



A New Approach to Provide High Water Permeable Polyethersulfone based Nanofiltration Membrane by Air Plasma Treatment

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In this study, polyethersulfone based nanofiltration membranes were modified by air plasma generated through dielectric barrier discharge to increase the membrane hydrophilicity aiming to improve the separation and antifouling characteristics. The effect of plasma time on the physico-chemical and separation properties of membrane was investigated. The PES nanofiltration membranes were fabricated by the solution casting technique associated with phase inversion method. The FTIR spectra showed formation of imine and amine functional groups on the membrane surface. The water contact angle decreased from 58° to 31° by plasma treatment which produces more hydrophilic surface. SEM and SOM images demonstrated that the surface morphology was changed due to ions collision with membrane surface bombardment. AFM results indicated that membrane roughness was initially enhanced by plasma treatment up to 1 minute, and then decreased again by a further increase of treatment time. Membrane water flux increased from $10.05 \text{ (L/m}^2\cdot\text{h)}$ to $35.17 \text{ (L/m}^2\cdot\text{h)}$ remarkably by plasma treatment up to 1 minute and then decreased again at longer treatment times. An opposite trend was observed for the salt rejection of membranes. The water flux was enhanced $\sim 270\%$ for the modified membrane at 2 min plasma treatment whereas rejection declined less than 18%.

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1. INTRODUCTION

Nowadays, membranes have become as the essential materials not only in industries but also in daily human life [1]. Nanofiltration (NF) is attractive and effective for treating industrial effluents. NF is also playing an important role in concentration/purification in food, pharmaceutical and chemical products industries, environmental protection as well as biological separation. The relatively low cost and energy consumption, easy scale-up, high flux and separation efficiency make it suitable compared to other separation methods [2-5]. Membranes are fabricated from different materials like metals, ceramics and polymers [6]. Polyethersulfone (PES) is one of the most important polymeric materials and is widely used in manufacture of membranes. PES based membranes have a outstanding physico-chemical stabilities as well as good

mechanical properties [7]. But they have some disadvantages that should be overcome. PES is a hydrophobic polymer and is easily susceptible for fouling [8, 9]. Various techniques have been utilized for the increase of membrane hydrophilicity. Polymers blending, utilizing of hydrophilic filler, chemical and plasma treatment and plasma-induced grafting polymerization are important ways for the aim [4, 10]. As one of the fastest and easiest way to modify the surface of polymers is plasma/corona treatment. Corona and plasma treatments are known as high technologies to enhance the wettability of polymers. Also the surface energy can be tailored according to the need using different treatment gases [3, 11]. Microwave induced plasma (MIP), radio frequency (RF), and dielectric barrier discharge (DBD) technologies have been used widely for batch applications of plasma treatment. Moreover, cold atmospheric pressure plasmas have been utilized to form new functional groups of heat-sensitive layers. It is of interest because of absence of a vacuum

