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Thin Film Heterogeneous Ion Exchange Membranes Prepared by Interfacial Polymerization of PAA-co-Iron-Nickel Oxide Nanoparticles on Polyvinylchloride Based Substrate

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A B S T R A C T

In this research, thin film heterogeneous cation exchange membrane was prepared by interfacial polymerization of *polyacrylic acid-co-iron nickel oxide nanoparticles* on PVC based substrate. Spectra analysis confirmed graft polymerization conclusively. The SEM images showed that polymerized layer covers the membranes by simple gel network entanglement. Results exhibited that membrane water content was decreased by graft polymerization of PAA/Fe$_2$NiO$_4$ nanoparticles on membrane surface. Membrane potential, transport number and permselectivity all were declined initially by PAA interfacial polymerization in NaCl ionic solution and then began to increase. The membrane transport number and permselectivity showed decreasing trend in bivalent (BaCl$_2$) ionic solution. The sodium flux and permeability were improved sharply by PAA graft polymerization on membrane surface and then decreased slightly by graft polymerization of PAA/Fe$_2$NiO$_4$ nanoparticles. Different behavior was found for barium flux and permeability. Membrane areal electrical resistance was also decreased by introducing interfacial graft polymerization on membrane surface.

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1. INTRODUCTION

Nowadays, global shortage of freshwater is a serious problem as the result of population growth and industrial activities [1, 2]. Membrane process is a promising, simple and energy-efficient technology for waste water treatment, ultra pure water production, food and pharmacy and biotechnological processes [3-12].

Among a wide range of commercial membranes, ion exchange membranes (IEMs) are considered as the advanced separation membranes which are applicable in fuel cells, sensors, chloro-alkali and electrodialysis [11, 12]. Electrodialysis is an electrically driven process based on ion exchange membranes for desalting brackish water, reconcentrating brine from seawater and etc. Therefore, the development of ion exchange membranes with acceptable physico-chemical

properties such as ionic flux, permselectivity and areal electrical resistance besides affordability is the aim of most researches [5, 11-13]. To achieve the desired membrane, IEMs' surface and structure are modified through different modification techniques. Some of them are variation of functional groups, utilization of different polymeric matrices, polymer blending, using various nanoparticles as additives, incorporation of highly soluble polymers and more uniform distribution of functional groups [5, 10-17]. Surface modification by grafting hydrophilic polymers on membrane surface and using nanoparticles as additive has been a key approach in recent years. Increasing membrane surface hydrophilicity and adsorptive characteristics through blending, coating and surface grafting could improve electrochemical properties of membranes [6, 7, 13, 18-22]. Currently, no researches have considered fabrication of grafted PAA/Fe$_2$NiO$_4$ composite ion exchange membrane and literature is silent on characteristics and functionality of cation exchange

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membranes modified with (PAA/ Fe₂NiO₄). In this research, surface modification of polyvinyl chloride based homemade heterogeneous cation exchange membrane was carried out to achieve efficient electrochemical properties applicable in electrodialysis. For the purpose, heterogeneous cation exchange membranes based on PVC were prepared by solution casting techniques using cation exchange resins as functional groups. The polymerization of polyacrylic acid (PAA) and Iron–nickel oxide (Fe₂NiO₄) was also utilized as modifier layer on membrane surface simultaneously by mixing Fe₂NiO₄ with hydrophilic acrylic acid monomer and grafting technique. By this method, polymerization occurs in both internal and external surfaces of membrane, which leads to ionic site formation within the membrane pores and surface [23]. Utilization of inorganic nano-materials into polymeric materials has been examined in many researches to enhance the physico/chemical characteristics and separation efficiency based on the synergism between the organic- inorganic components [24-26]. The effects of PAA and PAA/ Fe₂NiO₄ nanoparticles on physico-chemical properties of homemade heterogeneous cation exchange membranes were also investigated. During the experiments, sodium chloride (NaCl) and barium chloride (BaCl₂) were employed as monovalent and bivalent ionic solutions for the membranes characterization respectively.

The results are valuable for electro-membrane processes especially in electro-dialysis process for water recovery and waste water treatment.

