

Surface modification of cation exchange membranes by graft polymerization of PAA-co-PANI/MWCNTs nanoparticles

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Abstract—Surface modification of polyvinylchloride based heterogeneous cation exchange membrane was performed by graft polymerization of PAA and PAA-co-PANI/MWCNTs nanoparticles. The ion exchange membranes were prepared by solution casting technique. Spectra analysis confirmed graft polymerization clearly. SEM images illustrated that graft polymerization covers the membranes by simple gel network entanglement. The membrane water content was decreased by graft polymerization of PAA-co-PANI/MWCNTs nanoparticles on membrane surface. Membrane transport number and selectivity declined initially by PAA graft polymerization and then began to increase by utilizing of composite nanoparticles in modifier solution. The sodium and barium flux was improved sharply by PAA and PAA-co-0.01%wt PANI/MWCNTs graft polymerization on membrane surface and then decreased again by more increase of PANI/MWCNTs nanoparticles content ratio in modifier solution. The electrodialysis experiment results in laboratory scale showed higher dialytic rate in heavy metals removal for grafted-PAA and grafted-PAA-co-PANI/MWCNTs modified membrane compared to pristine one. Membrane areal electrical resistance was also decreased by introducing graft polymerization of PAA and PAA-co-PANI/MWCNTs NPs on membrane surface.

Keywords: Surface Modification, Heterogeneous Cation Exchange Membrane, Polyacrylic Acid-co-PANI/MWCNTs Composite Nanoparticles, Ionic Transport Property, Heavy Metal Removal

INTRODUCTION

In the field of separation and purification technology, ion exchange membranes (IEMs) have been used as active separators in various electro-membrane processes such as fuel cells, chloro-alkali and electrodialysis [1-3]. Electrodialysis is an electrically driven process for desalting brackish waters, reconcentrating brine from seawater and production of table salt as well as manufacturing chemical products. In IEMs charged groups are attached to polymer backbone and freely permeable to opposite sign ions under an electrical field influence [1-6]. Knowledge of the physico-chemical characteristics of ion exchange membranes is an important factor for their applicability in various processes [6,7]. Preparing inexpensive ion exchange membranes with special physico-chemical characteristics such as high ionic flux and selectivity, low electrical resistance and appropriate mechanical and chemical stabilities is a vital step in future applications [1-4,5,8].

High performance may be obtained by membrane modifications. Many researches have already been performed to improve the IEMs' physico-chemical properties, which resulted in various modification techniques. In recent years, the role of surface modification in determining the separation properties of membrane has

been obvious. Different methods such as graft polymerization, plasma modification, and flame treatment have been utilized in membranes surface modification to alter the physico-chemical properties of membranes without affecting bulk properties [9-14].

In the current research, surface modification of poly (vinyl chloride) based homemade heterogeneous cation exchange membrane was carried out to achieve efficient electrochemical properties useful in electrodialysis processes related to water desalination and water recovery.

The PVC based heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resins as functional groups agents. In situ polymerization of polyacrylic acid (PAA) and PANI/MWCNT composite nanoparticles was also used as membrane surface modifier by mixing PANI/MWCNT nanoparticle with hydrophilic acrylic acid monomer and grafting technique.

Recently, the use of nanoparticles because of their high activity is the concern of most researches [1,15,16]. The PANI/MWCNT nanoparticle is one of the advanced composite nano-materials which has been attracted a great deal of attention because of its interesting feature and capacity based on the synergism between PANI and MWCNT properties [17-27].

Currently no report have been considered surface modification of heterogeneous cation exchange membranes by graft polymerization of PAA and PAA-co-PANI/MWCNTs nanoparticles simultaneously. The effects of graft polymerization of PAA and PAA-co-PANI/MWCNT composite nanoparticles on electrochemical prop-

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erties of homemade heterogeneous cation exchange membranes were studied. Electrodialysis experiment was also performed in a laboratory scale unit to evaluate the electro-dialytic performance of modified membranes in heavy metal ions (Pb, Cu, Ni) removal from waste water. The results are valuable for electro-membrane processes, especially in electro-dialysis process for water recovery and waste water treatment. The correlation between the structure and properties of membranes was also studied.

MATERIALS AND METHODS

1. Materials

Polyvinylchloride (PVC, grade S-7054, density: 490 g/lit, viscosity number: 105 Cm^3/g) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as membrane matrix. Tetrahydrofuran (THF, molar mass: 72.11 g/mol, Density: 0.89 g/cm^3) was employed as solvent. Cation exchange resin (Ion exchanger Amberlyst, strongly acidic cation exchanger, H^+ form, 1.7 meq/g dry, density 0.6 g/cm^3 , particle size (0.355–1.18 mm) <90%) by Merck Inc., Germany, was used in membrane fabrication. Potassium persulfate (KPS, initiator), acrylic acid (AA, monomer) and ethylene glycol (EG, cross-linker) were obtained from Merck. Polyaniline/multiwalled carbon nano tube composite nanoparticles (PANI/MWCNTs, nano powder, 80 nm < particle size, including 10%wt MWCNTs and 90%wt) were provided from NANO-RADBEHAN company, Iran. All other chemicals were supplied from Merck. Throughout the experiment, distilled water was used. The chemical structure of PANI/MWCNTs composite nanoparticles is shown in Table 1.

2. Preparation of Heterogeneous Cation Exchange Membranes

The heterogeneous cation exchange membranes were prepared by solution casting technique and phase inversion method. For membrane preparation, resin particles were dried in oven at 30 °C for 48 h and then pulverized into fine particles in a ball mill (Pulverisette 5, Fritsch Co.) and sieved to the desired mesh size. The ion exchange resin with desired particles size (–300+400 mesh) was used in membrane preparation.

