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Nano-scale modification of polysulfone membrane matrix and the surface for the separation of chromium ions from water

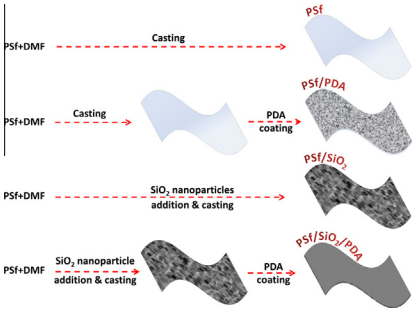
Samin Habibi [a], Ali Nematollahzadeh [a,*], Seyyed Abbas Mousavi [b]

[a] Chemical Engineering Department, University of Mohaghegh Ardabili, P.O. Box 179, Ardabil, Iran
[b] Chemical and Petroleum Engineering Department, Sharif University of Technology, Tehran, Iran

HIGHLIGHTS

- Four different bulk and surface modified polysulfone (PSf) membranes were prepared.
- SiO_2 nanoparticles and polydopamine (PDA) were used for the modification.
- PSf/SiO_2/PDA membrane showed smoother surface and more hydrophilic behavior.
- PSf/SiO_2/PDA membrane exhibited quite stable solution flux and robust structure.
- PSf/SiO_2/PDA membrane exhibited the best performance in the Cr(VI) removal.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, aiming at hexavalent chromium removal from aqueous solutions, different strategies were proposed for developing hydrophilic and surface functional polysulfone (PSf) membrane. In addition to PSf membrane, three different types of membranes were prepared by addition of SiO_2 nano-particles to the dope solution and/or by deposition of polydopamine (PDA) layer on the surface of the membranes. The membranes (i.e. PSf, PSf/PDA, PSf/SiO_2 and PSf/SiO_2/PDA) were characterized by different techniques. The membranes' transport properties and the separation performance were studied using a filtration unit operated at a continuous dead-end flow mode. The kinetics and the separation mechanism of Cr(VI) were investigated by tracing the effect of pH, initial chromium concentration and operation time. It was found that the surface and adsorption property of PDA layer is dependent on the substrate (PSf or PSf/SiO_2) on which it is grown. Reusability of the membranes was studied by repeating consecutive adsorption/desorption cycles. NaOH (0.05 M) showed the highest stripping capability. Among the membranes, PSf/SiO_2/PDA membrane with relatively smooth surface and robust structure over the operation time exhibited quite stable water flux (at 13 L m^{-2} h^{-1}) and superior separation performance (94% at pH = 3), which is quite encouraging from practical and industrial points of view.

1. Introduction

Removal of heavy metal ions from waters contaminated by effluent of different industries such as leather tanning, electroplating, wood preservation, paints, pigments, dye and textile, or polluted by natural or anthropogenic sources, is necessary from both the environmental remediation and economic points of view [1]. So far, several techniques have been developed for the removal of heavy metal ions from water and wastewaters, such as electrochemical deposition, adsorption on sorbents, ion exchange, chemical precipitation, flotation, and membrane filtration [2]. Among

* Corresponding author. Tel.: +98 45 33512910; fax: +98 45 33512904.
E-mail address: nematollahzadeha@uma.ac.ir (A. Nematollahzadeh).

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the different separation techniques, membrane separation has attracted more attention especially due to its operational feasibility, high rejection to the contaminants and low-cost of fabrication [2]. In addition, it is known that membrane process is more advantageous than ion-exchange resin process when solutions are to be treated at low cost [3]. However, membranes should be used in complementary with ion exchange resin process, in that below 500 ppm level ion-exchange resin process is more efficient and above that the membrane process is more efficient [3].

Polysulfone (PSf) is a widely used material in the preparation of membranes for the variety of membrane separation processes such as waste water treatment, gas separation and food and beverage processing. The polymer allows easy manufacturing of membranes owing to its excellent film forming characteristics, chemical inertness, mechanical strength, thermal stability, controllable size of pores and reproducible properties. However, the need for an efficient membrane especially for heavy metal ion separation necessitates the matrix or surface modification of the membranes. The necessity arises from the incapability of the manufactured membranes in rejection or adsorption of small molecules or stems from the hydrophobic nature of the membrane. The incapability can be offset by adding organic/inorganic compounds or nano-materials as a third component to the dope solution of the membrane. Frequently used additives include polyethylene glycol, polyethylene oxide, polyvinylpyrrolidone, propionic acid, surfactants, alcohols and water [4]. These additives are added in order to control the hydrophobicity, morphology and pore formation, and the interconnectivity, both by incorporating new functional groups into the polymer backbone of the membrane and by creating a spongy membrane structure through preventing the finger-like macrovoid formation. Besides the aforementioned organic modifiers, thus far different types of nano-materials such as TiO_2, SiO_2, Al_2O_3, ZrO_2, *etc*. [5], have been popularly incorporated into polymer matrix of membranes. Nano-materials with functional group such as amine, carboxyl, and thiol, can form coordinate bonds with heavy metal ions by donation of lone-pair electrons. They, in fact, can switch between the trapping and release of heavy metal ions with pH adjusting [6].

