

## Electrochemical characterization of mixed matrix heterogeneous cation exchange membranes modified by simultaneous using ilmenite-co-iron oxide nanoparticles

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**Abstract**—Mixed matrix heterogeneous cation exchange membranes were prepared by solution casting technique. Ilmenite-co-iron oxide nanoparticle was also employed as inorganic filler additive in membrane fabrication. The effect of the used additives on membrane electrochemical properties was studied. Membrane ion exchange capacity, membrane potential, transport number and selectivity all were improved by use of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in membrane matrix. Utilizing  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles in the casting solution also led to increase in ionic flux obviously. The modified membranes containing  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles showed higher transport number, selectivity and ionic flux compared to modified membrane containing ilmenite. Electrodialysis experiment in laboratory scale also showed higher cation removal for modified membrane containing  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles compared to other modified membranes and pristine ones. Results showed that membrane areal electrical resistance declined sharply by use of  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles in membrane matrix. Moreover, modified membrane containing ilmenite showed lower electrical resistance compared to others. Results showed that oxidative stability of membranes was decreased slightly by use of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in membrane matrix. The results revealed that modified membranes in this study are comparable with that of other commercial ones.

**Keywords:** Composite Ion Exchange Membrane, Ilmenite-co-iron Oxide Nanoparticles, Synergy, Electrodialysis, Adsorption-ion Exchange, Preparation/Characterization

### INTRODUCTION

Membrane technologies have obtained much attention in diverse industries and human life. Ion exchange membranes have been used widely as active separators in electrically driven processes such as electrodialysis for desalting brackish waters, reconcentrating brine from seawater and production of table salt. Ion exchange membranes are also efficient tools in resource recovery, food and pharmacy processing and environmental protection such as treating industrial and biological effluents as well as manufacturing of basic chemical products [1-5]. In IEMs charged groups attached to polymer backbone are freely permeable to opposite sign ions under an electrical field influence [6]. In such processes, ion interactions with membrane, water, and with each other occur in complex fashions. Knowledge of the electrokinetic properties of ion exchange membranes is a major contributing factor behind decisions about their applicability in specific separation processes and energy storage devices [2,7,8].

Preparing inexpensive IEMs with special physico/chemical characteristics may be a vital step in future applications [2,4]. Much research has already been carried out to improve the IEMs physico-chemical properties. Variation of functional groups type, selection

of different polymeric matrices, polymers blending, using of inorganic additives/filler, alteration of cross-link density and surface modification are the important techniques to obtain superior IEMs [1,2,9,10].

Utilizing inorganic particles or fillers into polymeric materials has been examined in many applications to enhance the physico-chemical characteristics and separation properties based on the synergism between the organic-inorganic components properties. Magnetic metal oxide (MMO) particles are a new class of advanced materials with very interesting features and capacity such as adsorption characteristics in metallic cation adsorption, which can provide unique characteristics for the membranes [1,5,11,12].  $\text{FeTiO}_3$  and  $\text{Fe}_3\text{O}_4$  particles are well known magnetic metal oxides which have gained a great deal of attention because of stable chemical property, safety toward the environment and high adsorption capacity due to valence states of ions in MMO structures [13-15]. The surface sites binding, electrostatic interaction and ligand combination are main factors for this adsorptive behavior. This characteristic acts as a driving force for cation transport from solution into membrane matrix, which can improve the ion exchange possibilities.

Currently, no reports have considered incorporating magnetic/adsorptive  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles into ion exchange membranes, and the literature is silent on characteristics and functionality of electrodialysis IEMs.

Preparing heterogeneous cation exchange membranes with specially adapted physico/chemical properties for application in elec-

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trodialysis processes related to water recovery and water treatment was the primary target of the current research. Mixed matrix (polyvinylchloride/ilmenite-co-iron oxide nanoparticles) heterogeneous cation exchange membranes were prepared by solution casting techniques. PVC is a flexible and durable polymer with suitable biological and chemical resistance [16,17]. Iron oxide nanoparticles ( $\text{Fe}_3\text{O}_4$ )/ilmenite ( $\text{FeTiO}_3$ ) were also employed as inorganic filler additive in membrane fabrication to improve the IEMs physico-chemical properties. The effect of used  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles on membranes properties was studied.

During the experiments, sodium chloride was employed as ionic solution for the membrane characterization. Electrodialysis experiment was also carried out in a laboratory scale unit to evaluate the electrodialytic performance of modified membranes in ions removal from waste water. The results are valuable for electro-membrane processes, especially the electrodialysis process for water recovery and water treatment.

