

Preparation and electrochemical characterization of polyvinylchloride/ FeTiO₃-co-Fe₃O₄ nanoparticles mixed matrix ion exchange membranes: Investigation of concentration and pH effects

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Abstract—Polyvinyl chloride based/FeTiO₃-co-Fe₃O₄ nanoparticles mixed matrix heterogeneous cation exchange membranes were prepared by solution casting technique. The effect of using filler additives in casting solution and also electrolyte concentration and pH on electrochemical properties of membrane was studied. Membrane potential, transport number and selectivity were improved by using FeTiO₃/Fe₃O₄ nanoparticles in membrane matrix. Utilizing FeTiO₃/Fe₃O₄ nanoparticles in membrane matrix also led to improvement of membrane ionic flux from 2.95×10^{-5} to 4.15×10^{-5} (mol/m²·s) obviously. Similar trend was also found for membrane electrical conductivity. Moreover, the transport number, selectivity and membrane electrical conductivity were enhanced by increase of electrolyte concentration. Prepared membranes exhibited higher transport number/selectivity at pH 7 compared to other pH values. Obtained results showed that the membrane electrical resistance decreased initially by increase of electrolyte pH sharply and then began to increase. Membranes exhibited lower selectivity for bivalent ions compared to monovalent type. Modified membranes containing FeTiO₃/Fe₃O₄ nanoparticles showed more appropriate electrochemical properties compared to other prepared membranes.

Keywords: Cation Exchange Membrane, Mixed Matrix, FeTiO₃-co-Fe₃O₄ Nanoparticle, Membrane Fabrication/Characterization, Electrolyte's Concentration/pH

INTRODUCTION

In the field of separation science and technology, membranes have obtained much attention in different industries [1-5]. Ion exchange membranes (IEMs) have been widely used as active separators in electrically driven processes such as electrodialysis for desalting brackish waters, reconcentrating brine from seawater and production of table salt. They are also efficient tools in resource recovery, food and pharmacy processing and environmental protection as well as manufacturing of basic chemical products [4-15].

In ion exchange membranes, charged groups are attached to polymer backbone and are freely permeable to opposite ions under electrical field influence [1,16]. In such processes, the ions' interactions with membrane, water, and with each other occur in complex fashions. Knowledge of the electrokinetic properties of ion exchange membranes is major factor behind decisions about their applicability in specific separation processes [2,13,17-19].

Preparing ion exchange membranes with special physicochemical properties may be a vital step in future chemical and treatment application [1,20,21].

Many researches have already been carried out to improve the

IEMs physicochemical properties. Variation of functional groups type, selection of different polymeric matrices, polymers blending, using inorganic additives/filler such as metal oxide and nano materials, alteration of cross-link density and surface modification are important techniques to obtain superior ion exchange membranes [1,2,5-7,10,13,22-27].

In this research polyvinyl chloride/FeTiO₃-co-Fe₃O₄ nanoparticles mixed matrix heterogeneous cation exchange membranes were prepared by solution casting technique using cation exchange resin powder as functional groups agent and tetrahydrofuran as solvent. The effect of using filler additive (FeTiO₃/Fe₃O₄ nanoparticles) and electrolyte conditions (type, concentration and pH) on membrane electrochemical properties was studied. The optimum concentration of FeTiO₃-co-Fe₃O₄ in casting solution has been studied and described earlier [1].

PVC is a flexible and durable polymer for application in chemical and medical processes [28-30] which has been used widely as membrane binder. The magnetic FeTiO₃ and Fe₃O₄ nanoparticles are also new class of advanced materials with very interesting features and capacity such as adsorption characteristic, which provides unique physico-chemical properties [31,32]. Utilizing inorganic particles, especially metal oxides, in polymeric materials has been examined in many applications to enhance the physico-chemical characteristics and separation properties of polymeric membranes based on the synergism between the organic-inorganic components

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properties [1,5,12,22].

The behavior of IEMs closely depends on the used electrolyte solutions. So, investigation of membrane electrochemical properties is necessary at different electrolytes conditions. The effect of electrolyte such as type (mono & bivalent ions), concentration and pH on membrane electrochemical properties was also studied.

