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Surface modification of polysulfone ultrafiltration membrane by in-situ ferric chloride based redox polymerization of aniline-surface characteristics and flux analyses

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Abstract−On the basis of the water-loving nature of Polyaniline (PANI), super hydrophilic polysulfone (PS) ultrafiltration membranes were prepared via in-situ polymerization of aniline on the surface of the membrane. Growing polyaniline in-situ leads to permeability enhancement of the ultrafiltration membrane. Surface-attenuated total reflection Fourier transform infrared spectroscopy, Atomic force microscopy, Scanning electron microscopy and energy dispersive X-spectroscopy and water contact angle demonstrated the successful attachment of PANI on PS membrane surface. Modified membranes containing increased amount of PANI were compared to the unmodified PS membrane to estimate the change in membrane performance, hydrophilicity and anti-fouling properties. PANI modified membranes showed higher water fluxes in comparison to unmodified membranes, while protein rejection was almost similar in both PANI modified and unmodified PS membranes. Atomic force microscopy and contact angle measurements confirmed increased membrane surface hydrophilicity with increasing PANI content. Fouling study and flux recovery experiments revealed that modified membranes exhibit higher flux recovery ratio (65%) and more stability to strong cleaning agents.

Keywords: Surface Modification, Ultrafiltration, PANI, Hydrophilicity, Stability

INTRODUCTION

Surface modification of polymeric membranes with hydrophobic surfaces is an effective technology for improving selectivity, flux enhancement, longevity with antifouling performance, as reported in the literature [1-9]. Enhancement of water permeability is basically due to the increase in hydrophilicity by generation of negative charge on the membrane surface and enlargement of pores that prevents natural bio-polymeric foulants to adhere membrane surface [10,11]. It is believed that hydrophilic surfaces are able to provide a buffer layer adjacent to the membrane surfaces with polar water molecules and enhance the membrane performance. A variety of works have been reported for hydrophilic modification of the polymeric membrane surfaces, such as blending, surface grafting, surface hydrolysis, surface/dip coating, dynamic forming, interfacial polymerization, plasma treatment, ion beam, electron beam, UV-photo-grafting polymerization, and chemical grafting polymerization [5,12-16]. For each category there are advantages and disadvantages. As example, grafting creates strong chemical attachment on the surfaces and ensures long-term stability but low efficiency and a multi-step process. Similarly, the coating may be simpler and easier process for industrial use, but the coating layer is readily removed and reduces longevity. On the contrary, the blending of hydrophilic additives provides heterogeneous phase morphology and reduces membrane strengths.

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In the previous few years, promising results of membrane modification were reported in terms of enhancement and anti-fouling properties using polyaniline (PANI) as hydrophilic modifier [17-19]. But most of the published works which support tremendous change in the properties of the membrane are basically achieved by alteration in the fabrication part: blending and doping of conducting/zwitterionic moieties in the casting solution. Technological importance of polyaniline for fabricating polymeric is well studied, especially for gas separation. PANI is better known as conducting polymers and in the form of emeraldine base [33]. PANI and its derivatives have been used to improve ultrafiltration membrane performance specifically for high permeability and excellent fouling resistance. PANI is added into the casting solution and then sulfonation of PANI is done by ex-situ/in-situ, leading to pore enhancement and negative charge generation on the surface of the membrane. Therefore, PANI and its derivatives have taken special attention of researchers for membrane modification due to its wide variety of applications based on the properties such as, ease of synthesis, low cost fabrication, anticorrosive, thermal and chemical stability [1,17,20,21]; above all, it has superb electrical conductivity when doped [21]. Addition of PANI in the blending/casting solutions at the fabrication stage receives so much attention because it improves pore size as well as hydrophilic nature in membranes, and deposition of nanostructure of conducting polymers allows morphological homogeneity and reproducible control of thickness by growing monolayers films. Moreover, PANI has a surface charge in aqueous medium aiding in charged based separation [17,22].

One of the most widely used commercially available membranes is polysulfone ultrafiltration (PS-UF) membrane. This membrane

has faced serious membrane fouling due to its hydrophobic surface characteristics and deterioration in separation efficiency and life [1,17,20,23-25]. Polysulfone membranes (PS) have been commonly used in the fabrication of ultrafiltration membrane due to outstanding chemical stability, heat resistance, mechanical properties and stability over a wide range of pH [1,2]. In spite of all these qualities, PS membranes deteriorate and lose their efficiency over a period of time as they are used in continuous operations. Natural organic matters which act as foulant are generally attracted towards hydrophobic surfaces and cause blocking of pores and ultimately a permanent flux decline happens [1,3]. Various techniques have been applied to improve hydrophilicity of PS-UF membrane surface for better performance as well as fouling resistance. The most well-known method that has been used for modification is blending due to its simplicity and comparatively low cost. But as mentioned above, this process has its own limitation. In contrast, membrane preparation from a polymer blend will produce hetero-structured membrane pores with different flux and selectivity. Also, the stability of the modified membrane may be another difficulty. Therefore, surface modification with preserving the originality of physicochemical properties is of great importance for the production of high performance UF membrane [2,10,26-28].

The versatile applications of PANI and its derivatives for the improvement of ultrafiltration membranes are well-known. A simple in-situ polymerization technique has been used for the hydrophilic modification of commercially available PS-UF membrane; using aniline as a monomer. In the present study, redox facile polymerization of aniline using Iron (III) chloride as an oxidant was used at room temperature for two days for the membrane surface modification instead of thermally initiated ammonium per sulfate (APS) polymerization. There is an advantage to use iron (III) chloride instead of APS because APS is stochiometrically consumed in the reaction and thus larger amount of monomer (Aniline) is required for bulk production, while in case of iron (III) chloride small quantity of monomer is sufficient [29-31]. Also, the conventional approach for making and deposition of PANI on the membrane surface may provide aggregated chains that are loosely packed [32], whereas at low temperature diffusion-controlled surface initiated redox polymerization produces densely polymer layers of PANI in-situ on the surface, as it provides much easier path for small monomer molecules to diffuse to the propagating immobilized chain ends [33]. We investigated the effect of monomer concentration on the surface hydrophilicity, fluxes and chemical stability of the coating layer. The modified membrane surfaces were characterized by the different morphological, spectral and physicochemical analyses. It is expected that PANI grown in-situ on membrane surface could provide a membrane with super hydrophilic nature and enhanced flux values.

