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IR-initiated preparation method of high performance nanofiltration membranes using graft polymerization of acrylic acid onto polyacrylonitrile surface

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Abstract−A new facile, cost-effective and safe approach is introduced for the modification of polyacrylonitrile (PAN) membrane surface by a polymerization process in order to improve hydrophilicity and antifouling. For this purpose, membrane activated by IR-initiated, and acrylic acid (AA) as a monomer was successfully grafted on the membrane surface. The surface properties of membranes were characterized by means of various techniques: infrared spectroscopy, zeta potential, water contact angle, atomic force microscopy (AFM), and scanning electron microscopy (SEM). The experimental results indicate that the membrane surface becomes more hydrophilic by reducing the contact angle from 67.1° to 52.5°. The existence of hydrophilic chains on the membrane surface facilitates the creation of a negative charge on the membrane surface unto −2.99 mV (from 3.51 mV in based-membrane). The separation performance of the modified membrane showed a desirable yield. For a membrane photografted for 25 min with acrylic acid solution (2 wt%), the retention of Na_2SO_4, $MgSO_4$, NaCl, and $CaCl_2$ was in the order of 81%, 67%, 34%, and 28%, respectively. The membrane retention is expressed the values of 90.37%, 87.17%, and 79.5% for Acid Blue 92, Acid Red 114, and Ibuprofen. The optimized NF membrane showed a permeability factor (Lp) of 6.48 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$. Furthermore, the surface modification of the PAN membrane via the IR-induced graft polymerization exhibits an enhancement of the membrane antifouling property.

Keywords: IR-Induced, PAN Membrane, Surface Modification, Acrylic Acid (AA), Graft Polymerization, Photoinitiator, Azo Dye

INTRODUCTION

Among the challenges that have appeared with the evolution of industries, is the entrance of chemical pollutants into the environment in diverse ways [1]. Recently, many studies have been accomplished to eliminate these pollutions and many investments in this field reveal the importance of this issue [2]. In this regard, membrane-based processes have been developed for separation, fractionation, and purifications of materials in various situations, and there is a significant expansion in this range due to the performance and facility of utilization [3]. Nanofiltration (NF), a pressure-driven membrane process, is extensively applied in various activities, including water purification, pharmaceutical, and chemical industries [4]. The surface of the membrane in the nanofiltration process has an ionic charge and these membranes are particularly employed in the separation of ionic compounds. Its advantages include low work pressure, high retention of multivalent ions, approximately low investment, cost-effective operational and preservation cost. Surface modification until formation nanofiltration range seems necessary to increase the efficiency of membranes and create desirable properties. So far, various methods, including chemical and physical, have been developed for this purpose [5]. The chemical method is done by blending polymers with more proper properties or joining polymer layers on the active surface of the membrane [6]. Chemical modification is usually an intricate process with expensive devices and requires a variety of materials and solvents. In addition, this method often leads to destruction or change in the porous structure of the membrane [7]. Physical modifications are the most promising method to improve the surface properties of membranes. Graft polymerization includes flame exposure, radiation, plasma, and ion beams, which can be efficiently modified by attaching the polymer layer to the surface [8]. Photochemical reactions are a class of reactions induced by the absorption of ultraviolet or visible beams. In these groups, the reactants are excited by light stimulation and transfer the highest energy level. Actually, it can be said that light in these reactions provides the required activation energy to perform the reaction. Then the excited state is inactivated by chemical processes and the expenditure of excess energy [9]. Photochemical modification of the surface of ultrafiltration (UF) membranes *via* UV photograft, by creating a new layer of polymer with unique and desired properties, reduces the size of membrane pores and can add electrical charges to the membrane surface. This increases membrane retention for salts and small organic molecules [10]. By graft polymerization of various monomers on the membrane surface, membranes with unique properties can be prepared. In this opinion, the kind of monomer employed is really important and can manage the size of the pores and the surface charge [11]. Herein, acrylic acid (AA) was used as a monomer. Acrylic acid is a hydrophilic monomer that holds an extensive field of employment in the linking process because of its C=C. Bequet et al.

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by using photo-induced grafting of AA on the surface of polysulfone ultrafiltration membrane developed nanofiltration membranes in the formation of plates and hollow fibers that were applied in water desalination [12]. Zhu et al. modified polyethersulfone membrane surface by Corona-treatment graft polymerization of AA and they improved permeability and antifouling characteristics of the membrane [13]. Employing plasma-initiated and acrylic acid grafting, Staňo et al. were able to improve the grafting degree of polypropylene (PP) membranes as separators in alkaline electrolysis [14]. In this work, the polyacrylonitrile (PAN) was studied for the preparation of the nanofiltration membrane by the graft polymerization of AA. Polyacrylonitrile membranes include a family of porous products. Compared with conventional commercial membranes that are made usually by a polyamide on the top of polyethersulfone or polysulfone supports, PAN-based membranes have great potential for use in filter membranes due to their controlled porosity, high thermal and chemical stability, resistance to most organic solvents, and low cost [15-17]. No toxicity has been identified for PAN in TOXNET Database [18]. In addition, the nitrile group acts as an electron acceptor and increases the ability to activate the base membrane against high wavelength radiation. In fact, this group helps to create radicals in the polyacrylonitrile base membrane and facilitates the polymerization reaction. The polyacrylonitrile used in this study is a textile waste that is inexpensive and available. Therefore, employing it as a desirable application is an advantage. Physical ways, which include a variety of monomer graft procedures on the membrane surface, have received more attention due to the simplicity and speed of the procedure. Plasma treatment [19-22] and the photopolymerization process [23-27] are the most widely employed techniques for vinyl monomer grafts. Most of these methods increase manufacturing cost and are also dangerous and destructive, so developing new initiating systems upon longer, safer, and cost-effective wavelength irradiation is a great challenge. In this study, a new method is introduced to modify the surface of the membrane by utilizing infrared radiation (IR). Electromagnetic radiation is classified into different spectral regions such as X-rays, UV, visible, and IR radiation. IR radiation ranging from 760 nm to 1 mm is non-ionizing radiation located 'below the red' adjacent to the red part of the visible radiation range and extending up to the microwave range. Extensive research has been carried out on thermal IR radiation. Some research has pointed out that infrared radiation (IR) heating in blanching, cooking, frying, food peeling, disinfection, and pest management could be able to improve the quality retention of food materials [28-30]. In another study, the effect of short and medium infrared radiation has been reported in the food drying industry [29,31]. IR radiation has been applied to the intensification of Reutealis trisperma biodiesel production with efficient productivity and less energy consumption [32]. However, few efforts have been reported for activation of reaction under infrared light, i.e., polymerization and modification of membrane. Infrared radiation is responsible for about 50% of the energy coming from the sun and is commonly used for different optical and biological applications, but ignored in industries such as membrane fabrication and separation. Infrared usually causes molecular vibrations and rotations due to rising temperatures [26]. Therefore, it is not normally able to react and modify the membrane surface. Here we developed a simple and easy way to provide this capability for infrared. Given the low beam intensity and the lack of photoactivity of the base polymer, a material that could both act as photoinitiator and enhance the intensity of the beam emitted was required. A photoinitiator in polymerization is a molecule in trace quantities that creates free radicals under the influence of light to start the reaction. Using a light absorption system that leads to the formation of active species is essential to initiate light polymerization [34]. Already dyes are used in a variety of applications as light-sensitive compounds [35]. Azo dye was appointed for this purpose. Azo dyes are a class of compounds containing N=N that can absorb visible light [36]. In this research, the surface of virgin membrane was modified with grafting via acrylic acid as the monomer. For this purpose, infrared radiation was used in a new idea. By adding Acid Red 114 (AR114) as an azo dye to the membrane, the connection of the monomer to PAN by infrared radiation is possible. Finally, the effect of monomer concentration and irradiation times on the performance of the modified membranes was evaluated (see Fig. 12).