The results are valuable for electro-membrane processes, especially electrodialysis process for water recycle and treatment.

MATERIALS AND METHODS

1. Materials

Polyvinylchloride (PVC, grade 7054, Density: 490 g/l, viscosity: 105 cm³/g) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as membrane binder. Tetrahydrofuran (THF, Merck Inc., Germany) was employed as solvent. Ilmenite (FeTiO₃, dark brown powder, average particle size <37 μm, Iran) and iron oxide nanoparticles (Fe₃O₄, nano-black-powder, nearly spherical, average particle size 60 nm, >55 m²/g SSA, MW: 213.53, China) were used as inorganic filler additives. Cation exchange resin (Ion exchanger Amberlyst[®] 15, strongly acidic cation exchanger, H⁺ form more than 1.7 milli equivalent/gr dry, density: 0.6 gr/cm³, particle size (0.355-1.18 mm) ≥90%) by Merck Inc., Germany, was also utilized in membrane fabrication. All other chemicals were supplied by Merck. Distilled water was used throughout the experiments.

2. Fabrication of Ion Exchange Membranes

Polyvinyl chloride-based heterogeneous cation exchange membrane was prepared by solution casting techniques using cation exchange resin powder as functional groups agent and tetrahydrofuran as solvent. The resin particles were dried in an oven (SANEE, V. S. Co) 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 (37-44 μm) was used in membrane fabrication. The preparation proceeded by dissolving the polymer binder (PVC) into solvent (THF) (polymer : solvent (1 : 20); (w/v)) in a packed glass reactor equipped with a mechanical stirrer (Model: Velp Scientifica Multi 6 stirrer) for more than 5 h. This was followed by dispersing a specific quantity of ground resin particle as functional groups agents (resin particle : polymer (1 : 1); (w/w)) and FeTiO₃ (16%wt) and Fe₃O₄ nanoparticles (2%wt) as additive in polymeric solution, respectively [1]. The mixture was mixed vigorously at room temperature to obtain uniform particle distribution. For better dispersion of particles and breaking up their aggregates, the solution was sonicated for 1 h by using an ultrasonic instrument. Then, mixing was repeated for another 30 min using a mechanical stirrer. The mixture was then cast onto a clean and dry glass plate at 25 °C. The membranes were dried at ambient temperature and then immersed in distilled water to remove THF completely. Finally, the membranes were pretreated by immersing in 0.5 M NaCl solution. The membrane thickness was measured by a digital caliper around 60-70 μm.

3. Test Cell

The electrochemical properties of membranes were measured by using a homemade test cell (Fig. 1) [1,22]. The cell consists of two cylindrical compartments made of Pyrex separated by membrane. One side of each vessel was closed by Pt electrode supported

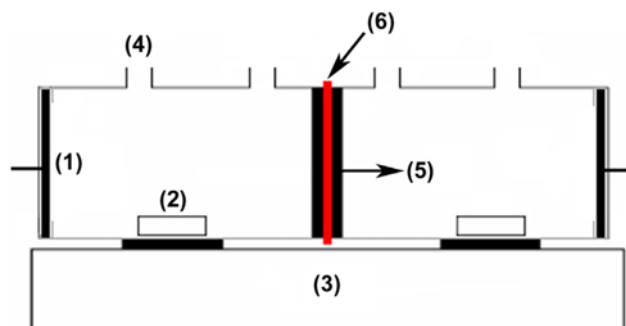


Fig. 1. Schematic diagram of test cell.

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

with a piece of Teflon and the other side was equipped with membrane.

4. Membrane Characterization

4-1. Morphological Studies

The behavior of prepared membranes is closely related to their structure, especially the spatial distribution of ionic site [21]. The structures of prepared membranes were examined by scanning optical microscopy (SOM Olympus, model IX 70) in transmission mode with light going through the membrane matrix.