EXPERIMENTAL DETAILS

1. Materials

Polysulfone UF flat-sheet membrane (MWCO 100 KDa) was purchased from Alfa Laval (India) Limited. Iron (III) chloride (Anhydrous, Emsure grade) was purchased from Merck Millipore (Germany) and used as slow catalyst in polymerization. Sodium hypochlorite with available chlorine (4-4.99%, Reagent grade) and aniline (≥99.5%, ACS reagent) were purchased from Sigma Aldrich (India). Bovine serum albumin (BSA, Molecular weight 69) was purchased from Sisco Research Laboratory (India). Pure water was obtained by using double distillation unit. Sodium hydroxide (Molecular weight 40) and hydrochloric acid (Molecular weight 36.5) were purchased from Thermo Fisher Scientific India Pvt. Limited (India).

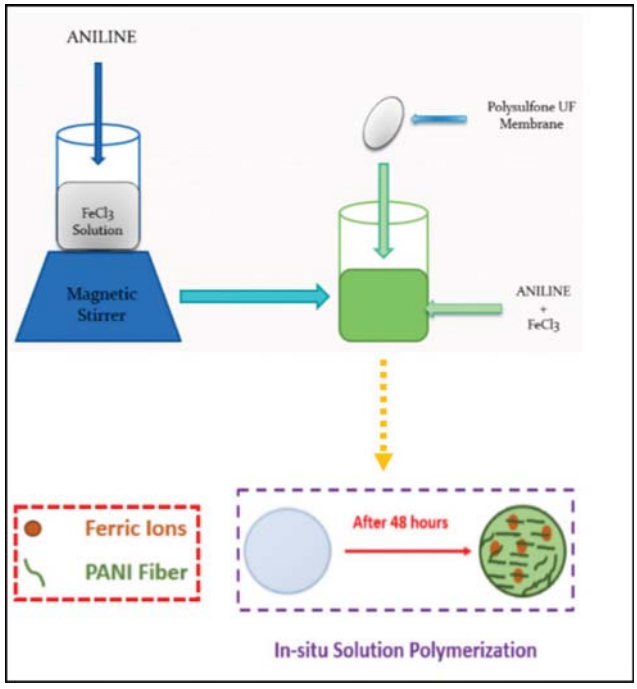

Fig. 1. Schematic diagram of PANI modified membrane.

2. Membrane Surface Modification

The membrane modification process is shown in Fig. 1. All the modified membranes were developed via in-situ solution polymerization of aniline using iron (III) chloride as an oxidant. In a typical procedure, iron (III) chloride was thoroughly dissolved in double distilled water by means of magnetic stirring. Subsequently, aniline in molar relation to iron salt (Aniline : $FeCl_3$=1 : 2) was added to the oxidant solution. This solution was further stirred for about ten minutes for uniform dispersion of reactants. Then pre-compacted membrane was dipped into this polymer solution and the mixture was allowed to polymerize under slow shaking (@110 rpm) for 48 hours at room temperature. After that, modified membranes were taken out and thoroughly washed with double distilled water for further use.

3. Dead-end Filtration Unit

A batch-cell made of stainless steel was used for the ultrafiltration experiments. A schematic presentation is shown in Fig. 2. The dead-end filtration unit has a feed capacity of 500 ml. A circular module with an inner diameter of 7.5 cm is provided below the feed tank to place the membrane. The effective membrane area for permeation has a diameter of 6.4 cm. Permeate was collected from the bottom of the system. All the membranes were pre-compacted for stabilizing the permeate flux. To maintain the TMP in the system, the feed tank is connected to a nitrogen gas cylinder.

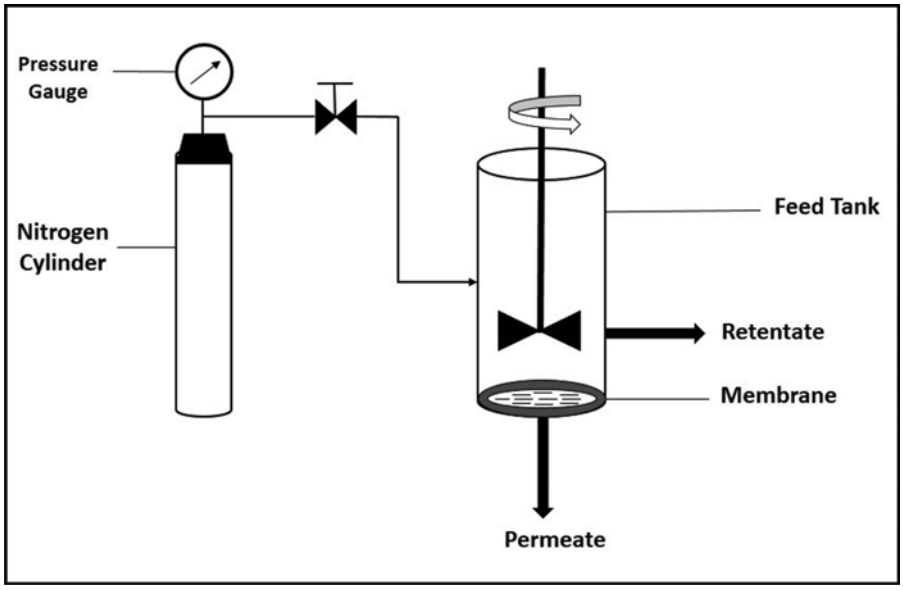

Fig. 2. Dead-end filtration unit.

4. Characterization of Modified Membrane Surfaces

4-1. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy

Bruker 3000 Hyperion microscope with Vertex 80 FTIR System, Germany, was used to confirm the PANI attachment on PS membrane surface. Each ATR- FTIR spectrum was collected over the range from 4,000 to 500 cm^{-1}. All the samples were vacuum dried at 40 °C prior to characterization.

4-2. Atomic Force Microscope

Heterogeneity or roughness developed on PS membrane surface after PANI modification was confirmed by atomic force microscopy (AFM). Surface roughness is described in terms of root mean square (RMS) value and peak to valley distance (Rpv) for modified and unmodified membranes.

4-3. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

Confirmation of PANI coating on the membrane surface was done by scanning electron microscopy (SEM). Surface and cross-sectional view of membranes were taken to ensure the attachment of polymer layer on the membrane surface. All the samples were dried before SEM analysis and for cross-sectional view images sample were cracked by using liquid nitrogen to get an idea about changes in pore structures.

4-4. Contact Angle Measurement

Kruss drop shape analyzer DSA25 was used to measure the contact angles of modified and unmodified membranes. Static contact angle over the sessile drop method was measured for all the membranes. All the membrane samples were vacuum dried prior to measuring the contact angle. For each sample five measurements were taken at different positions, and the reported results are the average of those five values. Wettability is directly dependent on the roughness of the surface: higher is the roughness more will be the contact angle and vice-versa.

5. Performance Evaluation of UF Membranes

Pure water flux of plain and modified membranes was calculated to estimate the performance of the modified surfaces. A batch-cell filtration unit with a feed capacity of 500 ml was used for the experiments. All the membranes were soaked over-night in double distilled water and compacted at 50 psi (>operating pressure) for about 4-5 hours prior to use. All the experiments were carried out at a constant TMP of 20 psi.

