Improvement of hydrophilicity properties of thin-film-based PVDF membrane by plasma irradiation for use in desalination

Scientific research paper

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ABSTRACT

Polyvinylidene Fluoride (PVDF) is one of the materials that has a great ability to form a membrane, but due to its hydrophobic nature, its use in nanofiltration membranes is problematic. A solution is proposed to solve the hydrophobicity problem of PVDF is nitrogen plasma irradiation. In this research, the effect of modifying the surface characteristics of PVDF membrane by N_2 plasma irradiation on filtration performance has been investigated. For this purpose, the modified membranes were evaluated by SEM, FT-IR, AFM, and CA analyses and compared with the control membrane. By gradually increasing the applied power of the irradiated plasma on the surface of the membranes, the hydrophilic properties and performance of the modified membranes are improved. The results indicate an improvement in the flux rejection and recovery rate in the modified membrane under N_2 plasma irradiation with super hydrophilic properties compared to the pure PVDF membrane. Based on the results of the experiments, the best flux recovery rate of 11.8 and 94% rejection can be obtained for the irradiated membrane with an applied power of 120W.

1 Introduction

Today, membrane processes have been widely used in various industries, such as dairy industries, water treatment, and oily wastewater treatment [1-3]. Membranes prepared for water purification processes mainly face basic problems such as precipitation of soluble pollutants, and hydrophobicity of membranes due to their inherent nature. Since the clogging property is mainly caused by the membrane's hydrophobicity [4-8], therefore, increasing the hydrophilicity of the membranes can prevent membrane clogging to a large extent. Phase inversion is the most common method of making polymer membranes, which can create two types of homogeneous and heterogeneous membrane structures by controlling the operating conditions and choosing the appropriate solvent and non-solvent for the polymer. In this method, the polymer is dissolved in a suitable solvent and a homogeneous solution is prepared with the appropriate concentration of the polymer in the solvent. Then the polymer solution is molded with the desired thickness and divided into two phases with different deposition techniques. One phase forms the membrane porosity and the other phase forms the

membrane framework. Among the polymers used for water treatment, PVDF has attracted a lot of attention due to its characteristics such as high mechanical strength, thermal stability, chemical stability, and high hydrophobicity. Among the difficulties of PVDF membranes, we can mention their weak wettability, which leads to low water flux in this type of membrane. Also, PVDF membranes are prone to clogging during membrane processes due to their hydrophobicity [9-11].

In general, surface modification methods are methods that change the chemical and physical properties of the surface such as surface tension and polarity, morphology, and surface hydrophilicity or hydrophobicity. However, most of the surface modifications are done on polymeric membranes in wastewater treatment processes to reduce clogging [12-14]. One of the biggest problems of using the membrane is its clogging. This phenomenon causes a decrease in the flux and an increase in the pressure on the membrane surface, and as a result, it causes an increase in the operation costs and life of the membrane. There are various methods to increase the hydrophobicity of membranes, such as surface modification and the use of hydrophilic nanoparticles in the membrane matrix, and physical methods such as plasma irradiation [15]. Chen et al. reported hexafluoropropylene-modified PVDF flat membrane by the electrospinning method with improved hydrophobicity in direct contact membrane distillation configuration for desalination [16]. Bai et al. reported the fabrication of a PVDF membrane modified with pDA material by the vacuum filtration method [17]. Li et al. reported the fabrication of PVDF membrane by layering method [18]. One of the most important problems of these chemical agents is their incompatibility with the environment therefore; methods should be chosen to improve this problem. The plasma irradiation process replaced the use of nanoparticles due to its reliability and reproducibility, cheapness, and uniformity of modification [19].

The uniformity of the coating resulting from plasma treatment is less visible in chemical coatings. The goal of many plasma applications in surface modification is to change the properties of the surface to increase or decrease its ability to adhere [20-21]. Modifying the surface of polymers with plasma has many applications in the medical, textile, and polymer membrane industries. Recently, Kiamehr et al. have subjected various types of membranes to plasma irradiation for

