

Original paper

Preparation and characterization of high flux PES nanofiltration membrane using hydrophilic nanoparticles by phase inversion method for application in advanced wastewater treatment

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ABSTRACT

In this research, in order to application of polymeric membrane for high quality treatment of wastewater, the synthesis, characterization, antifouling properties and performance of blended nanofiltration membranes were investigated. The chemical and physical characteristic influence of embedded hydrophilic dendrimer polycitrate-Alumoxane nanoparticles in membranes matrix was investigated by measuring permeability, filtration of fouling agent, water contact angle and the performance was assessed by calculating of Flux recovery ratio (FRR) and pure water flux. Also, to visual evaluation of thick of skin layer and pores shape, scanning electron microscopy (SEM) techniques was applied. The membrane surface hydrophilicity was improved by adding polycitrate-Alumoxane nanoparticles that can be attributed to the presence of hydrophilic functional groups on surface that was confirmed by contact angle experiments. The modified poly ether sulfone (PES) NF membrane revealed high resistance against fouling and high dye removal efficiency compared with that of the pristine PES. The FRR value of the PES membrane was increased from 39 to 98 % by blending 0.5 wt. % hydrophilic dendrimer polycitrate-Alumoxane nanoparticles. Also, Direct red 16 removal percentage was obtained 82 and 99 for unfilled and modified membrane, respectively.

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1. Introduction

The hydrophobic nature of poly ether sulfone (PES) polymer caused a high interfacial energy with water-rich media among other membrane materials such as polyacrylonitrile (PAN), cellulose acetate (CA), polyamide (PA) and polyamide-imide (PAI) that makes the unmodified PES membrane have a great desire to fouling during wastewater filtration. Therefore, worldwide usage of PES membranes is still greatly restricted by membrane fouling, which decreases the flux and enhances the operation cost by requiring extra process of cleaning (Zhu et al. 2013).

Many strategies include pretreatment of wastewater, chemical surface alteration (like hydrophobic or hydrophilic and negatively or positively charged surface), optimization of process variables, module arrangement optimization have been done to control membrane fouling that among these methods, improvement of surface hydrophilicity seems to be a capable way to reduce membrane fouling (Rana and Matsuura. 2010).

Several techniques have been performed for development of membrane hydrophilicity such as bonding of hydrophilic monomers onto the membrane surface, blending an amphiphilic terpolymer or phthalate plasticizers in the polymer matrix, functionalization of the polymer, coating of membrane surface with hydrophilic polymer, and embedding hydrophilic nanoparticles (Han et al. 2011; Wang et al. 2008; Rahimpour et al. 2009; Chang et al. 2009; Na et al. 2000).

Introducing hydrophilic inorganic Nps in the membrane matrix (embedding method) such as TiO₂ (Rahimpour et al. 2011), Al₂O₃ (Liu et al. 2011), SiO₂ (Yu et al. 2009), Fe₃O₄ (Zinadini et al. 2014), graphene oxide and carbon nanotubes can make better the hydrophilicity, the water permeability and the antifouling characteristic of synthesized

membranes. Boehmite is an aluminum oxide hydroxide (AlOOH) particle, containing OH groups bound to its surface. The formula of the boehmite exhibits an excess water from the properly crystallized boehmite form (AlOOH), principally due to physically adsorbed water on the crystallite surface (15 wt. % H₂O) (Deer et al. 1992). Therefore, using these nanoparticles as a base for preparation of hydrophilic nano materials could be promising.

Citric acid (CA) is a multifunctional chemical compound that supplies effective functionality contributed to the ester bond-crosslink formation and balance of the polymer network hydrophilicity. CA-derived biomaterials developments are dependent upon the significant requirements for many applications. Dendrimer polycitrate-Alumoxane is a derivation of CA which has abundant hydrophilic OH and COOH functional groups and make them strongly hydrophilic. In this paper, the successful fabrication of novel dendrimer polycitrate-Alumoxane-PES nanocomposite membranes by the phase inversion method was reported. The effect of nanoparticle concentrations on the hydrophilicity of membranes surface, permeability, morphology, and antifouling performance is investigated.

