Mixed matrix heterogeneous cation exchange membrane filled with clay nanoparticles: membranes' fabrication and characterization in desalination process

S. M. Hosseini, A. Seidypoor, M. Nemati, S. S. Madaeni, F. Parvizian and E. Salehi

ABSTRACT

In this research mixed matrix PVC based-co-clay nanoparticles heterogeneous cation exchange membranes were prepared by solution casting technique. The effect of clay nanoparticles concentration in the casting solution on membrane electrochemical properties was studied. Scanning optical microscopy (SOM) images showed uniform particles distribution and relatively uniform surfaces for the prepared membranes. The membrane water content was improved initially by an increase of additive content ratio up to 1%wt in casting solution and then it began to decrease by more additive concentration. Moreover, swelling was measured less than 5% in thickness and negligible in length and width for the prepared membranes. Membrane potential, transport number and permselectivity were improved by increase of nanoparticles loading ratio. Utilizing Cloisite nanoparticles up to 1%wt in the casting solution also led to an increase in permeability and flux for prepared membranes. The ionic permeability and flux were decreased again by a further increase in additive concentration from 1 to 4%wt. Also, membranes exhibited lower permeability and flux for bivalent ions in comparison with monovalent type. The membrane E-conductivity and mechanical strength was enhanced by an increase of nanoparticles concentration in membrane matrix. The modified membrane containing 1% wt clay nanoparticles showed more suitable electrochemical properties compared to others.

Key words | clay nanoparticles, desalination/water treatment, fabrication/electrochemical characterization, ion exchange membrane, mixed matrix

S. M. Hosseini (corresponding author)
A. Seidypoor
M. Nemati
F. Parvizian
E. Salehi
Department of Chemical Engineering, Faculty of Engineering,
Arak University,
Arak 38156-8-8349,
Iran
E-mail: sayedmohsen_hosseini@yahoo.com

S. S. Madaeni
Membrane Research Centre, Department of Chemical Engineering, Faculty of Engineering,
Razi University,
Kermanshah 67149,
Iran

INTRODUCTION

Nowadays, membrane technology has obtained much attention in diverse industries and human life. Among this, ion exchange membranes (IEMs) have been utilized 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 (Xu 2005; Kariduraganavar *et al.* 2006; Nagarale *et al.* 2006; Hosseini *et al.* 2014; Zarrinkhameh *et al.* 2014). In IEMs, charged groups attached to polymer backbone are freely permeable to opposite sign ions under an electrical field influence (Baker 2004). In such processes, ion interactions with membrane, water, and with each other occur in complex fashions. Knowledge of the electro kinetic properties of ion exchange membranes is a major contributing factor behind decisions about their applicability in specific separation processes and energy storage devices (Gohil *et al.* 2006; Dlugolecki *et al.* 2010; Hosseini *et al.* 2014).

Preparing ion exchange membranes with special physico/chemical characteristics may be a vital step in future applications (Kariduraganavar *et al.* 2006; Hosseini *et al.* 2014). Considerable research has already been carried out to improve the IEM 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 important techniques to obtain superior IEMs (Fathizadeh *et al.* 2011; Hosseini *et al.* 2013, 2014; Zendehnam *et al.* 2013; Zarrinkhameh *et al.* 2014).

Utilizing inorganic particles or fillers, especially nanomaterials, into polymeric matrixes has been examined in many applications to enhance the physico/chemical characteristics and separation properties based on the synergism between the organic-inorganic components (Xu 2005; Hosseini *et al.* 2014). Clay nanoparticle (NP) is well known as an inorganic material with very interesting features and capacity, such as high adsorption capacity, ion exchange property, low cost, stable property and safety toward the environment, which has been utilized in membrane fabrication (Lin *et al.* 2009; Ghaemi *et al.* 2011; Daraei *et al.* 2013; Rajabi *et al.* 2014).

Preparing heterogeneous cation exchange membranes with specially adapted physico/chemical properties for application in electrodialysis processes related to water recovery and water treatment was the primary target of the current research. For the purpose, mixed matrix polyvinylchloride-co-clay nanoparticles heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as the functional group's agent and tetrahydrofuran as the solvent. PVC is a flexible and durable polymer with suitable biological and chemical resistance (Harper 1975; Mark 1999). Clay nanoparticles were also employed as inorganic filler additive in membrane fabrication.

