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Fabrication of Gd_2O_3/PSF Membranes via Aqueous Phase Inversion Method

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ABSTRACT

The purpose of this study was to look into the effect of Gadolinium oxide (Gd2O3) concentration (0.5%, 1%, and 2%) on the performance of newly developed Gd2 O3 /PSF membranes A common phase inversion method was used to create the membranes. Pure water flux and bovine serum albumin (BSA) permeation tests were used to evaluate membrane performance. FTIR and contact angle measurements were used to characterize the membranes that were manufactured. The greatest percentage of BSA rejection was 53%. In this work, the optimum membrane (2% wt Gd2O3/17% wt PSF) successfully demonstrated 53% rejection with filtrate flux for about 8.7 L/m2.h at a pressure of 10 bar.

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INTRODUCTION

Membrane technology, especially microfiltration (MF) and ultrafiltration (UF) membranes is rapidly being employed in separation processes due to benefits such as 100% particle removal, reduced chemical usage, and a compact footprint, as well as financial, environmental, and safety advantages. Membrane characteristics have been adapted and altered to the specific job to date in order to benefit from a wide range of industrial applications, including the separation and purification of protein molecules [1-3].

The most prevalent protein in blood plasma, bovine serum albumin (BSA), is one of the most researched proteins in the serum albumin family. In terms of its role in the pharmaceutical and food industry, the separation of Bovine serum albumin (BSA) is one of the most important proteins that require membranes with high permeability and selectivity [4].

Gadolinium (Gd), is a member of the lanthanide family of elements that is mostly employed in the medical field as contrast and anti-cancer agent for Magnetic Resonance Imaging (MRI) and medication administration, as well as in the nuclear power industry [5, 6]. Due to its excellent properties and characteristics, such as mechanical strength, chemical and structural stability, and thermal resistance, polysulfone (PSF) is preferred as a membrane polymer for use in purification [7].

Some researchers examined the performance of a Gadolinium-based composite membrane for dye and arsenic removal from water. Zhao et al. recently completed a study employing gadolinium doped cobalt ferrite nanoparticles to remove Congo red [8]. Another recent work used Fe_3O_4-GO-Gd_2O_3 to treat polluted water and found that the poor adsorption capacity of 35.85 mg/g was attributable to material aggregation [9].

In this study, the performance of PSF and PSF/Gd_2O_3 membranes for BSA separation was investigated.

MATERIALS AND METHODS

Materials

The chemicals used in this work were PSF (with average Mw = 60,000 Da) was used as the polymer in the dope solution (Acros Organics). N,N Dimethylformamide was used as a solvent to prepare membrane cast solution (ISOLAB chemicals). Gadolinium oxide (Gd_2O_3) powder (99%, hydrophilic) was purchased from Nanografi A.Ş, Turkey. Ultra-pure water with 18.2 MΩ cm resistivity was used all experimental procedures. As a contaminant, bovine serum albumin (BSA) was used all experiments (Amresco Inc., USA).

Methods

Membrane fabrication

The Gd_2O_3/PSF membranes were fabricated by the typical phase inversion method. The casting solution consist of PSF; 17 wt % and 3 different concentrations of Gd_2O_3 (0.5 wt %, 1 wt % and 2 wt %) were dissolved in NMP. The solution was stirred for 24 h at 500 rpm around 20°C. Then, the solution was sonicated for 10 min for the exit of the air bubble. A schematic representation of the fabrication of Gd_2O_3/PSF membrane and dynamic membrane filtration process is presented in Fig. 1.

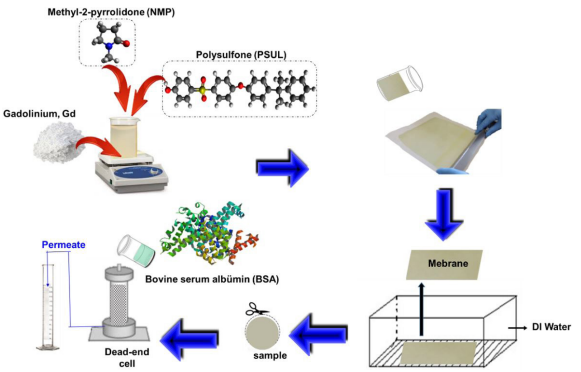


Figure 1. Schematic representation of the fabrication of PSF- Gd_2O_3 membrane and dynamic membrane filtration process.

