Surface Modification of Polyacrylonitrile Based Ultrafiltration Membrane

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ABSTRACT: Ultrafiltration membrane based on polyacrylonitrile prepared by phase inversion method using zinc chloride as an additive showed more than 90% rejection for BSA and 90–110 $lm^{-2} h^{-1}$ water flux. The surface modification of this membrane was studied using ethanolamine, triethylamine, sodium hydroxide, and potassium hydroxide solutions. The effect of base treatment time and temperature on water flux and rejection was investigated. The membranes exhibited swelling by NaOH treatment followed by deswelling by HCl post-treatment, similar to pH responsive membranes. The treatment by organic as well as inorganic bases improved water flux with a slight lowering in BSA rejection by dead-end mode type treatment. A 230% increase in water flux was achieved by sodium hydroxide treatment in crossflow mode without a noticeable pore swelling by SEM. The contact angle of the modified membranes was decreased as compared to the unmodified one indicating appreciable surface modification. As the treatment time or temperature increased, the ESCA analysis showed increased population of Na-carboxylate groups. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4378–4385, 2006

Key words: ultrafiltration; surface modification; polyacrylonitrile membrane; BSA rejection; chemical treatment

INTRODUCTION

Polyacrylonitrile (PAN) is widely used as UF-membrane material and is advantageous over other conventional polymers like polysulfone, polyethersulfone, etc. in certain respects. The former has more hydrophilicity, good solvent stability, and is cheaper than other materials. In addition, its chemical modification can be done easily to modify its properties. Its nitrile (—CN) group can be converted into various functionalities to offer membranes with better antifouling[1] and flux performance[2] due to increased hydrophilicity. The modification of PAN with bases is documented in the literature. Its modification using primary amine solution showed that the affinity to water increased with increasing the amine concentration.[3] Moreover, the modified polymer became water-soluble when a large amount of amine had reacted with PAN. The pervaporation membranes used for water–ethanol separation based on ethanolamine-modified PAN[4] showed that both the separation factor and permeate flux for water increased as ethanolamine component in the membrane increased. The hydrolysis of PAN microporous membrane by aqueous NaOH solution converted some PAN molecules into poly(acrylic acid) (PAA) and the pore diameter of the microporous membrane became larger with increasing hydrolysis time as verified by SEM micrographs.[5] On the other hand, NaOH-induced hydrolysis of nitrile groups on the PAN membrane surface resulted in decreasing pore diameter and the modified membranes were less prone for protein deposition.[1] Another study reported partial hydrolysis with NaOH, wherein, the nitrile groups of the PAN membrane were mainly changed to carboxyl groups, which improved membrane hydrophilicity and resulted in a negative surface charge.[6] The hydrolysis of PAN hollow fiber membranes by circulating NaOH solution of varying concentration at different temperatures produced a thin PAA layer, swelling of which reduced hydraulic permeability between pH 5 and 6.[7] It was also said that the number of carboxylic groups increased with increasing time, temperature, and concentration of NaOH solution. Oh et al.[2] studied the hydrolysis of PAN membrane by varying the NaOH solution concentration and time by keeping the temperature constant. At lower NaOH concentration, morphological changes were negligible and the hydrophilicity change was dominant; while at higher NaOH concentration, morphological changes became evident with increased hydrophilicity.[2] Effect of hydrolysis of annealed membrane was studied by Kim et al.[8] using different concentrations of NaOH and CH_3ONa. With an increasing treatment period of 1*M* NaOH or CH_3ONa, the rejection rate of PEG-600 was

decreased, whereas the permeability was considerably increased. However, when $2M$ NaOH or CH_3ONa was used, after 2 h treatment period the rejection rate of PEG-600 was increased, whereas the permeability was decreased. This was due to the change of surface morphology.

The PAN membranes used in this study exhibited a good combination of water flux and rejection. The water flux of 100 lm^{-2} h^{-1} at 1 bar transmembrane pressure, >90% BSA rejection, and 5-log reduction of hepatitis-A virus[9] showed its potential for removal of pathogenic species from drinking water. It was anticipated that appropriate surface modification of this membrane leading to increased hydrophilicity would improve the water flux. Though increased hydrophilicity using hydrolysis is reported in the literature, most of the treatments led to the reduction in porosity and hydraulic permeability due to pore swelling.[1,2,7,8] The objective of the present study was to systematically investigate the variation in water flux and BSA rejection, caused by surface modification of the PAN membrane using organic (ethanolamine/triethylamine) and inorganic bases (NaOH/KOH) while varying treatment conditions (time and temperature). The effect of modification method (dead-end versus crossflow) was also assessed.