2. EXPERIMENTAL STEPS

2. 1. Materials   Polyvinylchloride (PVC, grade S-7054, high porosity, bulk density (DIN-53466): 490 g/l, viscosity number (DIN-53726): 105 cm³/g) as binder. Tetrahydrofuran (THF) as solvent and cation exchange resin (Ion exchanger Amberlyst1 15, strongly acidic cation exchanger, H+ form more than 1.7 meq/g dry, spec. density 0.6 g/cm3, particle size (0.355–1.18 mm) < 90%) by Merck Inc., Germany, were also used in membrane fabrication. Potassium persulfate (KPS, initiator), acrylic acid (AA, monomer) and ethylene glycol (EG, cross-linker) were obtained from Merck. Iron–nickel oxide nanoparticle (Fe₂NiO₄, nano-powder, 50 nm particle size, ≥98% trace metals basis) by Aldrich as inorganic additive. All other chemicals were supplied by Merck Inc. Distilled water was used throughout the experiment.

2. 2. Preparation of Homemade Hetrogeneous Cation Exchange Membrane   Polyvinylchloride (PVC) based heterogeneous cation exchange membranes were prepared by solution casting technique using cation exchange resin powder as functional

groups agent and tetrahydrofuran as solvent. In order to undertake the membranes preparation, resin particles were dried in oven (SANEE. V. S. Co.) at 30 °C for 48h then pulverized into fine particles in a ball mill (Pulverisette 5, Fritisch Co.) and sieved to the desired mesh size. The ion exchange resin with desired particles size (−300 to +400 mesh) was used in membranes fabrication. The preparation proceeded by dissolving the polymers binder (PVC) into solvent (THF: PVC, (20:1) (v/w)) in a glass reactor equipped with a mechanical stirrer (Model: VelpSientifica Multi 6 stirrer) for more than 4h. This was followed by dispersing a specific quantity of grinded resin particle (Resin: Polymer binder, (1:1) (w/w)) as functional groups agents 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 30 min using an ultrasonic instrument. The excessive homogeneity and uniform distribution of resin particles, i.e. functional groups on the surface and in the bulk of membrane matrix provide superior ionic conducting regions in membrane to improve the membranes electrochemical properties. After the sonication stage, the mixing process was repeated for another 10 min using the mechanical stirrer. The mixture was then casted onto a clean and dry glass plate at 25 °C. The membranes were dried at ambient temperature until solvent evaporated and solidification was done totally. Then polymeric films immersed in distilled water. As the final stage, the membranes were pretreated by immersing in NaCl solution. The membrane thickness was measured 70 μm by a digital caliper device (Electronic outside Micrometer, IP54 model OLR).

2. 3. Surface Modification of Prepared Membranes via AA Polymerization   PAA and PAA/ Fe₂NiO₄ composite membrane was produced by polymerization method and grafting technique. Before modification, the homemade membranes were dipped in distilled water for 4 h to remove any pollutant. Then, homemade 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 to AA, 1:6.5 molar ratio) [23] and iron nickel oxide nanoparticles as additive (Fe₂NiO₄: 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. It is worth to mention that the modifier solution was mixed vigorously at room temperature and sonicated to obtain homogenously dispersed solution during the modifier preparation. After that, the membrane was heated at 90 °C for 4 h in oven (SANEE V. S. Co.). Finally, the membrane was washed sufficiently with

distilled water to remove the excess monomer and surfactant and then kept in water.

2. 4. Test Cell

The electrochemical measurements for the prepared membranes were carried out using the test cell, as reported earlier [24]. The cell consists of two cylindrical compartments (vessel, each 180 cm^3) made of Pyrex glass, which are separated by 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. In order to minimize the effect of boundary layer during experiments and to establish the concentration polarization on the vicinity of membrane's surface, both sections were stirred vigorously by magnetic stirrers (Model: VelpSientifica Multi 6 stirrer).

2. 5. Membrane Characterization

2. 5. 1. FTIR Analysis

Spectra measurements were carried out to prove the formation of PAA on membrane surface. FTIR spectra analysis was done using Galaxy series FTIR 5000 spectrometer. Scans were taken with 4 cm^{-1} resolutions between 200 and 4000 cm^{-1}.

2. 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 [27]. The structures of membranes were examined by scanning electron microscope (SEM, EM-3200, and KYKY). For the membranes scanning by SEM device, the samples were frozen in liquid nitrogen and then were cut to keep the original structure. After sputtering with gold, their observation was undertaken using the electron microscope.

