Surface Modification of PAN Hollow Fiber Membrane by Chemical Reaction

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Abstract: In this study, a new method was applied to achieve an efficient surface modification of Polyacrylonitrile (PAN) hollow fiber membrane. The surface modification dealt by immersion of PAN hollow fibers in hydroxylamine solution under various conditions (different solution concentrations and reaction time). The nitrile groups on the surface of the membrane were changed to form the amidoxime ($-C(NH_2)=N-OH$) groups. The surface modified membranes were assessed by pure water permeation test and the rejection of high molecular weight materials like Polyvinylalcohol (PVA) from water. Permeation test results showed that with increasing hydroxylamine concentration, the amount of water permeation reduces slowly, while the PVA-30 kDa rejection has been somewhat increased after surface modification. FTIR/ATR analysis confirms the presence of amidoxime groups on the membrane surface. Also, the water contact angel was decreased from 64 to 34 after reaction. The ability of silver ions absorption was also assessed for modified membrane. Finally, the antifouling property of the modified hollow fibers was assessed by milk solution ultrafiltration. The obtained results showed that the modified hollow fibers present better antifouling properties.

Keywords: Polyacrylonitrile, Surface modification, Hydroxylamine, Antifouling, Hollow fiber membrane

Introduction

Hollow fiber ultrafiltration membranes are widely used for water/waste water treatment and also as an RO pretreatment [1-3]. Because of its high degree of solvent resistance and good chemical and thermal stability, polyacrylonitrile has been successfully used in preparation of microfiltration and ultrafiltration membranes [4-6]. Moreover, because of its relatively active surface, chemical modification of PAN membrane can be easily done [7,8].

However, because of the relatively poor hydrophilicity and biocompatibility, advances in PAN membrane applications have been limited [9]. It is accepted that hydrophilic membranes present less fouling than hydrophobic membranes. Membrane fouling decreases the water permeation. Therefore, it increases the filtration cost [10-12]. To overcome these problems, a series of researches is required to improve the PAN membrane surface hydrophilicity by improving its antifouling property.

So far, various surface modification techniques such as plasma treatment, surface graft polymerization and chemical treatment for antifouling purpose of PAN membrane has been reported [9,10]. Among these, chemical modification is one of the most popular methods because it presents a membrane surface with types of functional groups and the modified surface is relatively stable. Active nitrile groups in PAN can be converted into various functional groups by specific reactions. In other words, by the nitrile alteration to other functional groups, a variety of functional materials are made.

For example, Higuchi *et al.* [13] formed NH_2 groups on the membrane surface by PAN membrane reaction with hydrazine. Also, the reaction of polyacrylonitrile with phenylhydrazine and paratoluenesulfamide was used for chelating ion exchange fiber synthesis [14].

Chemical modification with alkaline solutions is one of the easiest and the most well-known methods used for PAN membrane modification [15]. Several studies showed that PAN nitrile groups can be to an extent converted to carboxyl groups by an alkaline solution such as NaOH.

It has been reported that hydrolysis of PAN ultrafiltration membrane results in change of membrane pore size and augmentation of dextrin rejection [16,17]. Zhang *et al.* [2] 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 percent for intact fibers to nearly 87.23 percent for hydrolyzed ones.

Unlike the hydrolysis of inorganic bases such as NaOH and KOH, we can say that, no comprehensive study on polyacrylonitrile membrane modification, especially hollow fiber membranes, with hydroxylamine which is an organic base, has been done so far. In fact, hydroxylamine has been used in just limited number of studies for polyacrylonitrile fibers. For example, Saeed *et al.* [18] modified PAN nanofibers by reaction with hydroxylamine for the metal ions absorption improvement.

Previous results obtained by researchers showed that nitrile groups (-CN) in polyacrylonitrile can be changed to amidoxime ($-C(NH_2)=N-OH$) group through reaction with hydroxylamine, which this group has a very satisfactory situation according to its hydrophilicity [19,20]. Moreover, this group has shown potential for recovery of heavy metals from wastewater [18,19]. In other words, most of the transition

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metal ions can form stable complexes with electron-rich compounds and coordinate molecules containing O, N and S, e.g., hydroxyl groups (-OH), amine groups (-NH$_2$) and thiol groups (-SH) [21].