## MATERIALS AND METHODS

### 1. Materials

Polyvinylchloride (PVC, grade 7054, Density: 490 g/l, viscosity: 105  $\text{Cm}^3/\text{g}$ ) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as binder. Tetrahydrofuran (THF, Merck Inc., Germany) was employed as solvent. Ilmenite ( $\text{FeTiO}_3$ , dark brown powder, average particle size  $<37 \mu\text{m}$ , Iran) and iron oxide nanoparticles ( $\text{Fe}_3\text{O}_4$ , nano-black-powder, nearly spherical, average particle size 60 nm,  $>55 \text{ m}^2/\text{g}$  SSA, MW: 213.53, China) were used as inorganic filler additives. Cation exchange resin (Ion exchanger Amberlyst<sup>®</sup> 15, strongly acidic cation exchanger,  $\text{H}^+$  form more than 1.7 milli equivalent/gr dry, density: 0.6  $\text{gr}/\text{cm}^3$ , particle size (0.355-1.18 mm)  $\geq 90\%$ ) by Merck Inc., Germany, was also utilized in membrane fabrication. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used.

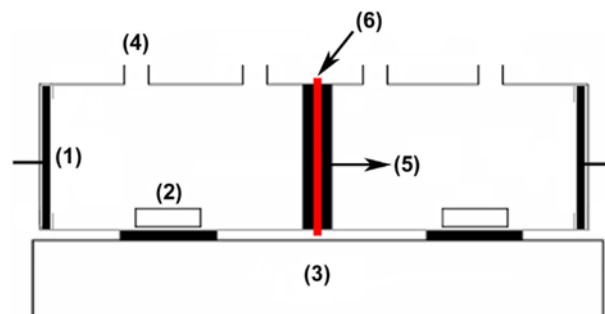
### 2. Preparation of Composite Ion Exchange Membrane

To undertake the membrane preparation, resin particles were dried in oven at  $30^\circ\text{C}$  for 48 h and then pulverized into fine particles in a ball mill and sieved to the desired mesh size. The ion exchange resin with desired particles size ( $-325 +400$  mesh) was used in membrane fabrication. The preparation proceeded by dissolving the polymer binder into THF solvent in a glass reactor equipped with a mechanical stirrer for more than 5 h. This was followed by dispersing a specific quantity of grinded resin particle as functional groups agents and  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles as additive in polymeric solution, respectively. The mixture was mixed vigorously at room temperature to obtain a uniform particle distribution in polymeric solution. In addition, for better dispersion of particles and breaking up their aggregates, the polymeric solution was sonicated for 1 h with an ultrasonic instrument. Then, the mixing process was repeated for another 30 min by the mechanical stirrer. The mixture was then cast onto a clean and dry glass plate at  $25^\circ\text{C}$ . The membranes were dried at ambient temperature and immersed in distilled water. As the final stage, membranes were pretreated by immersing in NaCl solution. The membrane thickness was measured by a digital caliper device around 60-70  $\mu\text{m}$ . The composition of casting solution is depicted in Table 1.

**Table 1. Compositions of casting solution used in preparation of homemade membranes<sup>a</sup>**

Membrane	(Additive; $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$ nanoparticles)
Sample 1 (S1)	Pristine/Unmodified membrane
Sample 2 (S2)	$\text{FeTiO}_3$ (16%wt), $\text{Fe}_3\text{O}_4$ (0%wt)
Sample 3 (S3)	$\text{FeTiO}_3$ (16%wt), $\text{Fe}_3\text{O}_4$ (1%wt)
Sample 4 (S4)	$\text{FeTiO}_3$ (16%wt), $\text{Fe}_3\text{O}_4$ (2%wt)

<sup>a</sup>(Polymer binder (PVC) : solvent (THF)) (w/v), (1 : 20); ((resin particle : polymer binder) (w/w), (1 : 1))



**Fig. 1. Schematic diagram of test cell.**

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

### 3. Test Cell

The electrochemical properties measurements were carried out using the test cell (Fig. 1). The cell consists of two cylindrical compartments made of Pyrex glass separated by membrane. One side of each vessel was closed by Pt electrode supported with a piece of Teflon and the other side was equipped with membrane. The membrane area was 19.63  $\text{cm}^2$ .

### 4. Membrane Characterization

#### 4-1. Morphological Studies

The behavior of the prepared membranes is closely related to their structure, especially the spatial distribution of ionic sites [18]. The structures of prepared membranes were examined by scanning optical microscopy in transmission mode with light going through the membrane. For the scanning, samples were cut in small pieces and after mounting between lamellas, observation was made by the optical microscope.