hydrophilicity and hydrophobicity [21-24]. Shen et al. used low-temperature plasma to create a rough structure and generate active groups on the surface of the membrane to improve the hydrophobic properties of the PVDF membrane [25]. Le et al. in order to decolorize, the PVDF membrane was developed by applying new plasma activation at different bonding times [26]. PVDF-CNHs composites were subsequently used for the first time in compatibilization studies. To increase homo-compatibility, new modifications were applied to the plasma surface in air, nitrogen, and ammonia, which have never been used before for CNHs [27]. Due to the modification of polymer surfaces by non-thermal nitrogen plasmas and nitrogen compounds (especially ammonia), the formation of various functional groups such as amine, amide, and imide groups is observed. The purpose of some work is to investigate common plasma processes such as continuous plasma, plasma pulse, and plasma bond polymerization in relation to the effect of their functionalization with primary amino groups using a mixture of nitrogen and hydrogen, ammonia, allylamine, and diamino cyclohexane [28]. Vandencasteele et al. studied the effect of applied power and time of N_2 or O_2 plasma treatment on the energy and composition of PTFE, PVDF, and PVF polymer surfaces [29]. Nitrogen functional groups on the surface of the membrane will be different according to the type of plasma gas selected [23-24].

Since there have been limited studies on N_2 plasma irradiation on PVDF, in this research, PVDF has been used as a substrate, which is included in the category of hydrophobic polymers. The surface modification was done by N_2 plasma with different applied powers, and this modification's effect on membrane performance (flux and selectivity) was investigated. Finally, according to the results related to the performance of the membranes, the best-irradiated power with the most excellent effect was reported as the optimal power of this irradiation.

2 Research materials and methods

2.1 Materials

Polyvinylidene fluoride (Kynar 761, Arkema) was used as the main polymer and membrane builder. Pure PVDF membrane was made by the phase inversion method. After drying the polymer at 80°C, a certain percentage of PVDF (15%) is dissolved in dimethylacetamide

solvent at 50°C. A specific percentage of ethylene glycol (EG) as a cavitation agent is slowly added to the resulting solution at a temperature of 50°C to create a homogeneous solution. After the solution is de-bubbled, the membrane is molded and placed in distilled water for 24 hours to exchange solvent/non-solvent. Then the membrane is dried at ambient temperature. Other used chemicals were obtained from Merck, Germany, and distilled water was used during the experiment. Sodium sulfate solution (mass number of sodium sulfate 142.04, from Merck-Germany) was prepared to measure the separation performance of modified membranes. These analyzes were performed at room temperature and finally compared with the separation performance of the control membrane.

2.2 Plasma

In this research, to achieve uniform and controlled plasma, the plasma device reported in the previous work was used [24]. Irradiated plasma depends on changing parameters such as chamber pressure, irradiation time, applied power, gas consumption, the distance between electrodes, etc. The material exposed to this radiation is the background to create the best modification in the desired surface. Only the surface part of the atomic layer with a thickness of less than 1 nm is modified. Therefore, by changing the morphology and chemical composition of this layer (which is altered by the plasma), we reach our goal of background correction [30]. According to the experimental details reported in the previous work, N_2 plasma with discharge power of 80, 100, 120, and 150 W was applied on the surface of PVDF membranes (Table 1). At the end, its performance in the desalination process was evaluated by the closed end tube method.

Table 1. Exercising powers in the process of Plasma treatment of membrane surface

Membrane	Power(W)
M_0	---
M_1	80
M_2	100
M_3	120
M_4	150

3 Methods of diagnosis

3.1 Optical emission spectroscopy analysis

In this method, the radiant plasma light is transferred from the quartz window of the chamber through an optical fiber to the spectrometer (Avantes; AvaSpec3648-USB2) and analyzed inside it.

3.2 Characterization of membranes

The characteristics of the surfaces before and after plasma treatment were investigated by the FTIR, AFM, SEM, and CA analyses according to the previous work [24].
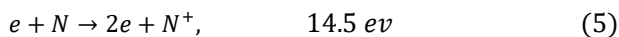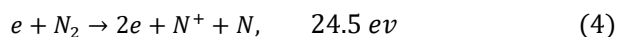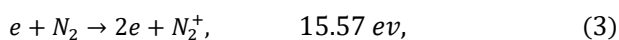
3.3 Membrane separation function

To determine the net water flux passing through each of the modified membranes, we placed them in a closed-end stirring cell device under a pressure of 0.5bar. By measuring Q the volumetric value of the flux (Lit), A the area of the active surface of the membrane (11.94 cm^2), and Δt and the relation J=Q/A (Δt), the flow rate can be estimated in terms of (Lit/(m^2.h)). Also, by measuring C_p and C_f, respectively, the concentration of sodium sulfate solution in the membrane leakage solution and the input feed solution, and using the relation of rejection%=1-(C_p/C_f)*100, it is possible to estimate the selectivity of the modified membranes [31, 32].