EXPERIMENTAL

1. Materials

Polyacrylonitrile (PAN) is a fiber made from textile waste and used as a membrane material. Dimethylformamide (DMF) from Chem Lab (Belgium) as solvent without further purification and polyethylene glycol (PEG) with average molecular weight from 600 to 3,000 Da from Merck (Germany) was applied. Acrylic acid (AA) supplied by Merck was used as a monomer for PAN modification. Acid Orange 7, acid red 114, and acid blue 92 from Yazd Alvan and other chemicals also were purchased from Merck company.

2. PAN-based Membrane Preparation

In this research, the flat sheet PAN-based membrane was prepared through phase inversion method. Initially, homogeneous polymeric solution containing PAN (18 w/w%), PEG2000 (4 w/w%), and DMF (78 w/w%) was mixed by a magnet stirrer at the rate of 250 rpm and heated at 65 °C for 24 hours in reflux system. Note that PEG2000 was added as a pore former. Finally, the dope solution was ultrasonically treated for about 15 minutes to remove bubbles and cast on a flat glass using an adjustable casting knife with a thickness of 255 μm. The basis of this research involves adding azo dye in an aqueous solution as non-solvent during the phase inversion process. The polymer film is immersed in a water bath containing 50 ppm AR114 for coagulation and remains for 24 hours. Here, the exchange between the solvent and nonsolvent in the water leads to the formation of the porous asymmetric PAN membrane. The permeability factor of virgin membranes (M_0) above 185 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$ was continuously measured.

3. Treatment of Polymer Membranes by IR-Irradiation

The IR system used in this study is PHILIPS/250W lamp, Korea. In the grafting polymerization step, prepared membrane containing the azo dye (membrane surface=374 cm^2) was dried and then dipped in a monomer (AA) solution at different concentrations. The virgin membrane was modified by IR-assisted grafting polymerization in the presence of AA. The samples were irradiated under IR lamp for 25 minutes at room temperature. The distance between

Table 1. Different polymerization conditions of membranes

Membrane	AA concentration (wt%)	Irradiation time (min)	Azo dye concentration (ppm)
M_0	-	-	-
M_1	1	15	50
M_2	2	15	50
M_3	3	15	50
M_4	4	15	50
M_5	2	10	50
M_6	2	20	50
M_7	2	25	50
M_8	2	30	50
M_9	3	25	50
M_{10}	2	25	40
M_{11}	2	25	70
M_{12}	2	25	100

the reaction solution and the light source was 30 cm. We used AR114 azo dye as photoinitiator. Various concentrations of AA (1, 2, 3, and 4 wt%), irradiation time (10, 15, 20, 25 and 30 min) and dye concentration (40, 50, 70, 100 ppm) were investigated and presented in Table 1 by M_n. The experimental conditions, such as monomer concentration, the distance between the IR source and the membrane and irradiation time, can influence the grafting rate. Therefore, situations must be constant and reactions controlled to determine the optimal monomer concentration and irradiation time. After irradiation, the modified membranes were immersed in water.

4. Filtration Measurements

Water permeation and retention of soluble ions are two important parameters in describing the performance of nanofiltration membranes. The filtration experiments were conducted in a cross-flow filtration system. The active membrane was placed inside the cell, and pure water or ionic solution with a specific concentration was filled in the feed tank. The filtration was carried out at pressure of 3 bar and room temperature (25 °C). After enough time and when the amount of permeation flux (F) was stable, the amount of output water was measured in units of time. The pure water flux (F) and permeability factor (L_p) were measured according to Eqs. (1), (2):

$$F=\frac{V}{A\times t}(L/m^2\cdot h) \tag{1}$$

$$L_p=\frac{F}{\Delta P}(L/m^2\cdot h\cdot bar) \tag{2}$$

The surface area of the membrane (A) was about 22 cm^2 and the pressure (ΔP) was 3 bar at room temperature (25 °C), where V is the volume of permeated water (liter) in 5 minutes.

To express membrane retention, the feed solution was prepared from 80 ppm of drugs and 60 ppm of dyes calculated according to the following equation:

$$R_{obs}(\%)=\left(1-\frac{C_P}{C_F}\right)\times 100\% \tag{3}$$

where R_{obs} is the observed retention of the solute, C_F and C_P are the feed and the permeate solution concentration, respectively. Retention of salts is an important parameter for evaluation of the membrane performance. Retention of 0.01 M NaCl, $CaCl_2$, Na_2SO_4, and $MgSO_4$ solutions was conducted using Eq. (3).

5. MWCO Measurement

The molecular weight cut-off (MWCO) is a key parameter for describing the efficiency of nanofiltration (NF) membranes. It refers to the molecular weight (Mw) of a solute having 90% retention [37]. Here PEG solute used for measurement of MWCO and analyzed by UV-Visible spectrophotometer (GBC Scientific Equipment Ltd., - Cintra 101 - UV-visible spectrometer, Australia) at a wavelength of 535 nm according to the method of Sabde et al. [38].

6. Characterization of the Membrane Surface

FT-IR analysis was done to detect the presence of functional groups and chemical structure of membranes before and after photopolymerization. FT-IR IBB Bomem MB-100, Canada was used for this purpose. Scanning electron microscopy (SEM, MIRA3 TESCAN) and atomic force microscopy (AFM, CP II/Veeco, USA) were used to evaluate the surface structure of the modified membranes and then compared with primary membranes. From AFM images were extracted morphological parameters and roughness value. To compare information about the hydrophilicity of the membranes, the contact angle was measured between water and membrane surface (Camera Model CAG-20). To determine the surface charge of membranes and describe their function, the zeta potential after grafting was measured (BROOKHAVEN OMNI/nano-book).

RESULT AND DISCUSSION

M_7 with the highest rate of salt retention provides the optimal conditions (2 wt% of AA under 25 min of IR irradiation, 50 ppm of Azo dye). Consequently, this membrane was employed to investigate parameters affecting the performance of modified membranes and analysis.