The preparation proceeded by dissolving the polymer binder (PVC) into THF solvent ((polymer binder: solvent) (w/v), (1 : 20))

in a glass reactor equipped with a mechanical stirrer (Model: Velp-Scientifica Multi 6 stirrer) for more than 6 h. This was followed by dispersing a specific quantity of grind resin particle ((resin particle: polymer binder) (w/w), (1 : 1)) as functional groups in polymeric solution. The mixture was mixed vigorously at room temperature to obtain uniform particle distribution in the polymeric solution. In addition, for better dispersion of particles and breaking up their aggregates, the solution was sonicated for 1 h using an ultrasonic instrument. The mixture was then cast onto a clean and dry glass plate at 25 °C. The membranes were dried at ambient temperature (25 °C) and immersed in distilled water. As the final stage, the membranes were pretreated by immersing in HCl and NaCl solutions. The membrane thickness was also measured as around 70 μm by a digital caliper device (Electronic outside Micrometer, IP54 model OLR).

3. Membrane Surface Modification by Graft Polymerization Method

PAA and PAA-co-PANI/MWCNTs composite membranes were prepared by graft polymerization technique (Fig. 1). Prior to modification, the homemade membranes were dipped in distilled water for 4 h to remove any pollutant. The prepared heterogeneous cation exchange membrane was clamped between two glassy frames. The modifier solution containing acrylic acid as monomer (AA, 20%wt), potassium persulfate as initiator (KPS, 1%wt), ethylene glycol as cross-linker (EG : AA, 1 : 6.5 molar ratio) [26] and Polyaniline/multiwalled carbon nanotube composite nanoparticles as additive (PANI/MWCNTs: 0, 0.01, 0.03, 0.5%wt) was poured on top of the prepared membrane and rolled by a soft roller to eliminate any bubble and make a uniform area. Note that the modifier solution was mixed vigorously at room temperature and sonicated to obtain homogeneously dispersed solution during modifier preparation. After that, the membrane was heated at 90 °C for 4 h in oven. Finally, the membrane was washed sufficiently with distilled water to remove the excess monomer and surfactant and then kept in water.

4. Test Cell

The electrochemical experiments for the prepared membranes used the test cell (Fig. 2). The cell consists of two cylindrical com-

Table 1. The chemical structures of PANI/MWCNTs composite nanoparticles

Material	Chemical structure
Polyaniline/multiwalled carbon nano tube composite nanoparticles (PANI/MWCNTs)	<p>The diagram illustrates the chemical structure of PANI/MWCNT composite nanoparticles. It shows the reaction of Aniline (a benzene ring with an NH_2 group) and MWNT (multiwalled carbon nanotube, represented as a cylinder). The reaction leads to Polyaniline (Emeraldine salt) - MWNT, which is a polymer chain with alternating benzene and quinoid rings, with NH^+ groups, attached to the MWNT. This intermediate then reacts with NH_4OH to form Polyaniline (Emeraldine Base) - MWNT, where the NH^+ groups are replaced by NH groups.</p>

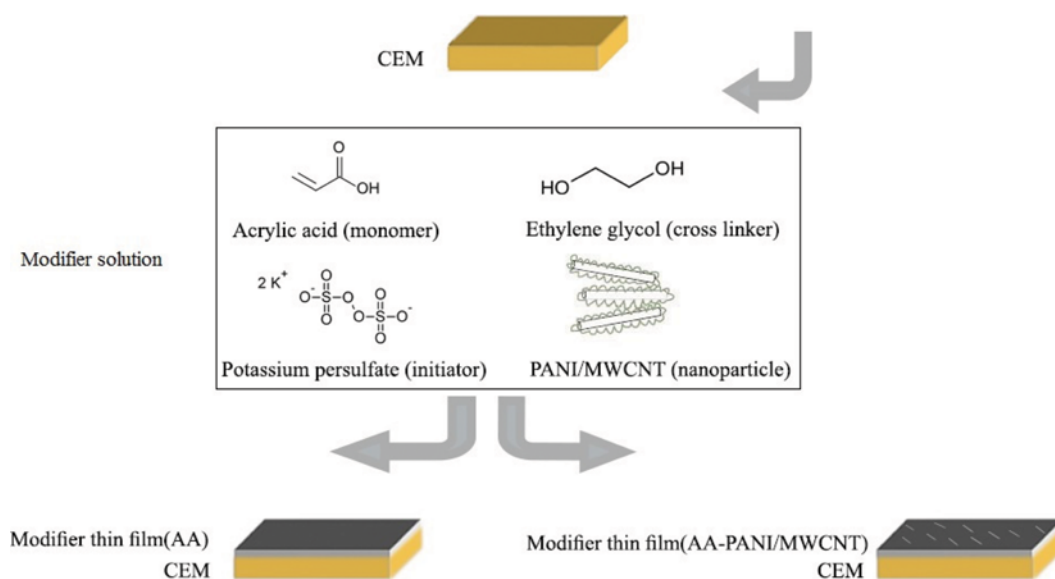


Fig. 1. Scheme of membranes surface modification by graft polymerization of PAA and PAA-co-PANI/MWCNTs nanoparticles.

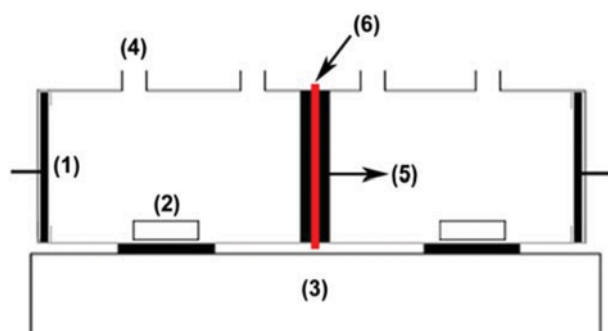


Fig. 2. Schematic diagram of test cell.