Currently no reports have considered incorporating clay nanoparticles into ion exchange membranes and the literature is silent on characteristics and functionality of electrodialysis IEMs.

The effect of used additives' concentration in the casting solution on membrane electrochemical properties was studied. During the experiments, sodium and barium chloride were employed as ionic solutions for membrane characterization. The results are valuable for electro-membrane processes, especially the electrodialysis process for water recovery and water treatment.

MATERIALS AND METHODS

Materials

Polyvinylchloride (PVC, grade 7054, Density: 490 g/L) supplied by BIPC Company, Iran, was used as binder. Tetrahydrofuran (THF, Merck Inc., Germany) was employed as solvent. Clay nanoparticle (Cloisite®15A, organically modified montmorillonite clay, quaternary ammonium compounds, bis (hydrogenated Tallow Alkyl) dimethyl, salt with bentonite, specific gravity 1.4–1.8, Southern Clay Products Inc., USA) was used as inorganic filler additive. 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/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.

Preparation of cation exchange membranes

In order to undertake preparation of the membranes, resin particles were dried in an oven at 30 °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 (polymer binder (PVC): solvent (THF)) (w/v), (1: 20)) in a glass reactor equipped with a mechanical stirrer for more than 5 h. This was followed by dispersing a specific quantity of ground resin particle ((resin particle: polymer binder) (w/w), (1:1)) as functional groups agents and clay nanoparticles (S_1: 0.0, S_2: 0.5, S_3: 1.0, S_4: 2.0 and S_5: 4.0%wt) as additive in polymeric solution, respectively. The mixture was mixed vigorously at room temperature to obtain 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 using ultrasonic instrument. Excessive homogeneity and uniform distribution of particles (resin, additive) in the membrane matrix provide superior conducting regions for the membranes and generate easy flow channels for counter-ions transportation. The presence of more conducting region on the membrane surface can also strengthen the intensity of the uniform electrical field around the membrane and decreases the polarization phenomenon (Kang et al. 2003). 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's conformation with particle surfaces and improves the membrane selectivity (Powell & Qiao 2006). 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 °C. The membranes were dried at ambient temperature and immersed in distilled water. In the final stage, membranes were pretreated by immersing in NaCl solution. The membrane thickness was measured by a digital caliper device around 60–70 μm. A summary of the membrane preparation procedure is given in Table 1.

Test cell

The membranes' electrochemical properties measurements were carried out using the test cell (Figure 1). The cell consists of two cylindrical compartments made of Pyrex glass which are separated by a membrane. One side of each vessel was closed by Pt electrode supported with Teflon
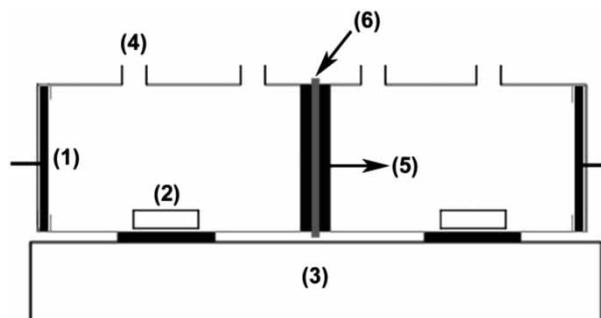
Table 1 | Flow sheet of membrane preparation procedure

The procedure for IEM preparation

Step 1	Resin particles drying (at 30 °C for 48 h)
Step 2	Resin particles pulverizing (−325 +400 mesh)
Step 3	Polymer dissolving into solvent (for 5 h)
Step 4	Resin particles and additive dispersing in polymeric solution
Step 5	Sonication of polymeric solution (for 1 h)
Step 6	Mixing of polymeric solution (for another 30 min)
Step 7	Casting (at 25 °C)
Step 8	Film drying (at 25 °C for 30 min) and immersing in water
Step 9	Membranes pretreatment by HCl and NaCl solutions

Figure 1 | Schematic diagram of test cell: (1) Pt electrode, (2) magnetic bar, (3) stirrer, (4) orifice, (5) rubber ring, (6) membrane.

and the other side was equipped with membrane. The membrane area was 19.63 cm².

Membrane characterization

Morphological studies

The behavior of prepared membranes is closely related to their structure, especially the spatial distribution of the ionic site (Li et al. 2005). 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 for scanning purposes.