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and possibility of materials treatment susceptible to heat. Plasma treatment changes the polymeric surface with no effect on bulk [2, 10]. Various researches have been carried out to improve the stability and separation characteristics of polymeric membranes by plasma treatment. Vidalis et al. [11] enhanced the surface hydrophilicity of reverse osmosis (RO) membranes by using plasma polymerization to reduce fouling. The results showed no flux decline for the modified membranes while flux decreased obviously for the pristine membrane. Moreover, flux recovery ratio after washing the membranes with water was higher than that of virgin membrane. In another study, Fisher et al. [12] modified surface of polysulfone (PSf) and polyethersulfone (PES) membranes by plasma treatment combined with in situ polymerization of hydrophilic acrylic acid layer. Ulbricht et al. [13] also studied the surface modification of microfiltration (MF) and ultrafiltration (UF) membranes by plasma polymerization of monomers and air plasma treatment. The effect of CO₂ plasma treatment on PSf UF membranes was investigated by Wavhal et al. [14]. Steen et al. [3] used H₂O plasma for treating PSf, PES and polyethylene (PE) membranes. The results showed an improvement in surface wettability. Pal et al. [15] considered PES as one of the most used materials for CO₂-plasma treatment, which improves the surface hydrophilicity and permanently. Moreover, using nitrogen-containing plasmas on PES UF membranes has been proposed as a good solution for inducing a permanent hydrophilic property to the membrane with lower fouling tendency. Tsai et al. [16] studied surface modification of PSf membranes by a cyclonic atmospheric pressure plasma. The membrane surfaces became highly hydrophilic when exposed to the cyclonic atmospheric-pressure plasma. Moghimifar et al. [17] modified the surface of PES ultrafiltration membrane by corona plasma-assisted coating of TiO₂ nanoparticles to improve the separation and antifouling properties of membranes. Sadeghi et al. [18] also investigated the effect of corona air plasma on PES UF ultrafiltration membranes to reduce membrane fouling during separation of oil/water emulsions. In this study, fabricated PES based NF membranes were modified by air plasma generated through dielectric barrier discharge to increase the hydrophilicity of membrane aiming to improve the separation and antifouling characteristics of them. The ionized nitrogen presents in the plasma ambient could react with PES membrane. This introduces imine and amine functional groups on the membrane surface which improves the charge and hydrophilicity of membrane. A few researches were found by the literature survey to modification of PES NF membrane by atmospheric pressure plasma generated through DBD. The PES NF membranes were fabricated by phase inversion method and then modified

by air plasma generated through DBD. The effect of plasma treatment time on physico-chemical and separation properties of membranes was investigated.

2. EXPERIMENTAL

2. 1. Materials Polyethersulfone provided by BASF (Ultrason E6020P, 58000 g/mol), polyvinylpyrrolidone (PVP) provided by Merck (25000 g/mol), N-N dimethylacetamide (DMAc, 87.12 g/mol) supplied by Merck and deionized water were used as polymer base binder, pore former, solvent and non-solvent.

2. 2. Fabrication of Membranes Casting solution technique and phase inversion method was used to preparation of PES membranes. The membranes fabrication was performed by dissolving a constant content of PES (18 wt. %) and PVP (1wt. %) in solvent (DMAc) with a stirrer for more than 4 h and then sonicated to break up air bubbles. The homogeneous solutions were poured and cast on smooth glass plates by an applicator in the thickness of 150µm. Then, they were immersed into deionized water bath as non-solvent. After precipitation of polymeric films, they were dipped in new deionized water containers (one day) to extract water soluble materials.

2. 3. Plasma Surface Treatment of PES Membrane

The used plasma generator (Figure 1) consisted of a fixed electrode as anode. The anode contained ten quartz tubes (5 mm diameter, 1 mm thickness). Copper wire was inside the tubes. The wires are connected to a metal probe which connected with high voltage power supply. The cathode was a metal grid wire with 5/2 mm diameter. After applying a voltage to electrodes, the electrical discharge occurs between them. Frequency and applied voltage were 7.5 KHz and 10 kV. PES membrane was placed on the cathode and the power supply was turned on. The plasma treatment time was adjusted from 1 to 4 minutes.

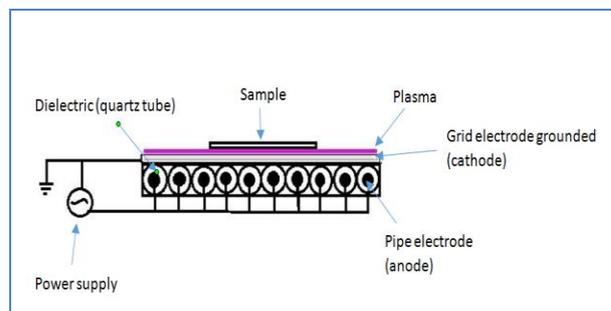


Figure 1. Scheme of the experimental setup for dielectric barrier discharge plasma generation

2. 4. Membrane Characterization

2. 4. 1. FTIR Analysis FTIR spectra measurements were carried out using Galaxy series FTIR, (Madison Instruments Inc., USA) to provide information about the chemical structure of membranes.