1. FT-IR Study

IR analysis was used to evaluate the structural characterization before and after membrane modification. The adsorption peaks presented in Fig. 1(a) are recorded for the research of the sublayer membrane before the joining of dye molecules. The notable peaks for the stretching vibrations of the -CH, -C≡N, -C=O, -C=N, and OH groups, respectively are present around 2,932 cm^{-1}, 2,243 cm^{-1}, 1,736 cm^{-1}, 1,628 cm^{-1}, and 3,628 cm^{-1} and also the peak at 1,449 cm^{-1} assigned as the bending vibration of the -CH_2 group. The appearance of peaks related to carboxyl and hydroxyl groups in the support membrane spectrum also indicates the presence of carboxylic groups in the polyacrylonitrile polymer chain. This means the impurity of the primary polymer fibers, which is really expected owing to its industrial quality. It is clear from the spectra of the grafted membrane that an increase in transmission peak intensity at 1,628 cm^{-1} and 3,629 cm^{-1} (Fig. 1(b)), is correlated to -C=O and OH functional groups in the monomer. These changes during the

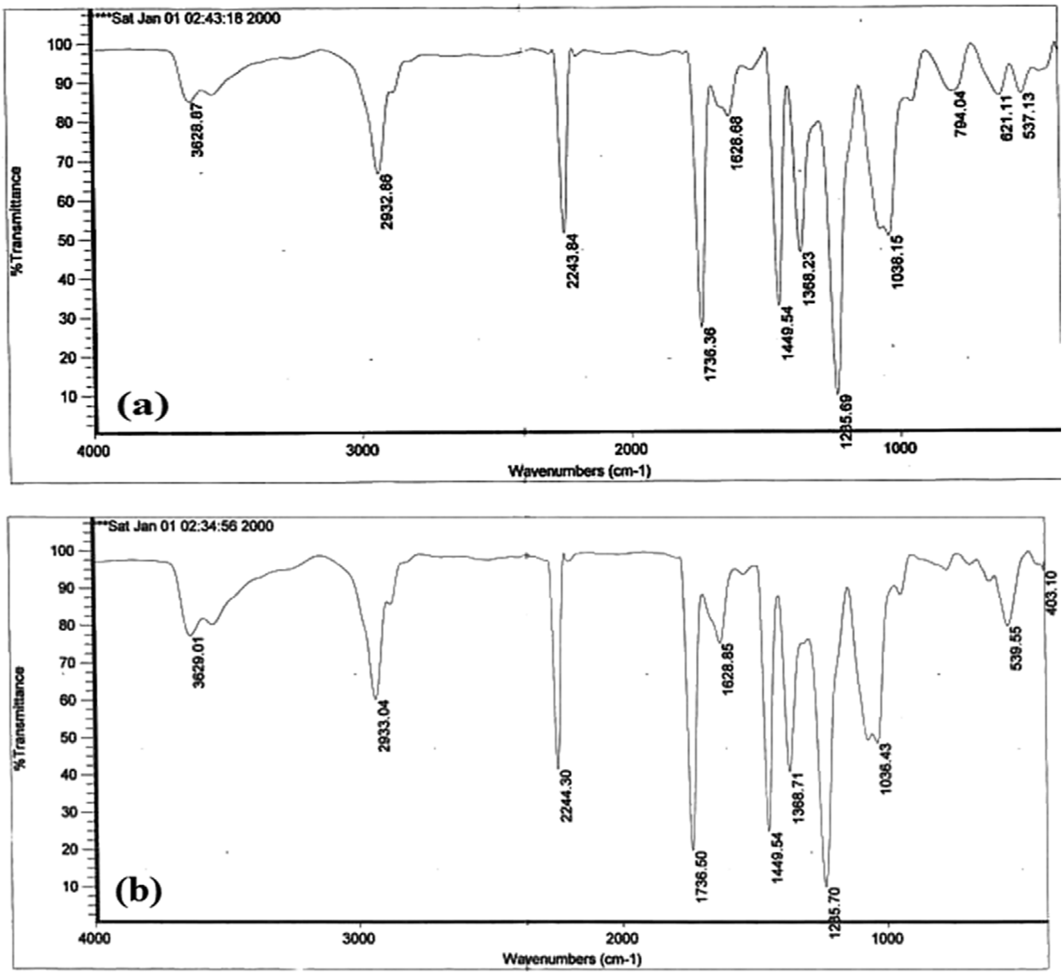
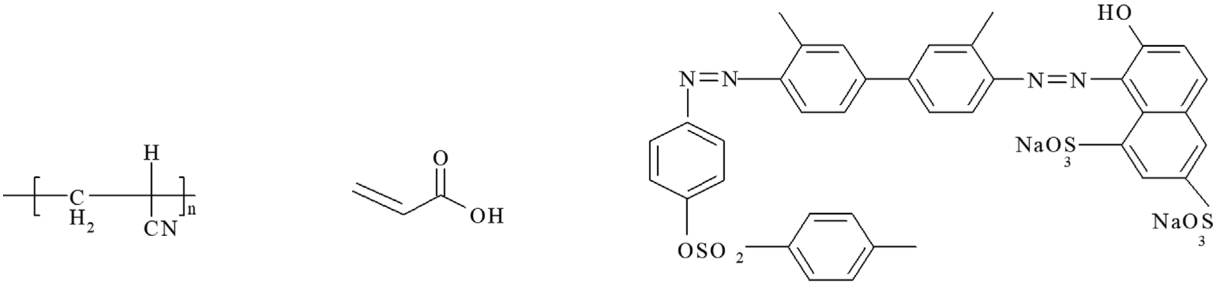


Fig. 1. FTIR spectra of virgin PAN (a) and IR treated PAN with 2%wt AA (b).



(a) (b) (c)

Fig. 2. Molecular structure of reactant utilized in the graft polymerization.

grafting of AA on the PAN membrane indicate successful photopolymerization.

During this method, the following reactants with the molecular structure displayed for graft polymerization were applied:

- Polyacrylonitrile (PAN) (Fig. 2(a)) as the base membrane.
- Acrylic acid as a hydrophilic monomer (Fig. 2(b)) to modify the membrane.
- Acid Red 114 dye (Fig. 2(c)) as a photoinitiator.

According to the following, it can be considered that AR114 can stimulate the base polymer in the presence of light by creating stable and multiple active groups as an effective initiator:

1. The behavior of azo (-N=N-) groups in the structure, which is easily broken down and produces free radicals.
2. Due to its color feature, it can increase the amount of radiation absorbed per unit area and enhance the light intensity [39,40].
3. The presence of OH group and methyl substitution on the dye compound assists to absorb longer wavelengths [39].

By irradiating the AR114 molecule, it absorbs infrared waves,

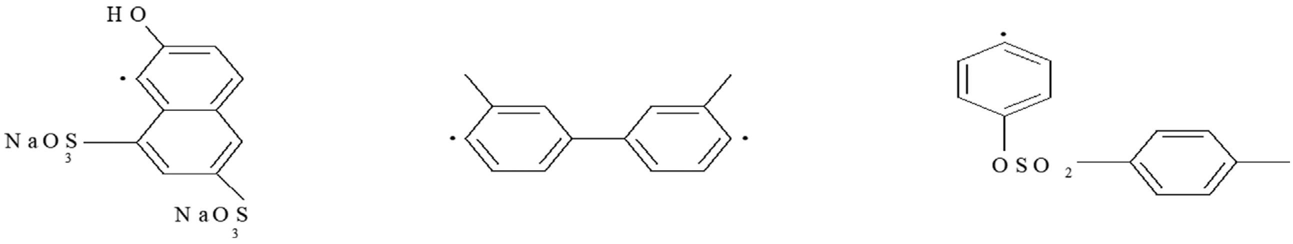


Fig. 3. Excited molecular structures of $A^{\bullet}$.