2. 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. Following equation [27-30] can be used in water content calculations:

$$Water\ content\% = (\frac{W_{wet} - W_{dry}}{W_{dry}}) \times 100 \qquad (1)$$

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

2. 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 [10, 30-34]. This parameter was evaluated for the equilibrated membrane with unequal concentrations of electrolyte solution ((NaCl (0.1 M/ 0.01 M) or BaCl$_2$ (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 [27, 30, 34-38] as follows:
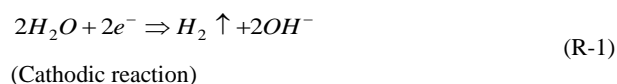
$$E_{Measure} = (2t_i^m - 1)(\frac{RT}{nF})\ ln(\frac{a_1}{a_2}) \qquad (2)$$

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 [10, 34-38]:
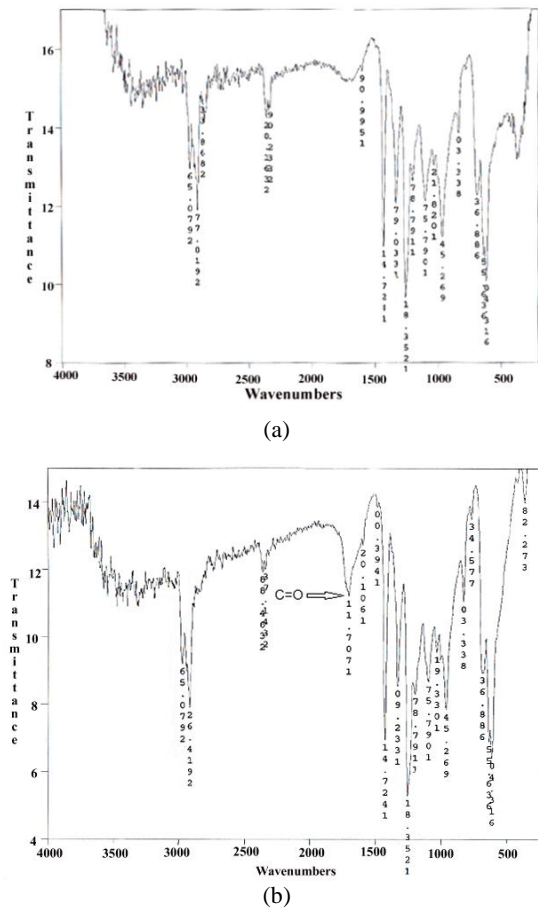
$$P_S = \frac{t_i^m - t_0}{1 - t_0} \qquad (3)$$

where, t_0 is the transport number of counter ions in solution [35].

2. 5. 5. Ionic Permeability and Flux of Ions

Ionic permeability and flux measurements were carried out using the test cell. A 0.1 M (NaCl or BaCl$_2$) solution 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. Cations pass through the membrane to cathodic section. According to anodic and cathodic reactions the produced hydroxide ions increase the pH of cathodic section.

$$2H_2O + 2e^- \Rightarrow H_2 \uparrow + 2OH^- \qquad (R-1)$$

(Cathodic reaction)

$$2Cl^- \Rightarrow Cl_2 \uparrow + 2e^- \qquad (R-2)$$

(Anodic reaction)

According to the first Fick's law, the flux of ions through the membrane can be expressed as follows [10-12, 27]:

(a)

(b)

Figure 1. The FTIR spectrum analysis of homemade membranes: (a) unmodified membrane, (b) modified membrane

$$N = P\frac{C_1 - C_2}{d} \tag{4}$$

where, P is coefficient diffusion of ions, d is membrane thickness, N is ionic flux and C is the cation concentration in the compartments.

$$N = -\frac{V}{A} \times \frac{dC_1}{dt} = P\frac{C_1 - C_2}{d} \tag{5}$$

$$C_1^0 = 0.1M , C_2^0 = 0.01M ,$$
$$C_1 + C_2 = C_1^0 + C_2^0 = 0.11M \tag{6}$$

where, A is the membrane surface area. Integrating Equation (5) was as follows:

$$\ln\frac{(C_1^0 + C_2^0 - 2C_2)}{(C_1^0 - C_2^0)} = -\frac{2PAt}{Vd} \tag{7}$$

The diffusion coefficient and flux of cations in membrane phase are calculated from Equation (7) considering pH changes measurements (Digital pH-meter, Jenway, Model: 2710) in cathodic section. Also,

these parameters can be determined by variations in conductivity in cathodic compartment as described earlier [10-12, 27].

