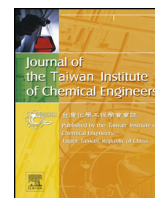




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Modified ultrafiltration membranes for humic acid removal

Alisa Mehrparvar, Ahmad Rahimpour*, Mohsen Jahanshahi

Membrane Research Group, Nanotechnology Research Institute, School of Chemical Engineering, Babol University of Technology, Babol, Iran

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ABSTRACT

Polyethersulfone (PES) ultrafiltration membranes were prepared via phase inversion induced by immersion precipitation with a blending method in different concentrations of two hydrophilic monomers, namely 3,5-diaminobenzoic acid (DBA) and gallic acid (GA). Herein we report the effects of these two monomers as additives in the casting solution on the morphology, performance, and antifouling properties of the membranes. The membranes were characterized in terms of pure water flux permeation, humic acid (HA) separation, membrane structure, and morphology. Experimental results show that the different component ratios of each monomer affected the structural property of blended membranes and surface roughness. The equilibrium water content (EWC) and water contact angle were measured to evaluate the change of hydrophilicity of the modified membranes. Trends exhibited that those two additives increased the hydrophilicity of the membranes because of their strong hydrophilic groups. The HA removal by the PES membrane increased considerably with the addition of DBA and GA in the casting solution. Moreover, the membranes prepared by adding DBA and GA in the PES casting solution exhibited better antifouling properties.

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1. Introduction

Membrane technology is an attractive and alternative separation approach due to its fast and energy-efficient process and its lack of need for a phase change [1]. Membranes have been used widely in many fields, such as chemistry, the pharmaceutical industry, food production, and especially in water and wastewater treatment [2–4]. Nowadays with the growing need for water supplements and wastewater treatment, modifying the membranes to give a superior performance, like performing higher fluxes with higher rejection and lower fouling, all of which reduces energy usage, becomes a target. In the water purification process, natural organic materials (NOM's) are removed by ultrafiltration (UF) or microfiltration (MF) because of their good properties in high-flux filtration. Usually, the efficiency of the water treatment does not meet the quality needs of the industrial process. A major hindrance is flux decline which results from fouling, thus making frequent membrane cleaning unavoidable, which seems to result in larger operating costs [5,6]. Obviously, improvement in membrane performance (mainly in water filtration) is the aim of modifications to the membrane polymer. In recent years many new polymeric materials have been developed. Polymeric

materials usually used in UF are polymers such as polyethersulfone, cellulose acetate, polyamide, and polyimide [7]. Among them, one of the most commonly used is polyethersulfone (PES) because of its good mechanical, chemical, and thermal stability. The disadvantage of PES is related to its relatively hydrophobic character [8–10], and the PES membrane is known as a high-fouling membrane for aqueous filtration. Fouling is the deposition of retained particles, macromolecules, colloids, etc. on the membrane surface or inside the pores in the pore wall. One disadvantage of fouling is the resulting decrease in the membrane flux, either temporarily or permanently [11]. It is generally accepted that better fouling resistance occurs when hydrophilicity is increased [12], because a more hydrophilic surface absorbs water molecules to make a layer between the membrane surface and organic molecules. Additionally, as many foulants are hydrophobic in nature, a hydrophilic surface has no tendency to absorb them. Most of fouling in water or wastewater may come from NOMs that are insoluble in water. One prominent NOM, which is used as a model in UF filtration tests, is humic acid (HA). The aggregation of HA on a membrane results in low filtration flux. Since HA is negatively charged as well as hydrophobic in nature, hydrophobic or negatively charged polymers can be used as main materials to both reduce adsorption of HA on the membrane surface due to the negatively electrostatic repulsion between HA molecules and the membrane surface [13,14] and also prevent the effect of flux decline made by fouling. Moreover, to have an incremental trend in filtration flux other hydrophilic polymers or additives can also be used [15]. Many investigations have been done to make membranes

* Corresponding author. Tel.: +98 111 3220342; fax: +98 111 3220342.
E-mail addresses: ahmadrahimpour@yahoo.com, ahmadrahimpour@nit.ac.ir
(A. Rahimpour).

hydrophilic [16–18]. Some methods, such as blending, chemical grafting, surface graft polymerization, and radiation induced grafting, have been developed to increase surface hydrophilicity [19–22].

Among these modification methods, blending was chosen for this study due to its simplicity, versatility, reproducibility, and environmental compatibility [23]. To increase the membrane hydrophilicity in the blending method, a hydrophilic additive is often blended with the membrane-forming polymer. Some additives that were used include polyvinylpyrrolidone (PVP) [24,25], poly-sulfoxideamide [26], polyethylene glycol (PEG) [27], and others.

In the present work, two organic additives, *i.e.* 3,5-diaminobenzoic acid (DBA) and gallic acid (GA), were used in different concentrations as hydrophilic additives in the PES casting solution. 3,5-Diaminobenzoic acid ($C_7H_8N_2O_2$) and gallic acid ($C_7H_6O_5$) are aromatic and polar with amine, hydroxyl and carboxyl groups which make them strongly hydrophilic, as shown in Fig. 1. The effects of additives on performance, morphology, hydrophilicity, and the fouling behavior of PES membranes during the filtration of humic acid (HA) were investigated. Also to characterize the modified membranes FTIR-ATR, AFM, SEM, EWC and contact angle were used. Therefore, the main effort of this strategy was based on the maximum permeate flow while having maximum HA solute rejection and less fouling behavior.