2. 4. 2. Water Contact Angle Water contact angle were measured to evaluate the hydrophilicity and surface wetting characteristics of membranes. To minimize the experimental error, contact angle was measured (at ambient conditions) in five locations and then their average was reported.

2. 4. 3. Scanning Electron Microscopy (SEM) and Scanning Optical Microscopy (SOM) The membranes surface was examined by scanning electron microscopy (SEM, Philips, Model XL30, Netherlands) and scanning optical microscopy (SOM Olympus, model IX 70).

2. 4. 4. Atomic Force Microscopy (AFM) For studying the effect of plasma treatment on the surface morphology and roughness of membranes surface, atomic force microscopy analysis was carried out. Then, the images analyzed by SPIP software.

2. 4. 5. Membrane Performance: Flux and Salt Rejection

The separation performance of membranes was investigated by a custom-made nanofiltration cell (Figure 2). The feed solution was prepared by dissolving Na_2SO_4 in deionized water (1000 ppm). The membranes' flux was examined by measuring water volume passed through the membranes as follow [19]:

$$J_v = Q/A (\Delta t) \quad (1)$$

where J_v ($\text{L}/\text{m}^2\cdot\text{h}$), Q (L), A (m^2), Δt (h) are the permeation flux, amount of passed water, membrane surface area and sampling time, respectively. The pressure was fixed at 5 bar. For salt rejection, the following equation was used [20, 21]:

$$\text{Rejection \%} = [1 - (C_p/C_f)] * 100 \quad (2)$$

Where C_p and C_f are the ion concentration in the permeation and in the feed.

3. RESULTS AND DISCUSSION

3. 1. FTIR Figure 3 shows the FTIR spectra of the pristine membrane and plasma treated PES membranes. Since more than 70% of the air is composed of nitrogen, ionized nitrogen present in the plasma ambient reacts with functional groups on the membrane surface, which causes formation of imine functional groups on the surface. The plasma treatment can also lead to the

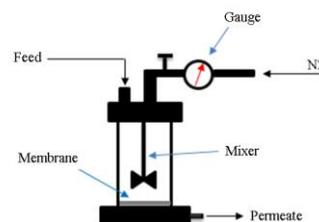


Figure 2. Schematic diagram of dead end cell

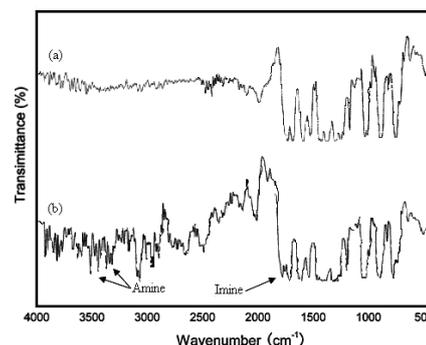


Figure 3. FTIR analysis of (a) pristine membrane and (b) plasma treated membrane

formation of amine groups on the membrane surface. As shown, the peaks at 3340.92 and 3477.87 cm^{-1} proves formation of secondary and primary of amine groups on the surface, due to the N-H bands vibration. The peak at 1655.03 cm^{-1} is assigned to the formation of imine functional groups by C=N band vibration. This is not visible for unmodified membranes.

3. 2. Water Contact Angle The results (Table 1) show that by increasing the treatment time, a significant decrease in water contact angle from 58° to 31° is obtained. This can be explained by formation of hydrophilic functional groups (amine and imine) on membrane surface due to plasma treatment. An increasing treatment time by introducing more hydrophilic agents on the membrane improves their surface wettability.