Water content

The water content was measured as the weight difference between the dried and swollen membranes. The wet membrane was weighed (OHAUS, Pioneer™, Readability: 10^{-4} gr, OHAUS Corp.) and then dried in an oven until constant weight was obtained. The following equation (Sata 2004; Li et al. 2005; Tanaka 2007) can be used in water content calculations:

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

Ion exchange capacity (IEC)

The IEC determination was performed using the titration method. For the IEC measurements, the membranes in acid form (H^+) were converted to Na^+ form by immersing

in 1 M NaCl solution to liberate the H^+ ions. The H^+ ions in solution were then titrated with 0.01 M NaOH and phenolphthalein indicator. The IEC can be calculated from the following equation (Sata 2004; Li et al. 2005; Kariduraganavar et al. 2006; Tanaka 2007):

$$IEC = \left(\frac{a}{W_{dry}}\right) \tag{2}$$

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

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 (Nagarale et al. 2004a, 2004b). This parameter was evaluated for the equilibrated membrane with unequal concentrations ($C_1 = 0.1$ M/$C_2 = 0.01$ M) of electrolyte solution at ambient temperature on either side of the 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 electrodes (through KCl bridges) and a digital auto multi-meter (DEC, Model: DEC 330FC, Digital Multimeter, China). The measurement was repeated until a constant value was obtained. Membrane potential ($E_{Measure}$) is expressed using the Nernst equation (Nagarale et al. 2004a; Gohil et al. 2006; Zarrinkhameh et al. 2014) as follows:

$$E_{Measure} = \left(2t_i^m - 1\right)\left(\frac{RT}{nF}\right)\ln\left(\frac{a_1}{a_2}\right) \tag{3}$$

where t_i^m is the 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 is also quantitatively expressed based on the migration of counter-ions through the IEMs (Shahi et al. 2003; Nagarale et al. 2004b, 2005; Gohil et al. 2006):

$$P_s = \frac{t_i^m - t_0}{1 - t_0} \tag{4}$$

where t_0 is the transport number of counter-ions in solution (Lide 2006).

Ionic permeability and flux

The ionic permeability and flux were measured using the test cell. A 0.1 M solution (NaCl/ $BaCl_2$) 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 the cathodic section and increase the pH of this region:

$$2H_2O + 2e^- \Rightarrow H_2\uparrow +2OH^- \quad \text{(Cathodic reaction)}$$

$$2Cl^- \Rightarrow Cl_2\uparrow + 2e^- \quad \text{(Anodic reaction)}$$
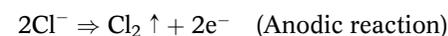
According to Fick's law, ionic flux through the membrane can be expressed as follows (Kerres et al. 1998; Li et al. 2005; Zarrinkhameh et al. 2014):

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

where P is ionic permeability (coefficient diffusion) of ions, d is membrane thickness, N is ionic flux, A is the membrane surface area, V_0 is the volume of each compartment in the used test cell and C is the cations concentration in the compartments.

The boundary conditions were as follows:

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

Therefore:

$$\int_{C_2{}^0=0.01}^{C_2} -\frac{d(C_1{}^0 + C_2{}^0 - C_2)}{(C_1{}^0 + C_2{}^0 - C_2 - C_2)} = \int_0^t P \frac{A}{V_0 d} \times dt$$

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

The ionic permeability (P) in membrane phase is calculated from Equation (7) considering pH changes in cathodic section (Digital pH-meter, Jenway, Model: 3510).

Electrical resistance

The electrical resistance of equilibrated membrane was measured in NaCl solution with a concentration of 0.5 M (at 25 °C). Measurement was carried out by an alternating current bridge with 1,500 Hz frequency. The membrane resistance is calculated using the different resistance between the cell (R_1) and electrolyte solution (R_2) ($R_m = R_1 - R_2$) (Sata 2004; Tanaka 2007). The areal resistance was expressed as follows:

$$r = (R_m A) \qquad (8)$$

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

Mechanical property

The tear resistance as a mechanical property of prepared membranes was tested according to ASTM1922-03. Before undertaking the tests, all samples were cut into standard shapes in ambient conditions. Three samples were used in each test and the average values were reported.

RESULTS AND DISCUSSION

Morphological studies

Scanning optical microscopy studies have been carried out to evaluate the condition of the resin particles (ionic sites) and nanoparticle spatial distribution in the membrane matrix.