#### 4-2. Ion Exchange Capacity (IEC)

The IEC determination was performed by using the titration method. To measure the ion exchange capacity, membranes were initially placed in 1 M HCl solution for 24 h to convert the exchange group to H type. Then membranes were washed and kept in water for 24 h at ambient temperature. A sufficient washing time was obtained through not exhibiting acidity which was recognized by the reaction with methyl red. Subsequently, membranes were immersed in 1 M NaCl solution for 24 h to liberate the  $\text{H}^+$  ions (the  $\text{H}^+$  ions in the membrane were replaced by  $\text{Cl}^-$  ions). The  $\text{H}^+$  ions in the solution were then analyzed with 0.01 M NaOH and phenolphthalein indicator (a meq). Finally, the membrane was wiped with filter paper and dried in oven for 4 h and then weighed ( $W_{\text{dry}}$ , gr).

IEC can be calculated from the following equation [12,19-21]:

$$\text{IEC} = \left( \frac{a}{W_{\text{dry}}} \right) \quad (1)$$

where  $a$  is the milli-equivalent of ion exchange group in membrane and  $W_{\text{dry}}$  is the weight of dry membrane (g).

#### 4-3. Membrane Potential, Transport Number and Permselectivity

The 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 with the external phase [19]. This parameter was evaluated for the equilibrated membrane with unequal concentrations ( $C_1=0.1 \text{ M}/C_2=0.01 \text{ M}$ ) of electrolyte solution at ambient temperature on either sides of membrane. 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. Membrane potential ( $E_{\text{Measure}}$ ) is expressed by using the Nernst equation [1,8,20] as follows:

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

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 and  $a_1$ ,  $a_2$  are solutions electrolyte activities in contact membrane surfaces.

The ionic permselectivity of membranes also is quantitatively expressed based on the migration of counter-ion through the IEMs [8,20,21]:

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

where  $t_0$  is the transport number of counter ions in solution [22].

#### 4-4. Concentration of Fixed Ionic Charge of Membrane

The greater conducting regions on the membrane surface can improve the membrane electrochemical properties and strengthen the intensity of uniform electrical field around the membrane [23]. The concentration of fixed ionic charge on membrane surface ( $Y$ ) has been expressed in terms of permselectivity as follows [20,21,24]:

$$Y = \frac{2C_{\text{Mean}}P_s}{\sqrt{1 - P_s^2}} \quad (4)$$

where  $P_s$  is the permselectivity and  $C_{\text{Mean}}$  is the mean concentration of electrolytes.

#### 4-5. Ionic Permeability and Flux

The ionic permeability and flux were measured by using the test cell. A 0.1 M solution (NaCl) 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 (10 V) 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.



According to Fick's law, ionic flux through the membrane can be expressed as follows [1,18,25]:

$$N = P \frac{C_1 - C_2}{d} \quad (5)$$

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

$$C_1^0 = 0.1 \text{ M}, \quad C_2^0 = 0.01 \text{ M}, \quad C_1 + C_2 = C_1^0 + C_2^0 = 0.11 \text{ M} \quad (6)$$

where  $A$  is the membrane surface area. Integrating of Eq. (7) was as follows:

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

The diffusion coefficient and flux of cations in membrane phase are calculated from Eq. (7) considering pH changes (Digital pH-meter, Jenway, Model: 3510) in the cathodic section.

#### 4-6. Electrodialysis for Ion Removal

The electrodialysis experiment was also in a homemade laboratory scale electrodialysis unit containing one cell pair of homemade cation exchange membrane and commercial anion exchange membrane with 19.63 cm<sup>2</sup> effective area to evaluate the performance of modified membranes for water treating in cations removal. DC electrical potential with constant voltage (15 V) was applied across the cell for one hour. A 0.1 M NaCl solution was utilized in the diluted section. The concentration of used electrolyte in electrode compartments was also 0.1 M. Commercial heterogeneous anion-exchange membrane (RALEX<sup>®</sup> 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% (gr absorbed water/gr dry membrane). The ion exchange capacity (IEC) was also obtained as 1.85 (meq/gr dry membrane). The volume of electrolyte solution was 180 cm<sup>3</sup>. The flux of cations was determined by considering conductivity variations in diluted compartment or pH changes in cathodic region.