TABLE 1. The effect of plasma treatment time on membrane water contact angle

Membrane	Contact angle ($^\circ$)
Pristine membrane (control)	58
Plasma treated (1 min)	52
Plasma treated (2 min)	45
Plasma treated (3 min)	37
Plasma treated (4 min)	31

Usually, increase of membrane surface wettability would improve the membrane rejection and antifouling performance but it is not always true and depends on the membrane structural properties and other physico-chemical ones [4, 7].

3. 3. Morphological Study: SEM, AFM and SOM Analysis

The SEM and SOM images (Figures 4 and 5) show that the surface morphology of membranes was changed due to plasma treatment. Plasma treatment of PES membrane up to 1 min leads to creation of micropores/valleys on the membrane surface, which is attributed to collision of ions with the surface. By increasing treating time from 1 to 4 min, the valleys disappeared and a more compact surface was produced. It is postulated that by increasing the possibility of ion collision at higher times, roughness is accordingly reduced by compression of the surface layer.

AFM images of membranes are shown in Figure 6. The images confirm the formation of valleys on the membrane surface at 1 min plasma treatment and a smoother surface for membranes with treatment time of 2 to 4 min. The calculated average roughness is given in Table 2. Roughness enhanced sharply by 1 min plasma treatment and then decreased for higher times. The membrane with rough surface has more ability to trap the rejectant which improves the selectivity in short-time however enhances the fouling happening [2, 4].

3. 4. Membrane Performance

3. 4. 1. Flux and Rejection Figure 7 and Table 3 showed that plasma treatment of membrane up to 1 min caused to increase of flux from 10.05 to 35.17 (L/m².h).

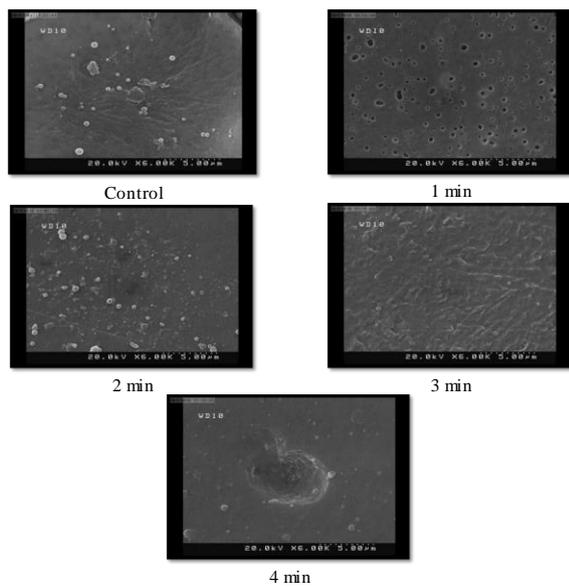


Figure 4. SEM surface images of prepared membranes

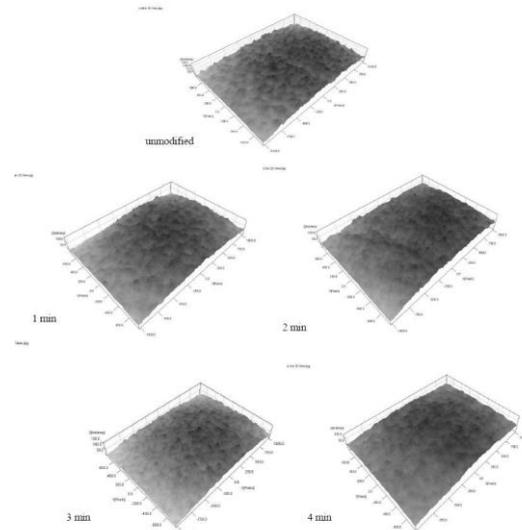


Figure 5. SOM images of the prepared membranes: pristine membrane and plasma treated membranes

