSO₄ salts with high purity (Merck) were used for the assessment of ion rejections. Distilled water was used throughout the study. The chemical structure of PES, CS and STPP is depicted in Fig. S1.

2. Membrane Preparation

2-1. Preparation of PES Support

PES ultrafiltration membranes were prepared with phase inversion process through immersion precipitation technique. The casting solution for polyethersulfone support was prepared by dissolving 15 wt% PES in dimethylformamide (DMF) as solvent containing 5 wt% polyvinylpyrrolidone (PVP), 5 wt% polyethylene glycol (PEG 600) and 3 wt% acrylic acid (AA) by stirring for 4 h at 50 °C. Stirring was at 300 rpm. After the formation of a homogeneous solution, the dope solution was held at ambient temperature for 24 h to remove all remaining air bubbles. Then, the dope solution was cast on a non-woven polyester (with 80 μm thickness) using a film applicator at ambient temperature without evaporation. After coating, the support was immersed into a distilled water bath for around 24 h for removing most of the solvent and water-soluble polymer.

2-2. Fabrication of PES/CS Composite NF Membranes

To investigate the effect of different conditions on the properties of thin layers, we prepared two types of membranes as follows:

- **Approach 1**: Coating method. The PES support was clamped between two Teflon frames that were 0.7 cm high with 7.5×20 cm² inner cavity. The membranes were prepared by dissolving chitosan at different concentrations of 0.5 and 1.5 wt% in 2 wt% aqueous acetic acid solution at room temperature. The temperature was increased to 60 °C to ensure the chitosan was dissolved. Then, the obtained solution was poured on the top of PES support membrane and allowed to wet for 60 min at room temperature. The surface was rolled with a soft roller to remove any small bubbles produced during the wetting procedure. The process for the preparation of TFC membrane using CS and STPP is given by Fig. S2.

- **Approach 2**: The chitosan solution flowing through the surface and pores of PES substrate. Chitosan solution was injected into the support membrane under the pressure of 0.2 MPa. The preparation method consisted of two stages, each with equal time. The conditions were then changed to surface flow mode in which chitosan solution flowed without applying any pressure.

Different concentrations of CS solutions (0.5 and 1.5 wt%) were chosen to fabricate the membranes. Between these two concentrations, 1.5 wt% of CS was preferred because of showing better performance in comparison with lower concentration (more detail is discussed in section 3.1). The membranes prepared with approaches 1 and 2 were dried in an oven at 70 °C for 45 min. Then, the dried membranes were neutralized by NaOH solution (0.1 M in 50 vol% water-ethanol mixture) for 30 min to ensure all chitosan acetate was converted to chitosan. Then, the membranes were cleaned by 50 vol% ethanol solution for 10 min to remove the remaining NaOH and repel the osmotic crack and were then washed with DI water for 30 min eventually. Finally, the membranes were dried at 25 °C. For cross-linking, the prepared chitosan solutions were mixed with 0.05, 0.1, 0.2 and 0.5 wt% STPP. Table 1 represents the composition of obtained thin layer membranes ("M" refers to the membranes prepared in approach 1 and "T" refers to the membranes in another one).