Surface modification or surface functionalization of membranes by different chemicals has received considerable scientific attention, as well. More recently flat polytetrafluoroethylene (PTFE) microfiltration membrane has been functionalized with hyperbranched polyamidoamine via UV irradiation for the removal of Cu^{+2} ions from aqueous solution [6]. Boltorn™ as an amphiphilic hyperbranched polymer has been self-assembled on the polyacrylonitrile ultrafiltration membrane for dye desalination [7].

Among different surface modifiers, polydopamine (PDA) has drawn considerable attention as a universal membrane surface modifier for improving hydrodynamic permeability and antifouling properties [8,9]. Bio-inspired research has found that 3,4-dihydroxyphenethylamine (i.e. dopamine) is able to undergo oxidative polymerization in aqueous solution and form strong adhesion to a wide range of substrates. In contrast to other well established techniques, such as mono-layer self-assembly and layer-by-layer assembly, surface modification by PDA is carried out in an *in situ* process [10]. The PDA coating on the surface of substrates is typically thin and offers highly robust structure at a wide range of pH and on pressure driven flow conditions [11].

Intrigued by the dormant potential of biopolymers and inorganic nano-particles and concerning the limitations of the existing membrane materials, we set out to modify polysulfone membrane matrix by SiO_2 nano-particles and modify the surface by polydopamine layer for the removal of heavy metal ions from aqueous solutions. Therefore, taking the advantageous of low cost, fast and convenient use of membrane and the capability of polydopamine as zwitterionic polymer for the adsorption of ions [12,13], we have introduced a new separation system for the removal of heavy metal ions from a diluted solution. In the studied system, hydrophilicity enhancement due to the presence of hydroxyl and amine groups on the membrane have caused to the priority of our investigation to the other methods of separation. Hexavalent chromium ion was used as a model pollutant to certify the separation capability of the modified membranes. To the best of our knowledge this is the first report on the simultaneous matrix and surface modification of PSf membrane using SiO_2 nano-particles and PDA layer for the heavy metal ion removal from water.

2. Experimental

2.1. Materials

PSf (Ultrason® S 6010) was obtained from BASF. Dopamine (3-hydroxy-tyramine-hydrochloride) was purchased from Sigma–Aldrich. Tris(hydroxymethyl)aminomethane hydrochloride (Tris–HCl), potassium dichromate, N,N-dimethylformamide (DMF), hydrochloric acid and sodium hydroxide were received from Merck. Silica nano-particles (AEROSIL200, particle diameter = 7 nm) was purchased from Evonik industries. All the chemical reagents used in this work were of analytical grade and used as received without further purification.

2.2. Preparation of PSf and PSf/SiO_2 membranes

PSf membrane was prepared by phase inversion method. Typically, PSf was dissolved in DMF (16 wt.%) and then vigorously stirred for 6 h until a clear homogeneous solution was obtained. The polymer solution was left still for 24 h to be degassed at room temperature. The solution was then casted onto a glass plate using an applicator with a precise gap of 200 μm between the applicator knife and the glass plate. Defect-free membrane was achieved by immersing the plate in a pure water bath.

PSf/SiO_2 composite membrane was prepared as follows. Dried nanosilica particles (SiO_2) were dispersed in DMF (1 wt.%). The mixture was ultrasonicated for 30 min with operating frequency of 30 kHz to ensure high degree of the SiO_2 nano-particles dispersion. Then PSf (16 wt.%) was added to the mixture. The final mixture was vigorously stirred for 6 h until a homogeneous solution was obtained. Subsequently, the mixture was left still for 24 h to be degassed at room temperature. Before the casting, the mixture was gently re-mixed to assure the homogeneity of the mixture. It is noteworthy to mention that penetration of air in the casting solution should be avoided; otherwise, the resultant membrane will suffer from air bubbles artifacts or defects.

The membranes were left in fresh deionized water to remove all the residual solvent and any detached silica nano-particles. Thereafter, the resultant membranes were stored in deionized water for further use.

2.3. Preparation of PSf/PDA and PSf/SiO_2/PDA membranes

The polydopamine coated membranes were prepared by continuous contact of PSf or PSf/SiO_2 membrane with dopamine solution. The dopamine solution was prepared by dissolving 20 mg dopamine in 10 mL Tris–HCl buffer (pH = 8.5, 10 mM). pH of the buffer was adjusted to 8.5 by addition of concentrated HCl solution. For the single-side coating, the membrane was fixed on a clean flat glass plate. A double open-ended cylindrical glass column was placed on the surface of the membrane and fixed by screws. Then the dopamine solution was poured into the column. The experimental setup is schematically shown in the Supporting Information (see Fig. S1). The coating was carried out by shaking