EXPERIMENTAL

Materials used and membrane preparation

The polyacrylonitrile (PAN) was received from IPCL, Vadodara. The viscosity averaged molecular weight of this material was 24,800. The NaOH, KOH, N,N-dimethyl formamide (DMF), ethanolamine (EA), triethylamine (TEA), zinc chloride ($ZnCl_2$), and HCl were of AR/GR grade. The nonwoven support fabric was procured from M/s. Freudenberg (Germany). Bovine Serum Albumin (BSA, fraction-v, ~99%) was obtained from M/s. Sigma chemicals (USA).

The flat sheet PAN-based ultrafiltration membrane was prepared by phase inversion method. A dope solution containing 120 g of vacuum-dried PAN and 27.2 g of $ZnCl_2$ in 653 g of DMF was prepared. It was degassed and then centrifuged at 2500 rpm for 3 h. The membrane was casted on moving nonwoven support using pilot scale continuous membrane casting facility at an ambient. The formed membrane had an average thickness of ~250 μm and was used for further investigations of surface modification.

Surface modification with dead-end mode

The PAN membrane surface modification by dead-end mode was performed using NaOH, KOH, TEA, and EA. The membrane with 10.7 cm^2 active area was mounted in a dead-end cell and 50 mL of base solution
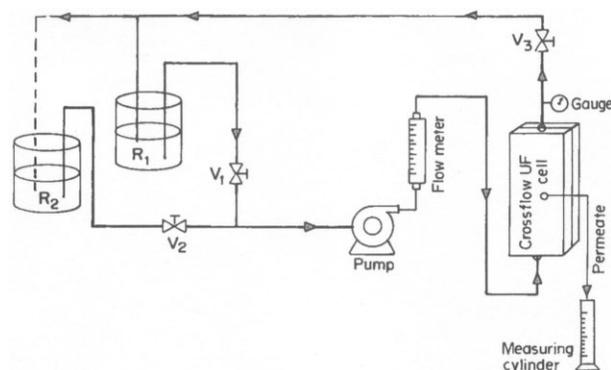

Figure 1 Schematics of crossflow set up.

was passed at 1 bar and then membrane was left under the base solution for predetermined time. The membrane was then thoroughly rinsed with water and finally 100 mL of water was passed through the membrane to remove base solution left into the pores. The water flux of modified membrane was recorded at 1 bar transmembrane pressure. In case of membrane treated with NaOH and KOH, a post-treatment of HCl was also performed by passing 30 mL of $0.1N$ HCl solution through the membrane, followed by thorough water washing till neutral to pH. The water flux after such treatment was again recorded at 1 bar pressure.

Surface modification with crossflow mode

The schematic of the crossflow setup used for this study is shown in the Figure 1. The reservoirs R_1 and R_2 filled with $1N$ aqueous NaOH solution and water, respectively were connected to the feed pump through valve V_1 and V_2. The NaOH solution was circulated at defined temperature through the crossflow cell containing PAN membrane having active area of 191 cm^2. The transmembrane pressure was kept at 1 bar throughout the treatment period by using throttle valve V_3 fixed at the retentate side of the cell. After predetermined time, the reaction was quenched by closing the valve V_1 and opening the valve V_2. The membrane was washed with water till neutral to pH. The water flux was recorded at 1 bar transmembrane pressure. Minimum of six repetitions with fresh membranes were done for a particular set of condition. The NaOH treatment was followed by post-HCl treatment by circulating $0.1N$ HCl solution kept in reservoir R_2. After collecting 150 mL of HCl solution in the permeate side at 1 bar pressure, the membrane was washed with distilled water by opening the valve V_1 till permeate showed neutral pH and then the water flux was recorded at 1 bar pressure.

Treatment of PAN powder

For IR investigations, the surface treatment of the PAN powder was done by using $2.5N$ aqueous NaOH

at 45°C and at varying treatment time of 0.5, 1, 2.5, and 5 h. The reaction was quenched by discarding the NaOH solution and gentle washing with water till neutral to pH. The 0.1N HCl treatment was also performed at ambient temperature followed by thorough water wash till neutral to pH.

Membrane characterizations

The membranes were analyzed for 0.1% BSA (68 kDa) rejection at pH of 7.5 (McIlvaine buffer). The concentration of feed, permeate, and retentate was determined by UV spectrophotometer (Shimadzu, Graphic printer PR-1) at 280 and 260 nm wavelength. At least six repetitions (±2% variation) were performed.