4 Results and discussion

4.1 Review of OES results

To check the type of N_2 plasma elements and its amount, OES analysis was performed. The intensity of the emission line of the excitation is higher and consequently, the light emission is more and more intense and as a result, the plasma environment is more active. Spectroscopy results show that N_2 plasma contains active elements such as (N, N^+, N_2^+, and N_2). Spectroscopic analysis was investigated for powers of 80, 100, 120, and 150W, which correlates with the evaluation of the intensity ratio of the N_2 plasma spectral lines as a function of power supply (Fig. 2). Several reactions are carried out inside the chamber, some of which are:

$$e + N_2 \rightarrow 2e + N_2^+, \qquad 15.57 \; ev, \qquad (3)$$

$$e + N_2 \rightarrow 2e + N^+ + N, \qquad 24.5 \; ev \qquad (4)$$

$$e + N \rightarrow 2e + N^+, \qquad 14.5 \; ev \qquad (5)$$

OES spectra related to pure N_2 plasma have several transitions related to ions and pure nitrogen atoms, the most important of which were observed at wavelengths 348, 354, 388, and 424cm^{-1}. According to the shape, it is expected that the power of the source affects the intensity of the emission lines. The intensity of the N_2^+ emission line grows faster than the N_2 emission line with increasing the source power. As the source current increases, the bombardment of positive ions from the cathode and the energy of secondary electrons increases, and at electron energies higher than the excitation threshold energy of N_2, the cross-section of the excitation level of $N_2(^3\Pi_{12})$ decreases drastically. The cross-section of N_2 ionization increases with more intensity than the cross-section of N_2 excitation, and the N_2^+ emission increases faster than the N_2 emission due to the upward trend of the ionization process from N_2 molecules to N_2^+ ions.

**Figure 2.** OES spectra of different RF powers.
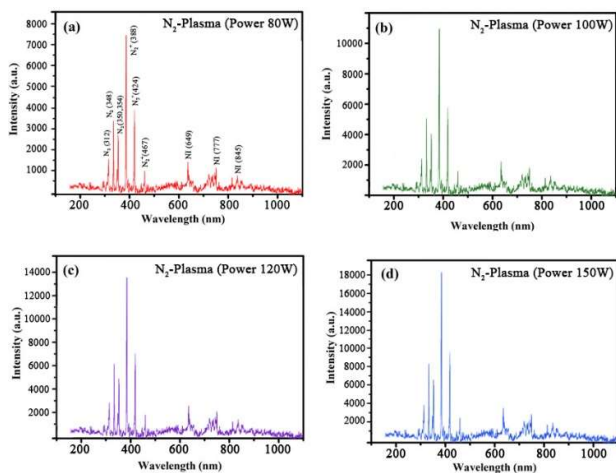
Also, the emission intensity of N and NI lines increases with the increasing power of the source, and slowly, a rapid increase in NI emission occurs compared to N emission, because NI is more sensitive to high-energy electrons than N.

4.2 Investigation of physico-chemical properties of membranes

To check the functional groups of the control membrane and the modified membranes, FTIR analysis was performed on the membranes. As shown in Fig. 3, various bonds such as CH, CF, and CC structures represent the PVDF membrane structure. N_2 plasma irradiation can be effective in solving the membrane structure and improves the thermodynamic, mechanical, and resistance properties of the membrane. The peaks are weak or removed from the pattern and instead, the peaks at 736, 1659, and 2784cm^{-1} were intensified in the modified membrane structure. This result indicated a phase change of the membrane, which resulted in an increase in its hydrophilic properties. On the other hand, the wavelength created in the range of 3000 to 3500 was characteristic of the NH structure. In addition, as seen in Fig. 3, the N-Methyl bond indicates the formation of a hydrophilic bond in the membrane structure, which was formed due to the increase in applied power.