2. Experimental

2.1. Materials

Polyethersulfone (PES Ultrason E6020P, $M_w = 58,000$ g/mol) and dimethylacetamide (DMAC) were supplied from BASF. Polyvinylpyrrolidone (PVP, $M_w = 25,000$ g/mol) and 3,5-diaminobenzoic acid (DBA, $M_w = 152.15$ g/mol) were obtained from Merck. Gallic acid (GA) and humic acid (HA) from Sigma–Aldrich were used. Humic acid solution was prepared by dissolving HA powder in 1 L distilled water. The pH value of HA solution was controlled at 6.9 ± 0.1 by 0.1 M HCl. The concentration of HA was 1000 mg/L in membrane test solution. Distilled water was used throughout this study.

2.2. Preparation of PES ultrafiltration membranes

PES membranes were prepared by phase inversion via immersion precipitation technique [28]. Different ratios of each additive were separately mixed with PES/DMAC casting solution containing PVP. These components were stirred at 200 rpm and 25 °C for 6 h. After complete mixing and formation of homogeneous casting solutions, the casting solutions were kept constant without any stirring for removal of bubbles. The solutions were sprinkled and cast on polyester non-woven fabric using a homemade casting knife with 75 μm thickness. The cast films were immersed in a water bath for immersion and membrane formation

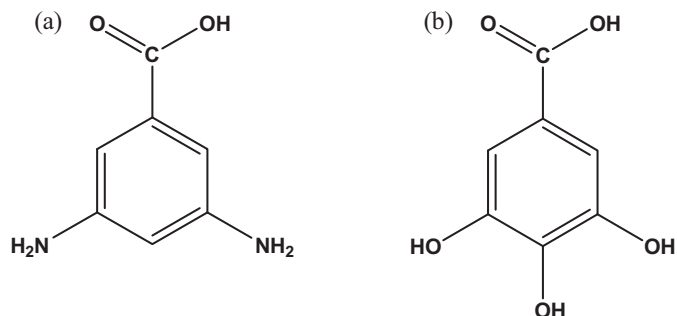


Fig. 1. Molecular structure of 3,5-diaminobenzoic acid (a) and gallic acid (b).

at room temperature without any evaporation. The prepared membranes were washed and stored in water for at least 1 day to completely leach out the residual solvents and additives. As the final stage, the membranes were dried by placing between two sheets of filter paper for 24 h at room temperature. The thickness of the membranes was about 100 μm . Table 1 classifies the materials and their weight percent in each membrane.

2.3. Characterization of membranes

2.3.1. Atomic force microscopy (AFM)

For analyzing the surface morphology and roughness of the membrane surface, The AFM images were obtained using a Dual scopeTM scanning probe-optical microscope (DME model C-21, Denmark). Small squares of prepared membranes (approximately 1 cm^2) were cut and glued on glass substrate and the membrane surfaces were imaged in a scan size of 5 $\mu\text{m} \times 5 \mu\text{m}$. The surface roughness parameters of the membranes which are expressed in terms of the mean roughness (S_a), the root mean square of the Z data (S_q) and the mean difference between the five highest peaks and lowest valleys (S_z) were calculated from AFM images by SPM DME software.

2.3.2. Scanning electron microscopy (SEM)

The cross section and surface morphology of PES ultrafiltration membranes were provided by scanning electron microscope (Hitachi FE-SEM S-4160). Small squares of prepared membranes (approximately 1 cm^2) were cut and cleaned with filter paper. After that, pieces were snapped in liquid nitrogen for 60–90 s and were frozen to give a generally clean break. Broken fragments of the membranes were kept in air for drying. The dried samples were gold sputtered to produce electric conductivity. After sputtering with gold, the cross section and surface morphology of PES ultrafiltration membranes were being viewed with the microscope at 15 kV.

2.3.3. ATR-FTIR spectra

Membranes were obtained for spectroscopic investigation by FTIR spectra and were recorded by the attenuated total reflection (ATR) technique using SHIMADZU FTIR-8400S spectrometer, with horizontal ATR device.

2.3.4. Contact angle measurements

To study the surface wettability of the membranes as a factor of each hydrophilic monomers concentration in the casting solution, water contact angle was measured. The hydrophilicity of membranes surface was estimated using a contact angle measuring instrument (OCA 15 plus, Data physics). De-ionized water was used in all measurements as the probe liquid. To reduce the experimental error, the contact angles were measured at three random locations and the average was reported.

2.3.5. Equilibrium water content (EWC) and membrane porosity

Equilibrium water content (EWC) is a parameter that deviously shows the hydrophilicity or hydrophobicity extent of a membrane [29]. Also, it can be used to exhibit the porosity of the membrane sub-layer. For measuring the EWC, the membranes were cut in size of 2 $\text{cm} \times 2 \text{cm}$ and then immersed in water for 24 h. The excess water on the surface of wet membranes were removed by a paper tissue and weighted after that. The wet membranes were put in an oven and dried for 48 h at 60 °C [30]. As a final level, dry membranes were weighted. To calculate the EWC at room temperature, Eq. (1) was used.

$$\text{EWC}(\%) = \frac{W_w - W_d}{W_w} \times 100 \quad (1)$$

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