The contact angle measurement of the dried membrane was done by the sessile drop method. A water drop of 4 μL was placed on a membrane surface. The measurement was repeated with at least eight different membrane samples and the data averaged (variation ±3–6°). Electron spectroscopy for chemical analysis (ESCA) spectra of membrane samples with their surface modified by crossflow method were recorded on a V.G. Scientific (UK) ESCA 3000, using Al Kα as an X-ray source (1486.6 eV), operated at 250 W of power, 50 eV pass energy, 4 mm slit, and a take-off angle of 30° in relation to the sample surface. The residual gas pressure in the spectrometer chamber during data acquisition was less than 10^{-8} Torr. The ESCA spectra were referenced to the C$_{1s}$ peak (285.0 eV). The surface analysis of the modified membranes was also done by attenuated total reflectance (ATR) spectroscopy (KRS crystal, Perkin Elmer, MA, USA) at an angle of 45°. The FTIR spectra of PAN powder before and after modification was recorded on Perkin-Elmer 16 PC FTIR. The scanning electron micrograph (SEM) of membrane cross section was recorded with Leica, stereoscan-440.

RESULTS AND DISCUSSION

Treatment of organic bases by dead-end mode

To select an appropriate modification agent and treatment conditions that would improve the water flux without causing the swelling, PAN membrane in this study was modified with ethanolamine, triethyl amine, NaOH, and KOH in dead-end mode and the effect on water flux was analyzed. For the modification with ethanolamine or triethylamine, the membrane was first dipped in 15 : 85 DMF : water (v/v) for 12 h to swell it to ease its reaction with these amines. At ~10% aqueous DMF, the degree of acrylamide grafting on PAN-based membrane was reported to be the highest.[10] Such pretreatment is also known for the reaction of PAN membrane with hydroxylamine and diethylaminoethylmethacrylate.[11] The DMF pretreatment did not cause

TABLE I
Change in Water Flux of PAN-Based Membranes Treated with 15% Aqueous EA and TEA in Comparison to Untreated Membrane and Their Rejection Properties

Treatment time (h)	Percent change in water flux		BSA rejection (%)	
	EA-treated	TEA-treated	EA-treated	TEA-treated
3	41	28	82	88
6	49	60	85	84
9	−12	78	82	84
12	−44	43	63	82

any damage to the pore morphology in the present case. This was confirmed by dipping the swollen membranes again in water for 24 h to extract back the DMF and then measuring the water flux, which was found to be identical with the initial water flux. After swelling by DMF, the membrane samples were dipped in 15% aqueous solution of ethanolamine or triethylamine for predefined time at an ambient. The results are summarized in Table I. It is seen that in the case of ethanolamine, water flux was initially increased by 49% at 6 h treatment, while it was increased by 78% after 9 h triethylamine treatment. The increase in water flux can be attributed to the increased hydrophilicity of the resultant membrane owing to the presence of amide and hydroxyl functionality as also shown by Todorov et al.[12] This led to a marginal reduction in BSA rejection. After 6 h treatment, the water flux of ethanolamine-treated membrane decreased abruptly due to the formation of cyclic intermediate as proposed by Hu and Chiang,[4] which is less hydrophilic. The reduction in water flux by triethylamine treatment was not as rapid. Though the reaction of PAN with organic bases like monoethanolamine, ethylene diamine, and hydroxylamine are well reported in the literature,[4,11,12] the reaction with triethylamine is not documented, to our knowledge. The PAN membrane modification using organic bases revealed that 9 h triethylamine treatment was the best treatment protocol.