- | | |
|------------------|-----------------|
| (1) Pt electrode | (4) Orifice |
| (2) Magnetic bar | (5) Rubber ring |
| (3) Stirrer | (6) Membrane |

partments (180 cm^3) made of Pyrex glass which are separated by the membrane. The membrane was fixed between rubber rings. One side of each vessel was closed by Pt electrode supported with a piece of Teflon and the other side was equipped with a piece of porous medium to support the membrane. The top of each compartment contained two orifices for feeding and sampling purposes. To minimize the effect of boundary layer during the experiments and also to establish the concentration polarization on the vicinity of membrane's surface, both sections were stirred vigorously by magnetic stirrers (Model: VelpScientifica Multi 6 stirrer).

5. Membrane Characterization

5-1. FTIR Analysis

FTIR spectra measurements provided information about the chemical structure of the unmodified and modified membranes. FTIR spectra analysis was done using Galaxy series FTIR 5000 spectrometer. Scans were taken with 4 cm^{-1} resolution between 200 and $4,000\text{ cm}^{-1}$.

5-2. Morphological Studies

The behavior of prepared membranes is closely related to their

structure, especially the spatial distribution of ionic site and particle distribution [28]. The structures of membranes were examined by scanning electron microscope (SEM, EM-3200, and KYKY). For the membrane scanning by SEM device, the samples were frozen in liquid nitrogen and then cut to keep the original structure. After sputtering with gold, their observation was undertaken using the electron microscope.

5-3. Water Content

The water content was measured as the weight difference between the dried and swollen membranes. The wet membrane was weighed (OHAUS, PioneerTM, Readability: 10^{-4} g , OHAUS Corp.) and then dried in oven until the constant weight was obtained. The following equation [28-31] can be used in water content calculations:

$$\text{Water content\%} = \left(\frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \right) \times 100 \quad (1)$$

Measurements were made three times for each sample and then their average value was reported to minimize the experimental errors.

5-4. Membrane Potential, Transport Number and Permselectivity

The membrane potential is algebraic sum of Donnan and diffusion potentials determined by the partition of ions into the pores as well as the mobilities of ions within the membrane phase compared with the external phase [31-36]. This parameter was evaluated for the equilibrated membrane with unequal concentrations of electrolyte solution (0.1 M/0.01 M) at ambient temperature on either sides of membrane using two-cell glassy apparatus. During the experiment, both sections were stirred vigorously to minimize the effect of boundary layers. The developed potential across the membrane was measured by connecting both compartments and using saturated calomel electrode (through KCl bridges) and digital auto multi-meter (DEC, Model: DEC 330FC, Digital Multimeter, China). The measurement was repeated until a constant value was obtained. The membrane potential (EMeasure) is expressed using Nernst equation [28,31,32-40] as follows:

$$E_{Measure} = (2t_i^m - 1) \left(\frac{RT}{nF} \right) \ln \left(\frac{a_1}{a_2} \right) \quad (2)$$

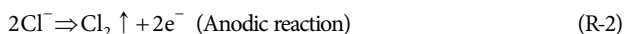
where t_i^m is transport number of counter ions in membrane phase, R is gas constant, T is the temperature, n is the electrovalence of counter-ion, a_1 , a_2 are solutions electrolyte activities in contact membrane surfaces and F is faraday constant. The ionic permselectivity of membranes also is quantitatively expressed based on the migration of counter-ion through the IEMs [35–40]:

$$P_s = \frac{t_i^m - t_0}{1 - t_0} \quad (3)$$

Where, t_0 is the transport number of counter ions in solution [37].

5-5. Ionic Permeability and Flux

The ionic permeability and flux were measured using the test cell (Fig. 2). A 0.1 M solution (NaCl or BaCl₂) was placed on one side of the cell and a 0.01 M solution on its other side. A DC electrical potential (Dazheng, DC power supply, Model: PS-302D) with an optimal constant voltage was applied across the cell with stable platinum electrodes. During the experiment, both sections were recirculated and stirred vigorously to minimize the effect of boundary layers. The cations pass through the membrane to cathodic section. Also, according to anodic and cathodic reactions the produced hydroxide ions remain in cathodic section and increase the pH of this region.



The flux of cations through the membrane is measured directly by considering pH changes (Digital pH-meter, Jenway, Model: 2710) in cathodic section.

The cation flux is also the sum of two terms, one due to the voltage difference, the other due to the diffusion caused by the difference in ion concentrations on each side of the membrane. Thus, the cations flux through the membrane can be written as follows [41]:

$$J^+ = \frac{t_i^m I}{F} + P \frac{C_1 - C_2}{d} \quad (4)$$

where, J^+ is total flux of cations, t_i^m is transport number of counter ions in membrane phase, I is the current, F is faraday constant, P is permeability of cations in membrane, d is membrane thickness and C is the cations concentration in the solutions compartments adjacent to the membrane surface. The cation permeability in membrane phase is calculated from Eq. (4).

5-6. Electrical Resistance

The electrical resistance of equilibrated membrane was measured in NaCl solution with 0.5 M concentration (at 25 °C). Measurement was by an alternating current bridge with 1,470 Hz frequency (Audio signal generator, Electronic Afzar Azma Co. P.J.S). The membrane resistance is calculated using the different resistance between the cell (R_1) and electrolyte solution (R_2) ($R_m = R_1 - R_2$) [31,36]. The areal resistance is expressed as follows:

$$r = (R_m A) \quad (5)$$

where, r is areal resistance and A is the surface area of membrane.