The membranes SOM images in transmission mode with light going through them are depicted in Figures 2 and 3. The polymer binder and ion exchange resin particles are clearly seen in the images. The used particles are observed as dark spots. As shown, dark regions are increased by an increase of additive loading. Images show a relatively uniform surface for the membranes. Also, particles (resin and clay) are uniformly distributed in the prepared membranes. The excessive homogeneity and uniform distribution of functional groups/clay NPs on the surface and in the bulk of membrane matrix provide superior conducting regions and generate easy flow channels for the transportation of counter-ions. The presence of more conducting regions on the membrane surface also strengthens the intensity of uniform electrical field around the membrane and decreases the concentration polarization phenomenon (Kang *et al.* 2003). Moreover, uniform distribution of particles increases the viscosity of casting solution (Powell & Qiao 2006) which reduces the evaporation rate of casting solvent. This improves the relaxation of polymer chains as well as its conformation with particles surfaces (Powell & Qiao 2006; Hosseini *et al.* 2014) which decreases the amount of cracks and fissures between binder and particles in the matrix of the membrane and improves the membrane selectivity.

Water content and ion exchange capacity

The results obtained (Figure 4) revealed that the increases of clay nanoparticles concentration up to 1%wt in the casting solution initially led to a slight increase in water content in prepared membranes. This is due to the hydrophilic characteristic of Cloisite nanoparticles which produces a more hydrophilic membrane by an increase of additive percentage in the casting solution and increases the amount of absorbed water in the membranes.

The membrane water content was decreased again by a further increase in additive concentration from 1 to 4%wt. This may be attributed to filling of voids and cavities by the clay nanoparticles at high additive concentration which occupy the free spaces in membrane matrix and reduces the amount of water molecules' accommodation. In fact, free spaces in the membrane matrix are surrounded by the nanoparticles and so decline water accommodation. The suitable amount of membrane water content can have
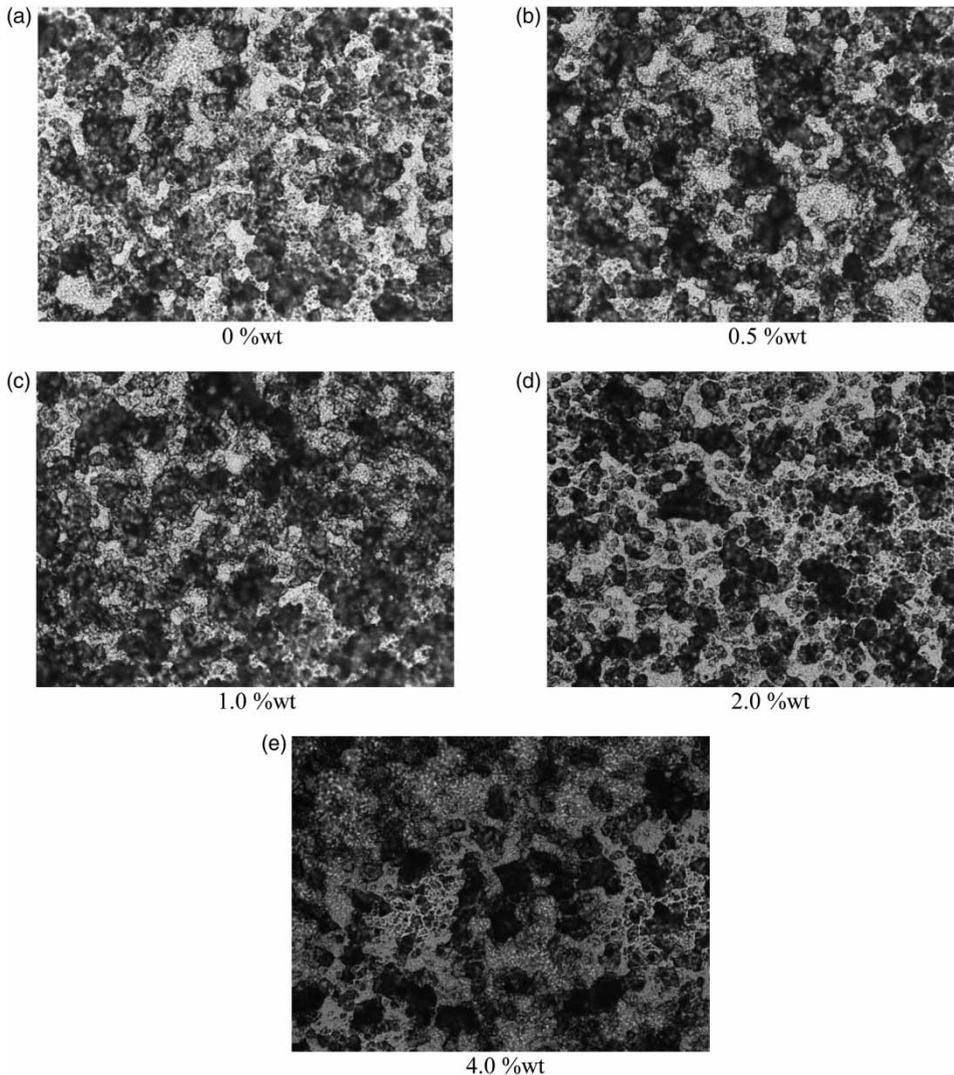
Figure 2 | The SOM images (10×magnifications) of prepared membranes with various ratios of clay nanoparticles content: (a) 0.0%wt; (b) 0.5%wt; (c) 1.0%wt; (d) 2.0%wt; (e) 4.0%wt.