Treatment of inorganic bases by dead-end mode

In the case of membrane modification by 1N NaOH or KOH, the water flux initially increased by ~50%, regains its original value (at 7.5 h for NaOH and at 10 h for KOH) and then decreased continuously by ~75% as seen in Figure 2(a,b). The post-HCl treatment to these membranes led to initial enhancement in water flux as revealed by increase in percent change in water flux (Δf), decreased slightly at 7.5 h treatment duration, again increased upto a maximum value of 152% for NaOH treatment and 133% for KOH treatment for 20 h duration, and then again declined for 25 h treatment duration for both the cases of NaOH and KOH pretreatments. These variations in water flux were associated with mar-
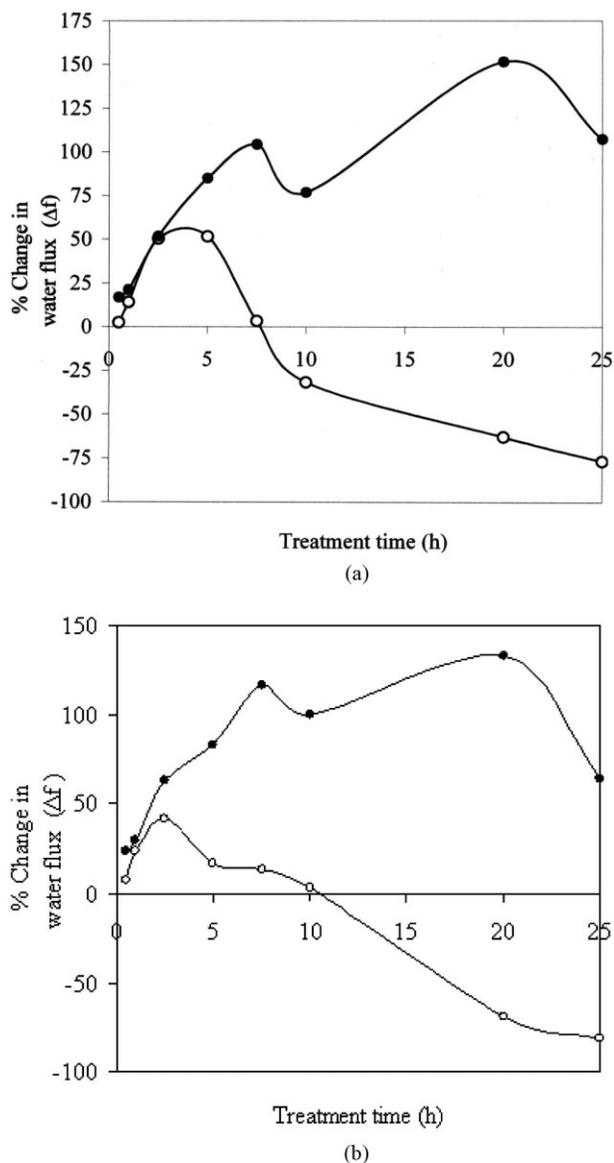
Figure 2 Variation in water flux (Δf) caused by treatment with dead-end mode in comparison to the untreated membrane; ($\bigcirc$) 1N NaOH treatment, ($\bullet$) 1N NaOH followed by 0.1N HCl treatment.

licity due to presence of both amide and carboxyl functionality. The presence of these groups at initial stages of reaction was confirmed by Bryjak et al.[1] by observing respective C=O bands in the IR spectra. As seen from Figures 2(a) and 2(b), the difference between percent change in water flux (Δf) for NaOH/KOH treatment and for post-HCl treatment becomes prominent only after the maxima was achieved by the base treatment (which is ~4 h for NaOH and 2.5 h for KOH treatment). After this time, a decrease in Δf by base treatment and its increase after post-HCl treatment could not be ascribed just to the surface hydrophilicity, but can better be correlated to the pore morphological changes. It is known that the NaOH treatment to PAN membranes resulted in reduction of pore size caused by swelling,[1,2,7,8] which in turn reduced hydraulic permeability[7] or PEG permeability.[8] The reduction in pore size was due to the swelling of the labile PAN chains on the membrane pore surface. In the present case, this type of swelling, though could be speculated for NaOH treatment, was not evident for the post-HCl treatment, since water flux still increases upto 20 h treatment duration [Figs. 2(a) and 2(b)]. This could be explained on the basis of reaction products formed after these treatments. During the initial stages of treatment, the population of amide and carboxylic groups are moderate and the increased surface hydrophilicity due to presence of both these groups is responsible for the increase in water flux for both base as well as post-HCl-treated membranes. As reaction time progresses, the population of carboxylic groups increases, leading to the decrease in water flux by base treatment (due to swelling). The presence of Na-carboxylate groups was confirmed by ESCA as shown in Figure 7. The intensity of Na increases as treatment conditions were made severe for coupons treated by crossflow mode as explained in the following section. It is postulated that in case of NaOH/KOH treatment, the swelling is predominantly due to the repulsive interaction of labile polymer chains bearing —COO⁻ group (as shown in Fig. 3), and not just by water uptake. The carboxyl functionality would re-

ginal changes in BSA rejection (Table II). Among various treatment durations, the lowest BSA rejection was 77–79%. The marginal changes in rejection are attributable to the changes in surface properties than to the pore morphological changes. The complex behavior of percent variation in water flux (Δf) and smaller changes in BSA rejection can be explained in terms of effects caused by the various intermediates formed as the reaction products of —CN functionality with NaOH/KOH at respective treatment duration. It is reported that the base initially converts —CN functionality to amide and cyclic intermediate,[13] though the presence of carboxylic groups at lower reaction time is also documented.[1,2] The initial increase in flux can be attributed to increased hydrophi-

TABLE II
Rejection Performance of Membranes Treated with 1N NaOH and 1N KOH, Followed by 0.1N HCl at 30°C by Dead-End Mode

Treatment time (h)	BSA rejection (%)	
	NaOH followed by HCl treatment	KOH followed by HCl treatment
0.5	92	82
1	93	83
2.5	84	84
5	79	77
7.5	84	85
10	90	99
20	100	87
25	92	91