4-2. Membrane Potential, Transport Number and Permselectivity

Membrane potential is the 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 to the external phase [6,26,33]. This parameter was evaluated for the equilibrated membrane with unequal concentrations of electrolyte solution on either side of the membrane. During the experiment, both compartments were stirred by magnetic stirrer to minimize the effect of boundary layer turbulence. The developed potential across the membrane was measured by connecting both compartments and using saturated calomel electrode and auto multimeter. Membrane potential (E_{Measure}) is expressed using Nernst equation [1,6,21,33-35] as follows:

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

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 and a_1 , a_2 are solutions electrolyte activities in contact membrane surfaces. The ionic permselectivity of membranes also is expressed based on the migration of counter-ion through the IEMs [5,6,33,35]:

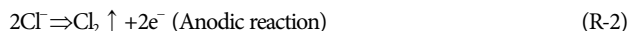
$$P_s = \frac{t_i^m - t_0}{1 - t_0} \quad (2)$$

where, t_0 is the transport number of counter ions in solution [36].

4-3. Ionic Permeability and Flux of Ions

The ionic permeability and flux were measured by using the test cell. A 0.1 M solution was placed on one side of the cell and a 0.01 M solution on its other side. A DC electrical potential with an optimal constant voltage was applied across the cell with stable plati-

num electrodes. 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.



According to Fick's first law, the flux of ions through the membrane can be expressed as follows [20,21]:

$$N = P \frac{C_1 - C_2}{d} \quad (3)$$

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

$$N = -\frac{V}{A} \times \frac{dC_1}{dt} = P \frac{C_1 - C_2}{d} \quad (4)$$

$$C_1^0 = 0.1\text{M}, C_2^0 = 0.01\text{M}, C_1 + C_2 = C_1^0 + C_2^0 = 0.11\text{M} \quad (5)$$

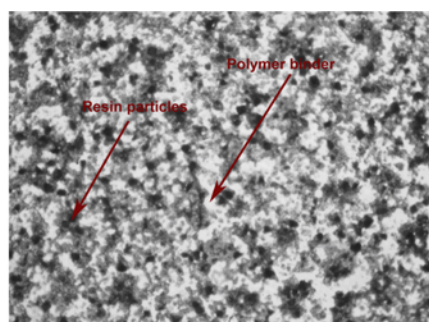
where, A is the membrane surface area. Integrating of Eq. (4) was as follows:

$$\ln \frac{(C_1^0 + C_2^0 - 2C_2)}{(C_1^0 - C_2^0)} = -\frac{2PA t}{Vd} \quad (6)$$

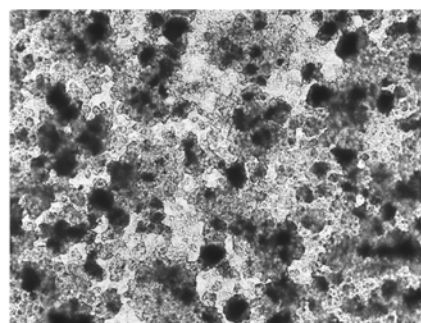
The diffusion coefficient and flux of cations in membrane phase are calculated by using Eq. (6) considering pH (Digital pH-meter, Jenway, Model: 3510) in cathodic section.

4-4. Electrical Resistance

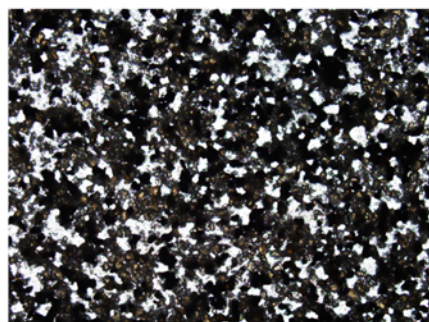
The electrical resistance of equilibrated membrane was measured in 0.5 M NaCl solution at 25 °C. Measurement was carried



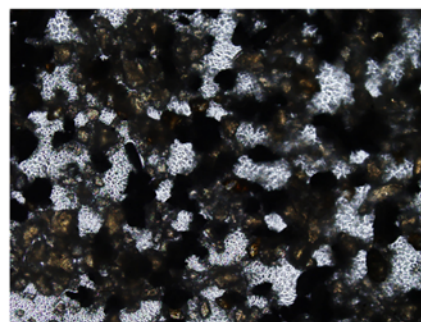
Unmodified/pristine membrane
(4X magnification)