5-7. Electrodialysis for Heavy Metal Ions Removal

The electrodialysis experiment was also on a laboratory scale electrodialysis unit containing a homemade cation exchange membrane and a commercial anion exchange membrane with 19.63 cm² effective area to evaluate the electrodialytic performance of the modified membranes for water treating in Cu, Ni and Pb, removal from waste water. Commercial heterogeneous anion exchange membrane (RALEX[®] AMH-PES), made by MEGA a.s., Czech Republic, was used in this study. The anionic membrane contains fixed quaternary ammonium functional groups. Water content of the commercial membrane was measured as 63% (g absorbed water/g dry membrane). The ion exchange capacity (IEC) was also obtained as 1.85 (meq/g dry membrane). Detailed membrane characteristics can be found elsewhere [42]. The electrolyte solution (Cu (SO₄)₂, Ni (Cl)₂ and Pb (NO₃)₂) of known volume (180 cm³) and concentration (0.01 M) was applied in the treated compartment, while 0.01 M NaCl solution was recirculated in the concentration compartments. The variation in concentration was determined by considering conductivity changes in treated compartment and also pH changes in cathodic region, respectively.

RESULTS AND DISCUSSION

1. FT-IR Spectra Analysis

The FTIR analysis of the unmodified (PVC based membrane) and modified membrane (grafted-PAA composite membrane) is shown in Figs. 3(a) and (b). The FT-IR spectra analysis clearly shows appearing the peak related to C=O, which decisively proves the graft polymerization of PAA. This is not visible for unmodified membrane.

2. Effect of Surface Modification on Membrane Morphology

The SEM study was conducted to evaluate the morphology of virgin and modified PAA-co-PANI/MWCNTs composite mem-

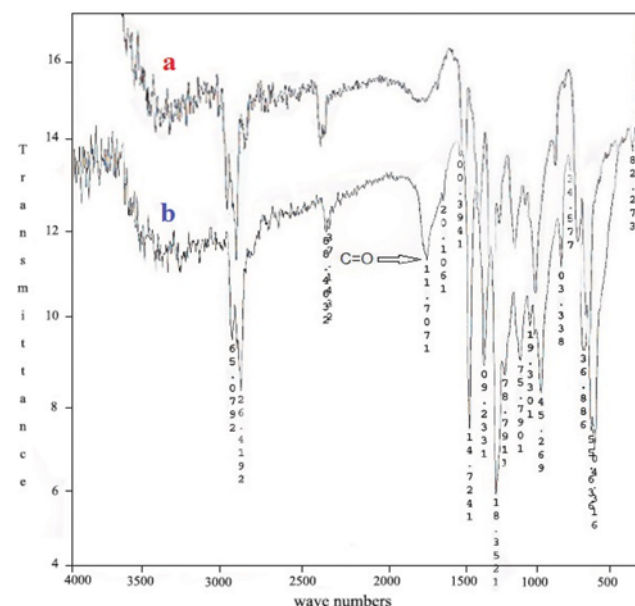
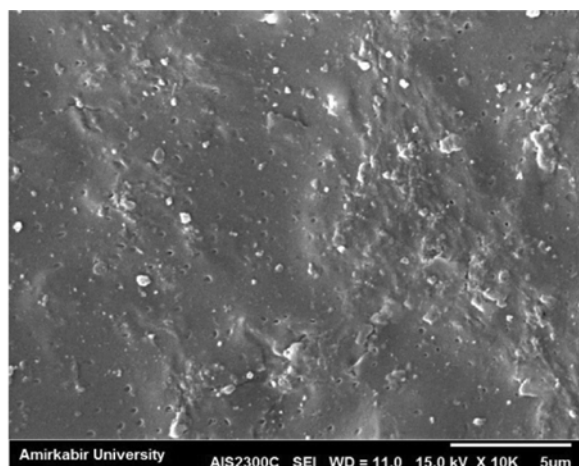
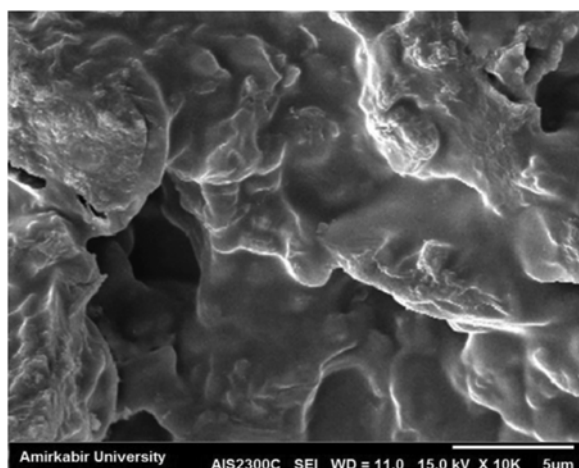


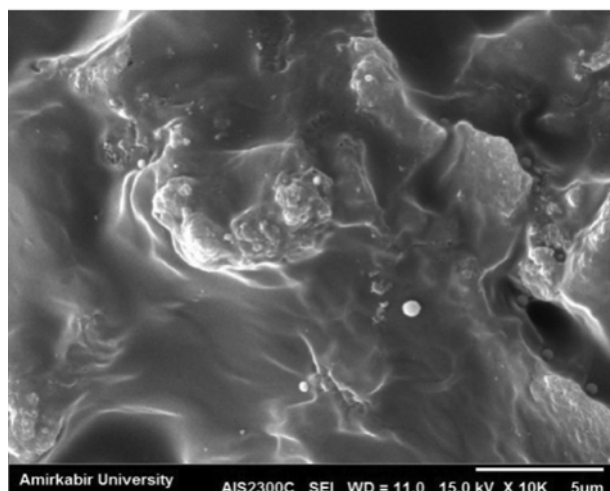
Fig. 3. The FTIR spectrum analysis of prepared membranes: (a) Unmodified membrane, (b) grafted PAA composite membrane.



