Development of a highly-permeable thin-film-based nanofiltration membrane by using surface treatment with Air-Ar plasma

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Abstract−Surface modification of thin-film nanofiltration membranes was carried out to produce high water permeable NF membranes by Air-Ar plasma treatment. The effect of composition of used gases on membrane properties was investigated. Results showed that the plasma treatment decreased the water contact angle obviously from 80.4° to 6.5°, which in turn would increase the membrane surface hydrophilicity. The results of FTIR spectra decisively confirmed the formation of hydrophilic nitrogen and oxygen compounds on the membrane surface. The SEM images of membrane surface also showed significant changes after plasma treatment. AFM analysis indicated smoother surface for the modified membranes compared to pristine membrane; the roughness declined from 55.85 nm for virgin membrane to 28.33 nm for modified membranes. The salt rejection was 90% for pristine membrane and 76.35% to 92.45% for the plasma treated membranes. The water flux for modified membrane treated by 50% Air-50% Ar plasma increased ~1,446.1% compared to the virgin membrane, whereas the selectivity declined only ~15.1%.

Keywords: Thin-film Nanofiltration Membrane, Surface Modification, Air-Ar Plasma, High Permeable Membrane, Trade Off, Permeability-selectivity

INTRODUCTION

Surface modification is a change in physico-chemical or biological characteristics of the surface of materials to improve their surface properties. There are different ways to modify a material's surface that are divided into three categories: mechanical, chemical, and physical [1,2]. In mechanical methods, the changes are of the order of micrometers or more; therefore, they are not suitable for surfaces with nano-micrometer dimensions. Chemical methods are not suitable for the environment because they can cause some adverse reactions and produce chemical waste. Therefore, physical methods such as heat, electric discharge, corona, ultraviolet radiation, gamma-ray, ion beam, electron beam, laser, and plasma have attracted more attention [3]. Membrane based separation processes have gained much attention in different industries and human life due to low energy consumption and high separation efficiency besides their environmental advantages. Among this, the construction of nanofiltration membranes (NF) with special properties and separation performance is of particular importance for producing clean water, water treatment and recycling. Recent findings provide useful guidelines and methods for designing and manufacturing of NF membranes with high efficiency, productivity, and optimal separation performance [4]. But the major problem faced during the process is the polarization and fouling phenomenon along with decrease of flux that makes for higher energy consumption, shorter lifespan and membrane performance unpredictable [5,6]. Various techniques are suggested to increase of membrane permeation, reducing of membrane fouling and preventing contaminant deposition to promote the separation efficiency, which includes the use of hydrophilic nanoparticles such as TiO$_2$ nanoparticles [7] and zeolite nanoparticles [8] into polymeric membranes and plasma treatment of membrane surface [5,6].

Surface modification by plasma treatment has been recognized as a new and effective solution to change the surface properties of materials in various industries [9]. Surface modification by plasma is carried out in order to reach four main effects on the surface of different materials, including etching, grafting, cleansing and activation of surfaces [10,11].

Also the type or the composition of used gases in plasma environment would determine the type of reactions and the different effects of plasma on the surface properties because of the unique chemistry of plasma belonging to each gas [12,13]. The reported study [14] showed that utilizing plasma containing oxygen gas could produce abundant carboxyl, carbonyl and hydroxyl groups on the PES membrane surface. Also, findings reveal that plasma radiation to the membrane can change the size of the pores along with the permeability [15]. In other study, Farokhi et al. [16] showed that the air plasma treatment of NF membranes for 2 min caused an increase of water flux of more than 270%, whereas rejection declined less than 18%. Saxena et al. [17] also applied Ar-O$_2$ plasma with different percentages of oxygen to surface modification of PES membranes. They reported more hydrophilic surface and an increase of ~44% permeability for the modified membrane. As recent studies have shown, surface modification of membranes by plasma treatment caused an increase of water flux, whereas the selectivity decreased and conversely. So, providing high water permeable NF