Bovine Serum Albumin rejection experiments

In the dead-end filtration module, the membranes bovine serum albumin (BSA) rejection performance was examined using aqueous solutions with the initial concentration of 2.5 g/L of BSA at 10 bar TMP. Deionized water (DI) was used to prepare the solutions, which were kept at room temperature. A UV spectrophotometer was used to determine the concentration of BSA solution in the filtrate at a wavelength of 278.5 nm. The rejection rate of the membrane was defined by Eq. 1.

$$R = \frac{C_1 - C_2}{C_1} X100\% \quad (1)$$

where R is the membrane rejection rate (%), C_1 is initial concentration of BSA in the permeate (g/L), C_2 is the BSA concentration in the feed solution filtrate (g/L).

Pure water flux

Water filtration experiments were performed in a dead-end stirred cell filtration system (Sterlitech, HP4750). The dead-end filtration system has a membrane surface area of 14.6 cm^2 and a volume capacity of 300 mL. The membranes that had been tested, PSF and PSF/ Gd_2O_3, were placed in the filtration cell, which was then filled with 250 ml of clean water. A nitrogen gas cylinder was connected to the membrane filtration cell. DI water was used in all experiments.

In the pure water flux experiments at a constant transmembrane pressure (TMP) of 10 bar at room temperature (25°C). The pure water flux was measured every 15 minutes. Eq. 2 was used to calculate the water fluxes of the PSF and PSF/Gd_2O_3 membranes.

$$J = V / \left(A \times \Delta t \right) \quad (2)$$

where J is the water flux (L/m^2h), V is the volume of permeate (L), Δt is time (h) and A is the effective membrane area (m^2).

RESULTS AND DISCUSSION

The zeta potential-pH behavior was characterized using a Nano ZS90 (Malvern, UK) equipment. 0.5 g Gd_2O_3 nanoparticles were conditioned in 50 mL of DI water for 30 min (1% solid ratio). The pH of the solution was adjusted by using 0.1 mol/L H_2SO_4 and 0.1 mol/L NaOH, and the solution was kept for 20 min to let the bigger particles settle.

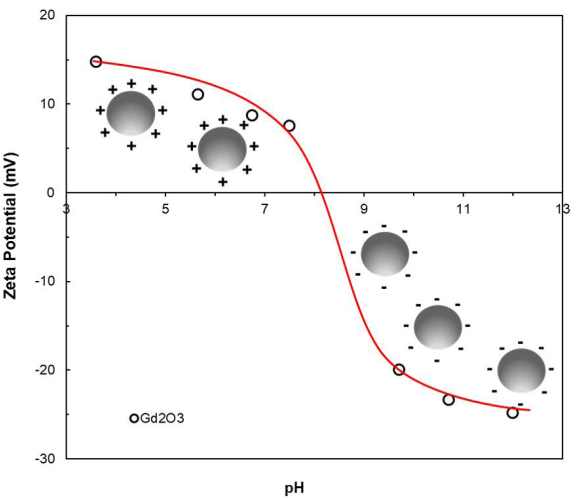


Figure 2. Zeta potential of Gd_2O_3 nanoparticles.

Fig.2 shows the pH dependence of the zeta potential of Gd_2O_3 nanoparticles. The isoelectric point (iep) was determined 8.1. Above the iep value, the Gd_2O_3 surface is negatively charged, while below the iep value the Gd_2O_3 surface is positively charged.