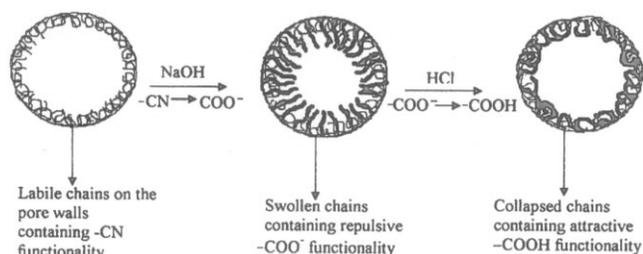**Figure 3** Schematic representation of pore swelling by NaOH treatment and regain of pore size by HCl treatment.

main in —COO$^-$Na$^+$ or COO$^-$K$^+$ form, which remains ionized, leaving net negative charge on the membrane surface and causing repulsive interactions among the labile chains bearing these groups. This chain repulsion predominantly causes the swelling, resulting in lowering in pore size and water flux. If it would have been just because of water uptake, the same behavior of swelling should have also been observed in the case of post-HCl treatment, and as a result, water flux in this case also would have decreased. Conversely, an increased water flux for 5–20 h post-HCl-treated membranes suggests that lowering in pore size caused by base treatment is absent. This is due to the collapse of swollen structure leading to increase in pore size as represented in Figure 3. This could happen since post-HCl-treated membrane now has carboxyl groups in the form of —COOH, which forms H-bonding with neighboring —COOH, creating attractive interactions that results in collapse of swollen structure into coiled one. This leads to an increase in pore size and the water flux increases due to the combined effect of changed pore size and increased hydrophilicity. The —COOH on labile PAN chains now behaves like a polyacrylic acid (PAA)-type structure. The behavior is similar to the observation of PAA grafted onto the pores of a polycarbonate membrane,[14] wherein, an increase in pH caused swelling, reducing the pore size and the permeability of the membrane. In the present case, an increase in water flux by post-HCl treatment was seen till moderate reaction has occurred upto 20 h treatment, after which, the Δf declined again. This could be due to formation of PAA-type layer with some unreacted —CN functionality on the membrane surface, which highly absorbs water, but remained water insoluble. The reason for this PAA insolubility can be as explained by Yang and Tong,[7] as not all the nitrile groups on the same molecular chain were converted into carboxylic group or the hydrolyzed molecular chains might be entangled with other nonhydrolyzed PAN chains. This study thus reveals that by carefully controlling hydrolysis conditions of PAN membranes, pores can be either swollen or deswollen, depending on pH and thus can act as stimuli responsive membranes or as membrane valve. This would need further investigations as the objective of next study. The base treatments with

larger treatment time, higher temperature, or concentration were not done, since the membrane surface turned yellow and got delaminated from the support backing after a membrane swelling. Further treatment to these swollen delaminated membranes led to dissolution of the membrane into the base solution due to formation of polyacrylic type material.

NaOH treatment in crossflow mode

The effect of base treatment by crossflow mode was also studied using 1N NaOH solution at different
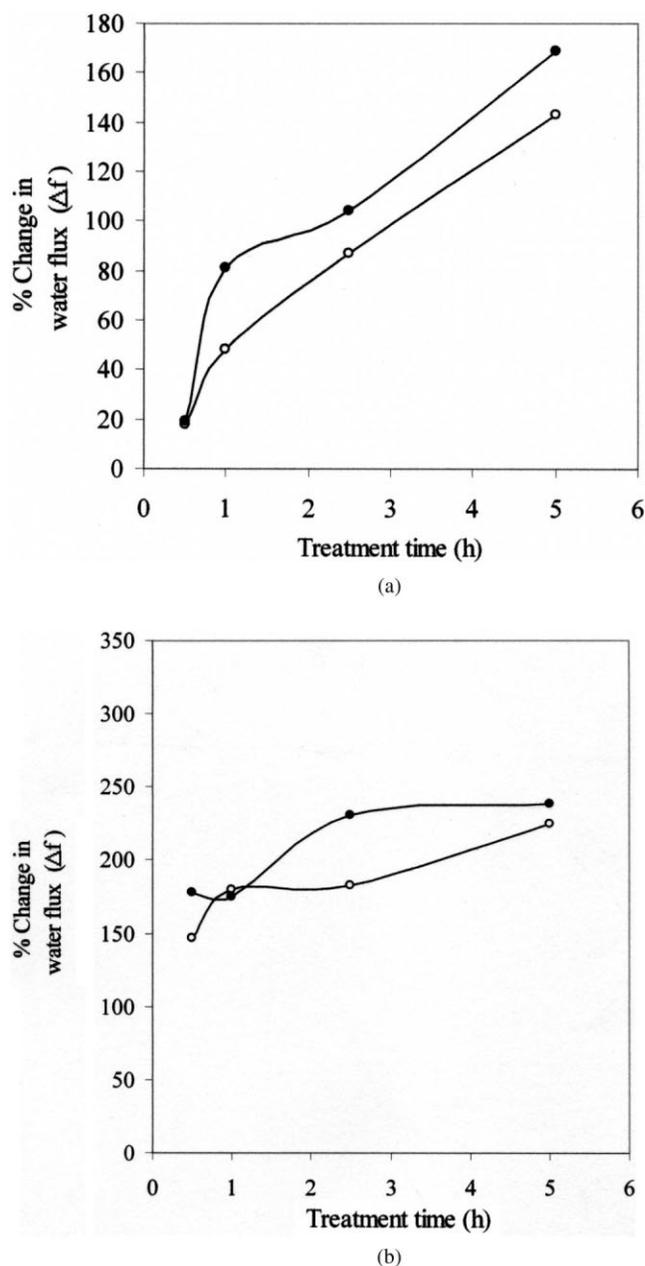