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membrane besides high selectivity was the main goal of the current study. For the purpose, surface modification of thin-film NF membranes was carried out by Air-Ar plasma treatment through a cleaner plasma device. We tried to find the optimum condition to promote permeability and selectivity simultaneously. The effect of various combinations of Air-Ar, with different percentages was studied. Argon gas is a noble gas that does not directly chemically react with the surface, but it can make smooth the surface by its bombardment, which would promote the antifouling ability of membrane by increase of membrane surface hydrophilicity. Besides, air gas could react with membrane surface, which leads to the formation of hydrophilic functional groups on the surface. This would enhance the surface charge density along with surface hydrophilicity. So, the combination of these two gases would provide unexpected characteristics based on the synergism effects between physical and chemical actions. Contact angle analysis, FTIR, SEM, AFM, XRD, water flux and the salt rejection were used in membrane characterization.

MATERIALS AND METHODS

1. Materials

A commercial thin-film composite nanofiltration membrane (three layers, PA thin-film; JMC-1812-100N, USA) was used in this study. All other chemicals were supplied from Merck Inc., Germany. Distilled water also was used throughout the experiment.

2. Plasma

Fig. 1 shows a schema of a vacuum cleaner plasma device made by SATIA Company that was used in this study. This type of plasma device requires much less gas, which is an advantage for expensive gases such as argon and helium. First, the existing air in the plasma chamber is discharged by a vacuum pump up to reach a pressure lower than 50 mtorr. Then, the selected gas enters the chamber to reach a steady-state gas stream. A high voltage with 13.56 MHz radio frequency is connected to the electrodes and plasma is formed between the electrodes for a certain period of time. During this period, the membrane is placed in the desired location and affected by the produced plasma. Finally, the voltage is terminated
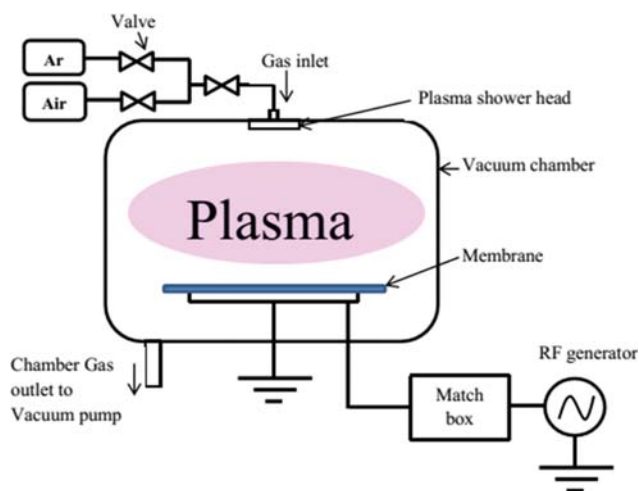

Fig. 1. A schema of used vacuum cleaner plasma device.

Table 1. The composition of used gases in plasma production

Membrane	(Air-Ar) ratio (v/v)
M_1	0% Air-100% Ar
M_2	100% Air-0% Ar
M_3	80% Air-20% Ar
M_4	20% Air-80% Ar
M_5	50% Air-50% Ar

Also (M_0) belongs to pristine membrane (control)

and air is entered into the chamber to increase the pressure up to atmospheric level. Then the modified sample can be removed from the device chamber. By this method, the superficial part of the atomic layer, even with thickness less than 1 nm, can be modified. The properties and chemical composition of the used part are also responsible for adhesion and the possible proper changes.

In this research, Ar-Air plasma with 25 W discharge power, 50 mtorr pressure during 120 s was applied to surface modification of thin-film NF membrane to produce high water permeable membrane. The composition of used gases in plasma generating is given in Table 1.

CHARACTERIZATION OF MEMBRANES

1. FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) was carried out using the ALPHA device at a range of wavelengths of 500-4,000 cm^{-1} to provide information about the chemical structure of membranes.