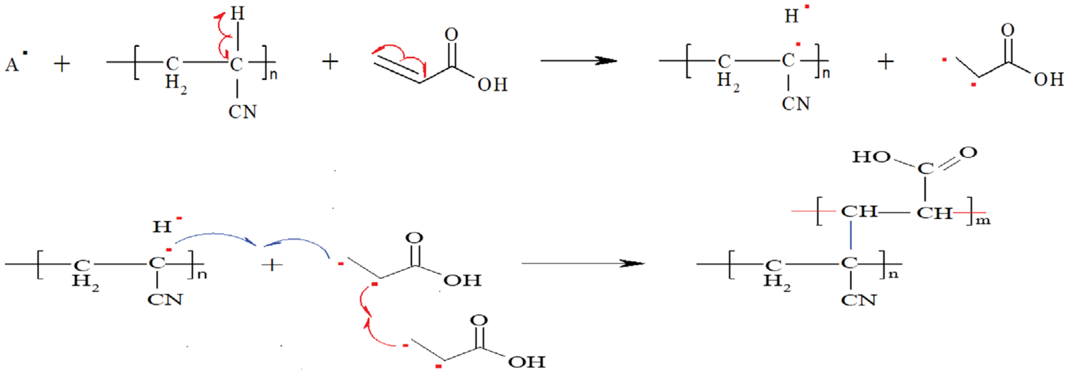


Fig. 4. The provisional mechanism of grafting AA as monomer on PAN membrane.

breaks them down, and creates free radicals according to Eq. (4):

$$A+h\nu\rightarrow A^{\bullet} \tag{4}$$

where A denotes the ground-state molecule, hν the absorbed photon, and $A^{\bullet}$ the molecule in an electronically excited state with an extra energy hν (as the equation indicates). $A^{\bullet}$ can be created in one of the radical forms of Fig. 3:

$A^{\bullet}$ as an energy-rich species excites polyacrylonitrile within a short period of time and grafting of monomer on the membrane surface according to Fig. 4.

The evidence below confirms the provisional mechanism of reaction drawn in Fig. 4.

- Analysis of the IR spectrum of the modified and unmodified membrane shows that the nitrile group peak has not changed. So this group has not been attacked.
- By comparison of the spectra of the membranes before and after IR-irradiation treatment enhanced peak intensity is visible and considering no reaction was performed in the absence of monomer, it can be maintained that the acrylic acid reacted with the substrate membrane.
- Additionally, peaks related to the color functional groups are not observed in the IR spectrum of the modified membrane, and this confirms the dye used acted as a photoinitiator.
- Discoloration of the membrane after irradiation is another reason to prove that the azo dye is degraded and acts as a photoinitiator.

2. SEM Images

Membrane morphological changes before and after graft polymerization were probed by scanning electron microscope (SEM) and Fig. 5 demonstrates typical images at different magnifications. It is the most commonly used means for direct observation in the study on the modification of membrane.

In Fig. 5, the modified membrane (b) after the formation of PAA new layer seems more cohesive and monotonic than the virgin membrane (a).

The images received from the cross-section of the membranes prepared through the grafting method are presented in Fig. 6(b). A porous and finger-like structure with a dense top layer is observed for the treated membrane. With graft polymerization, increment in agglomeration of PAA on the top and wall surface of the membranes, formation of denser skin-layers with increased thickness, organization of spongy canals and sub-layers with lower porosities are obvious. In addition, the uneven layer on the surface of the substrate membrane (Fig. 6(a)) is also arranged and evened.

3. AFM Analysis

AFM was used to characterize the changes in the roughness of surface morphology by the effect of graft polymerization, which is one of the best parameters for comparing different membranes. Roughness parameters can be correlated with membrane performance and surface properties, such as membrane fouling, pore size distribution and pure water flux. Two and three-dimensional images of unmodified and modified membranes are illustrated in Fig. 7(a) and 7(b), respectively. According to the presented figures, it can be reasoned that by IR-irradiation on the membrane, the surface roughness has significantly decreased. The virgin membrane prepared has rougher surfaces, whereas the treated membrane shows less roughness and smoother surfaces. During the grafting process and coverage of the PAA, the membrane had a noticeable reduction in roughness value from 39.15 nm to 19.92 nm. These variations are evidence of a reduction in membrane pore size that is proportional to the roughness [41,42]. The height of surface peaks, depth of valleys, and membrane roughness decrease with the polymer-

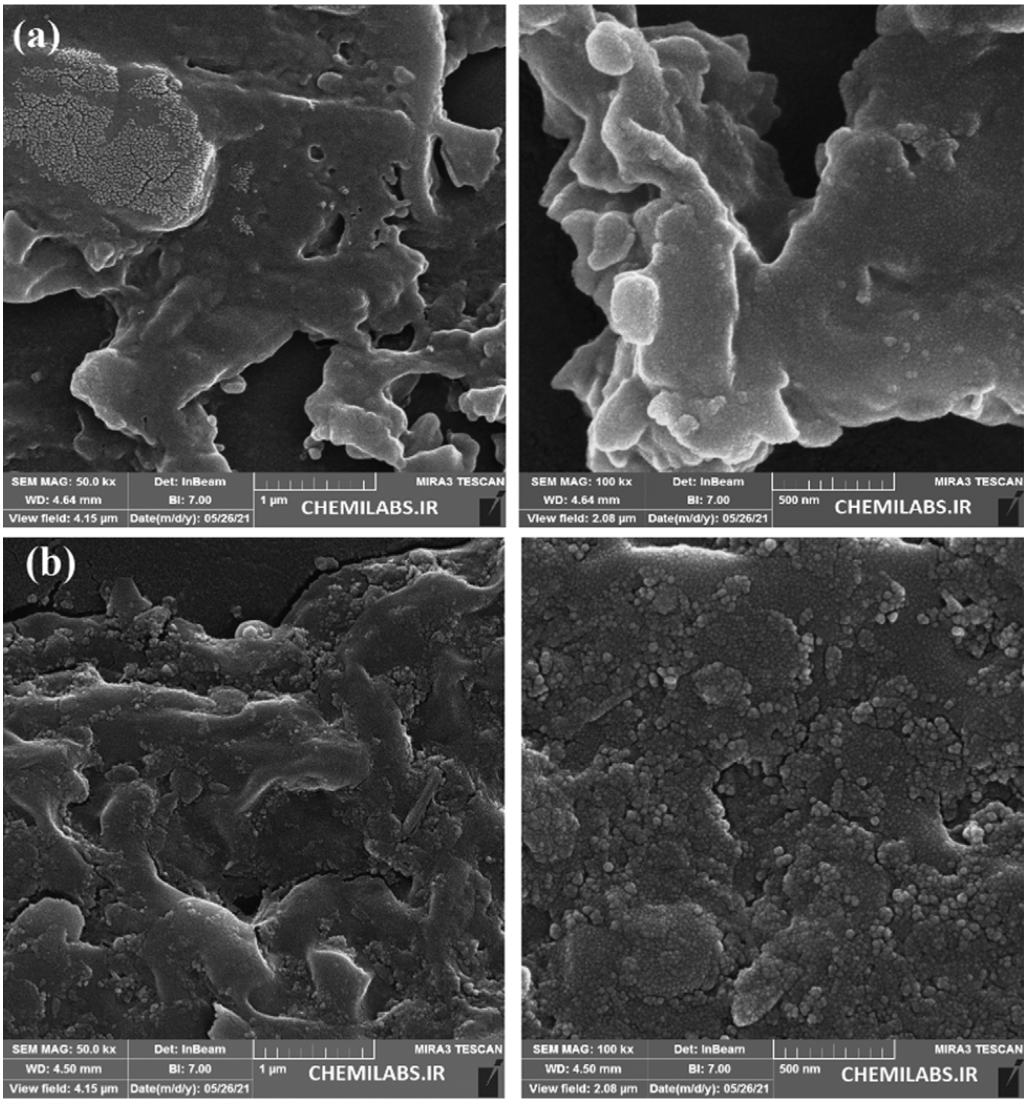
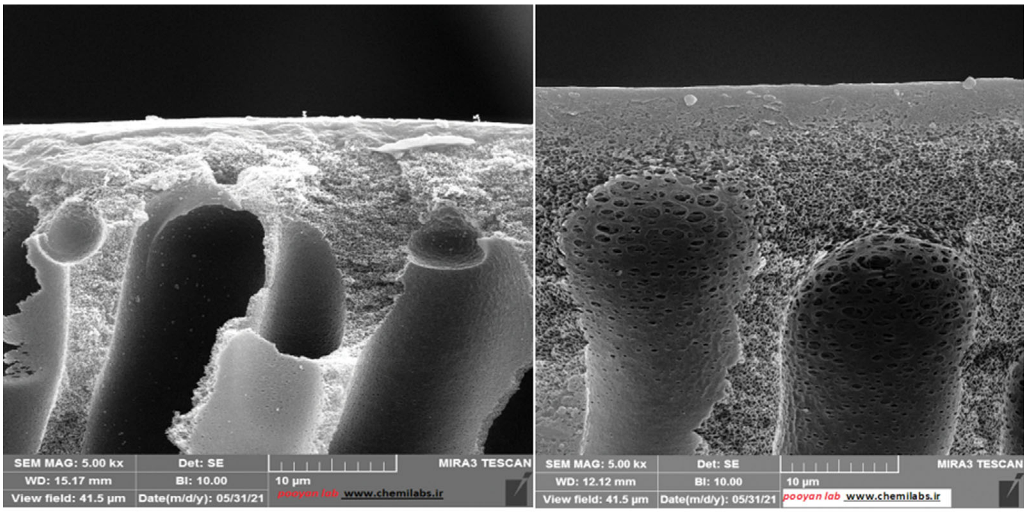