#### 4-7. Electrical 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 1,500 Hz frequency using conductivity cell (Fig. 2). The membrane resistance is calculated using the different resistance between the cell ( $R_1$ ) and electrolyte solution ( $R_2$ ) ( $R_m = R_1 - R_2$ ) [26,27]. The areal resistance was expressed as follows:

$$r = (R_m/A) \quad (8)$$

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

#### 4-8. Membrane Oxidative Stability

The prepared heterogeneous membranes were immersed into

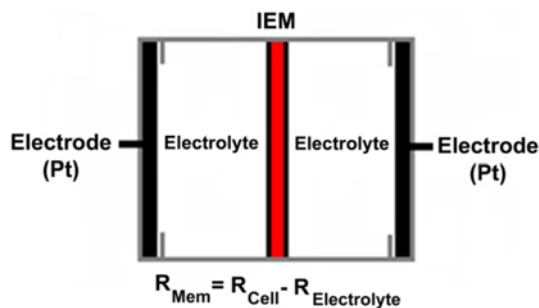


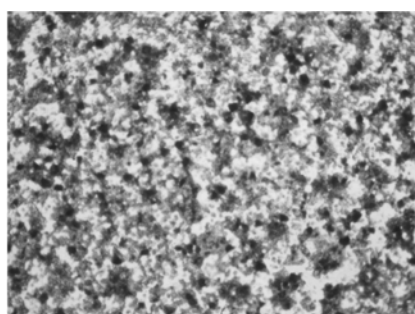
Fig. 2. The scheme of conductivity cell for membrane resistance measurement.

3%  $\text{H}_2\text{O}_2$  aqueous solution containing 4 ppm  $\text{Fe}^{3+}$  at 25 °C for up to 60 h. The weights of dried samples before and after the experiment were compared [28].

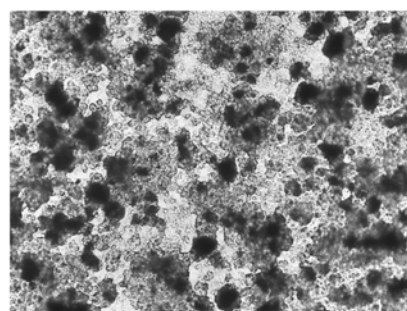
## RESULTS AND DISCUSSION

### 1. Morphological Studies

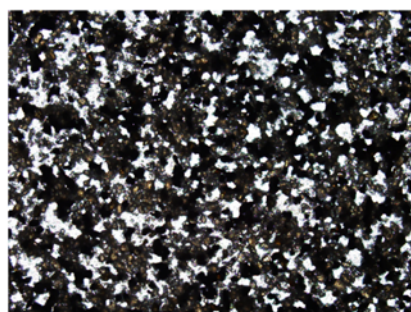
Scanning optical microscopy was used to evaluate the ionic/additive particles distribution in the prepared membrane. The SOM images are depicted in Fig. 3. The polymer binder, resin particles and used additive nanoparticles are seen in the images. As shown, the brightness of images was decreased or dark regions increased by increase of additive concentration in membrane matrix. Also exhibited was that particles were uniformly distributed in membrane matrix. It reveals that sonication/mixing has a significant effect on distribution of particles and results in formation of more uniform phase. Moreover, images show a relatively uniform surface for the membranes. Presence of MMO particles in membrane matrix provides more active sites for the membranes and generates easy flow channels for the ion transport. This strengthens the



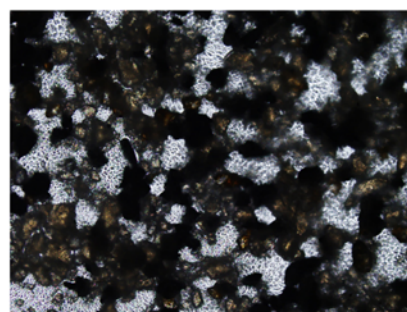
Unmodified/pristine membrane  
(4X magnification)



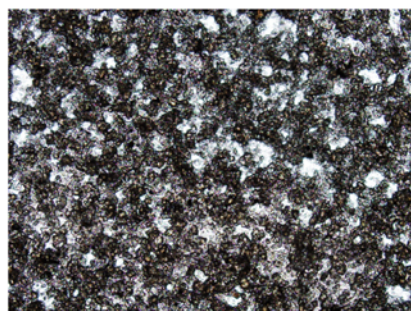
Unmodified/pristine membrane  
(10X magnification)



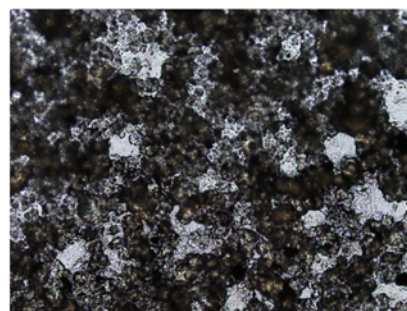
PVC/  $\text{FeTiO}_3$  composite membrane  
(4X magnification)



PVC/  $\text{FeTiO}_3$  composite membrane  
(10X magnification)



PVC/  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  composite membrane  
(4X magnification)



PVC/  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  composite membrane  
(10X magnification)

Fig. 3. The SOM images of prepared membranes with 4× and 10× magnifications; unmodified membrane, PVC/ $\text{FeTiO}_3$  composite membrane and PVC/ $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  composite membrane.