2. 5. 6. Electerical Resistance   The electrical resistance of equilibrated membrane was measured in NaCl solution with 0.5 M concentration (at 25 °C). Measurement was carried out by an alternating current bridge with 1470 Hz frequency. The membrane resistance is calculated using the different resistance between the cell (R_1) and electrolyte solution (R_2) ($R_m=R_1-R_2$) [10, 30] as follows:

$$r = (R_m A) \tag{8}$$

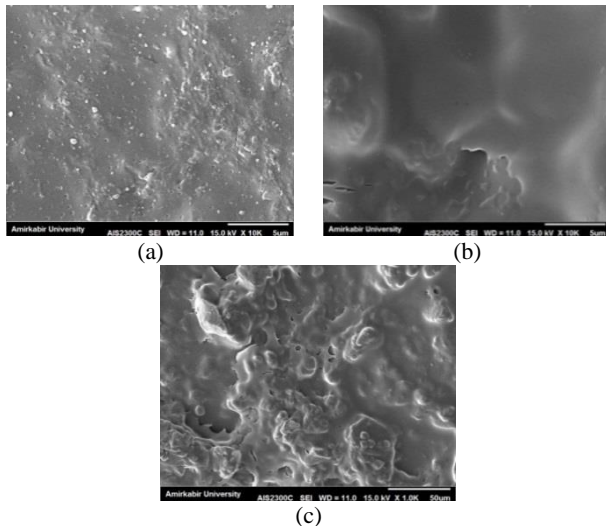where, r is areal resistance and A is the surface area of membrane.

3. RESULTS AND DISCUSSION

3. 1. FT-IR Spectra Analysis   The FTIR analysis of the unmodified (PVC membrane) and modified membrane (grafted-PAA on membrane surface) is shown in Figures 1 (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 peak is not visible for unmodified membrane.
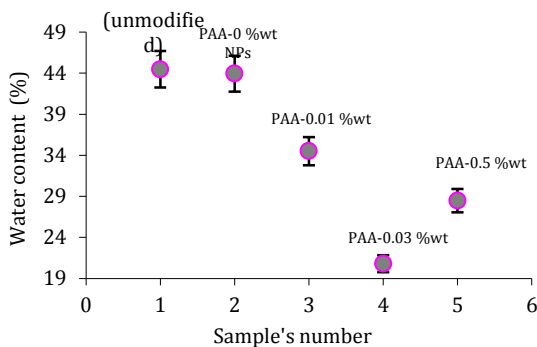
3. 2. Effet of Modification on Morphology of Membranes   The SEM studies have been carried out in order to evaluate the morphology of virgin and modified PAA/ Fe_2NiO_4 composite membranes. The SEM images are presented in Figures 2 (a), (b) and (c). The polymer binder and resin particles are clearly seen in the images. Figure2 shows that particles are uniformly distributed in prepared membranes. It reveals that sonication has a significant effect on distribution of resin particles in membranes matrix [12, 13, 24]. The excessive homogeneity and uniform distribution of resin particles on the surface and in the bulk of membrane matrix provide superior conducting regions in membrane and lead to membranes electrochemical properties improvement. Moreover, increase in conducting regions can strengthen the intensity of uniform electrical field around the membrane and decrease the concentration polarization phenomenon [39]. Furthermore, the sonication of solid particles increases the viscosity of casting solution by reducing aggregation and sedimentation. The increase in casting solution viscosity reduces the evaporation rate of casting solvent and improves the polymer chains relaxation as well as its conformation with particles surfaces. The conformation increases the polymer-particle interactions and promotes the compatibility of particles and binder [5, 12, 24]. This compatibility

reduces the amount of cracks and fissures between binder and resin particles in the matrix of membrane and improves the membrane selectivity. Also Figure 2 illustrates that the grafted-PAA/ Fe_2NiO_4 filled the cracks, voids and cavities in membrane by simple gel network entanglement. Figure EQ2 shows the formation of grafted-PAA/ Fe_2NiO_4 layer on the surface of modified PVC based membranes. Images show a relatively uniform surface for the membranes. The carboxylic groups of acrylic acid monomer can interact with the surface of nanoparticles and anchor to them by covalent attachment. Also, the grafting leads to minimizing agglomeration and strengthening the interaction between the nano particles and polymer matrix and allows monomer molecules to diffuse easily to the surface of the particles, enabling higher graft density, better control of molecular weight and polydispersity of the polymer chains [23].