Zhang *et al.* [19] modified amidoxime nanofibers by treatment of PAN nanofibers in hydroxylamine (NH$_2$OH) aqueous solution. Their results showed that amidoxime group can present high ability in metal ion absorbance such as Ag. Also in another study, after preparing amidoxime-modified polyacrylonitrile nanofibers, Zhang *et al.* [22] used it as laccase immobilization for dye degradation.

In this study, the purpose is to modify the surface of PAN hollow fiber membrane by reaction with hydroxylamine solution and also to compare the surface modified with unmodified hollow fiber membranes. For this purpose, unmodified and modified membranes were assessed by contact angle measurement, FTIR and pure water flux test. Moreover, the effect of hydroxylamine solution concentration and the reaction time on the PVA rejection and water permeation was investigated. Finally, modified membranes were used for ultrafiltration and their antifouling properties were also studied.

Experimental

Materials

PAN containing 92 percent acrylonitrile (AN) and 8 percent vinyl acetate (VA) was supplied from Polyacryl Company, Isfahan, Iran. It was dried at 70 °C for 30 min before using. Dimethylformamide (DMF) was purchased from Aldrich Company. Sodium carbonate (Na$_2$CO$_3$) of industrial grade was provided. Hydroxylamine hydrochloride (NH$_2$OH·HCl), silver nitrate (AgNO$_3$) and PVA with two molecular weights of 30 and 60 kDa were obtained from Merck Company.

Fabrication of PAN Hollow Fiber Membrane

PAN hollow fiber membrane was prepared through dry-wet spinning technique. Polymer solution, containing 18 percent PAN in DMF, was prepared by stirring the solution

Table 1. Spinning conditions for polyacrylonitrile hollow fiber membrane

Dope solution (Polyacrylonitrile/DMF) (wt%)	(18/82)
Bore fluid	Water
External coagulant	Water/DMF (90/10)
Air gap distance (cm)	50
Extraction pressure (kPa)	50
Dope flow rate (ml·min^{-1})	7
Bore fluid flow rate (ml·min^{-1})	5
Take-up speed (m·min^{-1})	9
Coagulant bath temperature (°C)	40
Spinneret dimension (OD/ID) mm	(1.3/0.64)

for 5 h and then it was kept for 1 day for degassing. Pure water was used as bore liquid. After leaving the spinneret and traveling a 50 cm air gap, the solution entered into the water/solvent bath and then hollow fibers were collected in water bath. Table 1 lists the spinning conditions for polyacrylonitrile hollow fiber membrane. Obtained hollow fibers were kept in another pure water bath for 72 h in order to withdrawal of remained solvent. The ID/OD of prepared PAN hollow fibers were about 0.6/1.25 mm.

Modification of Membrane Surface

The membrane samples were washed thoroughly with pure water before reaction with hydroxylamine. Then, to occur the reaction just on the outer surface of the fibers as far as possible, the two ends of fibers were clogged.

After that, aqueous solutions were prepared from hydroxylamine hydrochloric with three different concentrations and membrane samples were immersed in each hydroxylamine solution for 60 minutes. Also, in order to evaluate the reaction time effect, membrane samples in one of these concentrations (intermediate level of solution concentration) were reacted with hydroxylamine solution at 30, 60, and 90 minutes. At the end of the reaction, all samples were taken out and rinsed with pure water. In all cases, the reaction temperature was kept at 70±1 °C. All the modified sets of membranes obtained in different conditions are listed in Table 2.

It is noteworthy that according to previous reports, the best conditions for the reaction is pH=7 [21]. For this purpose, sodium carbonate was used to adjust the pH of the solution.

Figure 1 shows polyacrylonitrile reaction with hydroxylamine which leads to formation of amidoxime group.

Amidoxime is a group in which carbon is attached to the NH$_2$ and =NOH and consequently, the formation of this functional group can improve the hydrophilicity of the polymer.

Table 2. Modified PAN membranes at different conditions of reaction

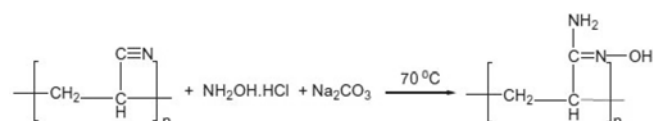| Sample name	Hydroxylamine hydrochloride concentration (g/l)	Na$_2$CO$_3$ concentration (g/l)	Reaction time (min)
PAN	-	-	-
APAN-1	5	3.75	60
APAN-2	17.5	13.12	30
APAN-3	17.5	13.12	60
APAN-4	17.5	13.12	90
APAN-5	30	22.5	60

Figure 1. Polyacrylonitrile reaction with hydroxylamine.