2. Materials and methods

2.1. Materials

Analytical grade dimethylacetamide (DMAc) as solvent and polyethersulfone (PES ultrason E6020P with MW= 58,000 g/mol) as a polymer were provided by BASF Company (Germany). Polyvinyl pyrrolidone (PVP) with molecular weight (PVP K30) of 25,000 g/mol was purchased from Mowiol, Germany. Aluminum nitrate [Al(NO₃)₃·9H₂O], sodium hydroxide, citric acid, and decane were provided from Merck. Distilled water was utilized during this study.

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2.2. Fabrication of asymmetric mixed matrix PES nanofiltration membranes

The immersion precipitation phase inversion technique was used for the preparation of asymmetric dendrimer polycitrate-Alumoxane-PES NF membranes. The components of casting solutions for unfilled and modified membranes are summarized in Table 1.

Table 1. The compositions of casting solutions.

Membrane type	PES (wt. %)	PVP (wt. %)	PC-Nanoparticle (wt. %)
Unfilled PES	20	1.0	-
Modified PES	20	1.0	0.5

The definite percentage of nanoparticles (0.5 wt. %) were added into DMAc and dispersed using DT 102H Bandelin ultrasonic (Germany) for 15 min to make better the homogeneity. After dispersing hydrophilic NPs in the solvent, PES and PVP were dissolved in the dope solution accompanied by continuous stirring for 24 h. After air bubbles removal, the membrane with the thickness of 150 μm was casted on glass plate. Then, the casted membrane was horizontally immersed in coagulation bath (distilled water) at room temperature for membrane solidification. Finally, to assure the perfect phase inversion

the membranes were immersed in fresh distilled water about one day. Afterward, the membranes were dried at room temperature.

2.3. Characterization of the prepared membranes

The wettability and hydrophilicity of solid membrane surface was quantified using the sessile drop contact angle that is measured by a contact angle goniometer (G10, KRUSS, Germany) at 25 °C and a relative humidity of 50 %. Also, to minimize the experimental error, the measurement of contact angle was done at least five random locations on each surface.

The cross sectional structure of the freeze-dried membranes was studied using Philips-X130 and Cambridge SEM. To provide electrical conductivity of the fractured membranes, the samples were sputtered with gold. The SEM analyze were performed in very high vacuum conditions operating at 20 kV.

2.4. Membrane performance measurements

In order to investigate performance of the prepared nanofiltration membranes, tests of the permeate flux, dye rejection and powder milk fouling in a homemade stirred dead-end system with a volume capacity of 150 ml and an effective membrane surface area of 12.56 cm^2 connected with a nitrogen gas line were done (Fig. 1).

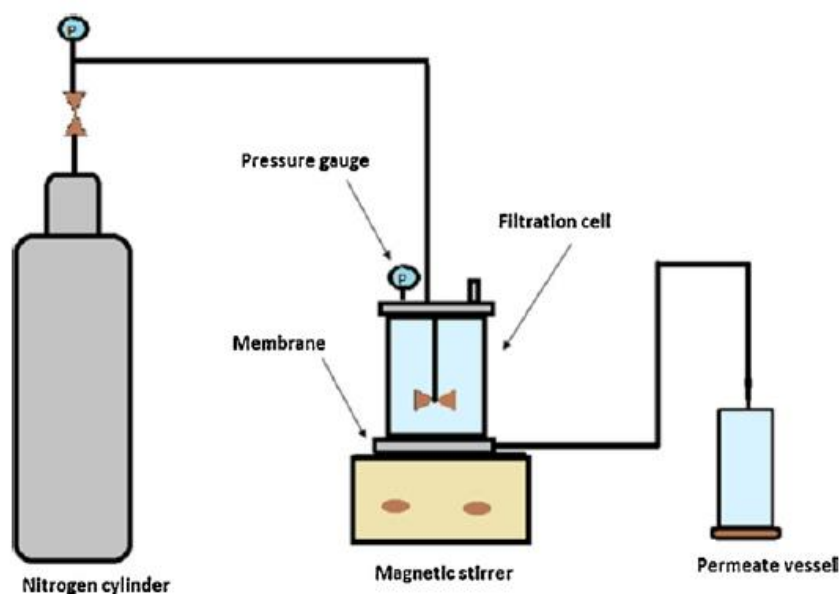


Fig. 1. Schematic of dead end system.