The pure water flux is calculated by the following formula:

$$J = \frac{V}{A * t} \tag{1}$$

where J is the volumetric flux, V is the permeate volume collected at a specified time, A is the effective membrane area, and t is the time required to collect the sample.

Protein rejection of the membrane was tested using 0.5 g/L (C_f) as initial BSA concentration. The protein concentrations in the feed solution (C_f) and the permeate solution (C_P) were measured using UV-vis spectrophotometer at a wavelength of 278 nm. Protein rejection was calculated using Eq. (2):

$$(\%)\ \text{Rejection} = \left(1 - \frac{C_P}{C_f}\right) \times 100 \tag{2}$$

The relative fouled flux ratio (RFR) was estimated using Eq. (3):

$$\text{RFR}\ (\%) = \frac{J_P}{J} \times 100 \tag{3}$$

where J_P is the permeate flux when the feed solution is replaced by protein solution such as BSA and J is the pure water flux.

To evaluate the antifouling property of membrane the flux recovery ratio was calculated by equation:

$$\text{FRR}\ (\%) = \frac{J_{w2}}{J_{w1}} \times 100 \tag{4}$$

where J_{w1} is the pure water flux and J_{w2} is the pure water flux of membrane after back flushing.

To explain flux decline mechanism, filtration resistance of mem-

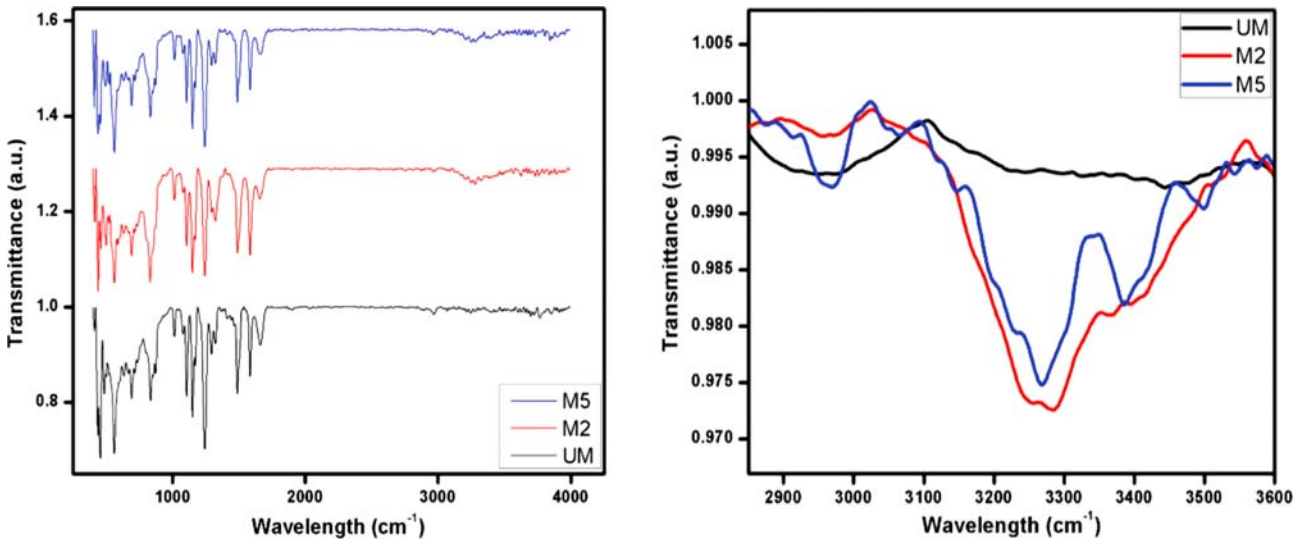

Fig. 3. ATR-FTIR spectra of unmodified (UM) and modified membranes (M2) and (M5).

branes was calculated in accordance with the resistance-in-series model. Permeation flux can be described as a function of transmembrane pressure (ΔP), viscosity of permeates (η), and the total filtration resistance (R_t). In case of pure water permeation, resistance offered by membrane towards mass transport is referred to as intrinsic membrane resistance (R_m). Membrane fouling (R_f) depends on several parameters like membrane material, solute properties and operating parameters. Reversible fouling results when the solute particles are loosely attached to the surface of the membrane and can be easily removed by simple cleaning techniques. When the solute gets adsorbed on the pore wall or surface of the membrane it causes irreversible fouling. The total filtration resistance (R_t) can be expressed as the sum of intrinsic membrane resistance (R_m), irreversible resistance (R_{ir}) and reversible resistance (R_r) and calculated by using Eq. (8) [23].

$$R_m = \frac{\Delta P}{\eta J_{w1}} \tag{5}$$

$$R_{ir} = \frac{\Delta P}{\eta J_{w2}} - R_m \tag{6}$$

$$R_r = \frac{\Delta P}{\eta J_P} - R_m - R_{ir} \tag{7}$$

$$R_t = R_m + R_c + R_f = R_m + R_c + R_{ir} + R_r \tag{8}$$

where R_c is the resistance provided by concentration polarization. In our case, osmotic effects and concentration polarization were considered negligible compared to membrane fouling.

6. Stability of Modified Membrane

Physical stability of the modified membranes was estimated by providing hydraulic back-flushing. Membrane was placed upside down in the filtration cell and feed tank was filled with double distilled water and 60 psi pressure was provided for about 10 minutes. After back-flushing, the membrane was placed upside above to measure the pure water flux under particular pressure. To evaluate the chemical stability of the polyaniline coating on membrane surface, modified membranes were dipped in three different cleaning solutions. Cleaning solutions were chosen to observe physical as well as chemical stability of the coating layer. Stability test was performed on the 5% PANI modified membranes (M5) as they were selected as the optimum one. These were dipped in NaOCl solution (available chlorine content=500 mg/L), NaOH solution (pH=13) and HCl solution (pH=2) for fifteen days and pure water flux was calculated with the interval of three days. Prior to calculating the pure water flux, each membrane was thoroughly rinsed by double distilled water.