2. XRD Analysis

For micro-structural studies of membranes, X-ray diffraction (XRD) patterns were carried out by X-ray diffractometer (XRD, model X' Pert Pw 3373, λ_G: 2.289 A$^\circ$, Philips, Holland).

3. SEM Analysis

The surface morphology and topography of membranes were examined by scanning electron microscope (SEM, AMETEK Co., USA). For the membrane scanning by SEM device, the samples were frozen in liquid nitrogen and then fractured. After sputtering with gold, their observation was undertaken using the electron microscope.

4. AFM Analysis

Atomic force microscopy (AFM) was used to analyze the surface morphology and roughness of membranes under contact mode. The AFM device was Dual Scope scanning probe-optical microscope. 3D surface images and average roughness were prepared using Nano-surf Easy Scan II software in the area of 10 μm×10 μm.

5. Water Contact Angle

Water contact angle was measured to evaluate the hydrophilicity and surface wettability of membranes. For the purpose, a drop of water was located on the surface by a Hamilton injector needle and than imaged with a 10-megapixel canon camera. To minimize the experimental error, the contact angle was measured (at ambient conditions) in five locations and then the average was reported.

6. Membrane Separation Performance

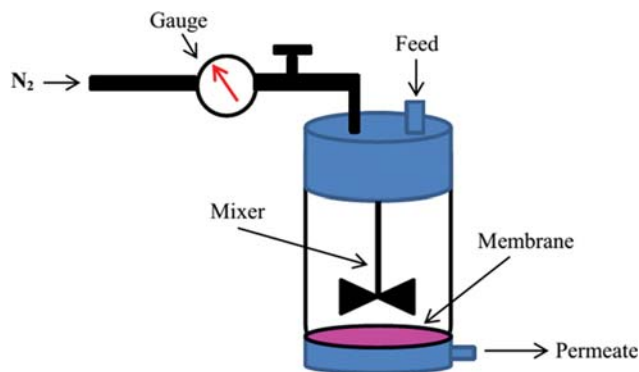The flux and salt rejection for the membranes were measured

Fig. 2. Schematic diagram of used filtration dead end cell in this study.

Fig. 3. FTIR spectral results for plasma treated membranes and pristine sample.

by a homemade dead-end filtration system containing a Pyrex-glass cell with an effective area of 11.94 cm². The schema of the used cell is shown in Fig. 2. During the experiment, feed solutions were agitated at 400 rpm using a magnetic stirrer to minimize the effect of concentration polarization. Initially, membranes were pressurized for 15 min. The filtration test was done at 6 bar pressure and ambient temperature. A 0.01 M Na_2SO_4 solution also used as feed solution. The flux was calculated by collecting the permeated water that passes through the membrane using the following equation [16,18]:

$$J_V = \frac{Q}{A(\Delta t)} \qquad (1)$$

where J_V (Lit/m²·h), Q (lit), A (m²) and Δt (h) are the flux, volume of permeation, membrane surface area and the filtration time, respectively.

The following equation was also used to investigate the salt rejection [18,19]:

$$\text{Rejection}\% = 1 - \left(\frac{C_p}{C_f}\right) * 100 \qquad (2)$$

where C_p and C_f are concentration of sodium sulfate permeate and feed, respectively, determined by a conductivity-meter device (OAHUS Co., USA).