(a)



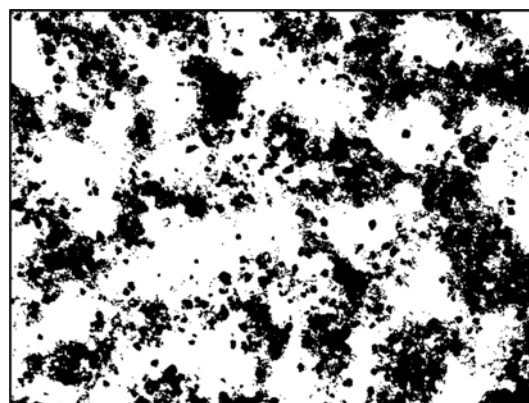
(b)



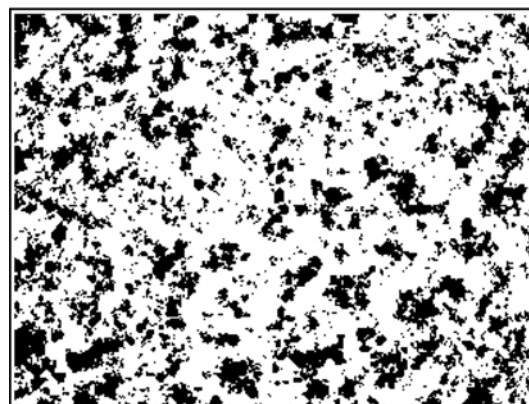
(c)

Fig. 4. The SEM images of prepared membranes; (a) unmodified membrane, (b) PAA grafted membrane, (c) PAA-co-PANI/MWCNT composite membrane.

branes. The SEM surface images of prepared membranes are depicted in Fig. 4. The polymer binder and resin particles are clearly seen in the images. The images illustrate that grafted-PAA-co-PANI/MWCNTs



(a)



(b)

Fig. 5. The effect of sonication on distribution of particles in prepared membranes: (a) Before sonication; (b) after sonication.

NPs filled the cracks, voids and cavities in membrane matrix by simple gel network entanglement. SEM images show the formation of PAA-co-PANI/MWCNTs thin layer on the surface of modified membranes. Also, images show a relatively uniform surface for the prepared membranes. During the polymerization process, carboxylic groups of AA monomers can interact with the surface of nanoparticles and anchor them by covalent attachment. Also, grafting leads to minimizing the particle agglomeration and strengthening the interaction between the nanoparticles and membrane matrix. Monomer molecules can diffuse easily to the surface of the nanoparticles, which leads to higher graft density, better control of molecular weight and polydispersity of the polymer chains [43].

The SOM image of pristine membrane in transmission mode is depicted in Fig. 5. The images also show the effect of ultrasonic method on prepared membranes. As shown, sonication has a significant effect on distribution of resin particles. Particles are also uniformly distributed in the prepared membranes. The excessive homogeneity and uniform distribution of resin particles on the surface and in the bulk of membrane matrix provide superior conducting regions for the membranes and generate easy flow channels for the counter-ions transportation, which improves electrochemical properties. Existence of more conducting region on membrane surface also can strengthen the intensity of uniform electrical field around the membrane and decrease the concentration polarization

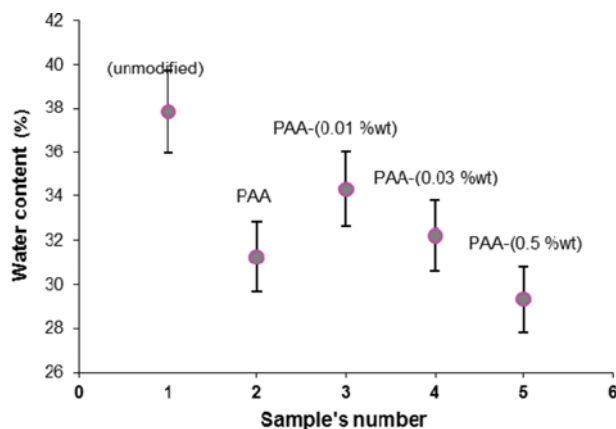


Fig. 6. The effect of PAA-co-PANI/MWCNT grafting on water content of prepared cation exchange membranes.

phenomenon [2-5,44,45]. Sonication of solid particles increases the viscosity of casting solution by reducing aggregation and sedimentation. This increases the casting solution viscosity and reduces the evaporation rate of casting solvent, which improves the polymer chain relaxation as well as its conformation with particle surfaces. The conformation increases the polymer-particle interactions and promotes the compatibility of particles and binder. This compatibility reduces the amount of cracks and fissures between binder and resin particles in the matrix of membrane and improves the membrane selectivity [2,3,6,44].

3. Water Content

Obtained results (Fig. 6) revealed that the water content of prepared membrane was decreased by PAA grafting on membrane surface. This might be due to voids and cavities filling by PAA, which can be prevailed upon the positive effect of PAA hydrophilic characteristic [43,44] and restrict the water molecules accommodation in membrane matrix.

The water content was increased again by using PANI/MWCNTs composite nanoparticles in modifier solution up to 0.01%wt. This may be due to increase in PAA-co-PANI/MWCNTs layer porosity by NPs' using which enhances the amount of water embedding. Moreover, utilizing of PANI/MWCNTs NPs increases the yield of polymerization by providing more surface area for AA monomer. This introduces more amount of hydrophilic PAA into membrane and improves the hydrophilicity. The inner diameter of nano-tubes is also large enough to accommodate the water molecules.

The membrane water content was decreased again by more increase in NPs' concentration in modifier solution. This is due to increase in membrane structure tightness and rigidity by more PANI/MWCNTs content ratio, which causes to lower membrane swelling and so water absorption. Moreover, diffusion of modifier solution into the membrane matrix occupies the free spaces in membrane matrix and so reduces the amount of membrane water content.