The stirring rate and operating pressure were adjusted to 500 rpm and 4 bar, respectively. After reaching steady state permeation, the water flux, $J_{w,1}$ ($\text{kg}/\text{m}^2 \text{ h}$), was computed using the equation (1), where M is the weight of the water permeates gathered (kg), A is the effective membrane area (m^2) and Δt is the sampling time (h).

$$J_{w,1} = \frac{M}{A \Delta t} \quad (1)$$

The prepared membranes were subjected to the synthetic colored feed with 30 mg/L concentration (typical value of Direct Red16 in wastewaters). For assessment of nanofiltration performance and dye removal capability, rejection (R) is determined as follow:

$$R (\%) = \left(1 - \frac{C_p}{C_f}\right) \times 100 \quad (2)$$

where C_p is the concentration of a particular component of permeate and C_f is the feed concentration.

2.5. Antifouling experiments

After performing water flux filtration, the dead end cell was refilled immediately with 8000 ppm concentration of powder milk solution as a strong foulant and permeation flux J_p ($\text{kg}/\text{m}^2 \text{ h}$) was measured by collection of the permeate at transmembrane pressure of 4 bar for 1 h. Then, the fouled membranes were rinsed with distilled water for 20 min, then the water flux of regenerated membrane for the second time, $J_{w,2}$ ($\text{kg}/\text{m}^2 \text{ h}$), was measured. The FRR as a suitable index of antifouling characteristic was computed as follow:

$$\text{FRR} (\%) = \left(\frac{J_{w,2}}{J_{w,1}}\right) \times 100 \quad (3)$$

Generally, higher FRR indicates better antifouling property of the prepared membrane.

3. Results and discussion

3.1. Morphology of the prepared membranes

In order to evaluate the changes induced in the skin-layer and sub-layer of the prepared membranes, the cross-sectional SEM images of the unfilled and modified nanocomposite membranes are displayed in Fig. 2.

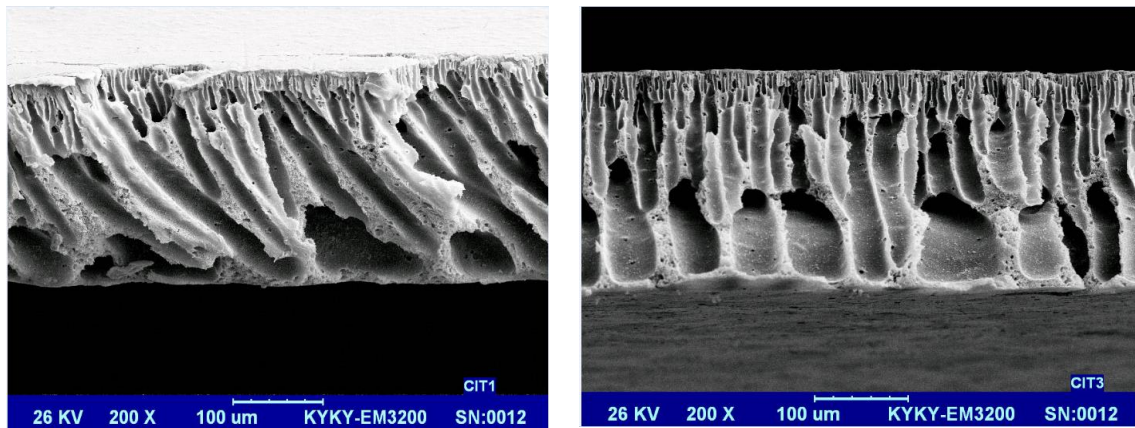


Fig. 2. Cross-section SEM images of the prepared membranes (left) Unfilled PES, (right) NPs 0.5 wt. %.

The membranes exhibited a typical asymmetric structure composed of a thin skin-layer and a porous bulk with a finger-like structure. From the Fig. seen, the addition of NPs caused a significant decrease in the top-layer thickness of the membranes. The addition of the dendrimer polycitrate-Alumoxane NPs increases the solution thermodynamic instability in the gelation bath (nonsolvent), and hydrophilic nature of the NPs increases the mass transfer rate between the solvent and the non-solvent in coagulation bath, which promotes a rapid phase inversion and results in large pore formation in low amount of the nanoparticles at the membrane skin-layer (Vatanpour et al. 2012).