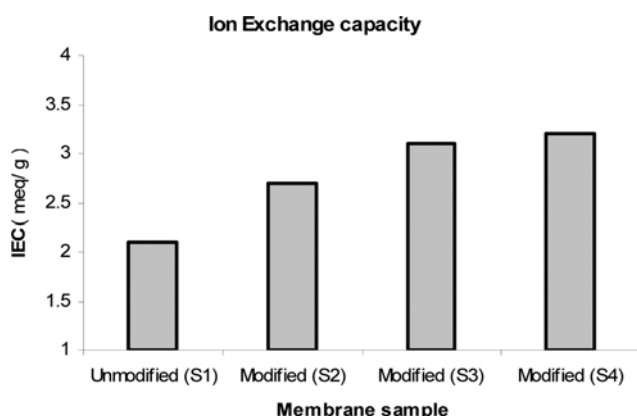


Fig. 4. Comparison between the ion exchange capacity of unmodified membrane and modified membranes (S2- S4).

intensity of a uniform electrical field around the membrane during ED process and decreases the polarization phenomenon [23]. Furthermore, uniform distribution of particles in polymeric solution increases the viscosity of solution and reduces the evaporation rate of solvent. This improves the polymer chain conformation with particle surfaces and improves the membrane selectivity [29].

## 2. Membrane Ion Exchange Capacity

IEC Results (Fig. 4) indicated that utilizing  $\text{FeTiO}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles in the casting solution led to an improvement in ion exchange capacity in the prepared membranes. This may be due to adsorption characteristic of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  particles which make superior interaction between ions and membrane surface and so facilitates the ion transport between the solution and membrane phase. This improves membrane ion exchange possibilities.

## 3. Membrane Potential, Permselectivity and Transport Number

It was found that membrane potential, transport number and permselectivity (Figs. 5, 6) all were improved in sodium chloride ionic solution by using  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in the casting solution. This is attributed to selective adsorption characteristic of used additive in metallic cations adsorption, which acts as a driv-

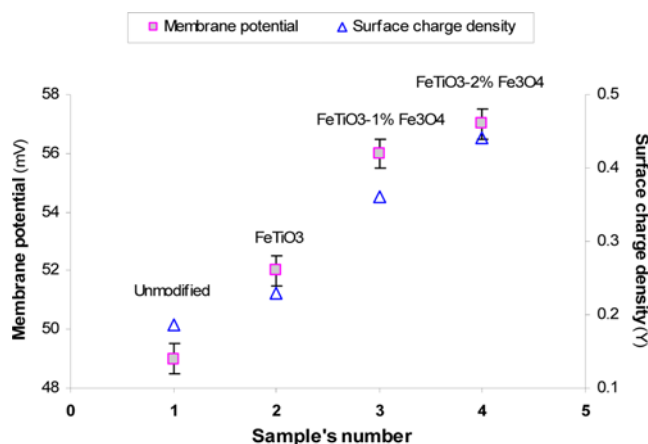


Fig. 5. Membrane potential and surface charge density of prepared ion exchange membranes modified by ilmenite/iron oxide nanoparticles.

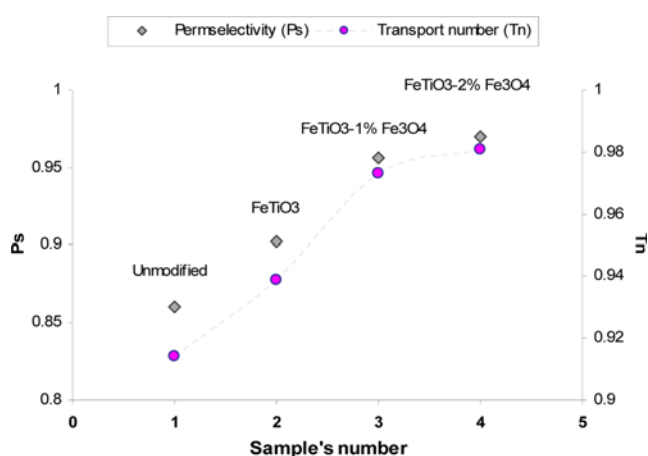


Fig. 6. Comparison between the transport number and permselectivity of prepared membranes; Pristine membrane and composite membranes containing  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles.

ing force for cation transport between solution and membrane, which increases the Donnan potential. Moreover, increase of ion exchange possibilities (Fig. 4) and membrane charge density (Fig. 5) improve the diffusion potential. This is responsible for the increment of membrane potential, transport number and selectivity [8,20].