RESULTS AND DISCUSSION

1. Surface Modification

ATR-FTIR spectra of pure polysulfone and PANI modified membranes are shown in Fig. 3. The characteristic band of pure polysulfone found at 1,148 cm^{-1}, 1,238 cm^{-1}, 1,294 cm^{-1}, 1,240 cm^{-1}, 1,487 cm^{-1}, and 1,584 cm^{-1} was attributed to symmetrical O=S=O stretching, asymmetrical O=S=O stretching, C-O stretching, benzenoid structure and quinoid structure, respectively [34,35]. In addition to quinoid (N=Q=N) and benzenoid (N-B-N) bands, the absorption band at 3,200 cm^{-1} to 3,500 cm^{-1} observed corresponds to the free N-H bond, clearly confirming the formation of polyaniline (PANI) [36,37]. The shifting of symmetrical and asymmetrical O=S=O stretching band to 1,150 cm^{-1}, 1,241 cm^{-1}, respectively, in polyaniline-modified polysulfone membrane spectra is due to the formation of hydrogen bond between oxygen atom and hydrogen atom; thus, it indicates the interaction between the polyaniline with surface of the polysulfone membrane. The carbon (C), nitrogen (N), oxygen (O), sulfur (S) and the iron (Fe) elements were observed by EDAX spectra Fig. 4, and the content of elemental measurements is mentioned in Table 1. The EDAX result reveals that in our long synthesis protocol, Fe, the catalyst, first gets absorbed on membrane surface and hence allows PANI to grow. Absorption on Fe leads to the strong attachment of PANI on the polysulfone surface. Table 1 shows that on the surface of the modified

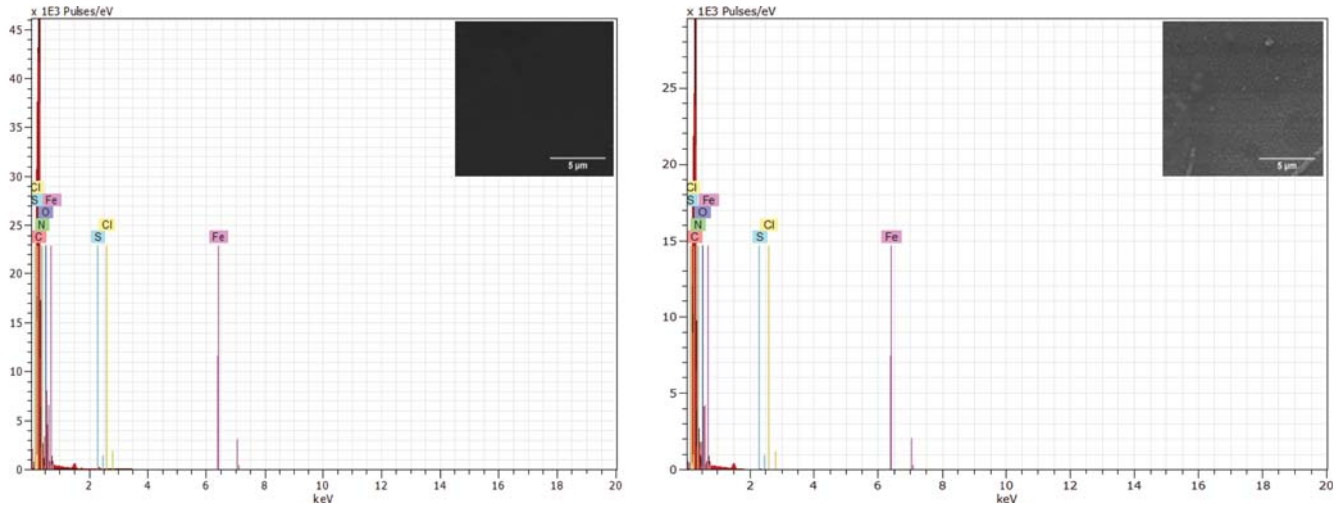

Fig. 4. EDX spectra (left) of the unmodified membrane (UM) and (right) modified membrane (M5).

Table 1. EDAX elemental analysis of modified and unmodified membranes

S.N.	Unmodified membrane (UM)		Modified membrane (M5)	
Elements	Weight%	Atomic%	Weight%	Atomic%
Carbon (K)	37.15	42.92	32.66	38.04
Nitrogen (K)	23.59	23.37	30.91	30.87
Iron (K)	-	-	0.67	0.17
Sulfur (K)	0.80	0.35	0.77	0.34
Oxygen (K)	38.46	33.36	34.99	30.59

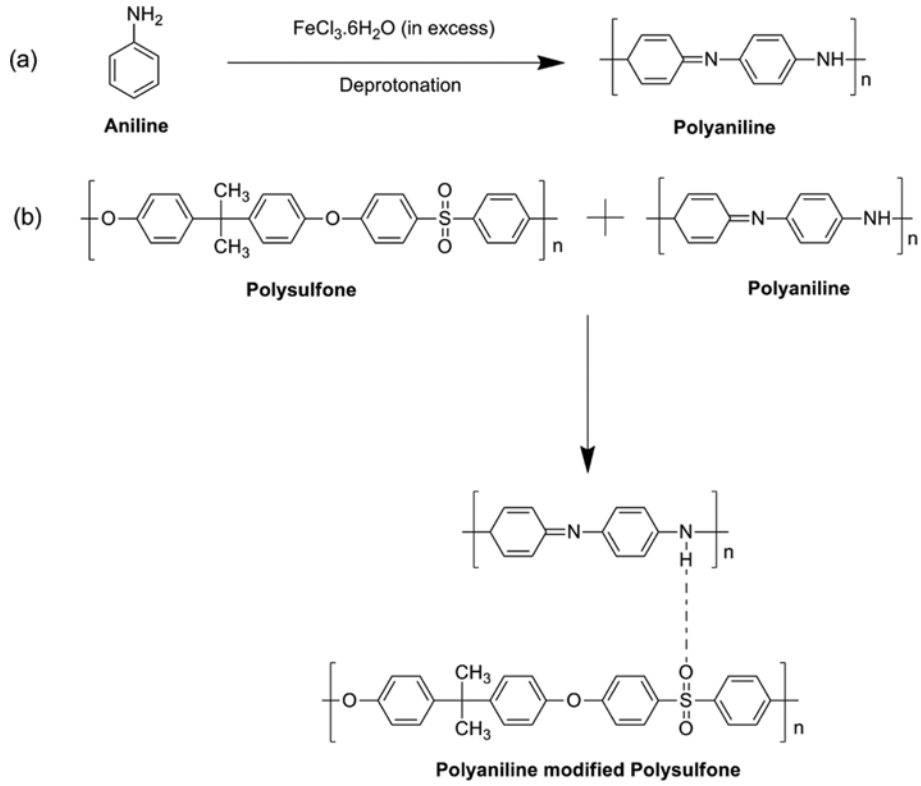

Fig. 5. Reaction mechanism of aniline with polysulfone.

membrane more N and Fe got absorbed [38]. Fig. 5. The suggested reaction mechanism was proposed by analyzing the results of ATR-FTIR spectra and the EDAX characterization. As discussed earlier, the polymerization of aniline occurs on the surface of PS membrane in the presence of excess Iron (III) chloride, used as a catalyst. Absorption bands develop in the range of 3,200 cm^{-1} to 3,500 cm^{-1} confirming PANI formation, and the shifting of symmetrical and asymmetrical O=S=O stretching in modified membrane spectrum indicates the interaction between polyaniline with surface of the polysulfone membrane, due to the formation of hydrogen bond between oxygen atom and hydrogen atom. In support of our suggested reaction mechanism some published work is referred here. Fan et al. [26] prepared PANI/PS composite membranes via filtration of PANI nanofibers in the form of aqueous dispersion through PS membrane as substrate. According to them, oxygen atoms in the ether bond (-O-) and sulfone group (O=S=O) of PS interacted with hydrogen atoms in the amine and protonated imine group of PANI by H-bonding, which caused the combination of PANI nanofibers and PS substrate membrane.