A suitable amount of membrane water content can have better control on the pathways of ion traffic and improve the membrane selectivity. Generally, high water content can provide more and wider transfer channels for co- and counter-ion transport and decrease the ionic selectivity and lead to a loose structure for the membranes but this is not always true and depends on the membrane struc-

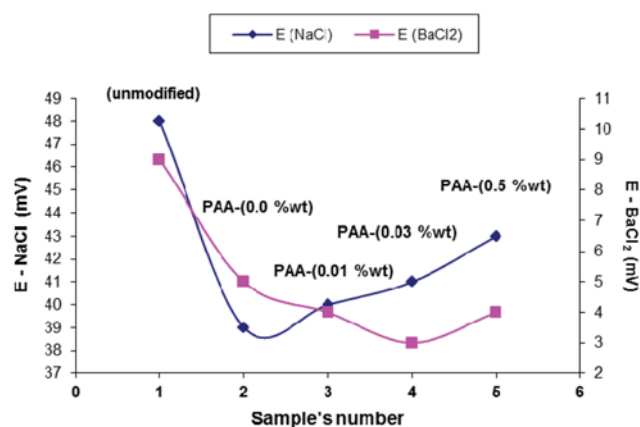


Fig. 7. The effect of graft polymerization on membrane potential in sodium chloride and barium dichloride ionic solutions.

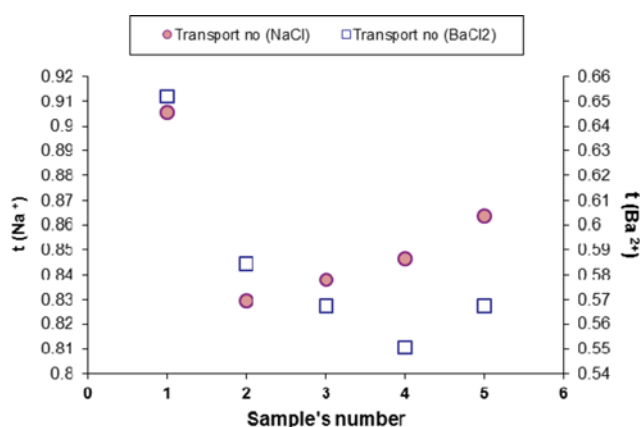


Fig. 8. The transport number of prepared membranes in sodium chloride and barium chloride ionic solutions.

ture and its properties. Measurements were made three times for each sample and then their average value was reported in order to minimize the experimental errors.

4. Membrane Potential, Permselectivity and Transport Number 4-1. Characterization in Monovalent Ionic Solution (NaCl)

Obtained results (Figs. 7-9) revealed that the graft polymerization on membrane surface caused a decline in membrane potential, permselectivity and transport number in sodium chloride ionic solution. It might be due to the isolation of resin particles by the grafted PAA which affects their performance. The pristine membrane contains sulfonate functional groups only while in modified membranes carboxylic groups are introduced to the surface and pores of membrane. Dissociation of different functional groups has high impact on the charged nature of membrane matrix which is dominant on ionic traffic. The sulfonate functional groups have much better dissociation behavior compared to carboxylic groups in the same conditions [33]. As seen in SEM images the polymerized PAA covers the resin particles and occupies the spaces around them, which restricts the accessibility of resin particle sulfonate groups by their surrounding in modified membranes. This means carboxylic group domination on membrane performance which is weaker than sulfonate groups. The membrane potential, transport

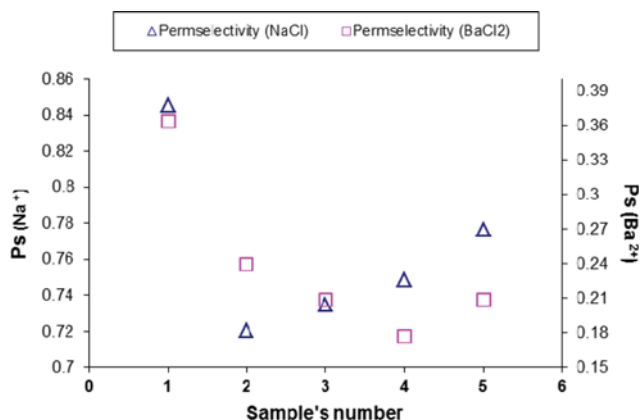


Fig. 9. Comparison between the permselectivity of prepared membranes (unmodified and modified membranes) in mono and bivalent ionic solutions.

number and selectivity were improved again by using of PANI/MWCNTs NPs in modifier solution. Utilizing of nanoparticles in modifier solution provides more appropriate site for PAA polymerization instead of PAA formation on resin particle surface and so prevents the sulfonate groups' isolation. This makes better the ionic pathways and generates suitable flow channels for easy passage of the counter ions. This happening declares the synergy phenomenon clearly by simultaneous use of carboxylic and sulfonate functional groups. Moreover, the channels in membrane matrix are occupied by PAA-co-PANI/MWCNTs and so they are narrowed by them as space limiting factors. This causes a strengthening of the ionic sites domination on ions traffic and makes difficult the co-ions percolation through the membrane.

4-2. Characterization in Bivalent Ionic Solution (BaCl₂)

The obtained results (Figs. 7-9) also showed lower membrane potential, transport number and selectivity for the modified membranes compared to pristine ones in bivalent ionic solution. This is attributed to weak dissociation of carboxylic group in modified membranes compared to sulfonate type. Also, the membranes exhibited lower potential, selectivity and transport number for bivalent ions in comparison with monovalent ones. The lower electrochemical properties of membranes for the bi-valent ions compared to monovalent type can be explained by the stronger bonds of bi valent cations with ion exchange functional groups, which poisons the membranes and decreases the membrane transport number and selectivity. In fact, bivalent cations have stronger electrostatic attraction with the oppositely fixed charge sites, and therefore they prevent functional groups dissociation. Furthermore, the larger radius of barium ions and their hydrated size in comparison with sodium ions makes lower membrane potential, transport number and permselectivity for the bivalent cation [1-3,28].