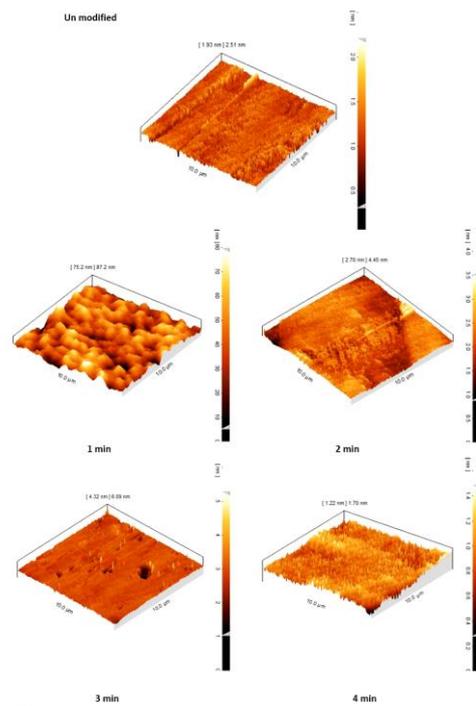


Figure 6. AFM images for prepared membranes

TABLE 2. Calculated average roughness for the modified and unmodified membranes

Membrane	Average roughness (nm)
Pristine membrane	1.25
Plasma treated (1 min)	13.86
Plasma treated (2 min)	0.84
Plasma treated (3 min)	0.38
Plasma treated (4 min)	0.26

This is due to increase of membrane surface hydrophilicity and roughness for modified membrane at 1 min plasma treatment which provides high surface area for that and enhance the flux. The membrane flux was decreased again by more treatment time due to formation of a compact surface layer. This increases membrane resistance which restricts the water flux. Opposite trend was also found for salt rejection. Decrease of salt rejection in modified membrane at 1 min plasma treatment is due to increase of surface roughness which increases the possibility of stagnant feed layer formation on membrane surface. This enhances co ions percolation though that which declines the selectivity. The increase of membrane salt rejection at higher time is due to formation of compact structure for the membrane which enhances salt retention. Increase of membrane surface hydrophilicity by increase of treatment time led to improvement of salt rejection for the modified membranes.

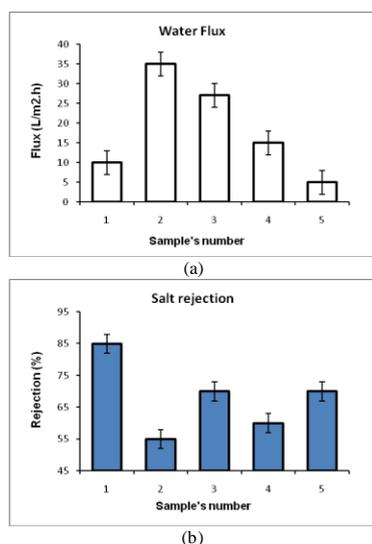


Figure 7. The effect of plasma treatment time on (a) membrane flux and (b) salt rejection

TABLE 3. The effect of plasma treatment time on membrane flux and salt rejection

Membrane	Flux (L/m ² .h)	Rejection (%)
Pristine	10.05	85.87
Plasma- 1 min	35.17	54.69
Plasma- 2 min	27.13	70.57
Plasma- 3 min	15.05	58.12
Plasma- 4 min	5.82	69.39

4. CONCLUSION

The PES-NF membranes were treated by atmospheric pressure air plasma generated through DBD to

providing high water permeable NF membrane. The effect of plasma time on the properties of the membranes was studied. FTIR spectra confirmed formation of imine and amine groups on the membranes surface. The water contact angle decreased from 58° for pristine membrane to 30° for modified ones. The SEM and SOM images indicated that the membrane surface was changed due to ion collision with its surface. AFM results revealed that surface roughness initially was enhanced by applying plasma up to 1 minute and then decreased again by more time. The water flux increased sharply by plasma time up to 1 minute and then decreased again at higher treatment times. An opposite trend was found for salt rejection. Results are valuable for modification of hydrophobic polymeric membranes especially PES to increase the hydrophilicity aiming to enhance separation characteristic and antifouling ability.