Zhu et al. [39] suggested a possible modification mechanism for their work. Coating of DOPA followed by heparin immobilization was explained thoroughly. The attachment of DOPA and heparin on the PVDF membrane was because catechol (DOPA) is easily oxidized into quionoe structure and these quionoe species are able to bond with the amine groups present in the heparin. This leads to the covalent immobilization of heparin on the PVDF/Poly (DOPA) composite membrane. In our work, the attachment of PANI on the surface of PS membrane was due to the absorption of Fe ions on the surface of the membrane. As the polymerization process is slow (48 hours), excess Fe ions have enough time to absorb and functionalize the membrane surface. Functionalized membrane surface takes part in the polymerization reaction and polysulfone is

Fig. 6. Photographs of pure PS membrane (Left) and PANI modified membrane (Right).

chemically attached to the polyaniline after the polymerization process (Fig. 6). Strong attachment of PANI on the PS membrane is actually due to the absorption of iron on the membrane surface. To evaluate the durability of the coating layer, stability experiments were performed which are discussed in the next segments.

2. Hydrophilicity and Morphology

According to the SEM images presented in Fig. 7 the incorporation of PANI develops a highly porous layer on the membrane surface. The surface view images give an idea that developed layer is certainly uniform, whereas the cross-sectional view images clearly describe the formation of macro-voids and finger-like structures due to the PANI modification [23]. Vertical and horizontal angled cross-sectional view images of modified membrane reveal that polymerization of aniline develops a layer of finger-like or channelized structures and it creates larger macro-voids. Due to these vertically aligned pore structures, an unrestricted and direct path is being offered to water for permeation, which absolutely enhances the permeability [1,40]. Contact angle versus PANI percentage plot

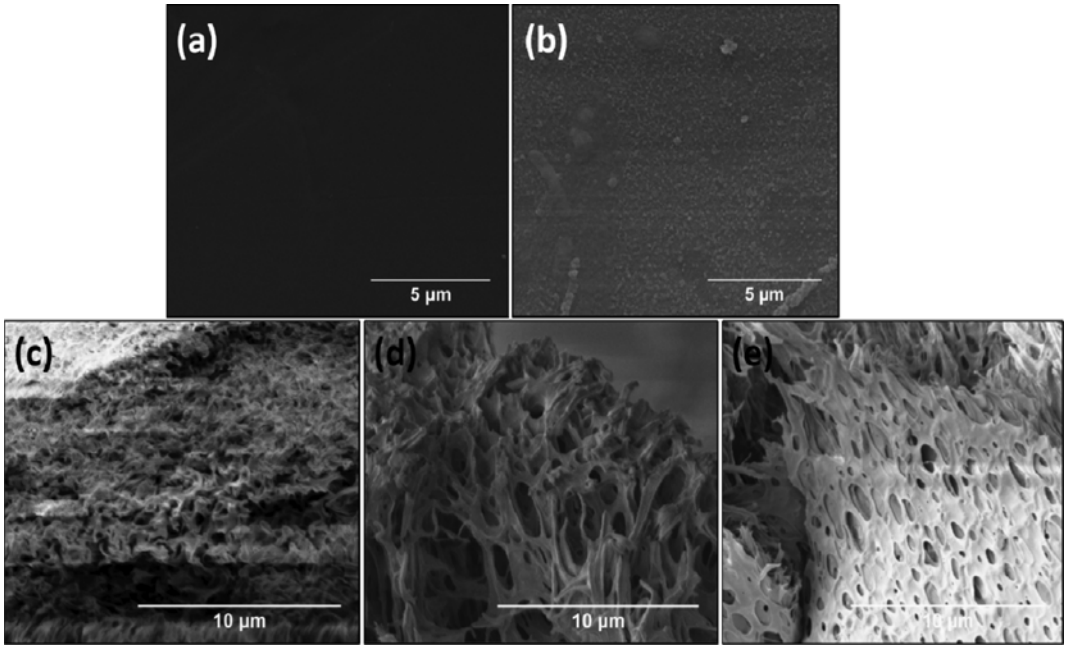

Fig. 7. FESEM images: (a), (b) Surface view of UM & M5 respectively, (c) Cross-sectional view of UM and (d), (e) Cross-sectional view of M5 respectively.

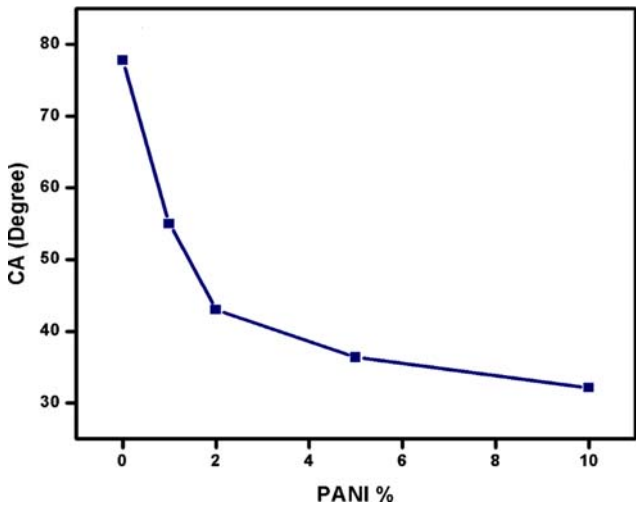

Fig. 8. Contact angle versus PANI %.

is shown in Fig. 8. The unmodified PS membrane due to its hydrophobic nature shows the highest value of contact angle: 77.8°. However, the contact angle of PANI modified membranes declined as the percentage of PANI increased in the coating solution. PANI nano-fibers were used for producing super-hydrophilic surfaces because they possess a higher value of surface free energy and hydrophilic property [27]. Lesser value of contact angle for modified membranes indicates that the hydrophobic nature of original PS membrane diminishes (Table 2). The lowest value of contact angle is 32.1° for 10% PANI modified membrane. Thus, it is confirmed that attachment of PANI via in-situ polymerization potentially improves the wetting ability of PS membranes, which was ultimately attributed to the porous nature of modified membranes and provides a basis for their antifouling properties [17,41,42]. The trend of lowering of contact angle is consistent with the study published by Mukherjee et al. [17], who reported that addition of PANI decreases the contact angle of membrane surface.