Fig. 5. SEM graphs of virgin membrane (a) and modified membrane with 2%wt AA (b).



(a) (b)

Fig. 6. SEM of cross-section of virgin membrane (a) and modified membrane with 2%wt AA (b).

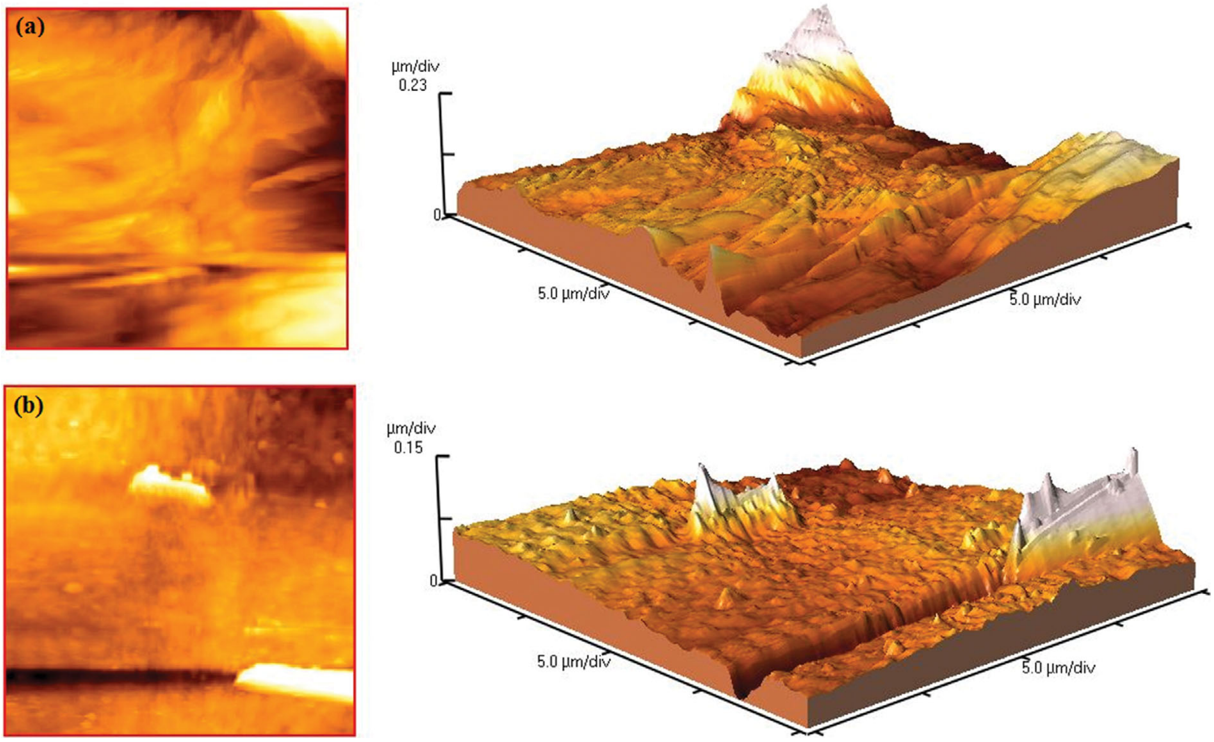
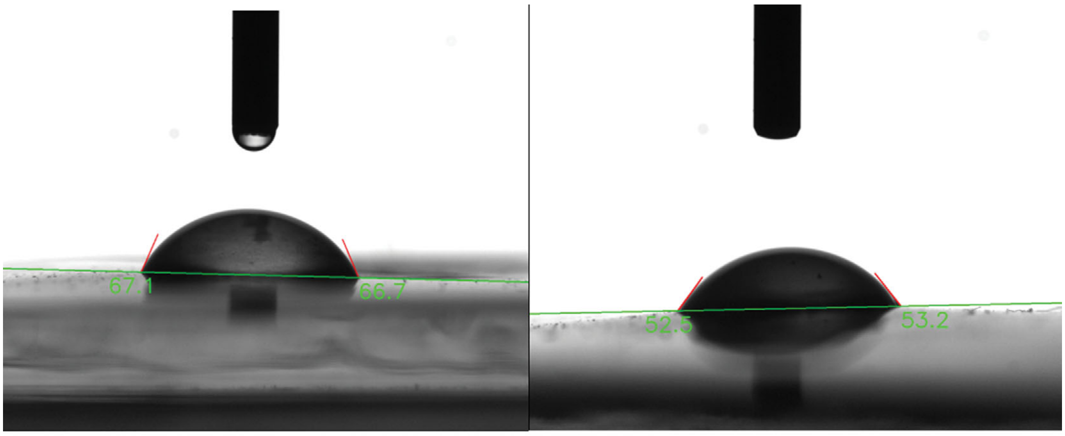


Fig. 7. AFM images of virgin and modified membranes: (a) PAN and (b) PAN-Irradiated.