RESULTS AND DISCUSSION

1. Investigation of Physic-chemical Properties of Membranes

The FTIR analysis of the membranes is shown in Fig. 3. The results for plasma treated membranes (M_1 and M_4) with 100% and 80% Ar show no significant changes compared to the pristine membrane (M_0). In M_1, the surface is bruised due to argon bombarding. Whereas argon, an inert gas, does not react with membrane surface and so no chemical change occurred. This is true for M_4 almost due to high percentage of argon (80%) that surface was bruised similarly and no significant chemical changes happened. For M_2, M_3, and M_5, the new peaks indicate the interaction of air molecules with the membrane surface. Similar trend was found for M_2 and M_3 due to high percentages of air in plasma production although M_5 showed stronger peaks than the other treated sam-
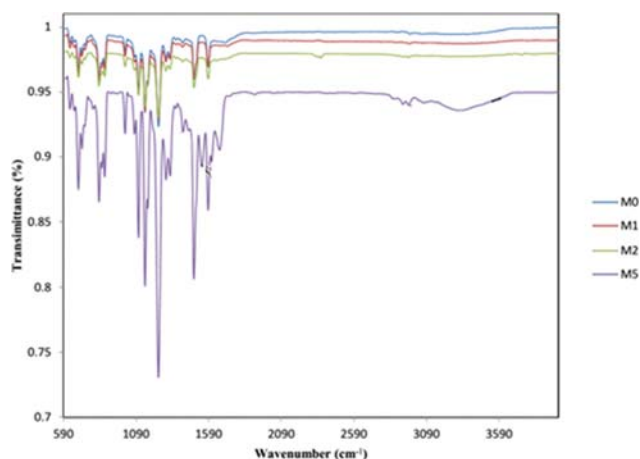
ples at 50%Air-50%Ar plasma condition. This may be assigned to key role of Ar atoms on the formation of functional groups on the membrane surface, which raises the synergetic effect. The process of surface bombardment by the atoms would be divided in two parts: I) the atoms of air plasma are smaller than argon and so rapidly bombard the membrane surface which causes much sputtering at the surface; II) the collisions of high speed air atoms with slower argon atoms increases the Ar-atom collisions with membrane surface and that causes the removal of some elements on the surface and promotes the possibility of air atom reaction to creation of more functional groups. The ionized nitrogen and oxygen molecules in plasma environment would react with active sites on the membrane surface. The peaks around 3,090 cm⁻¹, 3,280 cm⁻¹ and 1,440 cm⁻¹ are assigned to N-H and C-N stretches vibration of primary and secondary amines groups. The N-H bending
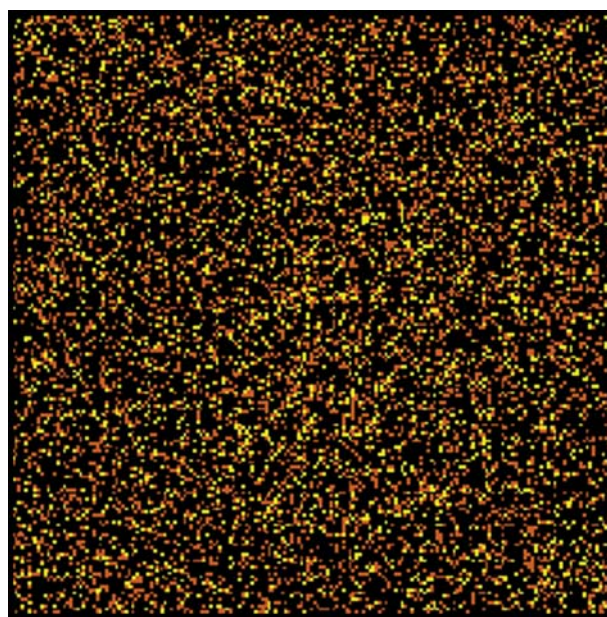

Fig. 4. EDX mapping of nitrogen for plasma treated membrane.

vibration at 1,540 cm^{-1} is also related to primary amines. The O-H stretches also appear in the same region simultaneously, which confirms the hydroxyl group formation. Moreover, the peaks appearing at 3,610 cm^{-1} and 1,650 cm^{-1} indicate the N-H and C=O stretching vibrations in amides. A comparison between spectra of the pristine and treated membranes also shows that the intensity of C-O peak at 1,260 cm^{-1} increased obviously. This may be explained by the fact that ionized oxygen attacks the membrane surface, causing C-O group formation, which would result in increase of membrane hydrophilicity [20].