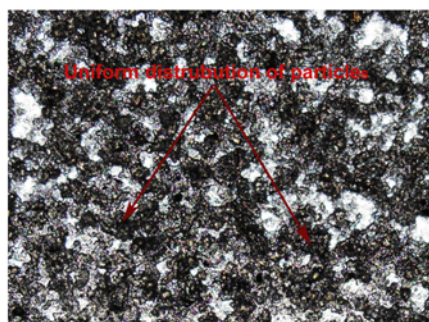
Unmodified/pristine membrane
(10X magnification)



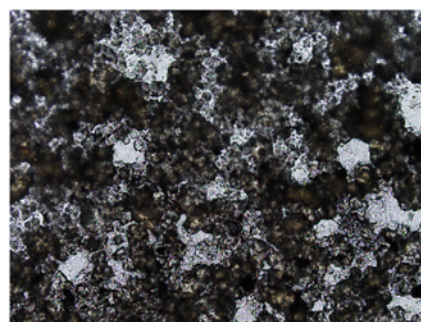
PVC/ FeTiO₃ composite membrane
(4X magnification)



PVC/ FeTiO₃ composite membrane
(10X magnification)



PVC/ FeTiO₃-co-Fe₃O₄ composite membrane
(4X magnification)



PVC/ FeTiO₃-co-Fe₃O₄ composite membrane
(10X magnification)

Fig. 2. The SOM images of prepared membranes with 4× and 10× magnifications; unmodified membrane, PVC/FeTiO₃ composite membrane and PVC/ FeTiO₃-co-Fe₃O₄ composite membrane (variation in membrane brightness by change of additive content).

out by an alternating current bridge with 1,500 Hz frequency. The membrane resistance was calculated by using the different resistance between the cell (R_1) and electrolyte solution (R_2) ($R_m=R_1-R_2$) [1,24,34]. The areal resistance was expressed as follows:

$$r=(R_m/A) \quad (7)$$

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

RESULTS AND DISCUSSION

1. Morphological Studies

Scanning optical microscopy has been used to study the distribution of resin and filler additive particles in membrane matrix. The SOM images are depicted in Fig. 2. As shown in SOM images, the brightness decreased or dark regions increased by increase of additive concentration in membrane matrix. Also, the images show that particles were distributed uniformly in membranes matrix. It reveals that sonication has a significant effect on distribution of particles and results in more uniform phase for the membranes. Moreover, the images show a relatively uniform surface for the membranes. Uniform distribution of particles in membrane matrix provides superior conducting regions for them and generates easy flow channels for counter ions transportation. Presence of more conducting region on membrane surface also can strengthen the intensity of uniform electrical field around the membrane and decrease the polarization phenomenon. Furthermore, uniform distribution of particles in polymeric solution increases the viscosity of casting solution and reduces the evaporation rate of solvent by breaking up particles' aggregations. This makes better the polymer chain conformation with particle surfaces and improves the membrane selectivity [1,37,38].

2. Membrane Potential, Permselectivity and Transport Number

Membrane potential, transport number and permselectivity (Figs. 3-5) were improved by using $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$ nanoparticles in membrane matrix. This may be attributed to adsorptive characteristic of the additives used, which enhances membrane charge density and improves the accessibility of ion exchange functional groups in membrane matrix. This makes better Donnan exclusion that is

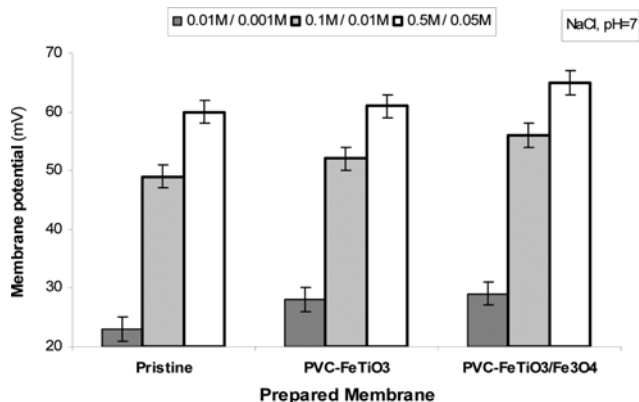


Fig. 3. The effect of electrolyte/sodium chloride concentration on membrane potential of prepared cation exchange membranes (pH=7).