Moreover, modified membranes containing  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles showed higher membrane potential, transport number, selectivity and charge density compared to modified membrane, including ilmenite. This may be due to the unique adsorptive characteristic of magnetic iron oxide nanoparticles, which makes superior interaction for the ions with membrane surface. Also, the high surface area to volume ratios of  $\text{Fe}_3\text{O}_4$  nanoparticles were favorable for diffusion of ions from solution onto the active sites of particles surface. The mechanisms of ion adsorption by magnetic metal oxide materials include surface sites binding, magnetic selective adsorption, electrostatic interaction and ligand combination [15]. Furthermore, as shown in SOM images, the interaction between  $\text{FeTiO}_3$  and  $\text{Fe}_3\text{O}_4$  particles enhances the possibility of particle dis-

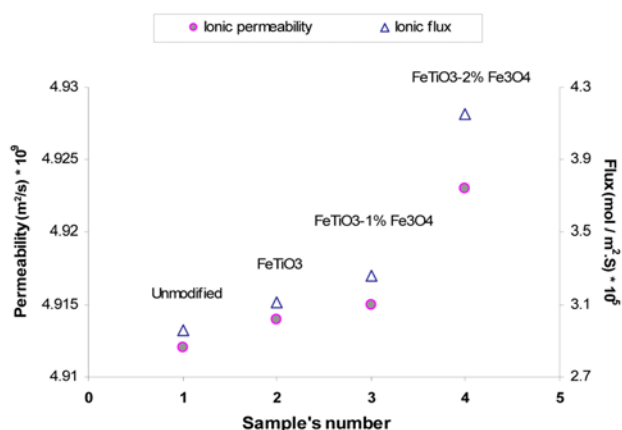


Fig. 7. Ionic permeability and flux of prepared cation exchange membranes with various ratios of additives: ilmenite-co-iron oxide nanoparticles.

tribution throughout the membrane matrix uniformly. This provides more conducting regions/active sites for the membranes.

#### 4. Ionic Permeability and Flux

During the experiment, ions pass through the membrane and reach a concentrated section. According to anodic and cathodic reactions, the amount of transported sodium ions through the membrane is equal to the produced hydroxide ions in the cathodic section. As shown in Fig. 7, utilizing  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in the casting solution sharply led to increase of ionic flux for sodium ions in prepared membranes. This may be due to the adsorption characteristic of ilmenite/iron oxide nanoparticles, which facilitates the ions transport between the solution and membrane phase and so increases the ionic permeability and flux. Also as mentioned, the potential and strong adsorptive affinity of iron oxide nanoparticles toward attraction of ions improves the ion traffic for the modified membrane containing  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles compared to others obviously.

#### 5. Electrodialysis for Ions Removal

Electrodialysis experiment was carried out in a laboratory scale unit to evaluate the electrodialytic performance of modified membranes for ions removal. The ionic flux/cation removal of unmodified membrane, modified membrane containing ilmenite and also

membrane including  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles are shown in Fig. 8. Results showed that ion removal was increased sharply by using  $\text{FeTiO}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles in the membrane matrix, which is assigned to the superior and unique adsorptive characteristic of MMO in cations adsorption, which enhances the ionic flux obviously in water treatment.

#### 6. Electrical Resistance

The membrane areal electrical resistance (Fig. 9) declined sharply by use of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in prepared membranes. This is due to the unique adsorption property of additive particles which facilitates ion transport between the solution and membrane. Moreover, modified membrane containing ilmenite showed lower electrical resistance compared to modified membrane including  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles. In general, less selective membranes have lower membrane resistance, but this is not always true and depends on the membrane structure and its properties [30]. A comparison between the electrochemical properties of prepared membranes in this study and some commercial membranes is given in Table 2. The modified membranes in this research showed higher selectiv-

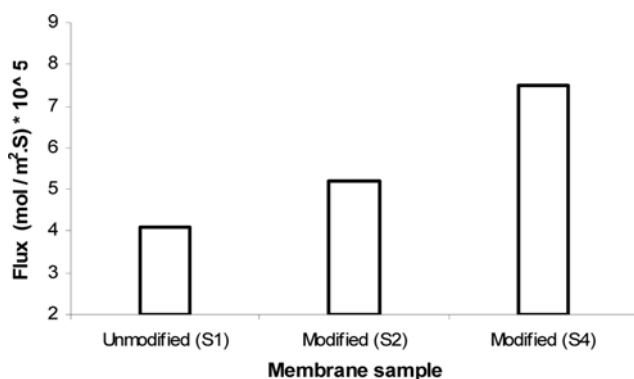


Fig. 8. The cations removal for pristine membrane (S1) and also modified membranes (S2, S4) in laboratory scale ED unit containing one cell pair.