AFM was performed to understand the morphological changes

Table 2. Monomer quantity and contact angle values of modified and unmodified membranes

S.N.	Code	Monomer quantity (ml)	Contact angle (degree)
1	Unmodified membrane (UM)	0	77.8°
2	Modified membrane (M2)	2	43°
3	Modified membrane (M5)	5	36°
4	Modified membrane (M10)	10	32.1°

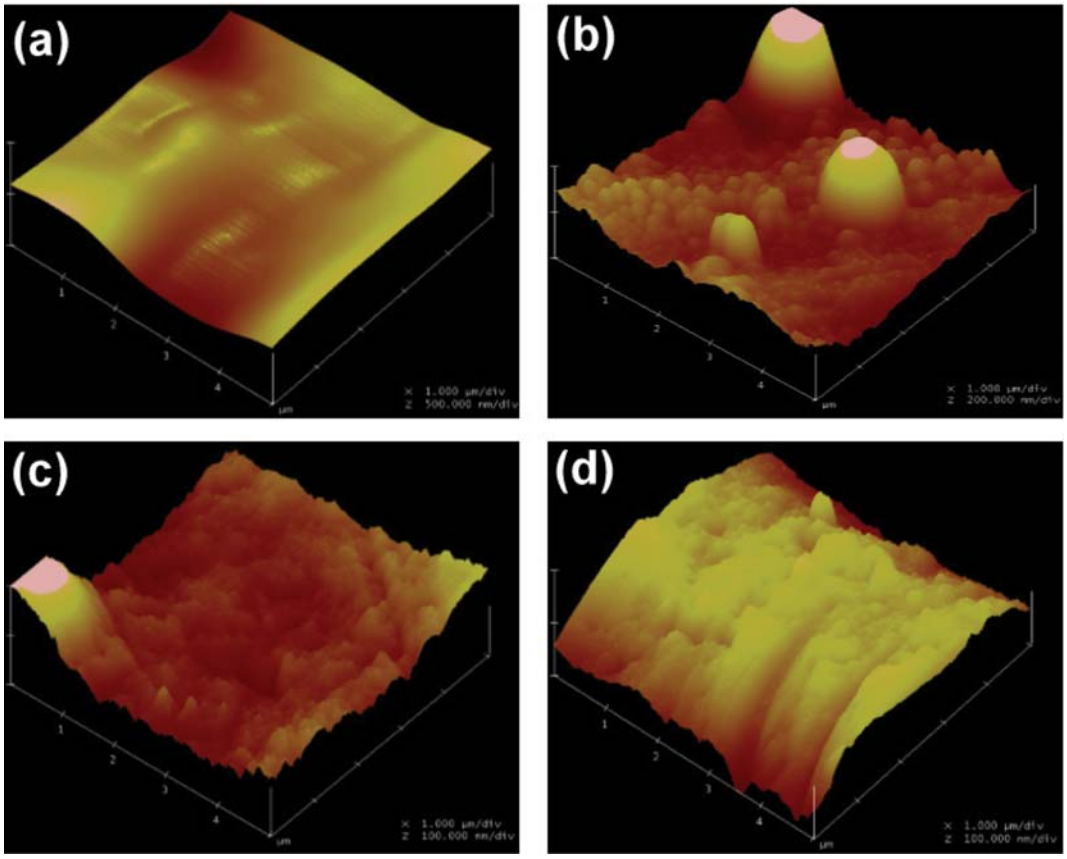

Fig. 9. AFM images: (a) UM, (b) M5, (C) UM treated with NaOCl, (d) M5 treated with NaOCl.

Table 3. Surface roughness parameters of unmodified (UM), modified membrane (M5) and after NaOCl treatment of UM and M5

Membrane	Z_{Range} (nm)	R_a (nm)	R_q (nm)
UM	288.13	40.29	50.75
M5	420.03	41.35	62.14
UM_{NaOCl}	200.61	17.27	25.81
$M5_{NaOCl}$	157.82	21.54	26.43

on the membrane surface due to PANI modification. Fig. 9 shows the AFM results of modified, unmodified membranes. Surface roughness parameters in terms of peak to valley (Z_{Range}) distance between the highest and lowest points, average roughness (R_a) and root-mean squared roughness (R_q) are calculated by using the following equations:

$$R_a = \frac{1}{n}\Sigma_{j=1}^{n}|Z_j| \quad (9)$$

$$R_q = \sqrt{\frac{\Sigma Z_i^2}{n}} \quad (10)$$

where Z is the average of Z in a given area, Z_i is the current value of Z, and N is the number of data points [43]. Table 3 presents the variation in roughness values of modified and unmodified membranes.

3. Membrane Performance

Fig. 10 shows the time-dependent pure water fluxes of the membranes during membrane compaction. A gradual decline in pure water flux is observed during membrane compaction. Simply, compaction can be defined as a compression of membrane structure under a transmembrane pressure difference, causing a decrease in membrane thickness. Usually, this compression reflects a mechanical deformation and is best represented as a compressive strain. In our case, during membrane compaction, the flux of unmodified PS membrane decreases from 186.736 to 180.702 L/m^2·h. It takes about 20 minutes to achieve steady state. As the result of enhanced porosity modified membranes show a sharp decline in flux in comparison to unmodified membrane. In-situ polymerization of aniline creates a sub-layer of macro-voids, which is the cause behind the severe flux decline in the modified membranes, and it also became affected by the monomer dose [1]. These modified membranes have more hydrophilic surface, better interlinked vertically aligned finger-like pores, higher porosity and larger surface area. The protein rejections of the modified as well as unmodified membranes were about 96% to 98% without significant changes Fig. 11 [2,27,42].

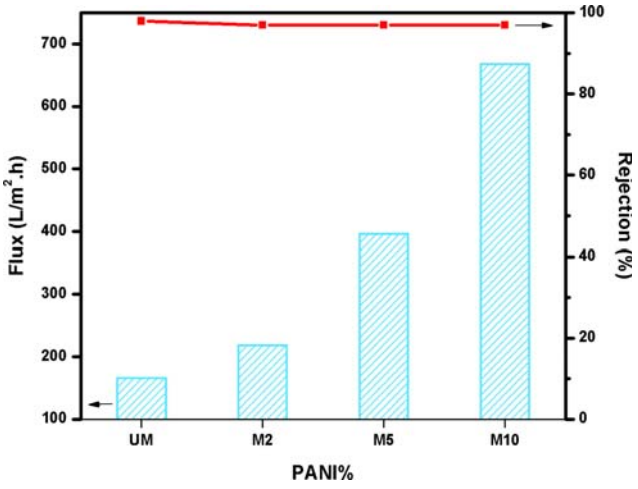

Fig. 11. Protein rejection of modified and unmodified membranes.