Figure 3. FTIR images of control and modified membranes.
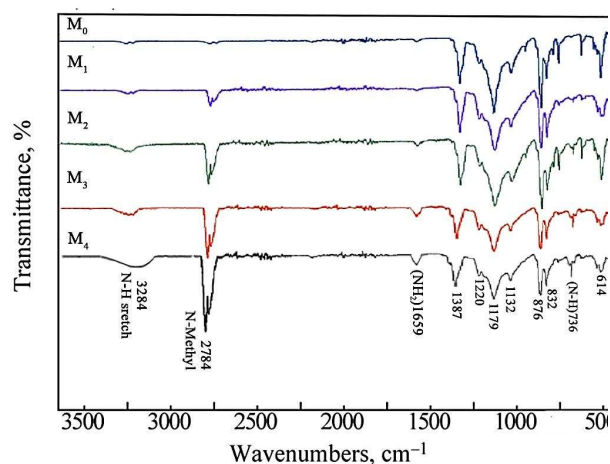
SEM images of the outer surface of the membranes modified by N_2 plasma irradiation are shown in Fig. 4. These results show that all the modified membranes have an asymmetric structure and are composed of a dense thin layer, which is similar to the results obtained in previous studies [33, 34]. These images showed that the modified surfaces had a drop in surface roughness and the average roughness was calculated by the SPIP 6.4.2 software. This decrease in roughness, of course, is achieved after an increase in membrane M_2, which can be said in the first minutes, the plasma bombards the surface, and because these samples are porous, more sputtering occurs on their surface, and after this sputtering and with continuing applying the plasma with more power, the surface becomes smoother and

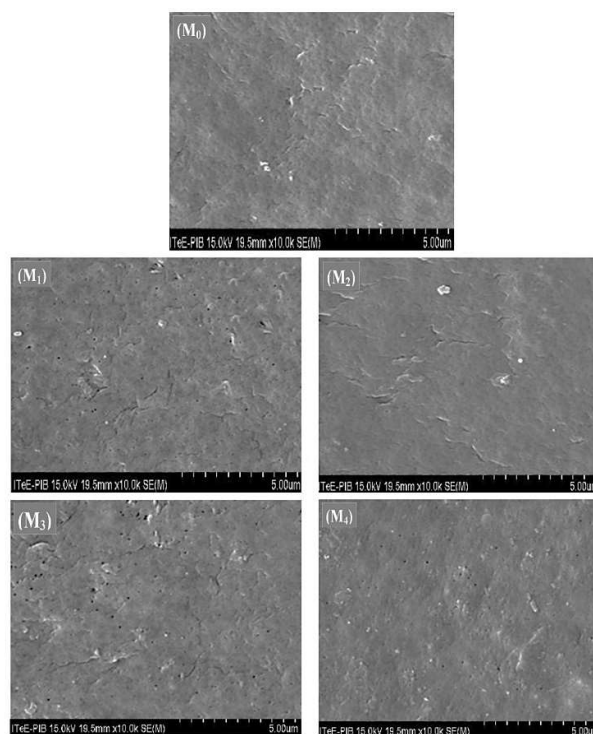smoother, and the plasma bombardment removes the roughness of the surface.

Figure 4. The SEM images of the control and modified membranes.

AFM analysis was used to evaluate the surface roughness before and after plasma N_2 treatment. Fig. 5 shows the three-dimensional images of the surface of membranes modified by N_2 plasma irradiation in a vacuum chamber with different applied powers. In different studies, researchers have considered the parameters of surface roughness and membrane hydrophilicity as determining factors in the amount of pollutant deposition on the surface of the membrane, and they consider the reduction of surface roughness as the reason for the reduction of membrane fouling [35]. Based on this, the surface roughness of the membranes modified in this research is reduced at first by increasing the power applied to the plasma generator in the vacuum chamber, and then with the further increase of this power, the roughness also increases (membrane M_2). This is due to the creation of surface sputtering at high applied powers, which is more likely to damage the outer layers of the surface. Of course, in the case of the modified membrane with a power of 150W, the proper distributions of functional groups on the surface and the uniform strokes created on the membrane surface have led to a smoother membrane surface.
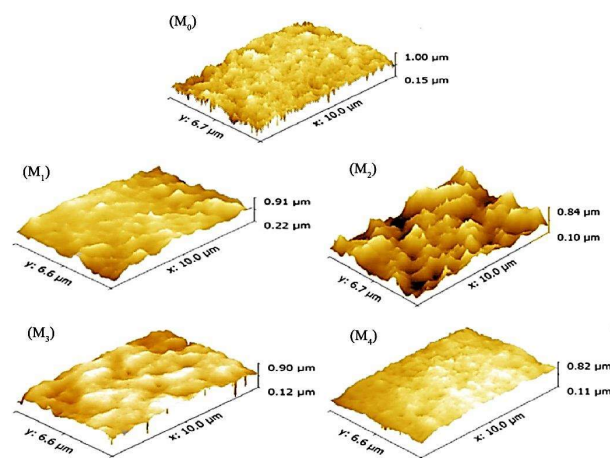

Figure 5. AFM images of control and modified membranes.