Also, the energy dispersive x-ray spectra (EDX) mapping of nitrogen (N) for the plasma treated membrane is given in Fig. 4; that exhibits the nitrogen compounds functional groups on membrane surface.
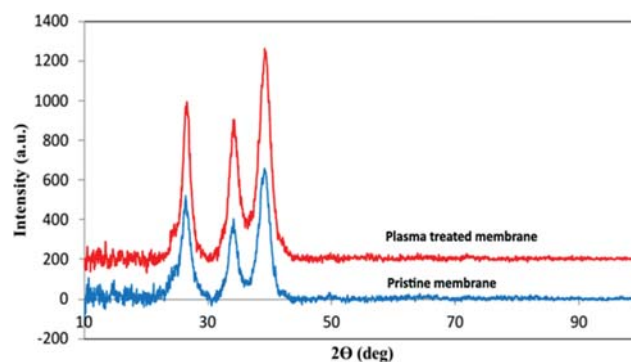

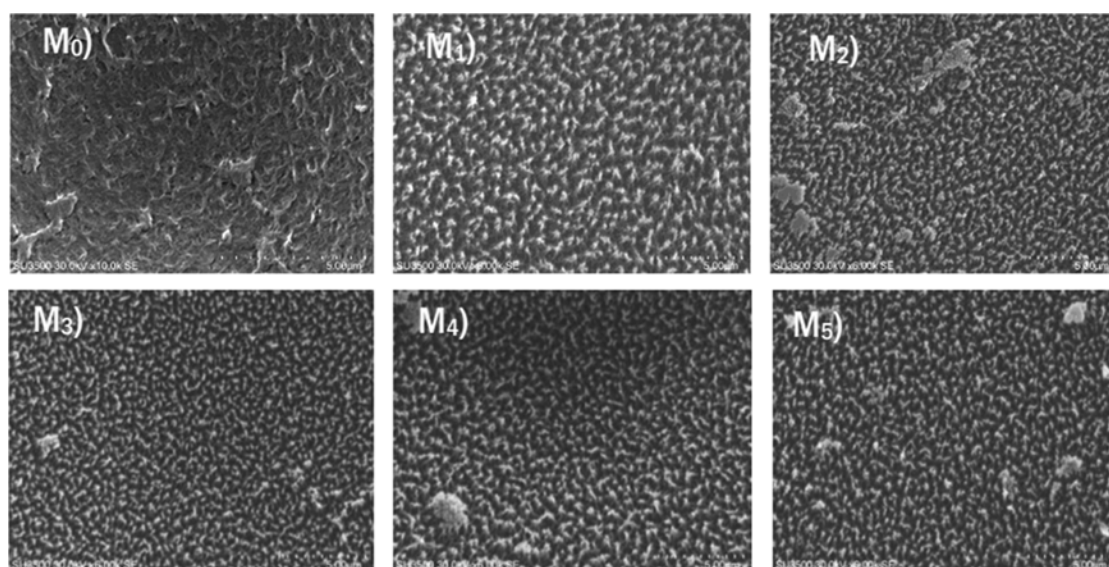Fig. 5. XRD pattern for plasma treated membrane and pristine sample.