(a) (b)

Fig. 8. Changes in the contact angles of water droplets on the virgin PAN membranes (a) and modified membrane (b).

ization of AA onto the pore surface and walls of the membrane. This event was clear by 3-dimensional AFM images up.

Decreasing membrane roughness has a great influence on reducing membrane fouling. According to a study by Chen et al. [43] about the effect of membrane roughness toward fouling, they resolved that the surface of the rough membrane enhances the tendency for surface fouling. Thus, the lower the surface roughness, the less likely it is that the fouling will adhere to the membrane surface. Liu et al. [44] also proved that soft membranes increase the resistance to fouling. Therefore, with the grafting of monomer on the membrane surface and a significant reduction in surface roughness, it can be expressed the anti-fouling property of the membrane has improved.

4. Contact Angle

Contact angle analysis was used to evaluate the hydrophilicity of the membrane surface. As seen from Fig. 8, the modification of the membrane surface is associated with a decrease in the contact angle (from 67.1° in unmodified to 52.5° in modified PAN membrane). This indicates the hydrophilicity of membrane was increased after the modification process. The presence of carboxyl as hydrophilic groups in the monomer improves the interaction with water molecules and reduces the contact angle.

5. Zeta Potential of Membranes

One of the great purposes for developing the membrane sur-

Table 2. The measurement of zeta potential

Membrane	Zeta potential (mV)	pH
M	3.51	5.697
M_7	−2.99	5.815

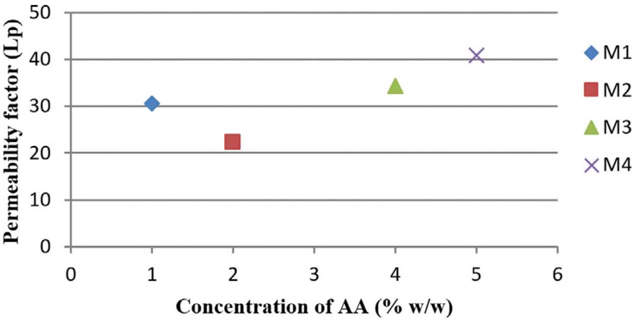


Fig. 9. Effects of acrylic acid concentration at constant exposure time on permeability factor (L_p).

face in this project is creating a negative charge on the membrane surface. For this, the zeta potential for base membrane and modified membrane with IR-radiation was measured and the outcomes are displayed in Table 2. The final results of the calculations obtained from the measurement of zeta potential show a negative charge on the membrane surface after surface modification. Since the linked monomer (AA) contains anionic groups that lead to high density of negative charges on the polymer surface, as expected, the value of zeta potential is negative.

6. Pure Water Flux Performance and Permeability Factor

Decrease of the pore size of the membrane results in reduced pure water flux and permeability factor. The effects of monomer concentration and irradiation time were investigated during the grafting process to optimize these properties. Initially, to optimize the concentration of acrylic acid, the irradiation time was set at 15 minutes and the permeability of the membrane at different concentrations of monomer was examined. Fig. 9 shows the effect of acrylic acid (AA) concentration with constant IR irradiation time.

The results of this study indicate that at constant irradiation time, the permeability factor at a concentration of 2%wt (M_2) gives a more favorable outcome. It appears that grafting is performed at high concentrations with lower intensity, which can be due to the less absorption of radiation by the membrane at high concentrations. If the concentration of the solution exceeds 2%wt, the radiation is absorbed by the solution and limits the reaching of the radiation across the surface of the membrane entirely, so the number of radicals created in the vicinity of the membrane surface is reduced. On the other hand, by extra reducing the concentration of the solution, the interaction between the membrane surface and the monomer is decreased and complete polymerization is not achieved, therefore increasing the pure water flux. After defining the optimal concentration of monomer, the influence of irradiation time on the permeability of pure water in several membranes was studied. Fig. 10 displays the effect of irradiation time on the permeability of pure water at constant AA concentration. While the duration of IR irradiation on the membrane surface increases, the monomer graft on the aperture and flank of the cavity advances, the cavity strait and the pure water flux decreases. At the constant concentration of monomer, the best IR activation time is 25 and 30 minutes (M_7 and M_8). Due to the suitability of short irradiation time, M_7 was considered optimal (The permeability factor of M_0=above 185 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$).

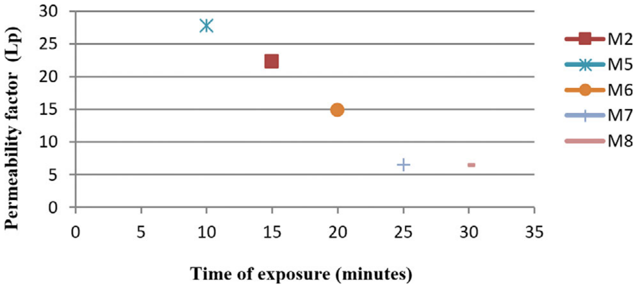


Fig. 10. Effects of IR exposure time at a constant concentration of 2%wt of AA on permeability factor (L_p).

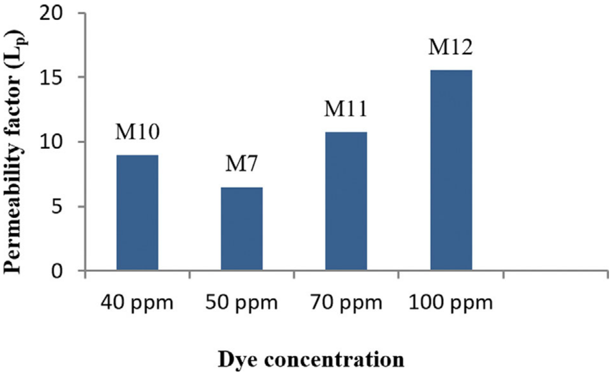


Fig. 11. Effects of the dye concentration on coagulation bath on permeability factor (L_p).

The consequences of Figs. 9 and 10 indicate that irradiation time and monomer concentration are two significant and powerful agents in membrane modification. M_7 and M_8 membranes exhibit the most suitable permeability factor for pure water, but since both membranes show an equal range of permeability, the M_7 membrane with more compressed irradiation time was chosen to continue working. Since azo dye was used as a photoinitiator in this work, the effect of dye concentration in coagulation bath was also examined and the results are shown in Fig. 11. It was observed that concentration higher than 50 ppm has the opposite effect on the reaction. Actually, the reason can be recognized as essentially a steric hindrance created by excess molecules and disturbed in the polymerization reaction, with the membrane surface. Therefore, the optimal color concentration was considered to be 50 ppm (The permeability factor of M_0=above 185 $L\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$).