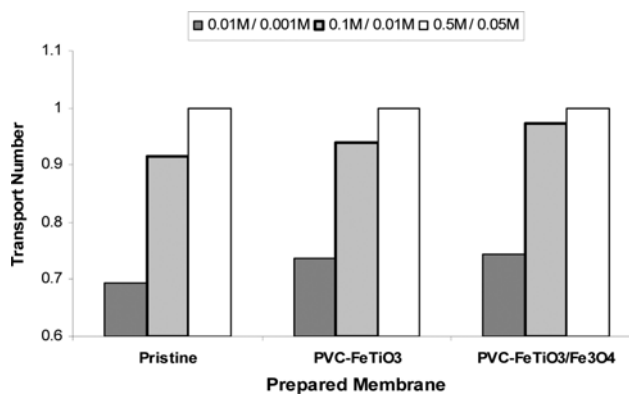


Fig. 4. The transport number of prepared membranes at different electrolyte concentration; Sodium chloride ionic solution (pH=7).

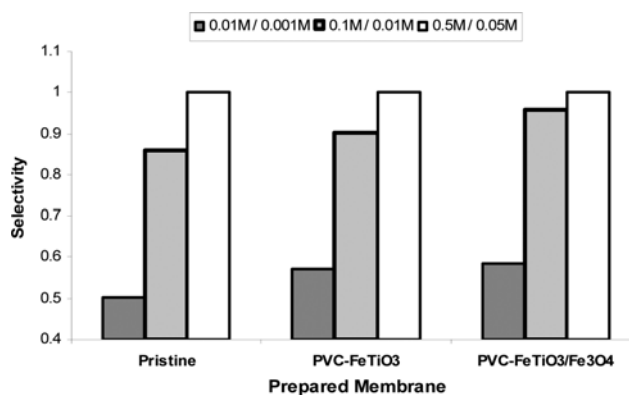


Fig. 5. The effect of electrolyte (sodium chloride) concentration on membrane permselectivity of prepared ion exchange membranes (at pH=7).

responsible for increment of membrane potential, transport number and selectivity [2,6,33]. Moreover, modified membrane containing $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$ nanoparticles showed higher transport number and selectivity compared to other modified membrane including FeTiO_3 . This is due to the unique adsorptive characteristic of magnetic iron oxide nanoparticles, which makes superior interaction for the ions with membrane surface. Moreover, as shown in SOM images, magnetic characteristic of Fe_3O_4 nanoparticles enhances the possibility of uniform particles distribution throughout the membrane matrix because of $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$ interactions.

2-1. The Effect of Concentration and pH on Transport Number and Selectivity

Results showed that (Figs. 3-5) membrane potential, transport number and permselectivity were improved by increase of electrolyte concentration (sodium chloride ionic solution). This may be attributed to high concentration of counter ions in electrolyte environment, which increases the possibility of counter ion interaction with membrane surface. This leads to enhanced Donnan exclusion. The obtained results are significantly in contrast with Donnan equilibrium theory [2,6,16,33,39].

The obtained results (Figs. 6-8) revealed that membranes have higher potential, transport number and selectivity at pH 7 com-

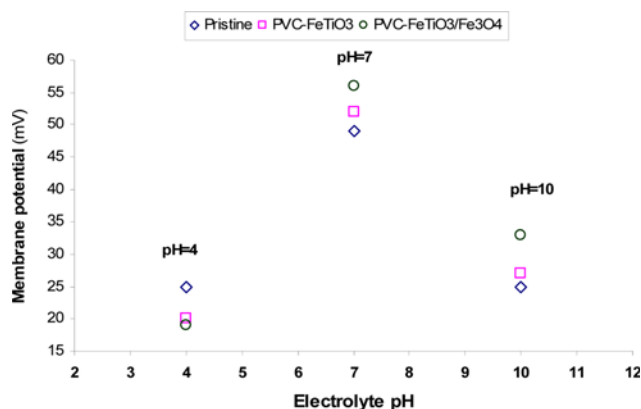


Fig. 6. The effect of electrolyte pH on membrane potential of prepared ion exchange membranes (NaCl, 0.1 M/0.01 M, ambient temperature).