Results obtained by other researchers showed that amidoxime group can coordinate with many metal ions becauseit is a bidentate ligand. Zhang *et al.* used amidoxime group to absorb silver ions, and in order to enhance the stability of the absorbed ion, reduced it to silver nanoparticles by a reducing agent [19].

In this study, in order to investigate the amidoxime group ability in metal ions absorbance, the APAN-3 membrane sample was selected. For this purpose, firstly, 1 g of silver nitrate was dissolved in 1000 m*l* of distilled water. Then, selected fibers were immersed in this solution for 36 h at room temperature to silver ions sit on the membrane surface.

Characterization of Membrane Surface

Contact angle is used as a measure for determining surface hydrophilicity. Contact angle of the dry membrane surface (either of the intact membrane or the modified one) was measured by tensiometric method, at 25 °C using DCA 100 (Portsmouth). The dynamic contact angle θ, was measured on the surface of the hollow fibers by the Tensiometer. This tensiometric method determines the advancing contact angle by measuring the force when a sample of fiber is brought into vertical contact with deionized water. As the forces of interaction and geometry of the solid were measured with a known surface tension of water, the dynamic contact angle can be calculated. Each measurement was done twice. Additionally, after membrane samples were rinsed by water and dried completely, surface analyses of modified membrane were carried out via ATR spectroscopy (Bruker, Tensor 27), and in the range of 4000-600 cm^{-1}.

Membrane Filtration Experiments

For performing filtration experiments, prepared hollow fiber membrane modules including eight fiber were used. In other words, for each group of the prepared membranes, eight fiber membranes were selected and cut and potted at both ends with epoxy resin in a designed module. In each module, about 20 to 21 cm of each fiber was left free as effective length to achieve about 65 cm^2 effective area in each module for permeation and other tests. Since the modifications are set only on the outer side of the hollow fibers, it is necessary that, the flow passing through membrane to be in the out-in mode. Figure 2 shows the experimental setup used in this study. Experiments were carried out at ambient temperature (25±1 °C).

For analysis and comparison of antifouling properties of unmodified and modified membranes, a solution of foam-free pasteurized milk (3 percent protein, 1.5 percent fat) was used. An approximate composition of used milk can be given as

· 90.1 % water (range of 89.5-90.7 %),
· 1.5 % milk fat (range of 1.0-5.5 %),
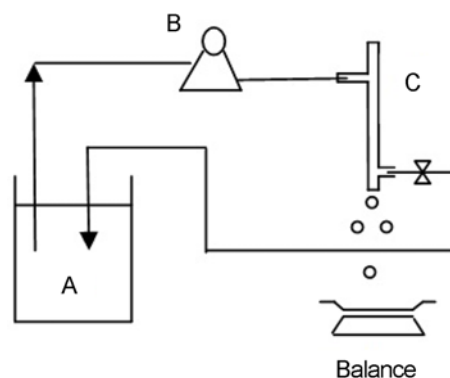· 8.4 % solids-not-fat (range of 7.9-10.0 %)

Figure 2. The schematic of used experimental setup; (A) feed reservoir, (B) pump, and (C) membrane module.

At first, each membrane sample was tested with pure water at pressure equal to 3 bar for 30 min. After that, the pressure was reduced and fixed at 2 bar. By weighing the permeate, the flux is determined and then it is calculated based on the following equation:

$$J = \frac{V}{At} \tag{1}$$

Here, V is volume of water (or solution) passing through membrane (L), A is the active surface of hollow fibers (m^2), and t is the permeating time (h).

Initially, a pure water flow at pressure of 2 bar is passed through membrane, and the flux is measured in each 5 min until reaching a fixed value which is defined as J_w. Immediately, the water is replaced by milk solution, and its flux (J_p) is determined by the same method and at the same pressure for time span of 3 h. After this time duration, the membrane is rinsed with pure water for 40 min by backwash method, so that reversible fouling (temporary fouling) becomes clear. Then, the pure water flux is measured (J_{wuf}).