Figure 4 Variation in water flux (Δf) caused by treatment at 30°C by crossflow mode in comparison to that of untreated membrane; (○) 1N NaOH treatment, (●) 1N NaOH followed by 0.1N HCl treatment.

TABLE III
Rejection Performance of Membranes Treated with 1N NaOH by Crossflow Mode

| Treatment time (h) | BSA rejection (%) | | | |
| | Membrane treated at 30°C | | Membrane treated at 45°C | |
	NaOH treatment	NaOH followed by HCl treatment	NaOH treatment	NaOH followed by HCl treatment
0.5	89	84	–	78
1	92	85	73	79
2.5	85	77	57	68
5	79	77	49	59

temperature and the membrane performance was compared with that of dead-end type treatment. Figure 4(a,b) shows the effect of treatment time on percent change in water flux (Δf) at 30 and 45°C treatment temperature, respectively. In both the cases, Δf increases with treatment time. In case of treatment at 30°C, the post-HCl-treated membrane had higher water flux, except for 0.5 h treatment. Such overlap of Δf is also seen for treatment at 45°C by crossflow mode [Fig. 4(b)] and also for dead-end type of treatments [Fig. 2(a,b)]. This overlap is observed at lower treatment times, indicating the membrane surface hydrophilicity leading to these enhancement in water flux is due not only to carboxyl groups but also to amide intermediates to a considerable extent. For 30°C treatment, the Δf starts rising from 20% and reaches to the maximum of 170% for the treatment period studied. In case of 45°C treatment, the extent of change in the water flux (Δf) is much higher even at smaller treatment time [Fig. 4(b)], owing to high reaction rate at higher temperature. The Δf reaches its maximum of 230% within 2.5 h and remains similar till 5 h time. The percent increase in water flux (Δf) was higher by crossflow type treatment than by dead-end type, indicating extent of hydrolysis is higher by earlier mode. This is possible as the base is constantly circulating through the membrane pores. All possible membrane surface as well as pore wall surface gets essentially treated with same feed concentration. The BSA rejection showed a general decrease for the membranes treated at 30 and 45°C (Table III). This may be attributed to the changes in surface hydrophilicity rather than to the morphological changes. The extent of decrease in rejection was higher for (i) 45°C treatment than for 30°C and for (ii) post-HCl-treated than NaOH-treated cases, depicting its dependence on extent of reaction as well as treatment type. The decrease in rejection also indicated that there is no pore swelling. The lowering in BSA rejection by crossflow type treatment was higher than by dead-end type, which could also be correlated to the extent of reaction. The SEM images of membranes treated at various conditions are shown in Figure 5. The treatment even at 45°C did not show appreciable morphological changes.

Contact angle, IR, and ESCA studies

The hydrophilicity of the membrane surface was studied by measuring contact angle of water by sessile drop method, for the membranes modified by crossflow mode that showed largest variation in Δf. The results are shown in Table IV. The decrease in contact angle was observed as the treatment time and temperature was increased, as anticipated.