(a)   (b)   (c)

Figure 2.The SEM images of prepared membranes; (a) unmodified membrane, (b) modified membrane (grafted-PAA), (c) modified (grafted-PAA/0.5% wt Fe_2NiO_4) composite membrane.

Figure 3. The effect of grafted-PAA/ Fe_2NiO_4 on water content of prepared cation exchange membranes.

3. 3. Water Content

Obtained results (Figure 3) revealed that the water content of prepared membrane decreased slightly by PAA grafting on membrane surface. This might be due to the voids and cavities filling by PAA which can be prevailed upon the positive effect of PAA hydrophilic characteristic [23, 24] and restricts the water molecules accommodation so declines the water content. Membrane water content continued its declining trend by adding then increasing nanoparticles percentage in modifier solution of membrane surface. This could be as the result of matrix rigidity by more nanoparticle content which causes to lower membrane swelling and 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. The suitable amount of membrane water content can have better control on the pathways of ions traffic and improve the membrane selectivity. Generally, high water content can provide more and wider transfer channels for co- and counter-ions transportation 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 structure and its properties. It is worth mentioning that measurements were carried out three times to minimize the experimental errors.

3. 4. Membrane Potential, Transport Number and Permselectivity

3. 4. 1. Characterization in Monovalent Ionic Solution (NaCl)

Experimental results show that the grafted-PAA modified membranes have lower membrane potential, transport number and selectivity (Figure 4-6) compared to unmodified membrane in sodium chloride ionic solution. This can be explained with respect to introducing carboxylic groups throughout the membrane matrix (surface and pores) during polymerization process. The pristine membrane contains only sulfonate functional groups while in modified membranes carboxylic groups are introduced to the surface and pores of membrane. Types and dissociation of different functional groups has high impact on the charged nature of membrane matrix and its characteristics. The sulfonate functional groups have much better dissociation behavior compared to carboxylic groups in the same conditions [27]. As seen in SEM images (Figure 2), the polymerized PAA covers the resin particles and also occupies the spaces around them so reduces the accessibility of sulfonate groups by their surrounding in modified membranes. This means carboxylic groups' domination on membrane performance occurs, which is weaker than sulfonate domination. Adding nano particles to polymeric solution resulted in improvement of membrane

potential, transport number and selectivity of modified membranes.

The increase of Fe_2NiO_4 particles concentration provides more appropriate site for PAA polymerization instead of PAA formation on resin particle surface and to prevent the sulfonate groups' isolation. This happening declares the synergy phenomenon clearly by simultaneous using of carboxylic and sulfonate functional groups. Moreover narrow ionic pathways in membrane surface are formed by adding nano particles as space limiting factor. Actually voids and cavities are occupied by nano particles and more strict channels are produced on membrane surface. Therefore, co-ions are less likely to pass and membrane potential, transport number and permselectivity will increase.
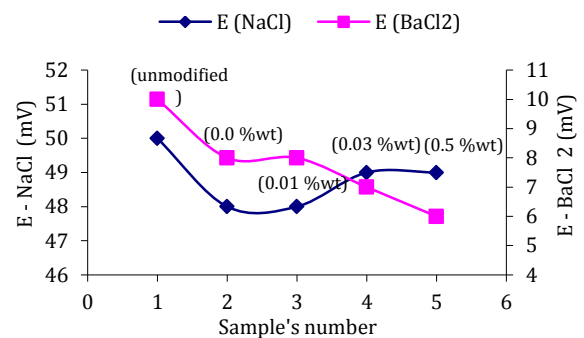
3. 4. 2. Characterization in Bivalent Ionic Solution (BaCl₂)
The obtained results (Figures 4-6) showed lower membrane potential, transport number and selectivity for the modified membranes compared to unmodified ones in bivalent ionic solution. This could be attributed to weak dissociation of carboxylic group in modified membranes compared to sulfonate groups. Also, the membranes exhibited lower potential, selectivity and transport number for bivalent ions in comparison with monovalent ones. These different behaviors can be explained with respect to the stronger bonds of bivalent ions with ion exchange functional groups [10-12] which poisons the membranes and decreases the membrane transport number and selectivity. In fact, bivalent ions have stronger electrostatic attraction by the oppositely fixed charge sites; therefore, they prevent functional group dissociation. Furthermore, the larger radius of barium ions and their hydrated size in comparison with chlorine ions make lower membrane potential, transport number and permselectivity for the bivalent ions.
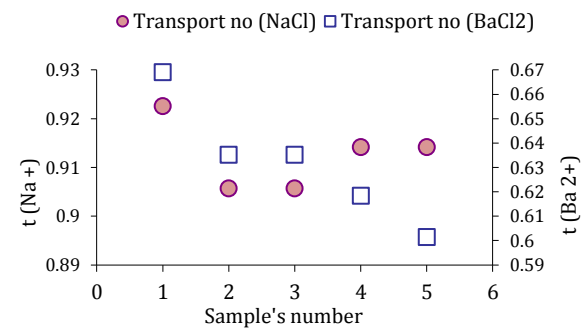
3. 5. Ionic Permeability and Flux

