

POLYETHERSULFONE MEMBRANES WITH INTEGRATED ADSORBENT PARTICLES FOR HEAVY METALS CAPTURE

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ABSTRACT

Novel polyethersulfone membranes with integrated submicron adsorbent particles were prepared by combining photoirradiation with liquid phase inversion. These particles consist of cross-linked poly(glycidyl methacrylate-co-acrylamido-2-methylpropane sulfonic acid), pGMA-AMPS. After membrane preparation, the epoxide groups were reacted with diethylene triamine to incorporate amine functionalities. Membranes were characterized using FTIR-ATR, SEM and dynamic adsorption of copper from a dilute solution. Effects of monomer concentrations on the properties and separation performance of membrane adsorbents are presented.

INTRODUCTION

Polyethersulfone (PES) is frequently used for making high performance ultrafiltration membranes [1]. Various functionalization methods, such as surface or bulk modification of PES material, are often used to incorporate desired functionalities or improve wettability [2]. Macroporous beads obtained by radical suspension polymerization of glycidyl methacrylate (GMA) are very attractive as adsorbents in biochemical and chemical separations [3], due to its ability to integrate separation and purification steps for processing large amounts of product in relatively short times [4]. In this paper, novel PES membranes with submicron crosslinked adsorbent particles of GMA-AMPS copolymer were prepared by combining liquid phase inversion with photopolymerization followed by amination of the epoxide groups under alkaline conditions.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA, reagent grade), trimethylolpropane triacrylate (TMPTMA), N-methyl-2-pyrrolidone (NMP, 99% purity), diethylene triamine (DETA, reagent grade), sodium hydroxide (NaOH), hydroquinone, 2-acrylamido-2-methylpropane sulfonic acid (AMPS) and copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, reagent grade) were purchased from Sigma Aldrich. Polyethersulfone (PES, Ultrason E 7020P) was provided by BASF. The photoinitiator (bis(2,4,6-trimethylbenzoyl)-phenyl-phosphine oxide (Irgacure 819) was obtained from Ciba SC as a gift. All chemicals were used without purification.

Membrane preparation

Sodium salt of AMPS was prepared by dissolving equivalent quantities of NaOH and AMPS, 0.1% hydroquinone in water followed by its crystallization upon acetone addition, filtration and drying under vacuum. Solutions of GMA, sodium salt of AMPS, cross-linker TMPTMA and solvent NMP were mixed in vials cooled with ice and protected from ambient light, then combined with PES solution and photoinitiator, cast on a glass plate, and exposed to UV irradiation under nitrogen blanketing. Irradiated films were immersed into water bath to prepare final membranes. Obtained membranes were functionalized with DETA by heating them in a solution containing 5g DETA and 100g distilled water for 8 hours at 80°C under reflux conditions.

Membrane characterization

FTIR-ATR analysis was conducted with Thermo Scientific Nicolet 6700 instrument equipped with Smart ATR Diamond accessory.

SEM analysis was performed with JEOL JSM-6610 L instrument using W filament as an electron source. Air-dried membrane samples were fractured after cooling in liquid nitrogen and sputtered with gold.

Feed solution containing 2 ppm Cu^{2+} in deionized water was permeated through membranes at 0.5 bar transmembrane pressure using a Millipore stirred cell, Model 8050. The concentration of Cu^{2+} in permeate was determined using Atomic Absorption Spectrophotometry.

RESULTS AND DISCUSSION

FTIR-ATR spectra of a typical PES membrane with adsorbent particles taken before and after functionalization are presented in Fig. 1. Strong carbonyl peaks at 1726 cm^{-1} and epoxide peaks at 907 cm^{-1} originate from GMA, while the peak at 1042 cm^{-1} corresponds to the sulfonic acid group present in AMPS. It can be seen that the epoxide peak at 907 cm^{-1} after functionalization was significantly reduced.