Table 2. Average Roughness of all membranes.

membrane	$R_a\ (\mu m)$
M_0	11.4
M_1	8
M_2	19
M_3	15
M_4	10

The effect of N_2 plasma applied power parameter on the surface hydrophilicity of modified PVDF membranes was investigated in comparison with the control membrane. The data obtained by measuring the water contact angle show a significant decrease in the value of the water contact angle for plasma-modified membranes compared to the control membrane. The $2\mu Lit$ drop placed by the syringe on the surface of the membranes after being imaged by a high-resolution camera, edited by Image J software, is shown in Fig. 6.

It is well-proven that Amin groups can increase the hydrophilicity of the surface. When N_2 plasma is applied to the surface of PVDF membranes, amine and imine groups are activated on the surface, which contributes to the reduction of the contact angle. Surface modification by plasma by creating functional groups containing nitrogen or oxygen leads to the hydrophilicity of the surface. The water contact angle of the raw sample is about 84°, after processing with N_2

plasma, the samples became hydrophilic, and the degree of hydrophilicity of the samples varies according to the power of plasma application. According to the data reported in Table 3, the highest level of hydrophilicity was for the membrane that was processed for 10s at a power of 120W, and the water contact angle for that sample is about 15°.
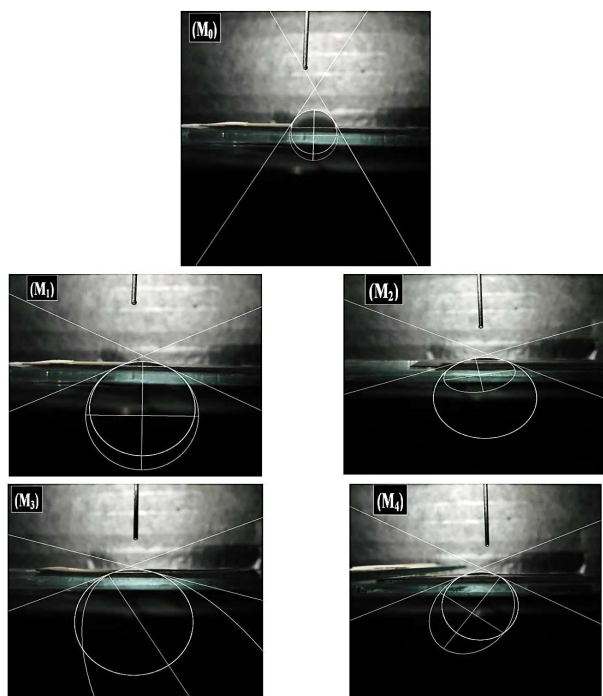

Figure 6. The contact angle of a water droplet on the surface of control and modified membranes.

Table 3. CA of all membranes.

membrane	Contact angle
M_0	84
M_1	31
M_2	26
M_3	15
M_4	22

As can be seen in Table 3, the hydrophilicity of the control PVDF membrane is relatively low and the contact angle is 84°. A step-by-step increase in the applied power of the irradiated plasma reduces the contact angle and improves the hydrophilicity of the

modified membranes using N_2 plasma treatment. In other words, the proper distribution of plasma particles in the radiation chamber leads to the reduction of the contact angle in exchange for the formation of functional groups and also changes the surface morphology. Here, the amount of applied power has an effect on this distribution, and in the M_3 membrane, due to the better distribution of functional groups, which was also confirmed in the SEM images, the improvement of hydrophilicity is more evident.

4.3 Membrane separation performance

The performance evaluation results of pure PVDF membrane and 4 different membranes irradiated at powers of 80, 100, 120, and 150W as modified membranes, in the separation process with feed with a salt concentration of 15000 ppm are presented in Fig. 7. Although the mechanism of salt separation in nanofiltration membranes is complex, this separation can be related to the molecular sieve (which depends on the average size of the nanofiltration membrane pores) and Donnan's limitation effect [36, 37]. Due to Donan's limitation effect, the concentration of ions on the surface of the membrane is not equal to their concentration in the solution. In other words, the concentration of ions opposite to the membrane charge on the membrane surface is higher than their concentration inside the solution. Then the concentration of ions with the same charge on the membrane surface is lower than their concentration inside the solution. When external pressure is applied to the membrane, water can pass through the membrane while the ions of the same name are repelled due to the Donnan repulsion effect. At the same time, due to the electrostatic balance, ions opposite to the charge of the membrane are also appalled. Therefore, due to the stronger electrostatic attraction of the divalent cation Mg^{2+} compared to the monovalent cation Na^+, the repulsion rate of $MgSO_4$ salt is lower than Na_2SO_4. Also, negatively charged nanofiltration membranes show more separation for divalent anions (SO_4^{2-}) than monovalent anions (Cl^-), because these membranes have stronger electrostatic repulsion.