better control on the pathways of ion traffic and improve the membrane selectivity. Additionally, high water content can provide more and wider transfer channels for co- and counter-ion transportation and decrease the selectivity and also lead to a loose structure for the membranes. However, this is not always true and depends on the membrane structure and its properties. The measurements were carried out three times for each sample and then their average value was reported in order to minimize experimental errors.

IEC results (Figure 4) indicated that utilizing clay nanoparticles concentration up to 1%wt in the casting solution initially led to an improvement in ion exchange capacity in prepared membranes. This may be due to the adsorption characteristic of Cloisite nanoparticles which makes superior interaction between the ions and the membrane surface. This facilitates the ions transportation between the solution and membrane phase and improves membrane ion exchange possibilities. The membrane ion exchange capacity was declined again by a further increase in additive concentration. This is because of the decrease in accessibility of resin particles in membrane matrix at a high additive content ratio which isolates the resin particles and reduces the accessibility of ion exchange functional groups by their surroundings.
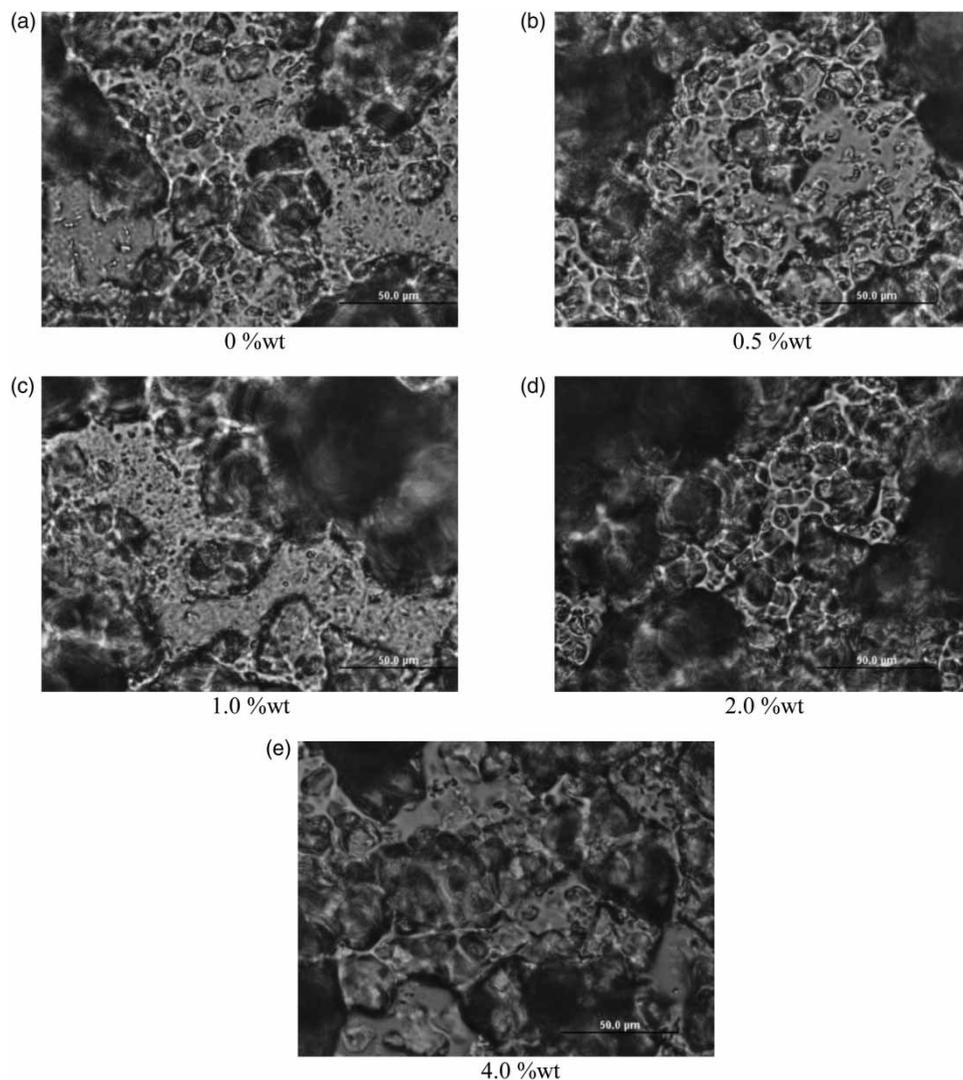
Figure 3 | The SOM images (100× magnifications) of home-made membranes with different concentration of clay nanoparticles: (a) 0.0%wt; (b) 0.5%wt; (c) 1.0%wt; (d) 2.0%wt; (e) 4.0%wt.