5. Ionic Permeability and Flux

During the experiment, ions pass through the membrane and reach the concentration section. Results (Figs. 10, 11) revealed that the ionic permeability and flux for both monovalent (sodium ions) and bivalent ions (barium ions) were increased initially by graft polymerization of PAA on membrane surface. Introducing carboxylic groups into membrane matrix during modification process

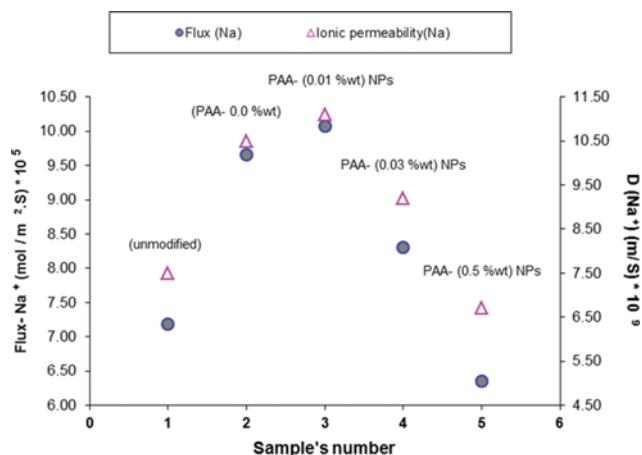


Fig. 10. Comparison between the ionic flux and permeability of prepared membranes in sodium chloride ionic solution.

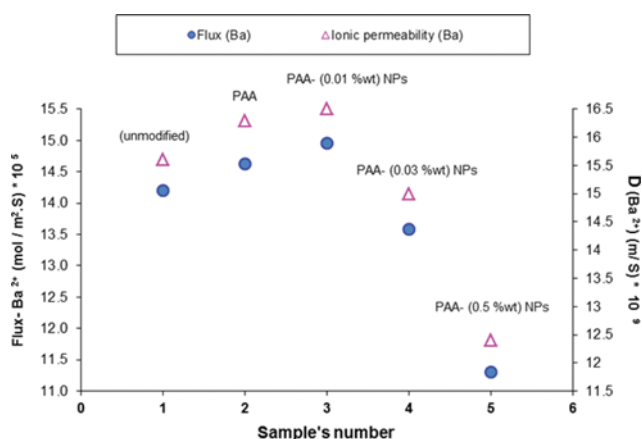


Fig. 11. Ionic flux and permeability for the prepared membranes in barium chloride ionic solution.

increases the ionic permeability and flux. The ionic permeability and flux were also improved by utilizing of PANI/MWCNT NPs up to 0.01%wt in modifier solution. This is attributed to adsorption characteristic of PANI/MWCNT nanoparticle which enhances the ion interactions with membrane surface and so strengthens the intensity of electrical field around the membrane and improves the counter ion transport.

Ionic permeability and flux showed decreasing trend again by more increase of nanoparticle concentration in modifier solution. This is attributed to formation of a tight and rigid layer of PAA-co-PANI/MWCNT on membrane surface at high nanoparticle content ratio, which makes difficult the ion transport and reduces the permeability and flux. Also, lower amount of water content for the prepared membranes declines the flux.

6. Areal Electrical Resistance

The electrical resistance has practical implications due to its relation with energy consumption in the process. The electrical resistance of pristine membrane (M_1) and superior membranes (M_2 , M_3) was measured in 0.5 M NaCl solution at ambient temperature. The membrane electrical resistance was measured <25, <13 and

$<22 \text{ ohm}\cdot\text{cm}^2$ for the membrane, respectively. The grafted-PAA composite membranes showed lower electrical resistance compared to unmodified ones. In general, less selective membranes have lower electrical resistances, but this is not always true and depends on the membrane structure and its properties [42]. The low electrical resistance for the grafted-PAA membrane is also because of formation of suitable ionic pathways in membrane matrix by simultaneous use of carboxylic and sulfonate functional groups, which in turn enhances ion transport and so lowers the areal electrical resistance. The electrical resistance of prepared membranes was increased again by utilizing of PANI/MWCNT NPs in modifier solution. This may be due to lower amount of water content and higher selectivity for PAA-co-PANI/MWCNTs composite membrane, which increases the membrane electrical resistance. A typical comparison between the areal electrical resistance of prepared membranes in this research and some commercial membranes [42,47,48] is given in Table 2.

7. Electrodialysis for Cu, Ni and Pb Ions Removal

Electrodialysis experiment was carried out in a laboratory scale unit to evaluate the electrodialysis performance of modified mem-

branes for Cu, Ni and Pb ions removal from waste water. The ionic flux for the prepared membranes (M_1 : unmodified membrane and M_2 , M_3 : modified membrane) were studied. Results (Fig. 12) showed that dialytic rate was increased sharply for heavy metal ion removal by AA polymerization on membrane surface which is assigned to less selective for grafted-PAA membrane. As seen in the figure, utilizing of PANI/MWCNTs composite NPs in modifier solution caused a decline in ionic flux for heavy metal ions, which is due to formation of narrow ionic pathways in modified membranes. The used nanoparticles limit the free spaces and so restrict the ion traf-

Table 2. A typical comparison between the areal electrical resistance of prepared membranes in this research and some commercial membranes [42,47,48]

Membrane	Areal electrical resistance ($\Omega\cdot\text{cm}^2$)
Pristine membrane (M_1)	<25
Grafted-PAA membrane (M_2)	<13
Grafted-PAA-co-PANI/MWCNTs membrane (M_3)	<22
Ionics Inc., USA, CR61-CMP	>11
Ionics Inc., USA AR112-B	20-28
MEGA a.s., Czech Republic, Ralex CMH-5E	<12
RAI Research Corp., USA, R-5010-H	8-12