As it is clear in Fig. 7, compared to the results obtained from the evaluation of the performance of the basic membrane, the flux of the modified membrane with the lowest applied power (80W) has decreased. The reason for this decrease in flux is to create a resistant layer on

the base membrane, which reduces mass transfer. Then, by increasing the amount of applied power on the surface of the base membrane up to 120W, the flux improved. This increase in flux is related to the increase in the hydrophilicity of the membrane. Because the membrane with more hydrophilic properties allows water vapor molecules to pass through it easily, increasing the flow rate. Also, the amount of salt removal has increased from 73% to 94% with the increase in applied power. It seems that increasing the hydrophilicity of the membrane has also increased the amount of membrane retraction. At higher values of an applied power of 150W, the membrane flux is somewhat reduced due to the accumulation of functional groups on the surface of the modified membrane and the reduction of the mass transfer rate. Therefore, increasing the applied power in very low values causes a decrease in the flux, in medium values it causes an increase in the flux, and further, with an increase in the amount of applied power, it causes a decrease in the flux. It is worth noting that an active layer applied on the surface of the base membrane simultaneously has two mutual effects on the flux. First, this layer as a resistant layer can affect the performance of the membrane by reducing the average size of the membrane pores. Secondly, it can facilitate the passage of water vapor through the membrane, which is due to the hydrophilic property of the surface, which can provide more paths for the passage of vapor. Also, a large amount of nitrogen functional groups causes accumulation and prevents the formation of a suitable dispersion on the surface of the base membrane. On the other hand, the accumulations created on the surface of the membrane cause the surface pores of the membrane to be closed and as a result, the passing flux decreases. Therefore, the value of 120W was considered the optimal applied power value. By using this optimal membrane, a flux of 11.8 $L/m^2.h$ and 94% salt removal was obtained.
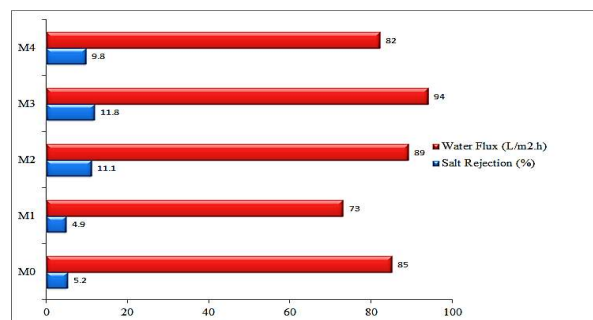

Figure 7. Flux and rejection resulting from control and modified membranes.

5 Conclusion

To choose the appropriate method for modifying the surface of a membrane, three factors must be considered: the chemical structure of the membrane, which indicates its strengths and weaknesses, the considered surface properties, and finally, the surface geometry, which is related to the presence or absence of porosity or physical and chemical heterogeneity on the surface. This research is aimed at investigating the surface modification of membranes with the help of plasma. Plasma modification and radiation, whose surface results are amine, carboxyl, hydroxyl, and aldehyde groups, are often used in plasma processing in medical fields. In plasma coating, the created coating has a high density and is relatively stable compared to the substrate modified by chemical methods. The main goal of this study was to improve the surface of the PVDF polymer nanofiltration membrane using nitrogen plasma layering. The effect of applied powers in plasma treatment on the surface the PVDF nanofiltration membrane was investigated and evaluated. The value of 94% was improved with the index layer. The amount of water contact angle as a measure of the water friendliness of the membrane showed a noticeable improvement in the effect of the index layer. The evaluation of the surface of the membranes with the images of the atomic microscope clearly showed the reduction of the roughness of the surface of the modified membranes. The results showed that the flux recovery rate for membrane M_3 as the optimal membrane was many times higher than that for the control membrane. According to the obtained results, it can be claimed that the layering caused by nitrogen plasma irradiation on the surface of the base membrane is a new and suitable method for the development of these membranes.

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