SEM analysis

The surface morphologies of the Gd_2O_3 powder and Ni-Zn MOF embedded membranes were assessed using a scanning electron microscope (Zeiss Gemini) with an app-

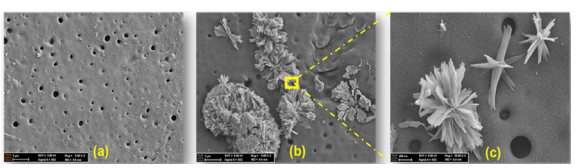


Figure 3. Schematic illustration showing the Scanning electron microscopic images of (a) PSF membrane, (b) Gd_2O_3/PSF membrane, and high-magnification of flower shape.

lied voltage of 10 kV. SEM images of the samples were given in Fig. 3.

As can be seen in Fig.3, the pure PSF membrane showed a clean and porous surface (Fig. 3a). The Gd_2O_3/PSF membrane (2 wt %) showed a porous surface with Gd_2O_3 particles (Fig. 3b). Some Gd_2O_3 nanoparticles formed aggregates embedded on the surface within the pores of the membrane (Fig. 3c).

FT-IR measurements

All FT-IR measurements were performed with an FT-IR spectrometer (Thermo Nicolet Avatar 370) for functional identification of PSF and embedded PSF membranes. The surface hydrophilicity of the Gd_2O_3 powder embedded in 3 different membranes was measured by a contact angle meter (Attention-Theta Lite, Biolin Scientific, Finland) with the sessile drop method.

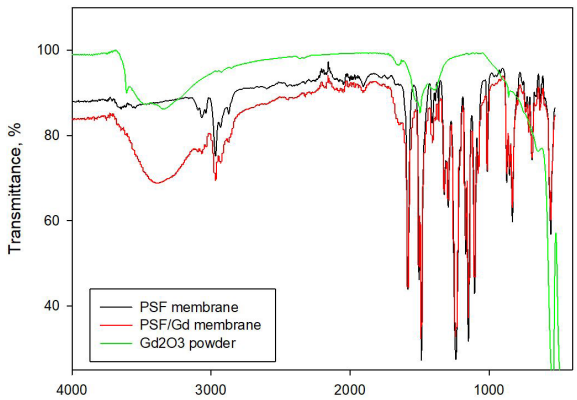


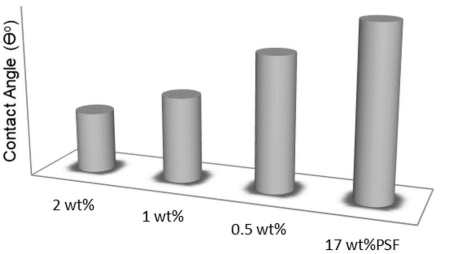
Figure 4. FT-IR spectra of PSF membrane and Gd_2O_3/PSF membrane and Gd_2O_3 powder.

Two spectra for PSF membrane and PSF/ Gd_2O_3 membrane were recorded in the region 400–4000cm^{-1}.

The peak at 1487 cm^{-1} and 1584 cm^{-1} which corresponds to an aromatic vibrational bonding of C=C in the polysulfone group [10]. OH stretching vibrations at 3646 cm^{-1} attributed to inner surface hydroxyl stretching [11]. For the Gd_2O_3/PSF membrane, the broadband at 3100–3500 cm^{-1} is attributed to O-H stretch [12]. As shown in Fig. 4, the new peaks at 470 cm^{-1} and 541 cm–1 assigned to the Gd–O vibration of Gd_2O_3. It shows that Gd_2O_3 particles are successfully incorporated into the PSF membrane. Therefore, the presence of Gd_2O_3 is the reason why the membrane becomes hydrophilic. Similar findings have previously been reported by [13, 14].

Membrane hydrophilicity

The hydrophobic or hydrophilic characteristics on the flat membrane surfaces (PSF and PSF/ Gd_2O_3 membranes (0.5 wt % Gd_2O_3, 1 wt % Gd_2O_3, and 2 wt % Gd_2O_3) were determined by contact angle measurements.