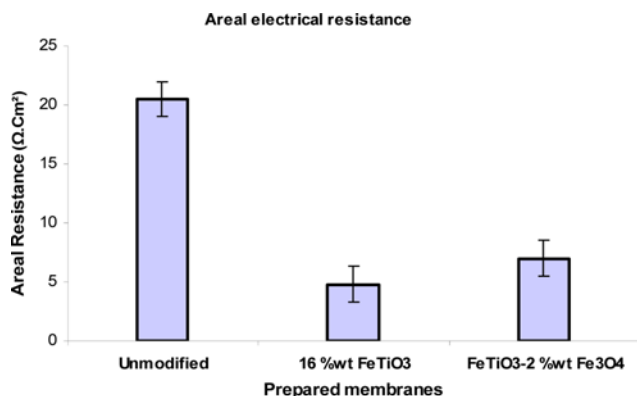


Fig. 9. The areal electrical resistance of prepared membranes: Unmodified membrane and modified membranes containing  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles.

Table 2. Comparison between the electrochemical properties of prepared membranes in this research and some commercial membranes [3,5,29]

Membrane	Permselectivity <sup>a</sup> (%)	Electrical resistance <sup>a</sup> (Ω cm <sup>2</sup> )
<b>Modified membrane (S4)</b>	>97	<7
RAI Research Corp., USA R-5010-H	95	8-12
Ionics Inc., USA, CR61-CMP	-	11
Ionics Inc., USA, CR67-HMR	-	7-11
FuMA-Tech GmbH, Germany FKB	-	5-10
Ralex® CMH-PES	>92	<10
Ionics Inc., USA (61CZL386)	-	9
CSMCRI, India (HGC)	87	4-6
Fumasep® FKE	>98	<3
Fumasep® FKD	>95	<3
Neosepta® CMX	>96	1.8-3.8

<sup>a</sup>Measured in sodium chloride ionic solution

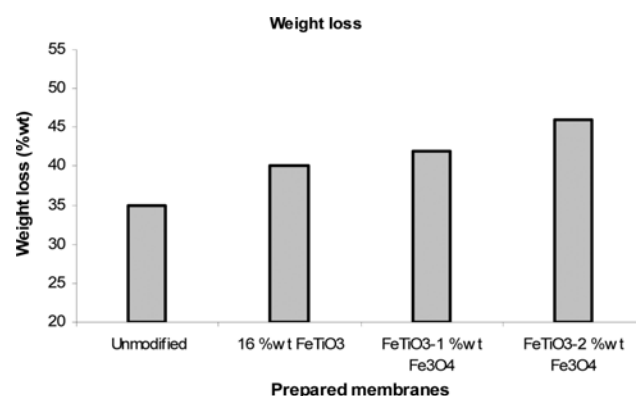


Fig. 10. The oxidative stability of prepared membranes: Unmodified membrane and modified membranes containing  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles.

ity and suitable amount of electrical resistance compared commercial ones.

### 7. Membrane Oxidative Stability

Prepared membranes were immersed in an oxidant aqueous solution for oxidative stability measurements. The results (Fig. 10) showed that oxidative stability of prepared membranes was decreased by use of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in membrane matrix. This may be attributed to the adsorption characteristic of used additive, which increases the possibility of oxidant diffusion in the matrix of membrane. Moreover, the nature of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles facilitates membrane oxidation.

### CONCLUSION

IEC results indicated that utilizing  $\text{FeTiO}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles in the casting solution led to an improvement in ion exchange capacity for the prepared membranes. Membrane potential, transport number, selectivity all were improved in sodium chloride ionic solution by using of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in the casting solution. Utilizing of  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles in the casting solution also led to increase in ionic permeability and flux for the membranes obviously. Electrodialysis experiment in laboratory scale also showed higher ion removal for modified membrane containing  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles compared to modified membrane containing ilmenite and pristine ones. The obtained results showed higher transport number and selectivity for the modified membranes containing  $\text{FeTiO}_3$ -co- $\text{Fe}_3\text{O}_4$  nanoparticles compared to modified ones including ilmenite. Also, the potential and strong adsorptive affinity of iron oxide nanoparticles toward attraction of ions improves ion traffic for the modified membrane containing  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles compared to others obviously. The results showed that membrane areal electrical resistance declined sharply by use of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in prepared membranes. Moreover, modified membrane containing ilmenite showed lower electrical resistance compared to modified membrane including  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles. The results showed that oxidative stability of prepared membranes is decreased by use of  $\text{FeTiO}_3/\text{Fe}_3\text{O}_4$  nanoparticles in membrane matrix. The obtained results revealed that modified membranes in this study are comparable with commercial ones. The results are valuable for electro membrane processes, especially electrodialysis process for water recovery and treatment.

