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# Improving antifouling performance of PAN hollow fiber membrane using surface modification method



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## ABSTRACT

In this study, a new approach to improve antifouling performance of polyacrylonitrile (PAN) hollow fiber membrane has been explained. Firstly, chemical modification with sodium hydroxide (NaOH) solution was performed on PAN membranes in various conditions, so that, as a result of hydrolysis, carboxyl groups emerge on membrane surface. Then, in order to improve surface hydrophilicity, the hydrolyzed membrane underwent a polyethylene glycol (PEG) deposition through a chemical reaction. Chemical changes in membrane were characterized via Fourier transform infrared spectroscopy/attenuated total reflectance (FTIR/ATR). In addition, measurement of contact angle and fouling test were performed to analyze hydrophilicity degree and performance of modified membrane, respectively. Results of measuring contact angle signified improvement of hydrophilicity of membrane after modification. Modified membranes showed lower tendency to foul during ultrafiltration (UF) of milk solution, which is confirmed by increase in flux recovery ratio (FRR) level following membrane modification. Three hours after hydrolysis process, though pure water flux through membrane reduced by 28% comparing with intact membrane, the level of polyvinyl alcohol (PVA-30 kDa) rejection and FRR increased 13 and 14%, respectively. Upon attachment of PEG to the membrane surface, the contact angle reduced from 64° for non-modified membrane to 21°.

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## 1. Introduction

Due to possessing some finest and superior properties including acceptable chemical stability, fair mechanical attributes, resistance against solvents, and being more economical than other polymers such as polysulfone and polyethersulfone, PAN has become one of the commonest polymers in membrane fabrication [1–3]. Nowadays, PAN ultrafiltration membranes have been extensively utilized in percolation of water/wastewater as a sub-layer in pervaporation process, and also as a pretreatment for reverse osmosis (RO) [4–6]. Although the broad use of PAN membrane is restricted by membrane fouling, which leads to lower permeation rate and shortening of membrane life [7,8], however, its chemical modification can be done easily. Development of membranes that inhibits the absorption of various foulants such as proteins which have drawn much of attention of many researchers. It should be noted that, foulants are prone to be easily absorbed onto the membrane surface or block the surface pores, decreasing the permeability and the final separation performance, depressing the lifetime

of the membranes, and subsequently causing more operation costs of the replacement and maintenance of the membrane modules. To improve the fouling resistance of membranes, membrane modification is a versatile method to reduce the operation cost.

Dai et al. [9] grafted a ring-opening glycomonomer D-gluconamidoethyl methacrylate (GAMA) onto the surface of the membrane to improve the antifouling property of PAN ultrafiltration membrane. The results revealed that by the surface glycosylation procedure, the hydrophilicity was enhanced and the FRR was increased after modification, but the loss of permeation flux was a problem when the grafting degree was too high.

In other work, Meng et al. [10] modified a PAN ultrafiltration membrane to improve protein antifouling capacity by grafting short-chain sulfonic type zwitterions. It was found that the modified membrane had excellent resistance to protein adsorption.

As stated before, chemical modification of PAN membrane can be done easily because of its rather active/ dynamic surface. Therefore, improving antifouling property of membrane in this polymer turns feasible accordingly [11,12].

Regularly, improvement of membrane surface hydrophilicity may delay fouling of membrane to some extent [13,14]. Based on this fact, various approaches of surface modification for PAN membrane including plasma treatment, surface graft polymerization, self-assembly,

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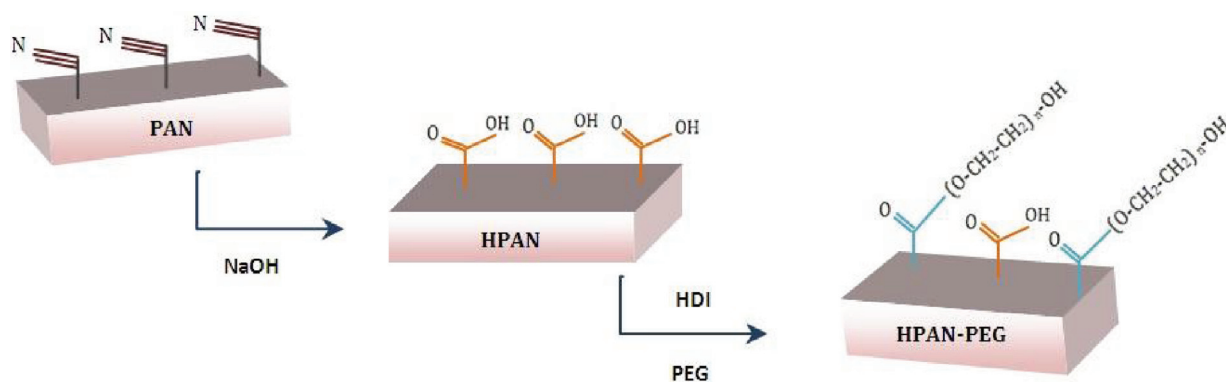


Fig. 1. Position of PEG conjugation to the surface of hydrolyzed membrane.

and chemical treatment have been reported [15]. Among these, chemical modification with alkali is one of the simplest, cheapest and commonest methods applied for PAN membrane; because it facilitates next modification processes. Many studies with different analysis method have proved that, by alkaline solution like NaOH, PAN nitrile groups can be converted somewhat to carboxyl groups. In this regard, Choi et al. [16] studied the effect of alkaline hydrolysis on chemical structure of PAN membrane by means of solid-state  $^{13}\text{C}$  NMR spectroscopy. Also, Xuan et al. [5] hydrolyzed PAN membranes to investigate the relationship between the electrokinetic property and permeation performance. It was observed that modified membranes had lower flux than unmodified ones.