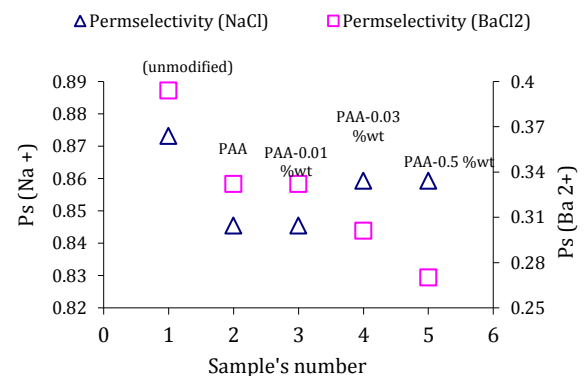### 3. 5. 1. Characterization in Monovalent Ionic Solution (NaCl)
During the experiment, ions pass through the membrane and reach the concentration section. Results (Figure 7) revealed that the ionic permeability and flux of monovalent ions (sodium ions) initially increased by grafting PAA on membrane surface. This is assigned to the dissociation of functional groups in membrane matrix. Introducing carboxylic groups to the membrane matrix during modification process and isolation of sulfonate groups by their surrounding in modified membranes makes a weaker domination of functional groups on ionic transfer and increase the ionic flux. Ionic permeability and flux showed a slight decreasing trend by adding Fe_2NiO_4 to polymer solution. This is attributed to formation of tight and rigid layer of PAA/ Fe_2NiO_4 on membrane surface at high nanoparticle concentration.

Figure 4. The effect of grafted-PAA/ Fe_2NiO_4 on membrane potential of prepared cation exchange membrane in sodium chloride and barium dichloride ionic solutions

Figure 5. The transport number of prepared membranes (modified by grafted-PAA/ Fe_2NiO_4)in sodium chloride and barium dichloride ionic solutions

Figure 6. Permselectivity of prepared cation exchange membranes in mono and bivalent ionic solutions

This makes the ions transportation difficult and reduces the permeability and flux.
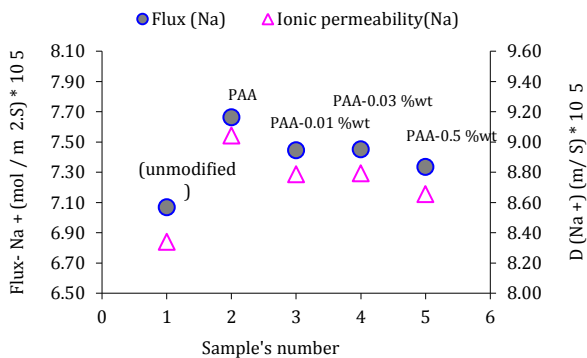
3. 5. 2. Characterization in Monovalent Ionic Solution (BaCl₂)
Results (Figure 8) show that PAA grafting on membrane surface caused the increase in barium permeability and flux in prepared membranes. It can be explained with respect to weaker dissociation of
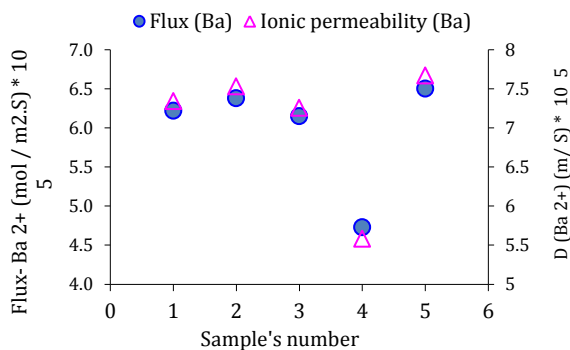
carboxylic groups than sulfonate groups. Barium permeability and flux then decreased obviously. This is due to large radius of barium ions which hinders the bariums' traffic through the membranes and also lower amount of water content.
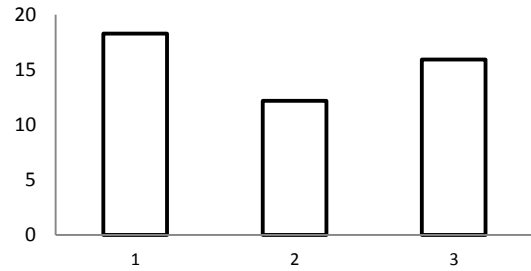
3. 6. Areal Electerical Resistance