Fig. 12 and 13 show rapid flux decline behavior of all membranes during BSA ultrafiltration. Comparing the flux decline trends for both pure water fluxes and BSA fluxes, it is clearly indicated that flux became stabilized after membrane compaction with a little decrease in initial flux values. On the other hand, flux dramatically reduced in protein filtration in a span of approximately ten minutes. Table 4 shows the average values of pure water and BSA fluxes for all membranes. Modified as well as unmodified membranes show nearly the same BSA flux values from the start till the end. Several mechanisms can attribute to the flux decline during

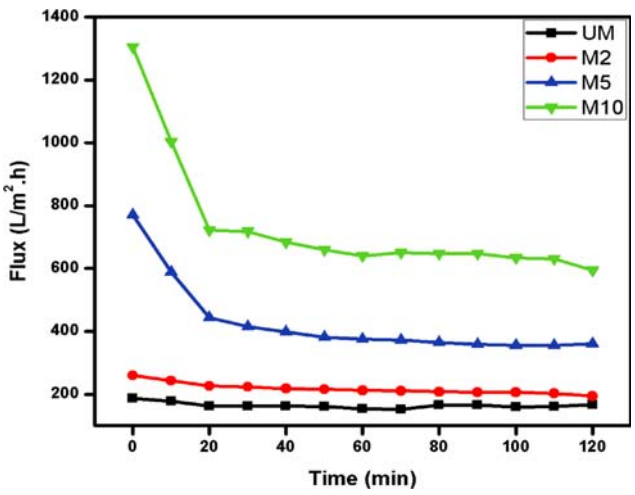

Fig. 10. Pure water flux versus time during compaction at 50 psi.

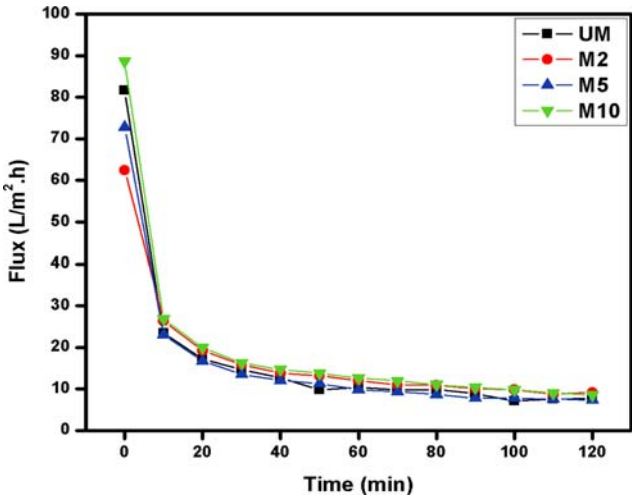

Fig. 12. Permeate flux versus time with BSA concentration 0.5 gm/L.

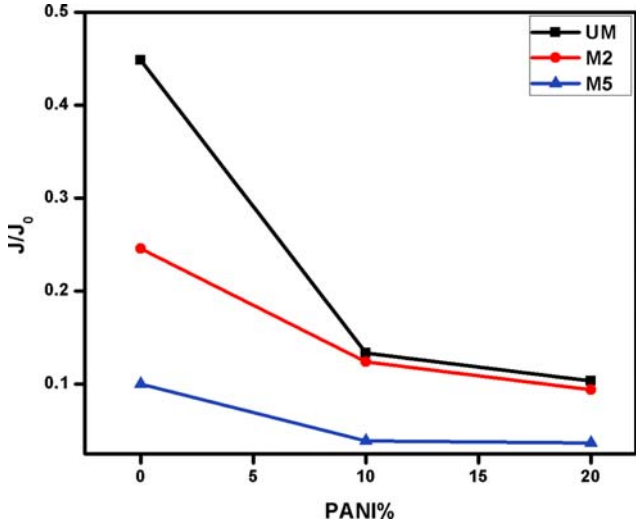

Fig. 13. Normalized water flux.

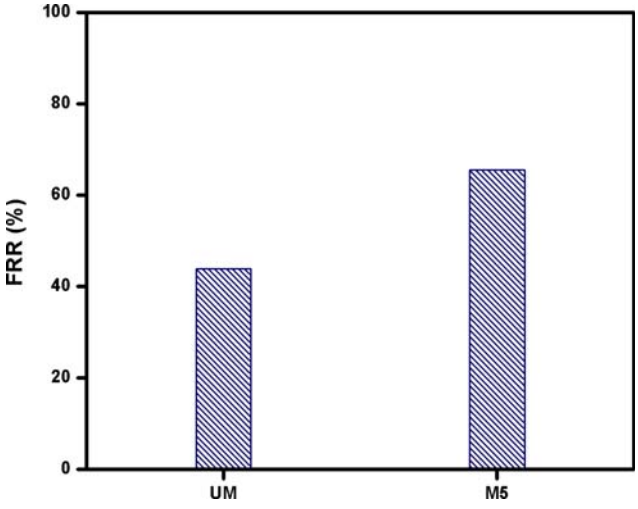

Fig. 14. FRR values of modified and unmodified membrane with BSA as feed.

Table 4. Summary of average pure water flux and BSA flux of plain and modified membranes and their relative fouled flux ratio

Membrane	Pure water flux ($L/m^2 \cdot h$)	BSA flux ($L/m^2 \cdot h$)	RFR%
UM	165.5871	16.98	10.25
M2	218.3535	17.17	7.86
M5	396.0864	16.42	4.14
M10	668.5673	18.18	2.71

Table 6. Specific flux values of modified and unmodified membranes before and after back-flush. Each membrane was back-flushed for about 30 minutes @ 60 psi. The flux values were measured @20 psi

Membrane	Flux before back-flushing ($L/m^2 \cdot h$)	Flux after back-flushing ($L/m^2 \cdot h$)
UM	16.98	72.71
M5	16.42	259.54

protein filtration, such as adsorption of protein on the surface of the membrane, pore blocking and cake filtration [1,23].

To evaluate membrane fouling, filtration resistance for unmodified and modified membranes was calculated by using Eqs. (5)-(8). Table 5 represents all the filtration resistance values, and the results clearly indicates that PANI modified membrane has very low value of irreversible resistance (R_{ir}) in comparison to unmodified membrane. Lowering of irreversible resistance value means that foulants are not easily adsorbed on the surface or the pore walls of the membrane. This may be due to the attachment of PANI on the PS membrane surface. Reversible protein adsorption causes the main reversible resistance, R_r, but that could be eliminated by simple cleaning procedures [23].