7. Salt Retention Performance

In terms of retention, feed solutions of Na_2SO_4, $MgSO_4$, NaCl, and $CaCl_2$ were selected. The pore flow in the membrane process can occur in the ion transfer mechanism or ion retention mechanism. In the transfer mechanism, the value of ion retention is based on the pore size, so that with larger pore size, the ion retention rate decreases. In the ion rejection mechanism, common ions with

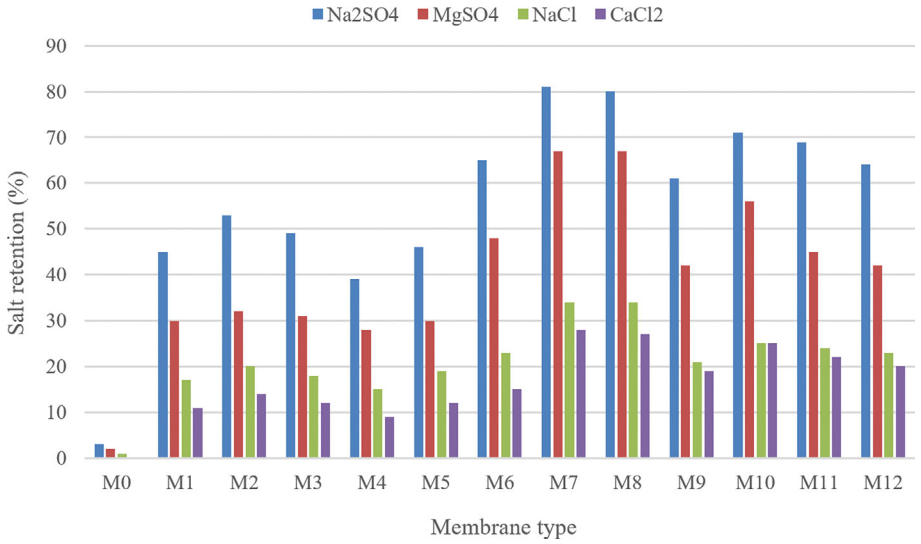


Fig. 12. Retention of membranes to different electrolytes (Na$_2$SO$_4$, MgSO$_4$, NaCl, and CaCl$_2$).

charges similar to the membrane surface are rejected by the membrane and equivalent number of counter-ions are retained to satisfy electroneutrality [24]. According to Fig. 12, the membrane modified with acrylic acid shows appropriate retention for salts and it can be seen the highest and lowest salts retention relates to Na$_2$SO$_4$ and CaCl$_2$, respectively. Generally, electrolyte solutes with higher anionic charge density ($SO_4^{2-}>Cl^-$) and with lower cationic charge density ($Na^+>Ca^{2+}>Mg^{2+}$) retain more efficiently in negatively charged NF membrane.

In Fig. 12, the impacts of monomer concentration and irradiation time also are displayed. As shown, M$_7$ (2%wt of AA, 25 min of IR-irradiation, 50 ppm of dye) provides the best performance in the retention of salts. This efficiency in membranes with different concentrations or different irradiation times is reduced. For example, M$_9$ (3%wt, 25 min, 50 ppm) or M$_6$ (2%wt, 20 min, 50 ppm) show a noticeable reduction in salt retention. The reduction of retention in membranes with differences in both concentration and irradiation time (i.e., M$_3$) is significantly less than the others. It can be concluded that M$_7$ provides the optimal conditions that have the highest rate of salt retention. Solute retention behavior of membranes is determined by charge effects and size pores. Therefore, by changing the irradiation time and concentration of the monomer from the optimal amount (2%wt of AA, 25 min of IR-irradiation, 50 ppm of dye), the surface of the membrane is not completely modified and due to the presence of incomplete grafting and larger pores, less retention in the membrane is observed. From separation graphs it is observable that salt retention is more sensitive to the monomer concentration rather than to the irradiation time (for example, salt retention rate in M$_9$ is lower than in M$_6$).

Under the same conditions, M$_7$ coated with 2wt% of AA under 25 min of IR irradiation had an extraordinary ability for salt retention of PAN membrane. Consequently, this membrane was employed to investigate parameters affecting the performance of these membranes and analysis.

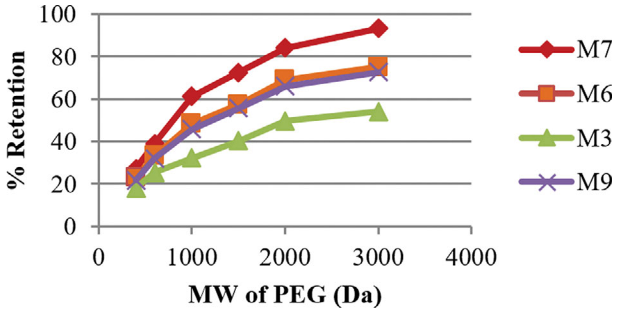


Fig. 13. MWCO of different membranes.

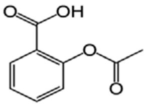
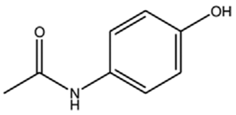
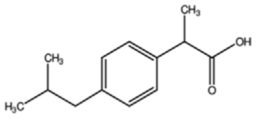
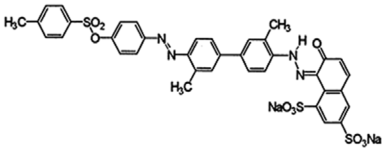
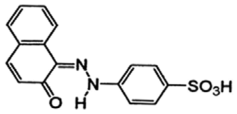
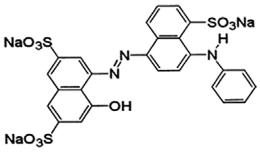
8. MWCO Measurement

According to the definition of MWCO, filtration tests membranes with the retention of different MW of PEG (1,000 ppm) were performed. To MWCO measurement, four M$_7$ (Optimal membrane in terms of salt retention), M$_6$ (with different irradiation time), M$_9$ (with different concentration), and M$_3$ (with differences in both concentration and irradiation time) modified membranes in the presence of AA were selected. The reason for selecting M$_9$, M$_6$, and M$_3$ is higher salt retention in membranes with differences in monomer concentration and irradiation time than the optimal value. Although predictions based on MWCO do not reflect the actual characteristics of the pores, however, a comparison among the membranes prepared in Fig. 13 explicates that M$_7$ with a concentration of 2%wt and irradiation time of 25 minutes has the best result with MWCO of approximately 2,500 Da. Retention behavior of modified membranes was studied and the effects of photopolymerization conditions like monomer concentration and irradiation time, on MWCO were measured. M$_6$ with a lower irradiation time and M$_9$ with a higher concentration did not show the desired results in MWCO measurements.

9. Membrane Performance Evaluation

To express the performance of the modified membranes, the retention rate of several pollutants with anionic group randomly was measured. The characteristics and conditions of the feed solutions used to determine retention are shown in Table 3.

Table 3. The characteristics and conditions of the feed solutions

Name of sample	Formula	Molecular structure	Molar mass (g·mol^{-1})	Concentration (ppm)
Aspirin	$C_9H_8O_4$		180.159	80
Acetaminophen	$C_8H_9NO_2$		151.165	80
Ibuprofen	$C_{13}H_{18}O_2$		206.285	80
Acid Red 114 (AR114)	$C_{37}H_{28}N_4Na_2O_{10}S_3$		830.8	60
Acid Orange 7 (AO7)	$C_{16}H_{11}N_2NaO_4S$		350.32	60
Acid Blue 92 (AB92)	$C_{26}H_{16}N_3Na_3O_{10}S_3$		695.58	60

Initially, solutions of each sample with defined concentration were employed for the filtration process through 3 bar pressure. Later, the absorption rate of feed solution and permeate solution collected in any test was estimated using a UV-VIS absorption spectrophotometer and, eventually, their retention percentage was calculated. The results for the solutions mentioned above are presented in Fig. 14.