In addition, it has been reported that hydrolysis of PAN UF membrane results in alteration of membrane pore size and augmentation of dextrin rejection [17,18]. Zhang et al. [4] studied the hydrolysis of PAN hollow fibers in the lumen side. They observed a subtle increment in separation of PEG-20 kDa, from almost 85.75% for intact fibers to nearly 87.23% for hydrolyzed ones.

By introducing proper active groups such as carboxyl groups, there will arise a potential for secondary modification processes (like PEG deposition) on membrane surface. The surface on which PEG is deposited (or so-called surface-immobilized PEG) delivers UF membranes resistant to cell adhesion and protein absorption [19].

In previous studies, maleic acid groups were usually used as functional sites to deposit PEG on PAN membrane surface. For instance, in researches done by Nie et al. [20,21], carboxyl groups on the surface of poly(acrylonitrile-co-maleic acid) (PANCMA) membrane were converted to hyperactive anhydride groups, which subsequently underwent a stratification reaction with PEG that included terminal hydroxyl group.

In this study, a new method for PEG immobilization/deposition on the surface of PAN membrane has been introduced to control fouling. For this purpose, after carboxyl groups were formed on membrane surface through hydrolysis, hexamethylene diisocyanate (HDI) was used as a crosslinker between carboxyl group and PEG (Fig. 1).

Then, modified membranes were used for UF process and their fouling release properties were studied.

## 2. Experimental

### 2.1. Materials

PAN (MW: 350 kDa) comprising 92% acrylonitrile (AN) and 8% vinyl acetate (VA) was supplied from Polyacryl Company, Isfahan, Iran, and before use, was dried at 70 °C for 30 min. Dimethylformamide (DMF), (purity: >99%) was purchased from Aldrich Company. Industrial type of NaOH was provided.

Table 1

Spinning conditions for PAN hollow fiber membrane.

Dope solution (polyacrylonitrile/DMF) (wt%)	(18/82) wt%
Bore fluid	Water
External coagulant	Water/DMF (90/10)
Air gap distance (cm)	50
Extraction pressure (kPa)	50
Dope flow rate (ml/min)	7
Bore fluid flow rate (ml/min)	5
Take-up speed (m/min)	9
Coagulant bath temperature (°C)	40
Spinneret dimension (OD/ID) (mm)	(1.3/0.64)

PEG with a molecular weight of 4000 Dalton was purchased from Kimia-Garan-e Emruz Company, Tehran, Iran. Acetone, ethanol (purity: >99%), HDI, and PVA (with two molecular weights of 30 and 60 kDa) were obtained from Merck Company, Germany.

### 2.2. Membrane preparation

PAN hollow fiber membrane was constructed through dry-wet spinning technique. Polymer solution, containing 18% PAN and 82% DMF was prepared by stirring for 5 h and then was kept for 1 day for degassing and debubbling. Pure water was used as bore liquid. After leaving the spinneret and traveling a 50 cm air gap, the solution entered into a water/solvent bath and then hollow fibers were collected. Table 1 lists the spinning conditions for PAN hollow fiber membrane preparation. Obtained membranes were kept in pure water for 72 h in order to withdraw residual solvent. The ID/OD of prepared PAN hollow fibers was about 0.6/1.25 mm.

### 2.3. Modification of membrane surface

In the first phase, for handling hydrolysis process, membrane samples were rinsed perfectly with pure water prior to use. Then, for the reaction occurs just on the outer surface of fibers as far as possible, the two ends of fibers were clogged.

Afterward, aqueous solutions of NaOH were prepared at 0.3, 1, and 1.7 molar concentrations; and membrane samples immersed in these solutions for about 3 h. Also, in order to investigate the effect of hydrolysis duration, membrane samples underwent reactions in 1 molar solution for 1, 3, and 5 h. Besides, in all cases, the temperature of hydrolysis reaction was maintained at  $27 \pm 1$  °C. The whole obtained modified membranes from different conditions are listed in Table 2. At the end of the reaction, all samples were taken out and rinsed with pure water, until the pH of rinsing water reached 7.

In the next phase, after formation of carboxyl groups on the membrane surface due to hydrolysis, HDI was employed as crosslinking agent between PEG and carboxyl group. To this end, the HPAN-3 membrane sample was chosen with moderate hydrolysis time and

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