3.2. Pure water flux and membrane hydrophilicity

The hydrophilicity of the membrane surface can be investigated by water contact angle measurement. Lower contact angle indicates that the membrane surface is more hydrophilic in nature. As shown in Fig. 3, by addition of polycitrate-Alumoxane nanoparticles to the casting solutions, the hydrophilicity of the mixed matrix membranes was improved. The contact angle of the 0.5 wt. % blended membrane was 54.2° , which is much lower than the unfilled membrane (62.8°). During membrane formation, the hydrophilic polycitrate-Alumoxane nanoparticles migrate towards the top surface of the membrane as the top layer was more exposed to water (non-solvent).

This migration decorates the functional groups of polycitrate-Alumoxane nanoparticles on the membrane top surface and improves the membrane hydrophilicity. By increasing of the membrane hydrophilicity with the nanoparticles addition, water molecules were attracted into the membrane matrix and promoted to pass through the membrane, thus enhancing the membrane flux. Fig. 4 reveals the pure water flux of the prepared membranes. As shown in this Fig., the trend of increasing in pure water flux is well matched with hydrophilicity improvement.

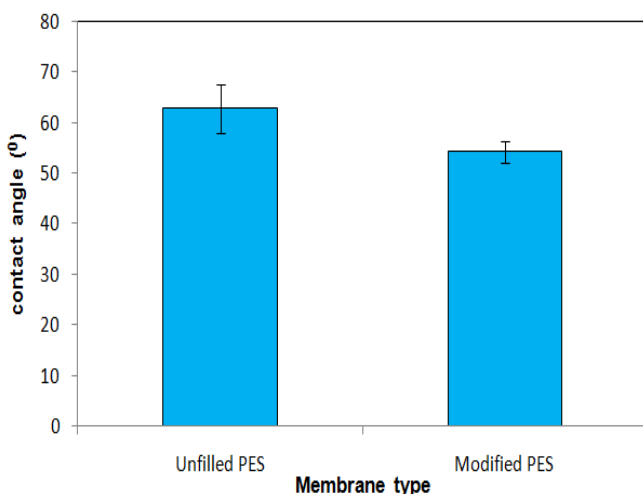


Fig. 3. Static contact angle of the prepared membranes.

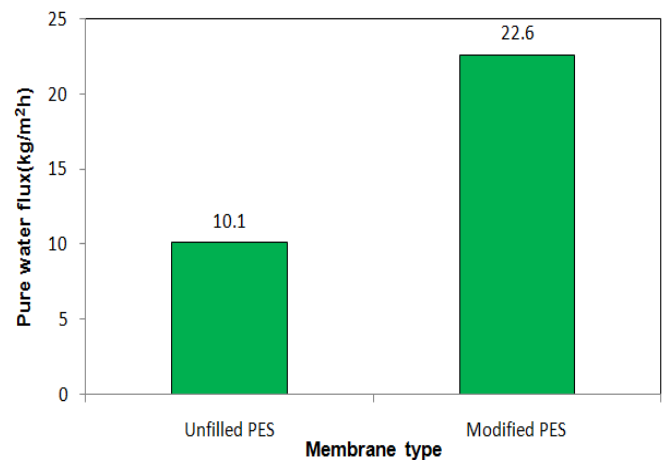


Fig. 4. Pure water flux of the prepared membranes (after 60 min).

3.3. Nanofiltration performance

The retention results of dye rejection after 60 min filtration of dye solution are shown in the Fig. 5. The rejection capability of the prepared polycitrate-Alumoxane NPs blended membrane was higher than that of unfilled PES membrane. Due to acidic functional groups of dendrimer polycitrate-Alumoxane, it can induce negative charge on the surface of the prepared membrane, causing high retention between negative dye and negative surface. The results showed that the behavior of the prepared nanofiltration membrane could be classified as Donnan exclusion mechanism (Sarkar et al. 2010), which is negatively charged. The membrane in contact with an aqueous solution gets an electric charge by dissociation of surface functional groups, causing electrostatic repulsion of the dye. Fig. 5. Dye retention performance of the prepared unfilled and modified PES membrane (4 bar, pH= 6.0 ± 0.1 , 30 mg/L Direct Red 16, after 60 min filtration).