According to the given results, the retention in the membrane modified with acrylic acid has significantly increased. Because of large pores and besides the lack of electrical charge on the surface of unmodified membranes, we see extremely limited retention. But after the membrane is exposed to radiation and photopolymerized, retention is effectively increased. Consequently, the performance of the modified membrane in eliminating anionic contaminants based on the Donnan effect [45] can be well observed. Acid Blue 92, despite having a lower molecular weight than Acid Red 114, records higher retention due to the larger number of functional groups (in AB 92, three groups of available sulfonic acid are observed in contrast to two groups of that in AR114). Acetaminophen has the lowest retention because of its lower molecular weight and the presence of an amino group in the structure. In addition, it is recognized that M_7 is also optimized for retention. The fouling phenomenon is one of the most serious limiting factors in the performance of membrane separation processes, which makes the use of this technology effective in terms of performance and lifespan. Changes in the separation achievement and a decrease in the amount of flux passing through the membrane during the separation process are due to the effects of fouling [46]. In surface modifications, antifouling properties of the membrane surface are enhanced. To prove this point, 60 ppm solutions of AR114 and AO7 and 80 ppm of Ibuprofen were selected, and then the filtration process was performed for 180 minutes at 3 bar pressure and 25 °C. The results of this experiment are presented in Fig. 15 (The permeability factor of M_0 for all reagents=above 185 L·m^{-2}·h^{-1}·bar^{-1}).

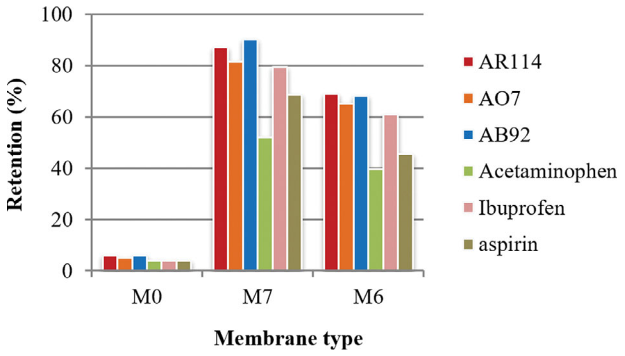


Fig. 14. Retention of different membranes.

While it is observed, a decrease in flux and also permeability coefficient due to precipitation of the particles on the membrane surface has occurred, but this fouling rate amount is really slight, and despite the time of 180 minutes later, there is no notable de-

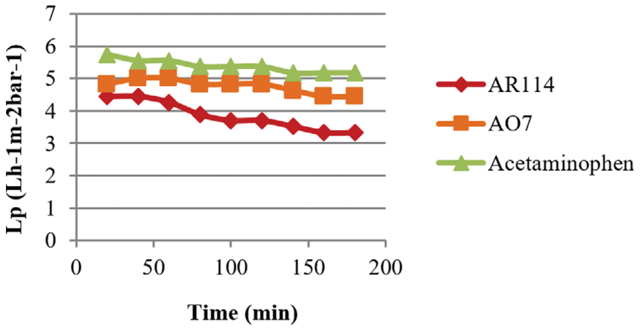


Fig. 15. Permeability coefficient of AR114 (60 ppm), AO7 (60 ppm) and Ibuprofen (80 ppm) as a function of time for M_7.

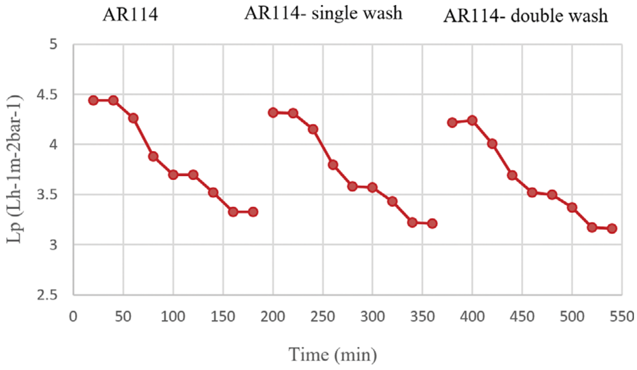


Fig. 16. Permeability coefficient of AR114 (60 ppm) Compared to once and twice washing and reuse.

crease in flux. With increasing molecular weight, more flux drop is seen, so that the AR114 exhibits more flux decline than the others. Note that since the amount of flux and consequently the permeability coefficient in the crude membrane is extremely high, measuring the fouling test for it seems pointless. According to the achieved outcomes, it can be recognized that modifying the membrane surface with this method improves the antifouling properties of the membrane and the membrane will not have a great flux decline over time. To clean the membrane, it was removed from the cell and immersed in distilled water for 20 minutes, and the contaminated surface was lightly washed. After rinsing the membrane, the fouling test was performed again in the same first way for Acid Red 114. This process was repeated for the second time and the results indicate that the membrane did not have many changes in the permeability coefficient even after being washed and reused twice.

As displayed in Fig. 16, the membrane exhibits only a 3% reduction in permeability factor for Acid Red 114 with a single wash and a 5% double wash.

CONCLUSION

So far, the membrane has been modified using various methods such as UV irradiation, plasma treatment, and gamma irradiation. In the meantime, it seemed necessary to use a safe method of radiation treatment that has low energy and at the same time can lead to great consequences. We started a new method to develop *via* IR-induced polymerization processes for rising membrane performance. To achieve this, it was important to create some changes in the membrane, for which purpose organic colored compounds in anti-solvent were utilized. The grafting process to AA concentration is more sensitive than irradiation time. Free radicals are created during irradiation and polymerization is initiated in the presence of a low amount of monomer. Monomer concentration (acrylic acid) and grafting time as grafting parameters were considered. Based on the checked parameters, sample number 7 (M_7) had the best result in this work. Increased hydrophilicity of the modified membrane, reduction of surface roughness which is associated with reduced membrane fouling, and enhanced retention of anionic drugs and dyes are the appropriate effects of this research. As mentioned, higher molecular weight molecules and more numerous anionic groups have more retention, so that among the chosen compounds, Acid Blue 92 with 90.37%, the highest, and Acetaminophen with 52% recorded the lowest retention rate. The optimized parameters were 2 wt% of AA and 25 min of IR activation time. The retention percentages obtained for Na_2SO_4, $MgSO_4$, NaCl, and $CaCl_2$ solutions were 81, 67, 34, and 28, respectively. A reduction in the contact angle value from 67.1 to 52.5 indicates an improvement in the hydrophilicity of the modified membrane. Additionally, the creation of a negative charge on the membrane by grafting with the change of zeta potential from 3.51 to −2.99 is quite noticeable. Therefore, surface analysis and evaluation of the performance of the modified membrane prove the development of membrane characteristics after the graft polymerization process by this method.

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SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at http://www.springer.com/chemistry/journal/11814.

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