The progress of the surface reactions was tried to monitor using FTIR-ATR spectroscopy at incident angle of 45°, but no significant information could be drawn. It is known that the penetration depth of the beam into the sample is variable but of the order of 0.5 to 10 μm.[15] The chemical modifications in the present case occurred predominantly at the membrane surface, which were masked and not seen in ATR spectra owing to the penetration depth. It was thus thought to treat PAN powder suspended in water by 2.5N NaOH at 45°C for various time and record the IR spectra. As seen from Figure 6, the characteristic broad —OH stretching peak near 3500 was seen for NaOH as well as post-HCl-treated powder. More significantly, a characteristic band for N—H stretching of primary amide (—CONH$_2$) was also observed in this region[16] till treatment duration of 2.5 h, confirming the presence of both amide and carboxylic acid for moderate treatment conditions. This suggests that if the PAN surface could be evenly treated, presence of both carboxyl and amide functionality would lead to an increased water flux at these moderate treatment conditions. In such case, the behavior of water flux after NaOH as well as post-HCl-treated membrane would be like as seen in Figure 4(a,b). Conversely, the dead-end type treatment would be more focused on membrane surface (and lesser into the pores), converting amide functionality also to carboxylic, leading to different behavior of water flux as seen in Figure 2(a,b). The appearance of Na at 1071.8 eV[17,18] in ESCA as a result of —COO$^-$Na$^+$ formation of membrane surface with increasing treatment severity is shown in Figure 7. For the membranes treated for 0.5, 2.5, 5 h at 30°C and for 5 h at 45°C using 1N NaOH solution, the intensity for Na increases. This increasing population of carboxylic groups
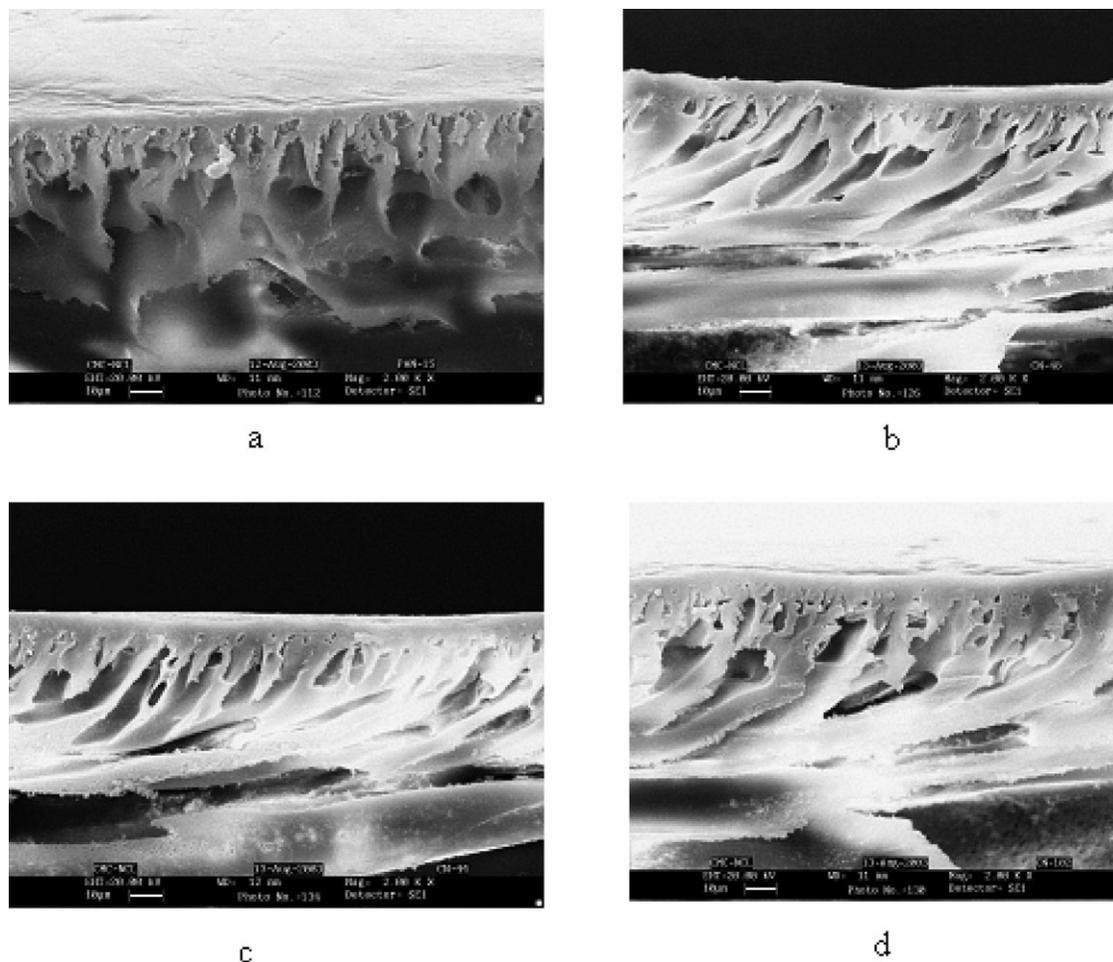
Figure 5 SEM of cross section of PAN membranes; (a) unmodified, (b) 1N NaOH treatment at 30°C for 5 h, (c) 1N NaOH treatment at 30°C for 5 h, followed by 0.1N HCl, (d) 1N NaOH treatment at 45°C for 5 h, followed by 0.1N HCl.

with the treatment time or temperature led to the observed variations in flux.