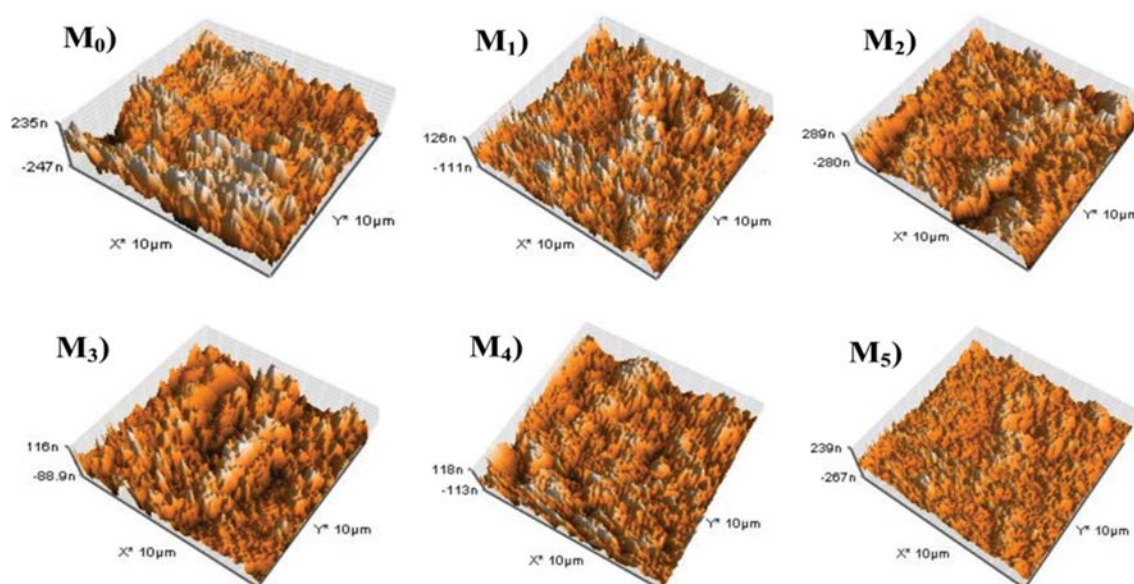Fig. 6. SEM surface images of plasma treated membranes and virgin membrane.

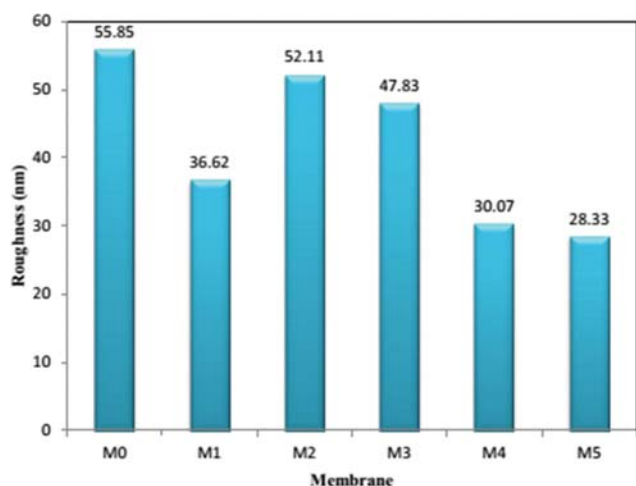Fig. 7. AFM images for modified membranes and virgin sample.

Fig. 8. Calculated average roughness for modified and unmodified membranes.

The X-ray diffraction pattern for modified and pristine membranes is presented in Fig. 5. As the results show, XRD patterns are the same for both samples, revealing that plasma modification does not change the physical property of the membranes.

The SEM and AFM images (Figs. 6 and 7) obtained from the surface of the membranes show that the surface morphology of membranes was changed due to plasma treatment.

The calculated average roughness for the membranes is also given in Fig. 8. As shown, all plasma treated membranes have smoother surface (28.33 nm to 52.11 nm) compared to virgin membrane (55.85 nm). This is due to ion collision with membrane surface that reduces the roughness by compression of the surface layer. Among the plasma treated membranes, M_2 and M_3 with high percentage of Air in plasma condition have rougher surface in comparison with other modified membranes. This is attributed to collisions of small and high speed air atoms with membrane surface, which causes more sputtering beside bombarding the peaks and making valleys again. But for M_1 and M_4 with high percentage of Ar in plasma, the bigger argon atoms hit the surface slowly and that makes the surface smooth by bruising the peaks. Also, M_5 at 50%Air-50%Ar plasma condition with 28.33 nm average roughness showed smoother surface compared to others; that is assigned to Air-Ar synergetic effects by the bombarding with a mixture of both small and big atoms in the plasma simultaneously.