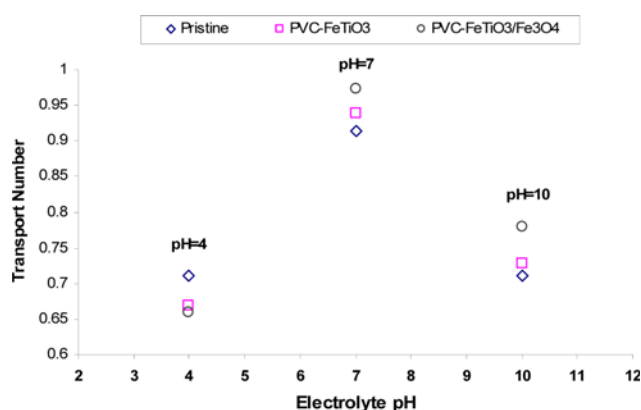


Fig. 7. Effect of electrolyte pH on membrane transport number of prepared membranes in sodium chloride ionic solution (0.1 M/0.01 M).

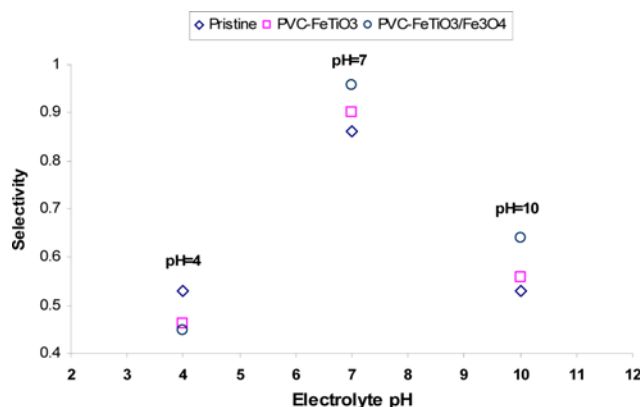


Fig. 8. The permselectivity of prepared membranes at various electrolytes' pH in sodium chloride ionic solution (0.1 M/0.01 M).

pared to other pH values. This is because of the difference in ionic functional groups' dissociation and charge density of filler additives at various pH values, which influences the charge nature of membrane matrix [26]. At suitable electrolyte pH, more dissociation of ion-exchange functional groups and higher charge nature

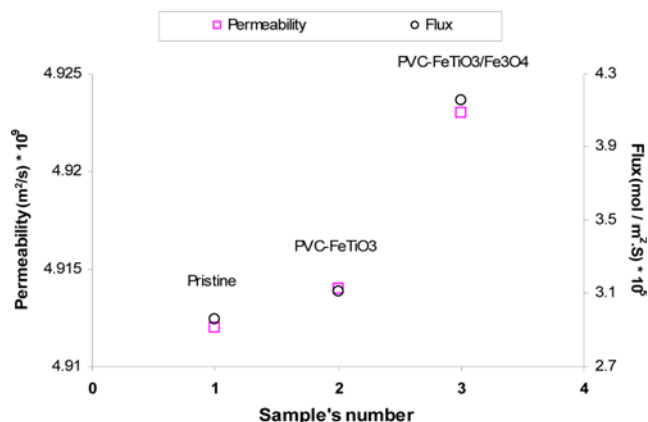


Fig. 9. The permeability and flux of prepared membranes in desalination of sodium chloride ionic solution.

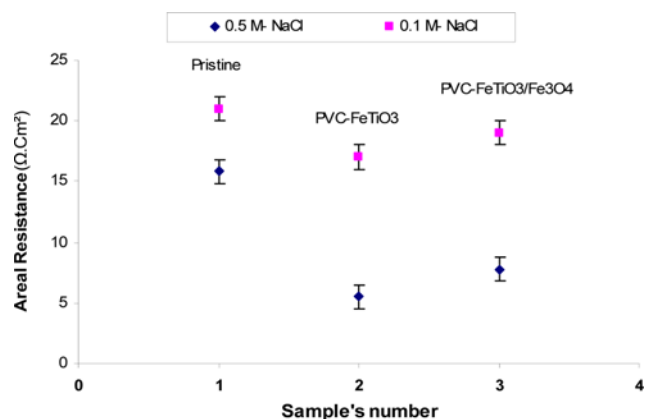


Fig. 10. Areal electrical resistance of prepared membranes at various electrolytes' concentration in sodium chloride ionic solution.

of membrane matrix facilitate the ions transport between the solution and membrane phase.