Pure polysulfone membrane and PANI modified membranes have almost similar BSA rejection in the range of 96%-98%. Fig. 14 shows the flux recovery (FRR) values of modified membranes and unmodified membrane were 65.53% and 43.91%, respectively. Enhanced FRR values of the modified membranes signify their better anti-fouling property, which was actually due to the increased surface hydrophilicity and better stability [1].

4. Stability of Coating Layer

In-situ polymerization of PANI on the membrane surface is very much similar to the dip coating method of surface modification. In case of surface modification by coating method, there is always a question about the durability of the coating layer for long term usage. Mechanical and chemical stability tests were conducted to confirm the stability of PANI modified membranes. To evaluate mechanical stability, hydraulic washing in reverse direction, back-flushing, was performed at a pressure of 60 psi, higher than the operating pressure. Table 6 presents the specific flux values of both modified and unmodified membranes. Fig. 14, in case of pure PS ultrafiltration membrane about 43% of the initial flux is recovered after back-flushing, whereas modified membrane recovered about 65% of their initial flux values [44]. These results clearly indicate that PANI modification eliminates the need for critical cleaning operations, and no peeling of coating layer was observed after intensive back-flushing.

Figs. 15 and 16 show that modified membrane dipped in NaOH (pH~13) and HCl (pH~2) solutions shows quite high initial fluxes. It is reported that these cleaning agents affect the hydrophilicity of

Table 5. Filtration resistances of unmodified membrane and modified membrane during BSA filtration

Membrane	R_m ($\times 10^9$)	R_{ir} ($\times 10^9$)	R_r ($\times 10^{10}$)	R_t ($\times 10^{10}$)	FRR%
UM	3.3	4.37	2.5	3.2	43.91
M5	1.4	0.74	3.18	3.39	65.53

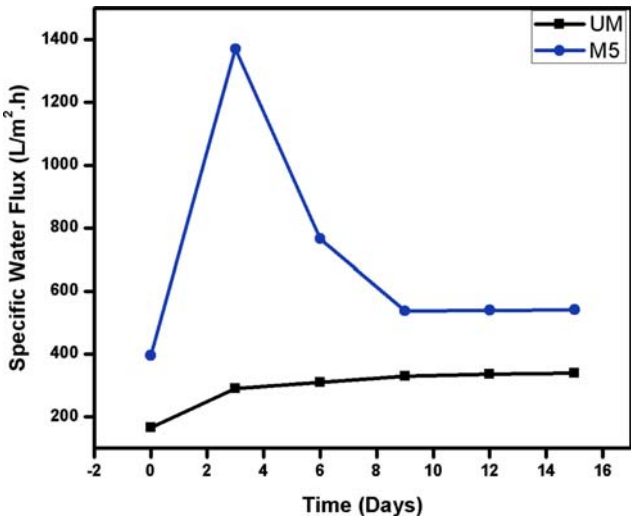

Fig. 15. Chemical stability test with HCl @ pH=2.

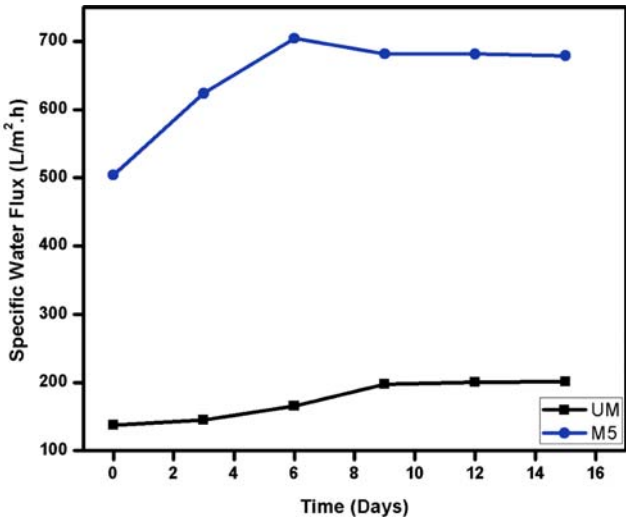

Fig. 16. Chemical stability test with NaOH @ pH=13.

the membrane surface. In case of unmodified membranes, the flux is slightly altered because of the natural hydrophobic surface. While the hydrophilicity of PANI modified membrane is already being altered, and after being exposed to much higher and much lower pH solutions, the hydrophilic nature is again targeted [45, 46]. Sharp shoot-up in the initial pure water fluxes, of modified and unmodified membranes is observed in the case of NaOCl cleaning (Fig. 17). Sodium hypochlorite is a well-known strong oxidizing agent. It is also found that NaOCl causes membrane swelling and can damage the membrane structure [47,48].

CONCLUSIONS

Commercially available PS membrane surface was modified via incorporation of in-situ polymerization of aniline. As the polymerization process is slow and the membrane surface itself takes part in the reaction, strong attachment of PANI on membrane surface

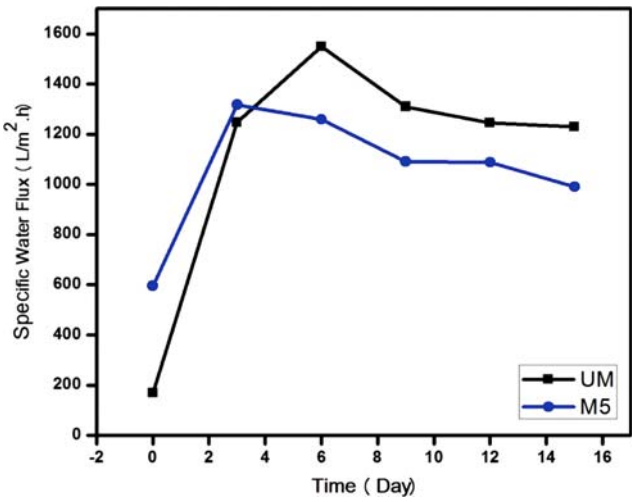

Fig. 17. Chemical stability test with NaOCl.

was observed. Development of PANI created a dense porous layer on the surface of the membrane, which was confirmed by SEM analysis. The contact angle of PANI modified membranes is much lesser (≈36°) in comparison to pure PS membrane (≈77°). Hydrophilic nature of PANI improves the surface hydrophilicity of PS membrane and thus became the reason for contact angle lowering. Even the anti-fouling properties were also altered because of PANI, and hydrophilicity was the reason behind it. BSA accumulation on the surface of PS membrane led to flux decline and irreversible fouling. Modified membranes showed flux recovery of about 65%, which confirmed that PANI modified membranes have improved anti-fouling properties. Channelization of flow also occurs due to the development of this porous layer, which ultimately enhances the permeability. The reliability of PANI layer attached to the PS membrane was proven by mechanical stability test and the durability was confirmed by long-term exposure of modified membranes in acidic, alkali and strong oxidizing agents. Our work provides an expedient method for the large scale/industrial preparation of super hydrophilic UF membranes.

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