Table 2 shows the water contact angle results for the plasma treated membranes and pristine membrane. The results exhibit more

Table 2. The effect of plasma treatment on water contact angle of membranes

Membrane	Contact angle (°)
M_0	80.4±1.3
M_1	12.1±1.8
M_2	10.1±1.5
M_3	10.0±1.3
M_4	13.5±1.7
M_5	6.5±1.8

hydrophilic surface for the plasma treated membranes compared to virgin ones. A significant decrease in water contact angle from 80.4° to 6.5° is obtained. This can be explained with respect to the smoother surface (Fig. 8) and formation of hydrophilic functional groups on the membrane surface (FTIR results) due to plasma treatment, which improves their surface wettability. Although membranes with higher surface roughness have higher surface area and consequently have more sites for interaction with H_2O molecules, the steric hindrance prevents H_2O molecules passing. Membranes with more surface roughness cannot have a systematically ordered network of hydrogen bonding between H_2O molecules that leads to increase of contact angle value [21]. M_1 and M_4 with high percentage of Ar in plasma, showed lower contact angle in comparison with pristine membrane. Whereas, argon as an inert gas is unable to chemically react with the membrane surface and cannot produce hydrophilic functional groups, so only the effective factor that makes these samples more hydrophilic than M_0 is surface smoothing. Also M_2 and M_3 with high percentage of Air in plasma showed rougher and more hydrophilic surface compared to M_1 and M_4. The air gas in plasma would introduce abundant hydrophilic functional groups into the membrane surface, which can be prevailing upon the negative effect of surface roughness and improve the surface hydrophilicity. Among the modified and virgin membranes, M_5 at 50%Air-50%Ar plasma condition exhibited more hydrophilic surface with 6.5° water contact angle due to smoother surface and more hydrophilic functional groups for this sample as compared to others.

2. Membrane Separation Performance

The results for the water flux and salt rejection are presented in Figs. 9 and 10, respectively. As seen, all modified membranes except M_2 have higher flux compared to virgin membrane. This low water flux for M_2 at 100% Air plasma may be attributed to formation of a compact structure for the treated membrane due to collisions of small and high speed air atoms with membrane surface, which causes more compactness for this sample. Also, the high water flux for M_5 is assigned to more hydrophilic surface and formation of abundant functional groups on M_5 as discussed before.

The increase of functional groups on the membrane surface promotes the charge density, and that enhances the Donnan exclusion and reduces the possibility of salt passage through the mem-
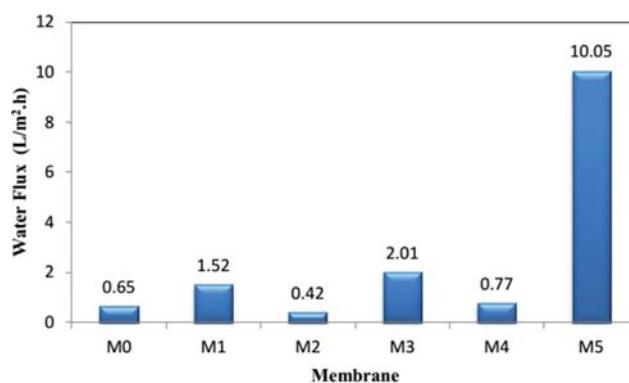