3. Ionic Permeability and Flux

The amount of transported sodium through the membrane is equal to produced hydroxide ions in cathodic section. Obtained results (Fig. 9) showed that utilizing FeTiO₃/Fe₃O₄ nanoparticles in the casting solution led to increase in sodium permeability and flux for the membranes sharply. This is due to adsorption characteristic of ilmenite/iron oxide nanoparticles, which facilitates the ion transport between the solution and membrane phase and so increases the ionic permeability and flux. Moreover, the strong adsorptive affinity of Fe₃O₄ nanoparticles toward attraction of ions improves the ion traffic for the modified membrane containing FeTiO₃-co-Fe₃O₄ nanoparticles compared to others obviously.

4. Electrical Resistance

Membrane electrical resistance (Fig. 10) was decreased sharply in 0.5 M NaCl ionic solution by using FeTiO₃/Fe₃O₄ nanoparticles in membrane matrix. This may be due to adsorption property of additive particles, which facilitates ion transport between the solution and membrane phase and so improves the membrane conductivity. The modified membrane containing FeTiO₃ showed lower

Table 1. Comparison between the electrochemical properties of modified membranes in this study and some commercial membranes [3,12,39]

Membrane	Permselectivity ^a (%)	Electrical resistance ^b ($\Omega \text{ cm}^2$)
PVC/FeTiO ₃ -co-Fe ₃ O ₄ composite membrane	>97	<7
Ralex® CMH-PES	>92	<10
Ionics Inc., USA (61CZL386)	-	9
RAI Research Corp., USA R-5010-H	95	8-12
FuMA-Tech GmbH, Germany FKB	-	5-10
Ionics Inc., USA, CR61-CMP	-	11
Neosepta® CMX	>96	1.8-3.8
CSMCRI, India (HGC)	87	4-6
Fumasep® FKD	>95	<3

^aMeasured in 0.1/0.01 M NaCl solution

^bMeasured in 0.5 M NaCl solution

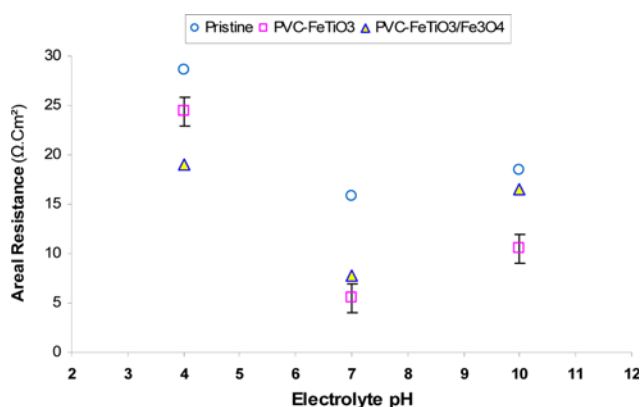


Fig. 11. The effect of electrolyte pH on membrane areal resistance of prepared membranes in sodium chloride ionic solution.

electrical resistance compared to modified membrane, including FeTiO₃/Fe₃O₄ nanoparticles. In general, less selective membranes have lower membrane resistances [39]. A comparison between the electrochemical properties of prepared membranes in this study and some commercial membranes is given in Table 1. Modified membranes showed higher selectivity and suitable amount of electrical resistance compared to commercial ones.

4-1. The Effect of Concentration and pH on Membrane Electrical Resistance

The effects of electrolyte concentration/pH on electrical resistance of prepared membranes are shown in Figs. 10 and 11. The significant increase in membrane resistance at lower salt concentration is attributed to diffusion boundary layer resistance, which is more significant at low salt concentration. Moreover, at high electrolyte concentration, the membrane swelling decreases the electrical resistance. The obtained results also showed that membrane electrical resistance was decreased initially by increase of pH and then began to increase. Variations of membrane conductance may be explained with respect to membrane functional groups dissociation at different electrolyte environments [19,26].