For assessing the antifouling property of membrane, flux recovery ratio (FRR) is determined from the following equation:

$$\text{FRR} \% = \left(\frac{J_{wuf}}{J_w}\right) \times 100 \tag{2}$$

Also, relative flux reduction (RFR) parameter could be calculated by this equation:

$$\text{RFR} \% = \left(1 - \frac{J_p}{J_w}\right) \times 100 \tag{3}$$

Here, the more FRR and the less RFR, the better antifouling property in membrane.

Separation test was also carried out with aqueous solution of PVA with molecular weights of 30 and 60 kDa at concentration of 0.3 wt.% (3000 ppm), and at the afore-mentioned conditions (pressure of 2 bar and ambient temperature). In order to prevent concentration polarization,

the feed was recirculated by the pump and permeate was gathered from inside. The rejection of solutes (R) is calculated by equation below:

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100 \qquad (4)$$

In this equation, C_p and C_f are concentrations of solute in permeate and feed, respectively.

The concentration of PVA in feed and permeate is evaluated after precisely weighing the dried/dehydrated polymer remaining after complete evaporation of water.

Determining the Ability of the Membrane to Silver Absorbance

Determining the absorbed silver amount can be calculated from concentration difference of silver nitrate solution before and after the exposure of fibers on them. For this purpose, the ICP spectrophotometer was used for determining the silver amount in the solution. The following equation can be used to calculate the amount of silver absorbance by the membrane:

$$q = \frac{(C_0 - C_1)V}{M} \qquad (5)$$

In which q is the silver absorbance amount (mg/m^2 or mg/g), C_0 and C_1 are the initial and final concentrations of the solution, respectively. V is the volume of the solution and M is the external surface area of the fibers or fiber mass.

Results and Discussion

In order to assess the effect of surface modification on properties of the obtained membranes, at first, the properties of unmodified membranes were analyzed. Prepared PAN hollow fiber membranes exhibited pure water flux equal to 56 LMH (cross-flow mode) at 2 bar. In addition, the rejection of PVA-30 kDa and PVA-60 kDa in this membrane sample were 55 % and 91 %, respectively.
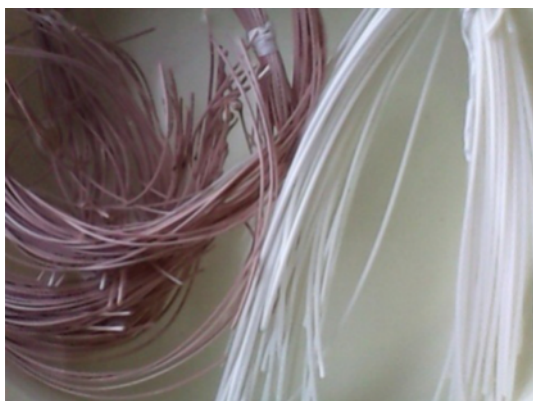

Figure 3. Membrane color change as a result of reaction with hydroxylamine.

By membrane reaction with hydroxylamine, and by reaction time, the membrane color in the solution starts to change, and alter from white to cherry color. Figure 3 shows the change in hollow fiber color because of reaction.

This changing color has been reported also in previous researches on PAN fibers [2]. The reason can be probably the long heating time during reaction process (temperatures > 60 °C).

Effect of Hydroxylamine Solution Concentration and the Time of Reaction on the Membrane Performance

In order to investigate the effect of hydroxylamine solution concentration during the reaction with membrane, membrane samples of PAN, APAN-1, APAN-3 and APAN-5 (Table 2) are evaluated. Figures 4 and 5 show the hydroxylamine solution concentration effect on the pure water permeation and PVA rejection, respectively.

As seen in Figure 4, with increasing the hydroxylamine solution concentration, water permeation reduces to 47 LMH thatmeans 16 % reduction in comparison with unmodified membrane. However, by increasing hydroxylamine concentration from 17.5 to 30 g/l, water permeation increased by very gentle slope.

Reduction in water permeation, whereas it seems by the rise of -OH and -NH$_2$ groups on the membrane surface, membrane becomes more active according to the hydrophilicity, maybe occurred as a process like steric hindrance (or swelling the unstable chains of the polymer), because this phenomenon has been confirmed by many studies on polyacrylonitrile with bases such as NaOH and KOH [15,25].