CONCLUSIONS

An increase in the water flux was achieved by surface treatment of PAN membranes either by organic bases (TEA, EA) or by inorganic bases (NaOH, KOH), the latter being more effective. The morphological

TABLE IV
Contact Angle of Surface Modified Membranes

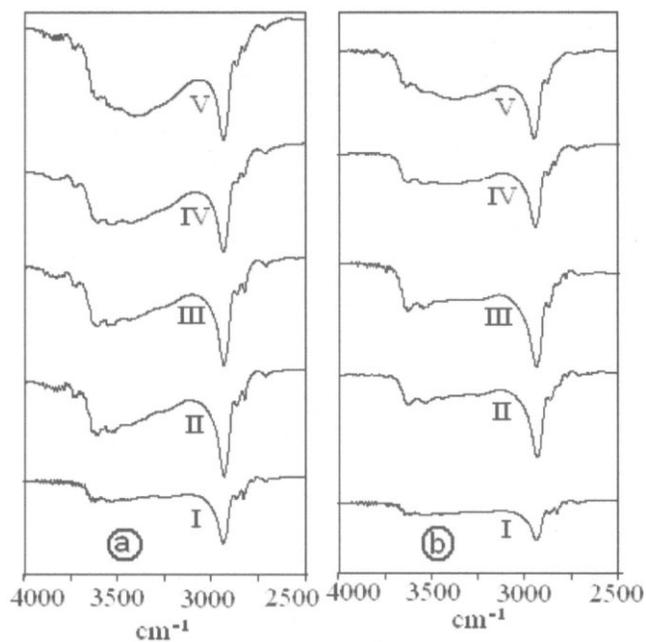| Time (h)	Contact angle for membrane treated at 30°C		Contact angle for membrane treated at 45°C	
	NaOH treatment	NaOH followed by HCl treatment	NaOH treatment	NaOH followed by HCl treatment
0.5	68	66	–	60
1	61	58	58	58
2.5	59	61	62	54
5	60	61	55	55

Figure 6 FTIR spectra of PAN powder treated at 45°C with (a) 2.5N NaOH solution, (b) 2.5N NaOH, followed by 0.1N HCl; I: unmodified, II: 0.5 h, III: 1 h, IV: 2.5 h, V: 5 h.
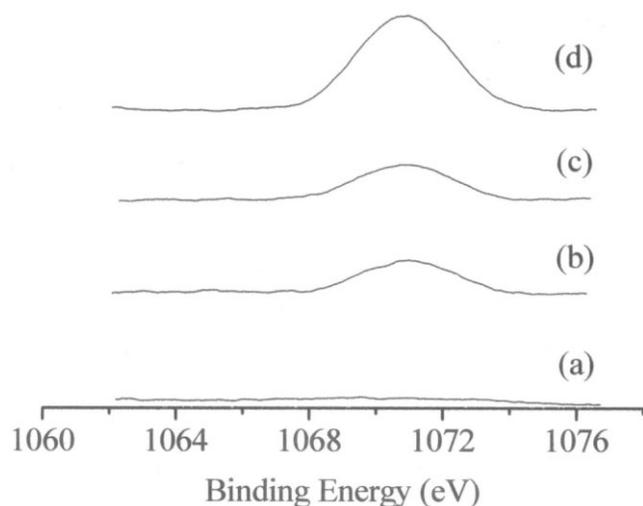
Figure 7 Occurrence of Na by ESCA for membranes treated at 30°C with 1N NaOH at (a) 0.5 h, (b) 2.5 h, (c) 5 h, and (d) 45°C for 5 h.

changes leading to large pore size variations were not evident from the different flux behavior offered by NaOH and post-HCl treatment. This also shows that the PAN surface modification has a potential to offer membranes that are pH responsive. The SEM also depicted absence of noticeable changes in membrane pore size. The treatment by crossflow mode was more effective than by dead-end mode. A maximum increase of 152% in water flux was achieved by dead-end mode within 20 h, while crossflow offered maximum increase of 230% in just 2.5 h duration at 45°C. The extent of percent change in water flux was highly dependant on treatment mode (dead-end or crossflow) and treatment temperature. The variations in BSA rejection and water flux are attributed mainly to the surface hydrophilicity. This investigation shows that the optimum surface modification of PAN membrane by bases can lead to a large improvement in the water flux, without causing pore swelling.

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