5. ACKNOWLEDGMENTS

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6. REFERENCES

1. Bagheripour E., Hosseini S. M., Hamidi A. R., Moghadassi A.R., "Fabrication and Characterization of Novel Mixed Matrix Polyethersulfone Based Nanofiltration Membrane Modified by Ilmenite", *International Journal of Engineering, Transactions A: Basics*, Vol. 30, No. 1, (2017) 7-14.
2. Moghadassi A. R., Bagheripour E., Hosseini S. M., Parvizian F., "Fabrication of (Acrylonitrile Butadiene Styrene/Poly Ethylene Glycol) Nanofiltration Membrane: the Effect of PEG Concentration and Operating Conditions on Membrane Performance", *International Journal of Engineering, Transactions A: Basics*, Vol. 31, No. 10, (2018) 1609-1616.
3. Steen M. L., Jordan A. C., Fisher E. R., "Hydrophilic modification of polymeric membranes by low temperature H₂O plasma treatment", *Journal of Membrane Science*, Vol. 204, No. 1 (2002) 341-357.
4. Hosseini S. M., Amini S.H., Khodabakhshi A. R., Bagheripour E., Van der Bruggen B., "Activated carbon nanoparticles entrapped mixed matrix polyethersulfone based nanofiltration membrane for sulfate and copper removal from water", *Journal of the Taiwan Institute of Chemical Engineers*, Vol. 82, (2018) 169-178.
5. Bagheripour E., Moghadassi A. R., Hosseini S. M., "Preparation of Polyvinylchloride Nanofiltration Membrane: Investigation the Effect of Thickness, Prior Evaporation Time and Addition Polyethylene glycol as Additive on Membrane Performance and Properties", *International Journal of Engineering, Transactions C: Aspects*, Vol. 29, No. 3 (2016) 280-287.
6. Rushton A., Ward A. S., Holdich R. G., "Solid-liquid filtration and separation technology", John Wiley & Sons, VCH (2008).
7. Bagheripour E., Moghadassi A. R., Hosseini S. M., "Incorporated Poly Acrylic Acid-co-Fe₃O₄ Nanoparticles Mixed Matrix Polyethersulfone based Nanofiltration Membrane in Desalination Process", *International Journal of Engineering, Transactions C: Aspects*, Vol. 30, No. 6, (2017) 821-829.