Fig. 9. The water flux for the plasma treated membranes and pristine sample.
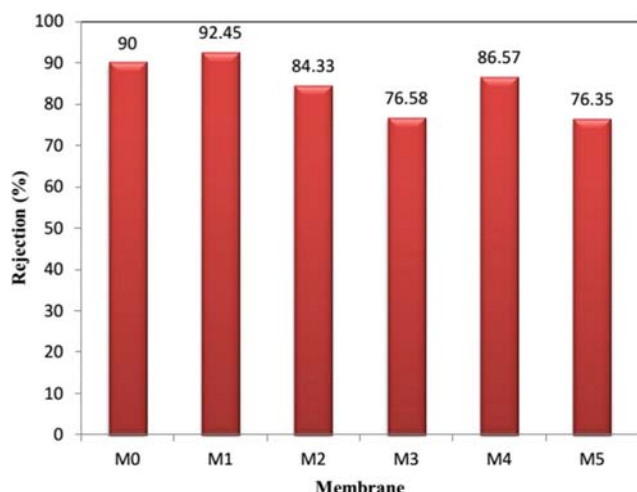
Fig. 10. The effect of plasma treatment on salt rejection of membranes.

Table 3. Changes in flux and rejection for modified membranes compared to virgin ones*

Membrane	Flux ratio (%) (J/J_0)	Change in rejection (%)
M_1	+133.8	+2.7
M_2	−35.3	−6.3
M_3	+209.2	−14.9
M_4	+18.4	−3.8
M_5	+1,446.1	−15.1

*Pristine membrane (M_0): water flux (J_0): 0.65 (L/m²·h); salt rejection: 90%

branes. Moreover, increase of surface hydrophilicity and reduction of surface roughness reduces the polarization phenomenon by movement of water molecules on the membrane surface during the separation process, which would keep the amount of salt rejection almost constant. The salt rejection measured 76.35% to 92.45% for the plasma treated membranes. The best salt rejection also was found 90% for virgin membrane; however, its flux was not considerable.

The salt rejection of modified samples was changed (+2.7 to −15.1%) compared to virgin sample, whereas the water flux through the membrane increased markedly up to more than >14 times for M_5 compared to the pristine membrane (Table 3).

Also, a typical comparison between the obtained results for modi-

fied membranes in this study with that of earlier reports studies was done and included in Table 4. As seen, the modified membrane in this study is comparable to that of other reported ones.

Separation experiments were repeated after two weeks again and the results were evaluated. The results showed changes of less than 4% for the modified membranes.

CONCLUSION

Surface modification of thin-film NF membranes was carried out to produce high water permeable NF membranes by Air-Ar plasma treatment. The effects of different concentrations of Air-Ar plasma generating gases on physico-chemical properties and separation performance of membranes were investigated. It was found that the plasma treatment of membranes clearly caused a decrease of water contact angle. The FTIR results also confirmed the formation of hydrophilic nitrogen and oxygen compounds on the membrane surface. The SEM and AFM images showed significant changes after plasma treatment. Results indicated smoother surface for the plasma treated membranes compared to virgin membrane. The average roughness was calculated as 55.85 nm for virgin membrane and 28.33 nm for M_5 at 50% Air-50% Ar plasma condition. The salt rejection measured 76.35% to 92.45% for the plasma treated membranes. The best salt rejection also was found 90% for virgin membrane; however, its flux was not considerable. Results showed that the salt rejection of modified samples was changed (+2.7 to −15.1%) compared to virgin sample, whereas the water flux through the membrane increased markedly up to more than >14 times for M_5 at 50% Air-50% Ar plasma compared to the pristine membrane.

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Table 4. Comparison between the membranes in this study with some earlier reports

Membrane	Pressure (bar)	Flux (L/m²·h)	Rejection (%)	Ref.
Pristine membrane (Thin-film NF)		0.65	90.00 (Na_2SO_4)	
Plasma treated membrane (M_1)	6	1.52	92.45 (Na_2SO_4)	This study
Plasma treated membrane (M_5)		10.05	76.35 (Na_2SO_4)	
Air-plasma treated PES-NF membrane	5	>27	70.57 (Na_2SO_4)	[16]
PES-NF membrane (citric acid as additive)	10	>54	89.36 ($MgSO_4$)	[4]
[PES-CoFe$_2$O$_4$/CuO NPs] NF membrane	5	>35	95 (Na_2SO_4)	[18]
PES-APTS-GO membrane	4	9.9	51.6 (MgSO4)	[2]

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