3.4. Antifouling properties of the membranes

Results of the fouling parameters are shown in Fig. 6. Comparing FRR as the most demonstrative factor in the antifouling capability of the prepared membranes indicates that addition of polycitrate-Alumoxane nanoparticles might be influential on the fouling reduction. The FRR for the unfilled PES membrane (39 %) was lower than the FRR for the membranes prepared by embedding nanoparticles (81 %). This indicates the high antibiofouling property of the modified membrane was induced by polycitrate-Alumoxane nanoparticles. The smoother and high hydrophilic surface of membrane indicates reversible attachment of the foulants on the membrane top surface and a higher flux recovery ratio. The higher FRR is an index of better antifouling property for the membrane.

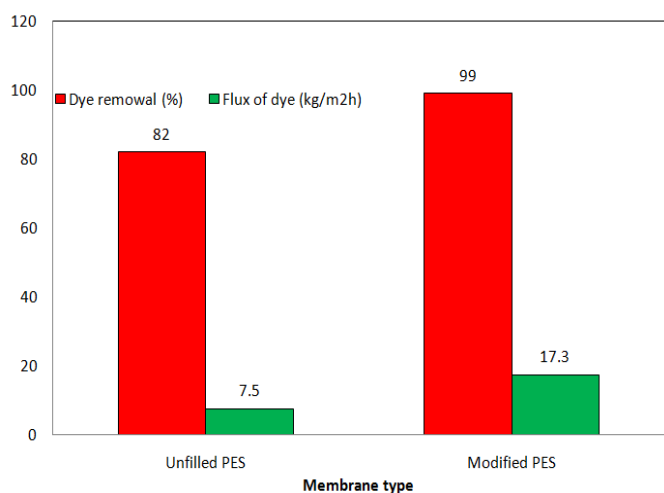


Fig. 5. Dye retention performance of the prepared unfilled and modified PES membrane (4 bar, pH= 6.0 ± 0.1, 30 mg/L Direct Red 16, after 60 min filtration).

Addition of nanoparticles results in partial blockage of membrane surface pores and reduces the pore radius of membrane surface. Since the roughness of membrane surface depends on pore size and pore density, the reduction of pore size may lead to creation of smoother surface. The trend of FRR is matched by hydrophilicity of the membranes. Hydrophilic surface of membranes can form a water layer by adsorption of water molecules, which retards the adsorption of protein and other fouling agents (Zinadini et al. 2014).

4. Conclusions

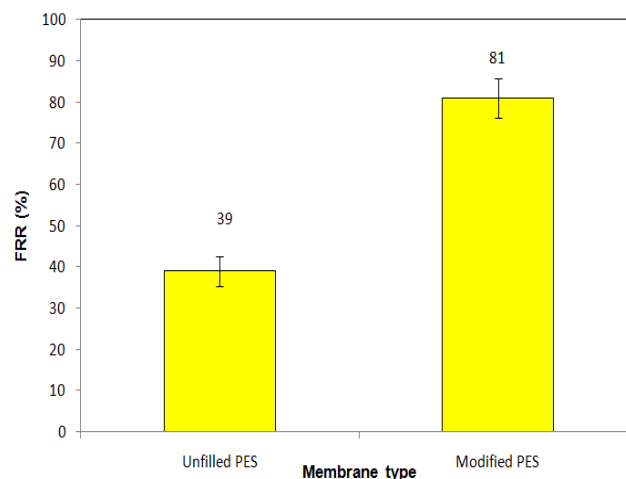


Fig. 6. Water flux recovery ratio of the unfilled and modified PES membranes after milk powder fouling (average of three replicates was reported).

This was an attempt to study the effectiveness of the dendrimer polycitrate-Alumoxane nanoparticles on the characteristics of the PES mixed matrix membranes. The influences of blended NF membranes were investigated by pure water flux, dye removal and fouling measurements. The results indicated that the hydrophilic branch of dendrimer formed on the nanoparticles is located on the surface of membrane by migration of the nanoparticles to the surface that enhanced the membrane hydrophilicity as well as the surface properties. A significant improvement was observed in fouling prevention and dye removal in the prepared modified membrane compared with that of the unfilled PES.

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