To minimize the experimental errors, the electrical resistance of three samples was examined. The electrical resistance has practical implications due to its relation with energy consumption in the process. The grafted-PAA/Fe_2NiO_4 composite membranes showed lower electrical resistance compared to unmodified ones (Figure 9). In general, less selective membranes have lower electrical resistances but this is not always true and depends on the membrane structure and its properties. The low electrical resistance for the grafted-PAA and grafted-PAA/ Fe_2NiO_4 modified membrane is also because of formation of suitable ionic pathways and flow channels in membrane matrix by simultaneous using of carboxylic and sulfonate functional groups which in turn enhances the ions transportation and so declines the areal electrical resistance.

Figure 7. Comparison between the ionic flux and permeability of prepared (virgin and modified) membranes in sodium chloride ionic solution

Figure 8. Ionic flux and permeability (bivalent ions) for the prepared (unmodified and modified) membranes

Figure 9. The effect of grafted-PAA/Fe_2NiO_4 on the areal electrical resistance (ohm.cm^2)of prepared membranes

4. CONCLUSION

The FT-IR spectra analysis obviously proves the graft polymerization of PAA on membrane surface. SEM images show that particles are uniformly distributed in prepared membranes. Images illustrates that the grafted-PAA/ Fe_2NiO_4 filled the cracks, voids and cavities in membrane by simple gel network entanglement. Images also show a relatively uniform surface for the membranes. Obtained results reveal that by grafting PAA/ Fe_2NiO_4 on membrane surface membrane water content decreased. Membrane potential, permselectivity and transport number in monovalent solution initially declined then started to increase while these parameters showed a decreasing trend in bivalent solution. Ionic permeability and flux of ions for both mono and bivalent solution increased initially then had a slight decreasing trend for monovalent and a nearly sharp one for bivalent solution. Modified membranes showed a lower areal electrical resistance.

5. ACKNOWLEDGEMENT

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Thin Film Heterogeneous Ion Exchange Membranes Prepared by Interfacial Polymerization of PAA-co-Iron-Nickel Oxide Nanoparticles on Polyvinylchloride Based Substrate

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چکیده

در این پژوهش غشاهای تبادل کاتیونی ناهمگن با استفاده از پلیمریزاسیون آکریلیک اسید به همراه نانوذرات اکسید آهن/نیکل بر پایه پلی وینیل کلرایدی تهیه گردید. آنالیز طیف سنجی، تشکیل شدن پلی اکریلیک اسید را به صورت قطعی تایید نمود. نتایج عکسبرداری SEM نشان می دهد که لایه نانوکامپوزیتی تشکیل شده سطح غشا را پوشانده است. همچنین نتایج نشان می دهد که میزان محتوای آب غشاها در اثر تشکیل لایه نانوکامپوزیتی پلی اکریلیک اسید–نانوذرات اکسید آهن/نیکل کاهش یافته است. پتانسیل، عدد انتقال و انتخاب پذیری غشاها، در محلول یک ظرفیتی، در ابتدا با ایجاد پلیمریزاسیون بین سطحی، یک روند کاهشی و سپس روندی افزایشی نشان داد. همچنین عدد انتقال و انتخاب پذیری غشاها در محلول دوظرفیتی عملکردی کاهشی نشان داد. فلاکس سدیمی با ایجاد پلیمریزاسیون بین سطحی پلی آکریلیک اسید بر پایه پلی وینیل کلرایدی در ابتدا افزایش چشمگیری داشت و سپس با افزودن نانو ذرات به تدریج کاهش یافت. رفتاری کاملا متفاوت برای فلاکس باریم مشاهده شد. مقاومت الکتریکی سطحی غشاها نیز در اثر پدیده پلیمریزاسیون بین سطحی کاهش یافت که این مسئله بر کاهش میزان مصرف انرژی سیستم بسیار تاثیرگذار است.

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