	2 wt%	1 wt%	0.5 wt%	17 wt%PSF
Contact angle	74 ±2	76 ±4	80±2	83 ±3

Figure 5. Contact angles of PSF membrane and PSF/ Gd_2O_3 membranes (0.5 wt % Gd_2O_3, 1 wt % Gd_2O_3, and 2 wt % Gd_2O_3)

As can be seen in Fig.5., a significant decrease in the contact angle of water drops from 83±3° for the PSF membrane surface to 9±2.5° for the surface of 2 wt % Gd_2O_3 embedded PSF membrane. This decrease of contact angle revealed Gd's hydrophilic property, which is clarified by the presence of the polar -OH groups on the Gadolinium(III) hydroxide hydrate surface [15].

Water filtration and rejection of BSA experiments

The capacity of the membrane to filter solutions, also known as flux or permeability, is a key metric for its performance. Another critical parameter is the membrane's capacity to remove components or particles from the solution, typically known as solute rejection [16].

Pure water filtration tests were performed on PSF membranes with three varied concentrations of Gd_2O_3 concentration (0.5wt %, 1 wt %, and 2wt %) to determine their permeability.

The pure water fluxes of PSF, 0.5 wt % Gd_2O_3, 1 wt % Gd_2O_3, and 2 wt % Gd_2O_3 were determined at 10 bar using a dead-end filtration system, and the results are shown in Fig. 6, where the pure water fluxes of 17 wt % wt PSF, 0.5 wt % Gd_2O_3, 1 wt % Gd_2O_3, and 2 wt % Gd_2O_3 are 81.6, 8.5, 14.3 and 18.1 L m-2 h-1, respectively.

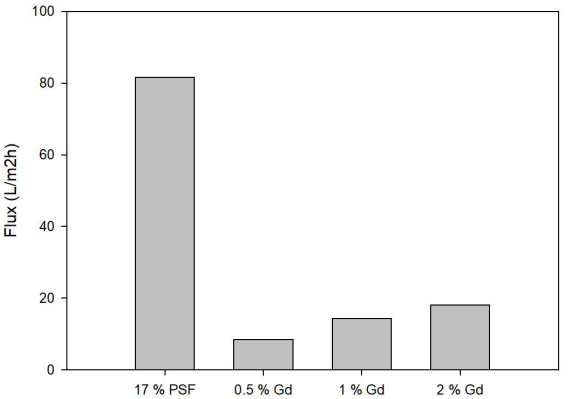


Figure 6. Pure water flux of 17 wt % PSF; 0.5 wt % Gd2O3, 1 wt % Gd_2O_3, and 2 wt % Gd_2O_3 membrane.

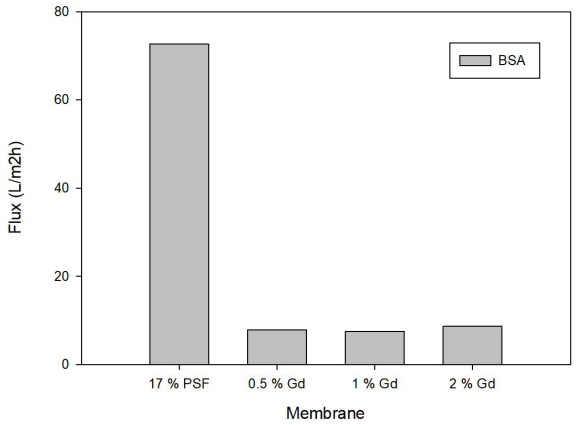


Figure 7. BSA flux of 17 wt % PSF; 0.5 wt % Gd2O3, 1 wt % Gd_2O_3, and 2 wt % Gd_2O_3 membrane.

The membranes BSA rejection performance was investigated in the dead-end filtration module using aqueous solutions with an initial concentration of 2.5 g/L of BSA at 10 bar TMP. BSA flux and BSA rejection values of prepared PSF and PSF/ Gd_2O_3 membranes are given in Figs 7-9.

The permeability of BSA was measured when the pure water was replaced with a BSA solution, and the flux of these membranes significantly reduced as shown in Fig 5 where the BSA fluxes of 17 wt% PSF, 0.5 wt % Gd_2O_3, 1 wt% Gd_2O_3, and 2 % wt Gd_2O_3 are 72.6, 7.9, 7.5 and 8.7 L m^{-2} h^{-1}, respectively.