In Figure 5 we observe that with increasing in hydroxylamine solution concentration, the rejection of PVA has been increased. When this figure is compared with Figure 4, we realize that reduction in water permeation and increasing in the rejection amount can be due to the possible porosity reduction. A major reason for this phenomenon can be steric hindrance.

In order to evaluate the effect of reaction time with hydroxylamine solution, we have also compared the membrane samples of PAN, APAN-2, APAN-3 and APAN-4. Figure 6 shows the effect of reaction time on the pure water permeation.
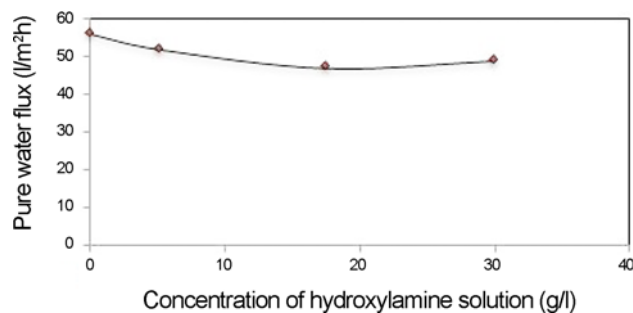
According to Figure 6, as we expected, with the increasing

Figure 4. The effect of concentration of hydroxylamine solution on permeation of pure water.
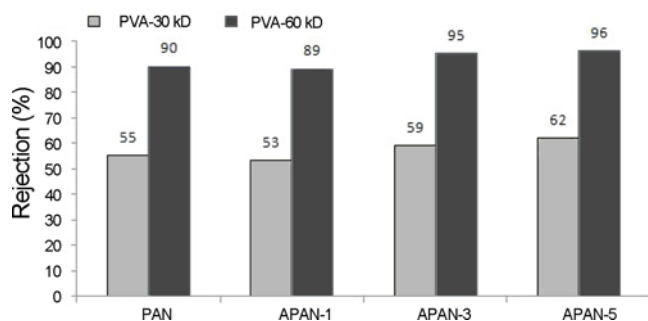
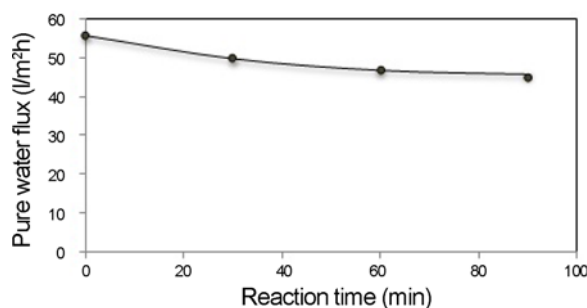**Figure 5.** PVA rejection of unmodified and modified membranes.

Figure 6. The effect of reaction time on the pure water permeation.

time of reaction, a similar trend to increasing concentration has been seen in water permeation. It may be concluded that both the increasing time of reaction and the solution concentration have the same effect on membrane performance.

Results of FTIR and Contact Angle

As seen in Table 3, contact angel for the membrane after the reaction with hydroxylamine, has been reduced to 34 degrees (water contact angle for unmodified membrane was 64 degree), and this means the increasing of hydrophilicity of membrane which cause the formation of amidoxime hydrophylicity group on the membrane.

Results obtained from Fourier Transform Infrared (FTIR) spectroscopy, for modified and unmodified hollow fiber membranes, have been depicted in Figure 7.

In the diagram related to PAN sample, regardless to previous investigations [2,15,26], the peak observed at 2937 cm^{-1} can be attributed to C-H bond, or so-called CH stretching. The peak at 2243 cm^{-1} is related to the nitrile group (-CN). At 1452 cm^{-1}, possibly there is a peak related to another sort of C-H bond. After the reaction occurs on the membrane surface, the spectrum of APAN-3 is obtained.

For this range, it can be seen that between 3100 cm^{-1} and 3500 cm^{-1}, a broad and noteworthy peak has been appeared. This peak can be attributed to -OH group. Also at 1660 cm^{-1} and 1608 cm^{-1}, two new and pretty clear peaks seen which according to previous studies might be related to C=N and NH groups [18,20]. However, unlike these two peaks which are relatively clear, there is a small peak at 914 cm^{-1} which

Table 3. Obtained water contact angles for intact and modified PAN hollow fiber membranes

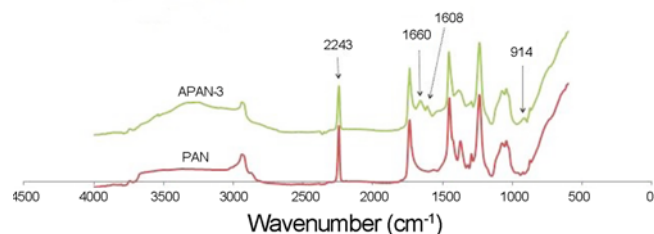| Sample name	Contact angle (degree)
PAN	64
APAN-3	34

Figure 7. FTIR spectroscopy for modified and unmodified PAN hollow fiber membranes.

might be related to N-O.

