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Preparation of modified polyethersulfone nanoporous membranes in the presence of sodium tripolyphosphate for color separation; characterization and antifouling properties

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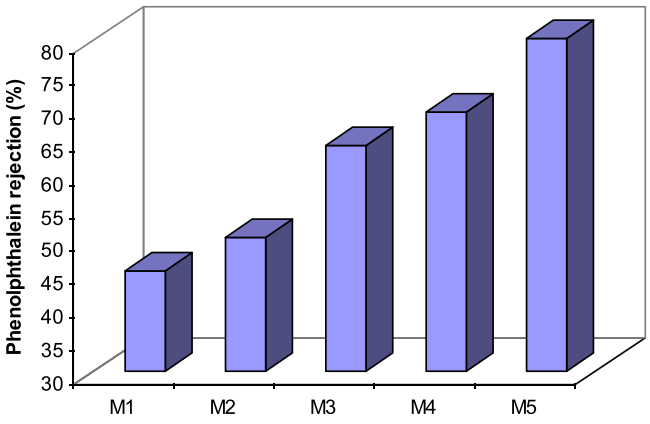
HIGHLIGHTS

- Changing the separation performance of the membranes by adding a multi-functional group salt
- Alteration in the surface properties and surface pore sizes of the membranes
- Increasing the color separation capability from 45 to near 80%
- Improving the antifouling properties of the modified membranes

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the effect of sodium tripolyphosphate (STPP) salt as an inorganic additive was investigated to show the obtained changes in the structure, separation performance, and antifouling properties of the nanoporous polyethersulfone (PES) membranes. Different concentrations of STPP (0.5, 1.0, 1.5 and 2.0 wt.%) were utilized. Some characterization methods like SEM, AFM, water contact angle, and zeta potential test were used to investigate the changes. According to the results, the phenolphthalein separation capability of the membranes increased from 45% to near 80%. In addition, the separation performance of the prepared membranes against methyl orange was over 70% which was increased to near 83% in the presence of STPP. The rejection capability of the neat PES membrane for Na_2SO_4 was 39% which significantly increased to near 74% for the membrane composed of 1.5 wt.% STPP. The flux recovery ratio (FRR), which refers to the antifouling property of the membranes, developed from 57% to near 94%. SEM and AFM images clearly showed that a dense and compressed skin layer was formed in the presence of STPP. On the other hand, the alteration in surface charge of the STPP-modified membranes improved the separation behavior of the prepared membranes.

1. Introduction

The methods of purification of waters and wastewaters can be generally classified into three groups: chemical, physical, and biological methods. Pressure driven membrane processes have found numerous

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applications in water treatment and wastewater purification [1]. The membrane separation process has been used in many applications such as pharmaceutical, chemical, paper, textile, industrial water production, wastewater treatment, water softening, and separation of compounds having different molecular weights. Many applicable polymers, such as polyethersulfone possess excellent mechanical as well as a high thermal stability, which make them ideal materials for membrane preparation. However, a main drawback for application of polyethersulfone membranes is hydrophobic property resulting in low flux. So, some researchers offer the hydrophilic polymers such as poly (vinyl alcohol), cellulose acetate, and polyacrylonitrile to investigate the separation processes of membranes [2–8]. However, these membranes did not exhibit good thermal and dimensional stability or chemical resistance.

Polymeric membranes have been used for a variety of industrial application, such as microfiltration, ultrafiltration, nanofiltration, reverse osmosis and gas separation [9]. Polyethersulfone (PES) with high mechanical, thermal and chemical resistance is classified as a high-Tg polymer and widely used in manufacturing asymmetric membranes [10,11]. PES has shown a favorable temperature resistance, wide pH tolerances and good resistance against chlorine and chemicals [12]. There are several ways to fabricate polymeric membranes, such as track etching, sintering, stretching and phase separation processes. Obtained morphology strongly depends on the properties of the materials and the process condition. A well-known procedure to fabricate membranes is the immersion precipitation process [13,14]. In this process an asymmetric structure is resulted, leading to a dense top layer and a porous sub layer. Addition of tiny amount of organic/inorganic additives into the dope solution shows the outstanding effects on morphology and performance of membranes [15–17]. Polyethyleneglycol (PEG) and polyvinylpyrrolidone (PVP) were largely used in casting solution to change the membrane morphology and performance [18–20]. The presence of these additives causes low fouling, high flux, selectivity, etc. [21–28].

In this study, sodium tripolyphosphate (STPP) as an inorganic salt and additive was used in the casting solution to investigate the effect of different concentrations of STPP on the performance and morphology of the PES membranes. Some characterization methods like AFM, SEM, zeta potential and water contact angle were utilized to show and investigate the changes in the membrane characteristics. A dead-end filtration cell was used to investigate the separation behavior and antifouling properties of the prepared membranes.