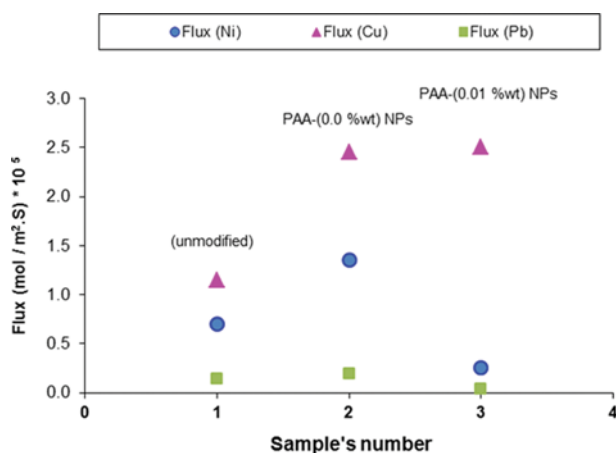


Fig. 12. The ionic flux of prepared membranes (M_1): unmodified membrane, (M_2): grafted-PAA membrane and (M_3): grafted-PAA-co-0.01%wt PANI/MWCNTs) for Cu, Ni and Pb ions removal (dialytic rate) in water treating electrodialysis experiment process.

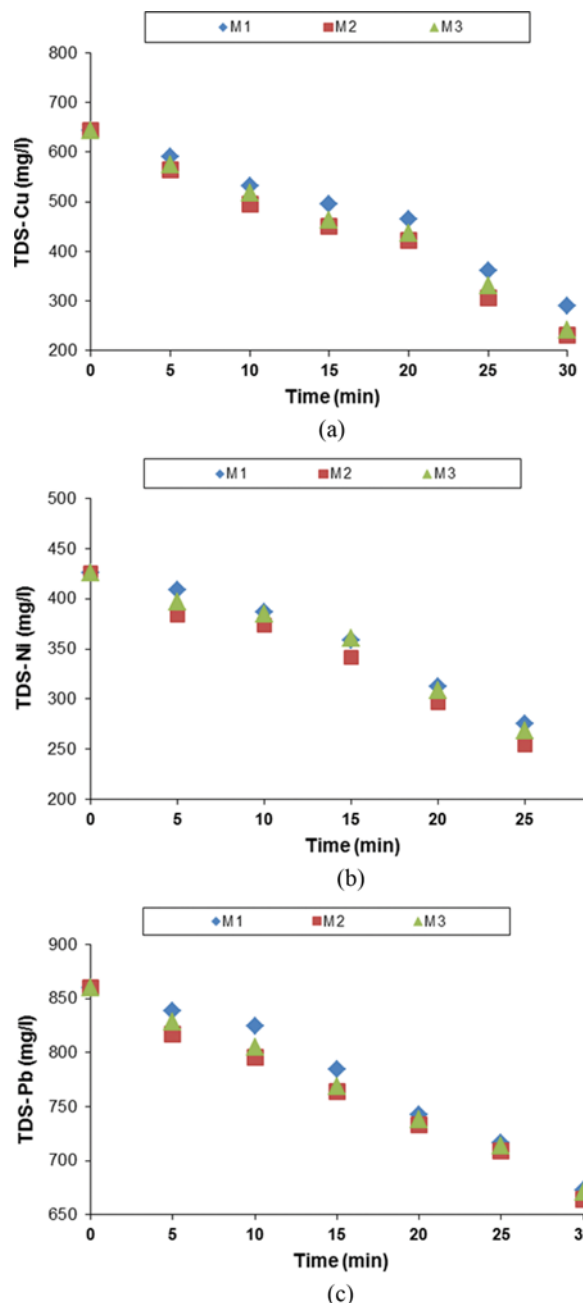


Fig. 13. The TDS variations with time in treated (*diluted*) region during the electrodialysis experiment for Cu, Ni and Pb ions removal from waste water.

fic. Moreover, strong affinity of heavy metals on active sites of PANI/MWCNT nanoparticles does not allow cations to release from membrane surface and reach to the concentrated region [46,49]. Results clearly showed that ionic flux for Pb ions is less than Ni and Cu. This different behavior can be explained with respect to the radius of lead ions and their hydrated size in comparison with copper and nickel ions. The TDS variations in treated region during the experiment are depicted in Fig. 13. As shown, total dissolved solid decreased over time in the treated compartment during the electrodialysis process, which is an indicator of ion passage through the membrane.

CONCLUSION

The FT-IR spectra analysis clearly proves the polymerization of PAA on membrane surface. SOM images show uniform resin particles distributed for the prepared membranes. Also, SEM images illustrate that the grafted PAA-co-PANI/MWCNT NPs filled the cracks, voids and cavities in membrane matrix. Images also show a relatively uniform surface for the homemade membranes. The modified grafted-PAA and grafted-PAA-co-PANI/MWCNTs membranes show lower amount of water content compared to pristine ones. Membrane potential, transport number and permselectivity all declined initially by PAA graft polymerization and then began to increase by increase of NPs concentration in modifier solution. The sodium and barium flux and permeability were improved sharply by PAA graft polymerization on membrane surface. The sodium and barium flux were enhanced again by utilizing of PANI/MWCNTs nanoparticles concentration up to 0.01%wt in modifier solution and then showed decreasing trend by more NPs content ratio. Membrane areal electrical resistance was also decreased by introducing graft polymerization on membrane surface. The electrodialysis experiment results in laboratory scale show higher dialytic rate in heavy metals removal for grafted-PAA and grafted-PAA-co-PANI/MWCNTs modified membrane compared to pristine one.

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