The flux differences are explained by the fact that as the membrane surface becomes rough and the pore structure inside the membrane becomes more complicated, the membrane pores become blocked, decreasing BSA flux [17]. The adsorption or deposition of protein molecules inside the membrane pores, which causes antifouling activity within the membranes by the partial blocking of membrane pores, is responsible for the decrease in water flux of BSA aqueous solution [18].

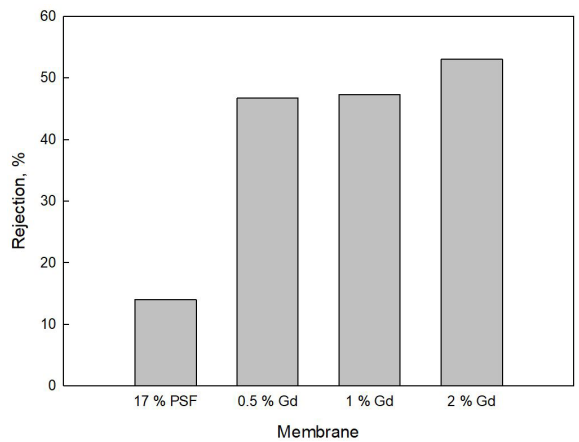


Figure 8. The BSA rejection for prepared membranes (17 wt % PSF; 0.5 wt % Gd_2O_3, 1 wt % Gd_2O_3, and 2 wt % Gd_2O_3).

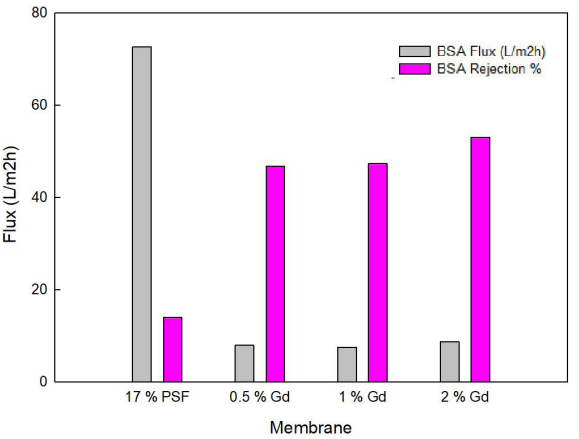


Figure 9. The BSA rejection for prepared membranes (17 wt % PSF; 0.5

PSF and PSF/Gd BSA rejection values ranged from 14% to 53%. PSF/ Gd_2O_3 membranes were shown to reject more than 45% of the BSA, with the PSF 2 wt % Gd_2O_3 nanocomposite membrane showing the highest BSA rejection at 53 %.

Fluxes and rejection of BSA solutions were measured and the results were shown in Fig. 9. The increased concentration of Gd_2O_3 in the membranes was evaluated using BSA flux and BSA rejection ratio. Rejection of BSA increased when BSA flux decreased. Many variables affect membrane permeability, including membrane shape, surface roughness, surface pore size, and surface hydrophilicity.

CONCLUSION

The present study examines the rejection of BSA with a newly developed Gd_2O_3/PSF membranes. The following conclusions can be drawn;

- BSA rejection increased with increasing Gd_2O_3 concentration. Therefore, this is also enhanced the Gd_2O_3 /PSF membrane separation performance.
- FT-IR spectra suggest the presence of chemical bonding with Gd_2O_3 and functional groups.
- A significant decrease in the contact angle of water drops from 83±3° for the PSF membrane surface to 9±2.5° for the surface of 2wt % Gd_2O_3 embedded PSF membrane.
- PSF/Gd_2O_3 membranes showed better BSA rejection than pure PSF membrane.
- The highest BSA rejection efficiency was observed with 2 wt % Gd_2O_3, at pH 8.

CONFLICT OF INTEREST

Authors approve that to the best of their knowledge, there is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper.

AUTHOR CONTRIBUTION

All authors contributed to the study conception and design. Material preparation, data collection and analysis

were performed by Ayse Gul,Dilek Senol-Arslan and Nigmet Uzal. The first draft of the manuscript was written by Dilek Senol-Arslan and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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