2. Experimental

2.1. Materials

Polyethersulfone (PES Ultrason E6020P with MW = 58,000 g/mol) was supplied by BASF Company (Germany). Polyvinylpyrrolidone (PVP, 25,000 g/mol), dimethylacetamide (DMAc), sodium tripolyphosphate (STPP), NaCl, Na_2SO_4 salts and phenolphthalein (all from Merck) were used in this work. NaCl and Na_2SO_4 were chosen to investigate the rejection capability of the membranes. Bovine Serum Albumin powder [some properties are followed: assay > 96%, mol wt.; 66 kDa, pH ≈ 7, solubility > 40 mg/mL in H_2O], methyl orange and phenolphthalein were obtained from Sigma. Distilled water was used throughout the study.

2.2. Fabrication of PES membrane

At first, the different concentrations of STTP (0.5, 1.0, 1.5 and 2.0 wt.%) were dissolved in DMAc and the obtained solutions were exposed to ultrasonic for 2 h to achieve better dissolving of sodium tripolyphosphate (STPP). Then, PES and PVP with 20 and 4 wt.%, respectively; were added to the solution. The obtained polymeric solution was stirred for 24 h at 50 °C in 300 rpm. After formation of a homogeneous solution, the dope solution was held at the ambient temperature for around 24 h to remove the air bubbles. Afterwards, the dope solution was cast on the glass plate at 250 μm height using a film applicator at room temperature and in 30% humidity without evaporation. After coating, the membrane was immediately immersed into a distilled water bath for at least 24 h to guarantee complete phase separation. The composition of the prepared membranes was depicted in Table 1.

2.3. Characterization methods

The atomic force microscopy (AFM, non contact mode) was used to analyze the surface morphology and roughness of the membranes. The AFM apparatus was a DualScope™ scanning probe-optical microscope (DME model C-21, Denmark). Small squares of the prepared membranes (1 cm^2) were cut and glued on a glass substrate. The membrane surfaces were analyzed in a scan size of 10 μm × 10 μm.

The cross-section and surface morphology of the membranes were examined by using a scanning electron microscope-Philips model X130 (SEM). The membrane samples were frozen in liquid nitrogen and fractured to the pieces with 1 cm^2. Afterward, they were sputtered with gold and viewed at 25 KV.

The static contact angles were measured using a contact angle measuring instrument (G10, KRUSS, Germany). Deionizer water was used as the probe liquid in all measurements and the contact angles between water and the membrane surface were measured for the evaluation of the membrane hydrophilicity. To minimize the experimental error, the contact angle was measured at five random locations for each sample.

The ion rejections were investigated by measuring the permeate conductivity using a conductivity meter (Hanna 8733 Model, Italy) and then it compared to the feed conductivity.

To determine the charge of the membrane surface, the zeta potential (which is the potential at the shear plane between the solution and the membrane) was determined from streaming potential measurements. In these measurements, a streaming potential is induced when ions within an electrical double layer are forced to move along with a flow, thereby generating a potential difference. The relationship between the measurable streaming potential ΔE and the zeta potential ξ is given by the Helmholtz–Smoluchowski equation, using the Fairbrother and Mastin approach [29]:

$$\xi = \frac{\Delta E \eta \kappa}{\Delta P \varepsilon} \tag{1}$$

where η is the viscosity, κ is the conductivity, ΔP is the applied pressure and ε is the permittivity. The zeta potentials of the prepared membranes were measured by Electro Kinetic Analyzer (EKA 1.00, Anton-Paar, Swiss) equipped with a plated sample cell. In the experimental set-up a 0.001 M KCl solution was applied. Zeta potential was measured 4 times and a mean value was calculated.

A dead-end system was utilized to investigate the performance of prepared membranes (Fig. 1). The membrane surface area in the filtration cell was 12.5 cm^2. The flux of each membrane was determined at 10 minute intervals under 0.8 MPa. The experiments were carried out at 25 °C. The permeation rate and salt rejection were determined for all membranes using NaCl and Na_2SO_4 solutions in 1000 ppm concentration. The rejection was obtained by following equation:

$$R\% = \left[1 - \frac{\lambda_p}{\lambda_f}\right] \times 100 \tag{2}$$

where λ_p and λ_f are the ion conductivity in the permeate and feed, respectively. In addition, we used methyl orange as an azo color and phenolphthalein for determination and comparison of the separation power of the prepared membranes. For all of the runs, the average data and standard deviation (S) were reported.