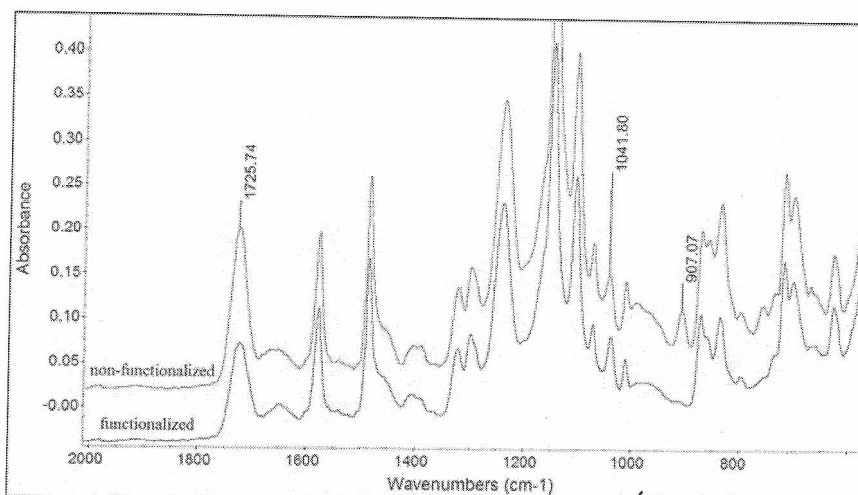


Figure 1. FTIR-ATR spectra of a membrane (11% PES, 2 mmol/g GMA, 1 mmol/g AMPS and 15 mol % TMPTMA), before and after functionalization

Fig. 2 presents SEM images of a membrane with initial concentrations of 2.0 mmol/g GMA and 1.0 mmol/g AMPS. The interconnected structure of crosslinked pGMA-AMPS submicron particles embedded within porous PES membrane is clearly visible.

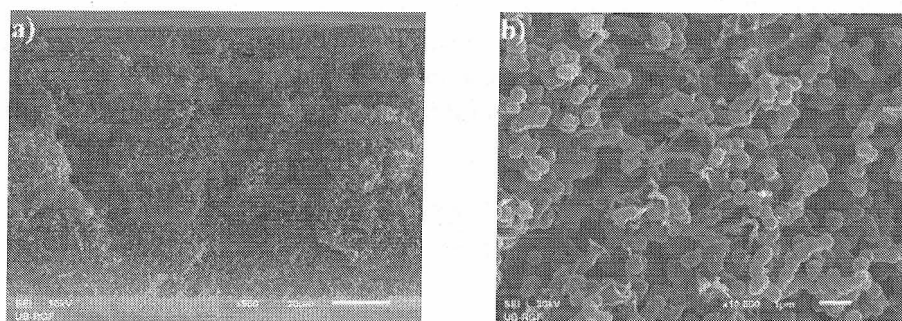


Figure 2. SEM images of a PES membrane with 2.0 mmol/g GMA and 1.0 mmol/g AMPS: a) cross-section, b) middle part at 10k magnification.

The separation performances of functionalized and non-functionalized membranes are shown in Fig. 3. Heavy metal capture occurs by electrostatic binding between sulfonic group present in AMPS and Cu^{2+} , while, in the case of functionalized membranes, by additional chelating action of the amino groups. Best separation performance was achieved with the functionalized membrane with 1 mmol/g AMPS and 2 mmol/g GMA.

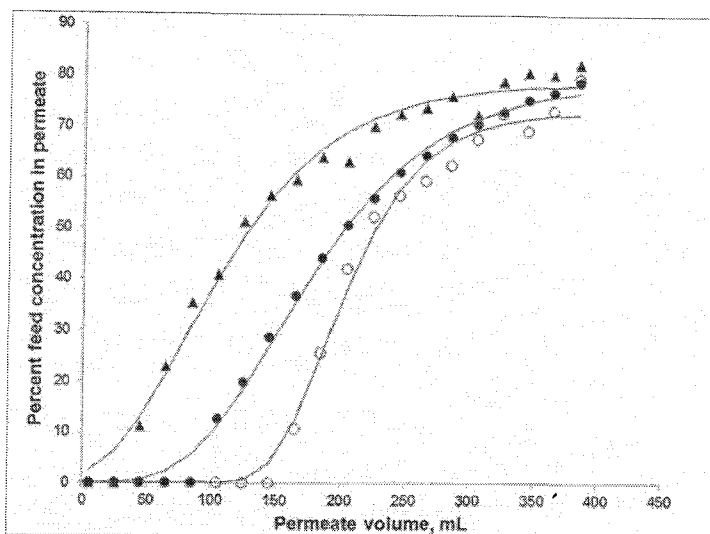


Figure 3. Filtration of Cu solution through functionalized PES membranes made with 0.75 mmol/g sodium salt of AMPS (▲) and 1.0 mmol/g sodium salt of AMPS (○) and non-functionalized membrane with 1.0 mmol/g sodium salt of AMPS (●)

CONCLUSION

Novel PES membrane adsorbers were prepared by combining liquid phase inversion with photopolymerization followed by post-amination. SEM images show interconnected network of submicron particles. Dynamic adsorption performance of these membranes using a dilute Cu^{2+} solution indicated that they could be useful for capture of heavy metals.

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