Analyses of the Antifouling Property and Silver Absorption Amount

In order to assess the performance of modified membranes against fouling, samples of PAN, APAN-3 and APAN-5 membranes were examined throughout milk ultrafiltration. Figures 8 and 9 show obtained results from milk ultrafiltration test for these samples.

From Figures 8 and 9, it can be concluded that with this reaction, FRR amount increases and RFR amount decreases. In other words, it was observed that with the reaction of membrane with hydroxylamine, the membrane resistance to fouling of milk has somewhat increased. Perhaps the main reason for this phenomenon, is the formation of amidoxime groups on the membrane surface which cause the improvement of hydrophilicity. The obtained data showed that the flux recovery rate has been increased from 64.2 % for the PAN membrane sample to more than 71 % for the APAN-3 membrane. In comparison to other researches which tried to enhance the antifouling properties of PAN membranes by surface modification, the obtained results in this study are acceptable. For example, Dai *et al.* [27] grafted a ring-
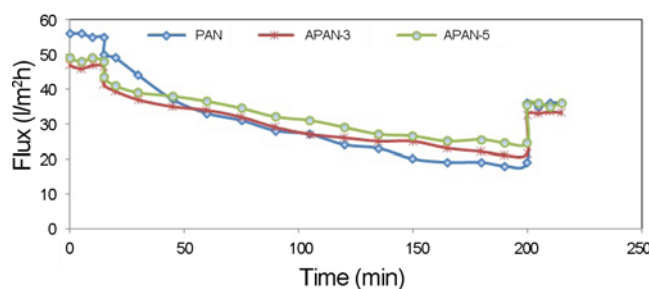

Figure 8. Flux change of solution permeation versus time for unmodified and modified membranes.
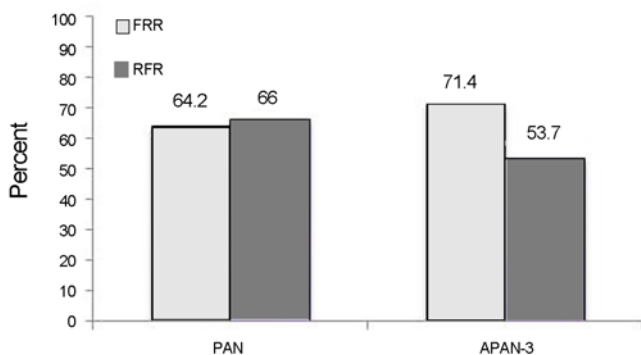
Figure 9. FRR and RFR changes for unmodified and modified membranes.

opening glycomonomer d-gluconamido ethyl methacrylate (GAMA) onto the surface of the membrane to improve the anti-fouling property of PAN ultrafiltration membrane. The results revealed that by the surface glycosylation procedure, FRR was raised from 28.6 % to 37.9 % when the grafting degree was 41.2 μg/cm^2. In another work, Nieet *et al.* decreased RFR from 37 % to 26 % by grafting of polyethylene glycol on the PAN membrane's surface [28].

Test result of ICP spectrophotometer showed that the modified PAN membranewith hydroxylamine can present the relatively high absorption of silver, so that each gram of the membrane can have the absorption ability of 23.8 mg of silver, or in other words, each square centimeter of membrane surface can absorb 0.28 mg of silver.

Conclusion

In this work, chemical modification with hydroxylamine hydrochloride solution was performed on PAN hollow fiber membrane. By the membrane reaction with hydroxylamine, nitrile groups on the membrane surface of PAN have relatively become amidoxime hydrophilic groups.

It was seen that, due to the reaction, the water permeation was reduced and the rate of molecular weight rejection had an approximately ascending pattern. On the other hand, they could be signs of membrane porosity reduction.