5. Characterization of Membranes in Bivalent Ionic Solution

During the ion removal or concentrating of solutions, scale formation of bivalent ions on membrane surface is a serious prob-

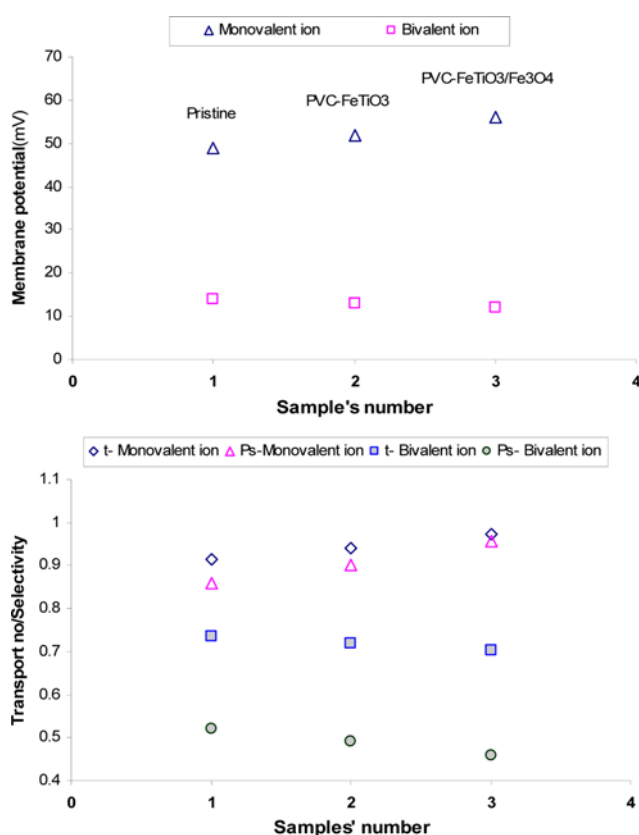


Fig. 12. Comparison between the membrane potential, transport number and selectivity of prepared membranes in mono and bivalent ionic solutions.

lem that is due to hydroxide formation. Obtained results showed lower potential, selectivity and transport number for the prepared membranes in bivalent ionic solution compared to monovalent ionic solution (Fig. 12). This may be due to stronger bonds of bivalent ions with ion exchange functional groups [2,26], which decreases the membrane electrochemical properties. In fact, bivalent ions have stronger electrostatic attraction with fixed opposite charge sites of membranes and so prevents their dissociation. Furthermore, the larger radius of bivalent ions and their hydrated size in compari-

son with monovalent type are other reasons for lower membrane potential, transport number and permselectivity [2,17,21].

CONCLUSION

Preparing mixed matrix ion exchange membranes with special physico-chemical characteristics for the application in water recovery and treatment was the primary target of the current research. PVC/FeTiO₃-co-Fe₃O₄ nanoparticle heterogeneous cation exchange membranes were prepared by solution casting technique. The effect of filler additives (FeTiO₃/Fe₃O₄ nanoparticles) and electrolyte conditions (type, concentration and pH) on membrane electrochemical properties was studied.

Membrane transport number, selectivity and charge density all were increased by using FeTiO₃/Fe₃O₄ nanoparticles in prepared membranes.

Utilizing FeTiO₃/Fe₃O₄ nanoparticles also led to increase of sodium flux from 2.95×10^{-5} to 4.15×10^{-5} (mol/m²·S) obviously.

Obtained results also showed higher transport number, selectivity and flux for the modified membranes containing FeTiO₃/Fe₃O₄ nanoparticles compared to other modified membrane including FeTiO₃.

Moreover, membrane areal electrical resistance declined sharply by using of FeTiO₃/Fe₃O₄ nanoparticles in membrane matrix from 15.8 to 5.5 (ohm·cm²).

The membrane potential, transport number and selectivity were improved by increase of electrolyte concentration. Also, prepared membrane showed higher potential, transport number and selectivity at pH 7 compared to other pH values.

The electrical resistance of membrane also was decreased by increase of electrolyte concentration. The membrane electrical resistance was also decreased initially by increase of pH value and then began to increase.

Prepared membranes exhibited lower potential, selectivity and transport number for barium ions compared to sodium ions.

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

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