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### REFERENCES

1. M. Zarrinkhameh, A. Zendehnam and S. M. Hosseini, *Korean J. Chem. Eng.*, **31**, 1187 (2014).
2. S. M. Hosseini, A. Gholami, P. Koranian, M. Nemati, S. S. Madaeni and A. R. Moghadassi, *J. Taiwan Inst. Chem. Eng.*, In Press, DOI: 10.1016/j.jtice.2014.01.011.
3. R. K. Nagarale, G. S. Gohil and V. K. Shahi, *Adv. Colloid Interface Sci.*, **119**, 97 (2006).
4. M. Y. Kariduraganavar, R. K. Nagarale, A. A. Kittur and S. S. Kulkarni, *Desalination*, **197**, 225 (2006).
5. T. Xu, *J. Membr. Sci.*, **263**, 1 (2005).
6. R. W. Baker, *Membrane Technology and Applications*, 2<sup>nd</sup> Ed., Wiley, England (2004).
7. P. Dlugolecki, B. Anet, S. J. Metz, K. Nijmeijer and M. Wessling, *J. Membr. Sci.*, **346**, 163 (2010).
8. G. S. Gohil, V. V. Binsu and V. K. Shahi, *J. Membr. Sci.*, **280**, 210 (2006).
9. A. Zendehnam, M. Arabzadegan, S. M. Hosseini, N. Robatmili and S. S. Madaeni, *Korean J. Chem. Eng.*, **30**, 1265 (2013).
10. S. M. Hosseini, S. S. Madaeni, A. Zendehnam, A. R. Moghadassi, A. R. Khodabakhshi and H. Sanaeepur, *J. Ind. Eng. Chem.*, **19**, 854 (2013).
11. L. Y. Ng, A. W. Mohammad, C. P. Leo and N. Hilal, *Desalination*, **308**, 15 (2013).
12. S. M. Hosseini, S. S. Madaeni, A. R. Heidari and A. Amirimehr, *Desalination*, **284**, 191 (2012).
13. T. Fujii, M. Yamashita, S. Fujimori, Y. Saitoh, T. Nakamura, K. Kobayashi and J. Takada, *J. Magn. Magn. Mater.*, **310**, e555 (2007).
14. A. T. Raghavender, N. H. Hong, K. J. Lee, M. H. Jung, Z. Skoko, M. Vasilevskiy, M. F. Cerqueira and A. P. Samantilleke, *J. Magn. Magn. Mater.*, **331**, 129 (2013).
15. P. Xu, G. M. Zeng, D. L. Huang, C. L. Feng, S. Hu, M. H. Zhao, C. Lai, Z. Wei, C. Huang, G. X. Xie and Z. F. Liu, *Science of the Total Environment*, **424**, 1 (2012).
16. E. Mark, *J. Polymer Data Handbook*, Oxford University Press Inc., New York (1999).
17. C. A. Harper, *Handbook of plastic and elastomers*, New York, McGraw-Hill (1975).
18. X. Li, Z. Wang, H. Lu, C. Zhao, H. Na and C. Zhao, *J. Membr. Sci.*, **254**, 147 (2005).
19. R. K. Nagarale, G. S. Gohil, V. K. Shahi and R. Rangarajan, *Colloids Surf. A*, **251**, 133 (2004).
20. R. K. Nagarale, V. K. Shahi, S. K. Thampy and R. Rangarajan, *React. Funct. Polym.*, **61**, 131 (2004).
21. R. K. Nagarale, V. K. Shahi and R. Rangarajan, *J. Membr. Sci.*, **248**, 37 (2005).
22. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 87<sup>th</sup> Ed. Boca Raton, CRC Press (2006).
23. M. S. Kang, Y. J. Choi, I. J. Choi, T. H. Yoon and S. H. Moon, *J. Membr. Sci.*, **216**, 39 (2003).
24. V. K. Shahi, G. S. Trivedi, S. K. Thampy and R. Rangarajan, *J. Colloid Interface Sci.*, **262**, 566 (2003).
25. J. Kerres, W. Cui, R. Disson and W. Neubrand, *J. Membr. Sci.*, **139**, 211 (1998).
26. Y. Tanaka, *Ion exchange membranes: Fundamentals and applications*, Netherlands: Membrane Science and Technology Series Elsevier (2007).
27. T. Sata, *Ion exchange membranes: Preparation, characterization, modification and application*, Cambridge/United Kingdom: The Royal Society of Chemistry (2004).
28. J. Schauer and L. Brozova, *J. Membr. Sci.*, **250**, 151 (2005).
29. C. E. Powell and G. G. Qiao, *J. Membr. Sci.*, **279**, 1 (2006).
30. P. Dlugolecki, K. Nijmeijer, S. Metz and M. Wessling, *J. Membr. Sci.*, **319**, 214 (2008).