The results of evaluating the contact angel showed the increase of the surface hydrophilicity after the appearance of amidoxime groups. Surface modified membranes showed high flux recovery during filtration process, indicating that the anti-fouling performance of the PAN membrane was enhanced by the surface modification strategy.

References

1. W. X. Bao, Z. L. Xu, and H. Yang, *J. Sci. China, Ser. B: Chem.*, **52**, 683 (2009).
2. G. Zhang, X. Song, J. Li, S. Ji, and Z. Liu, *J. Membr. Sci.*, **350**, 211 (2010).
3. A. Sueoka and K. Takakura, *Polym. J.*, **23**, 561 (1991).
4. H. R. Lohokare, M. Muthu, J. Agarwal, and U. Kharul, *J. Membr. Sci.*, **320**, 159 (2008).
5. Z. G. Wang, L. S. Wan, and Z. Xu, *J. Membr. Sci.*, **304**, 8 (2007).
6. T. Barroso, M. Temtem, T. Casimiro, and A. Aguiar, *J. Supercrit. Fluids*, **56**, 312 (2011).
7. S. Mei, C. Xiao, X. Hu, and W. Shu, *Desalination*, **280**, 378 (2011).
8. T. D. Tran, S. Mori, and M. Suzuki, *Thin Solid Films*, **515**, 4148 (2007).
9. G. Zhang, H. Meng, and S. Ji, *Desalination*, **242**, 313 (2009).
10. X. Zhao, Y. Su, W. Chen, J. Peng, and Z. Jiang, *J. Membr. Sci.*, **415**, 824 (2012).
11. X. Qiao, Z. Zhang, and Z. Ping, *Sep. Purif. Technol.*, **56**, 265 (2007).
12. M. Kurihara and Y. Himeshima, *Polym. J.*, **23**, 513 (1991).
13. A. Higuchi, P. Wang, T. Tak, T. Nohmi, and T. Hashimoto, *ACS Symposium Series*, **744**, 228 (1999).
14. S. Yan, M. Zhao, G. Lei, and Y. Wei, *J. Appl. Polym. Sci.*, **125**, 382 (2012).
15. H. R. Lohokare, S. Kumbharkar, Y. Bhole, and Y. Kharul, *J. Appl. Polym. Sci.*, **101**, 4378 (2006).
16. M. C. Yang and J. H. Tong, *J. Membr. Sci.*, **132**, 63 (1997).
17. I. C. Kim, H. Yun, and K. H. Lee, *J. Membr. Sci.*, **199**, 75 (2002).
18. K. Saeed, S. Haider, T. Oh, and S. Y. Park, *J. Membr. Sci.*, **322**, 400 (2008).
19. L. Zhang, J. Luo, T. Menkhaus, H. Varadaraju, Y. Sun, and H. Fong, *J. Membr. Sci.*, **369**, 499 (2011).
20. Y. C. Chu, C. H. Tseng, K. T. Hung, C. Wang, C. Y. Chen, and J. Inorg, *Organomet. Polym. Mater.*, 309 (2005).
21. Q. Feng, Q. Wang, B. Tang, A. Wei, X. Wang, Q. Wei, F. Huang, Y. Cai, D. Hou, and S. Bi, *J. Polym. Int.*, **62**, 251 (2012).
22. P. Zhang, Q. Wang, J. Zhang, G. Li, and Q. Wei, *Fiber. Polym.*, **15**, 30 (2014).
23. M. E. McComb and H. D. Gesser, *J. Appl. Polym. Sci.*, **65**, 1175 (1997).
24. P. K. Neghlani, M. Rafizadeh, and F. Taromi, *J. Hazard. Mater.*, **186**, 182 (2011).
25. Y. H. Choi, C. M. Choi, D. H. Choi, Y. Paik, B. Park, Y. K. Joo, and N. Kim, *J. Membr. Sci.*, **317**, 84 (2011).
26. K. Parashuram, S. K. Maurya, H. H. Rana, P. S. Singh, P. Ray, and A. V. Reddy, *J. Membr. Sci.*, **425**, 251 (2013).
27. Z. Dai, L. Wan, and Z. Xu, *J. Membr. Sci.*, **325**, 479 (2008).
28. F. Nie, Z. Xu, Q. Yang, J. Wu, and L. Wan, *J. Membr. Sci.*, **235**, 147 (2004).