8. Zhao C., Xue J., Ran F., Sun S., "Modification of Polyethersulfone Membranes- A Review of Methods", *Progress in Materials Science*, Vol. 58 (2013) 76-150.
9. Luo M. L., Zhao J. Q., Tang W., Pu C. S., "Hydrophilic modification of poly(ethersulfone) ultrafiltration membrane surface by self assembly of TiO₂ nanoparticles", *Applied Surface Science*, Vol. 249 (2005) 76-84.
10. Khulbe K. C., Feng C., Matsuura T., "The Art of Surface Modification of Synthetic Polymeric Membranes", *Journal of Applied Polymer Science*, Vol. 115 (2010) 855-895.
11. Vidalis I., "Surface hydrophilic modification of RO membranes by plasma polymerization for low organic fouling", TU Delft, Delft University of Technology, (2010).
12. Wavhal D. S., Fisher E. R., "Membrane surface modification by plasma-induced polymerization of acryl amide for improved surface properties and reduced protein fouling", *Langmuir*, Vol. 7, No. 19, (2003) 79-85.
13. Liu Z. M., Xu Z. K., Wan L. S., Wu J., Ulbricht M., "Surface modification of polypropylene microfiltration membranes by the immobilization of poly (N-vinyl-2-pyrrolidone): a facile plasma approach", *Journal of Membrane Science*, Vol. 249, (2005) 21-31.
14. Wavhal D. S., Fisher E. R., "Modification of polysulfone ultrafiltration membranes by CO₂ plasma treatment", *Desalination*, Vol. 172, (2005) 189-205.
15. Pal S., Ghataka S. K., Deb S., Das Gupta S., "Characterization of CO₂ plasma treated polymeric membranes and quantification of flux enhancement", *Journal of Membrane Science*, Vol. 323 (2008) 1-10.
16. Tsai C. Y., Chang Y. C., Huang C., "Surface Hydrophilization of Polysulfone Membrane by Cyclonic Atmospheric Pressure Plasma", Osaka University, (2011).
17. Moghimifar V., Raisi A., Aroujalian A., "Surface modification of polyethersulfone ultrafiltration membranes by corona plasma-assisted coating TiO₂ nanoparticles", *Journal of Membrane Science*, Vol. 461, (2014) 69-80.
18. Sadeghi I., Aroujalian A., Raisi A., Dabir B., M. Fathizadeh, "Surface modification of polyethersulfone ultrafiltration membranes by corona air plasma for separation of oil/water emulsions", *Journal of Membrane Science*, Vol. 430 (2013) 24-36.
19. Han R., Zhang S., Liu C., Wang Y., Jian X., "Effect of NaA zeolite particle addition on poly (phthalazinone ether sulfone ketone) composite ultrafiltration (UF) membrane performance", *Journal of Membrane Science*, Vol. 345, No. 1, (2009) 3455-3462.
20. Lee H. S., Im S. J., Kim J. H., Kim H. J., Kim J. P., Min B. R., "Polyamide thin-film NF membranes containing TiO₂ nanoparticles", *Desalination*, Vol. 219 (2008) 48-56.
21. Hegde C., Isloor A. M., Padaki M., Fun H. K., "Synthesis and performance characterization of PS-PPEES nanoporous membranes with nonwoven porous support", *Arabian Journal of Chemistry*, Vol. 6, (2013) 319-326.

A New Approach to Provide High Water Permeable Polyethersulfone based Nanofiltration Membrane by Air Plasma Treatment

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در این پژوهش غشاهای نانوفیلتراسیون بر پایه پلی اتر سولفون با استفاده از پلاسمای هوا از طریق تخلیه سد دی الکتریک و به منظور بهبود خاصیت آبدوستی غشا، خواص جداسازی و ضد گرفتگی مورد اصلاح قرار گرفت. اثر پلاسمای بر خواص شیمی-فیزیکی و جداسازی غشاها مورد بررسی قرار گرفت. غشاها با استفاده از تکنیک قالب گیری محلول پلیمری و تغییر فاز تهیه شد. نتایج طیف سنجی مادون قرمز تشکیل گروه های عاملی آمین و ایمین را بر سطح غشاها تایید کرد. زاویه تماس آب در اثر اصلاح پلاسمایی از 58 تا 31 درجه کاهش یافت که نشان از بهبود آبدوستی سطحی غشاها بود. تصاویر میکروسکوپ الکترونی و نوری تهیه شده از سطح غشاها نشان می دهد که ساختار سطحی آنها در اثر برخورد یونها تغییرات آشکاری داشته است. نتایج آنالیز میکروسکوپ اتمی حاکی از آن است که در ابتدا زبری سطح غشاها در اثر درمان پلاسمایی تا 1 دقیقه افزایش داشته و سپس با افزایش بیشتر زمان درمان پلاسمایی مجددا کاهش یافته است. همچنین میزان فلاکس آب غشاها در ابتدا در اثر استفاده از درمان پلاسمایی تا 1 دقیقه از 10.05 (L/m².h) تا 35.17 (L/m².h) افزایش داشته و در ادامه با افزایش بیشتر میزان زمان درمان پلاسمایی کاهش می یابد. رفتار متفاوتی برای پس دهی میزان نمک با درمان پلاسمایی مشاهده شد. در غشایی که به میزان 2 دقیقه تحت درمان پلاسمایی قرار گرفته بود فلاکس آب به میزان 270 درصد افزایش یافت درحالیکه میزان پس دهی تنها 18 درصد کاهش داشت.

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