Membrane potential, permselectivity and transport number

It was found that membrane potential, transport number and permselectivity (Figures 5 and 6) were all improved in sodium chloride ionic solution by using clay nanoparticles in the membrane matrix. This is attributed to the adsorptive characteristic and ionic transport property of clay nanoparticles. Moreover, filling of the pathways by the nanoparticles narrows the ionic channels in the membrane matrix and improves the ionic site dominations on ions traffic. The high surface area to volume ratios of nanoparticles was also favorable for diffusion of counter-ions from solution onto the active sites of particles surface in the membrane matrix which makes superior interaction between the ions and membrane surface. This improves the Donnan exclusion that is responsible for the increment of membrane potential, transport number and selectivity (Nagarale *et al.* 2004b; Gohil *et al.* 2006).

Ionic permeability and flux

During the experiment, ions pass through the membrane and reach the concentrated section. According to anodic
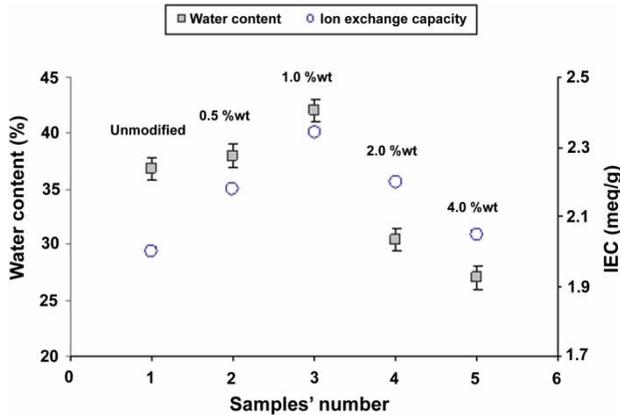
Figure 4 │ The effect of clay nanoparticles concentration on water content and ion exchange capacity of prepared mixed matrix heterogeneous cation exchange membranes.
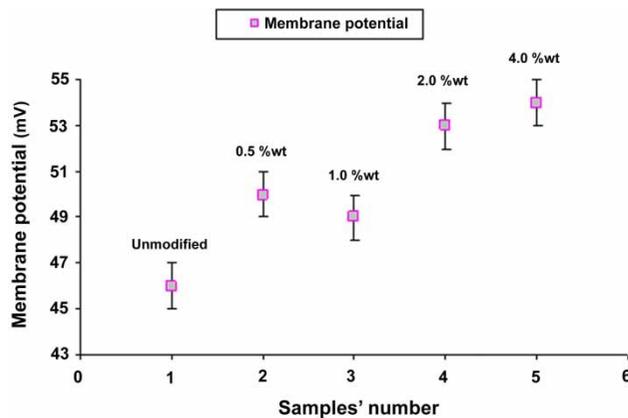

Figure 5 │ The effect of clay nanoparticles concentration on membrane potential of prepared mixed matrix ion exchange membranes.
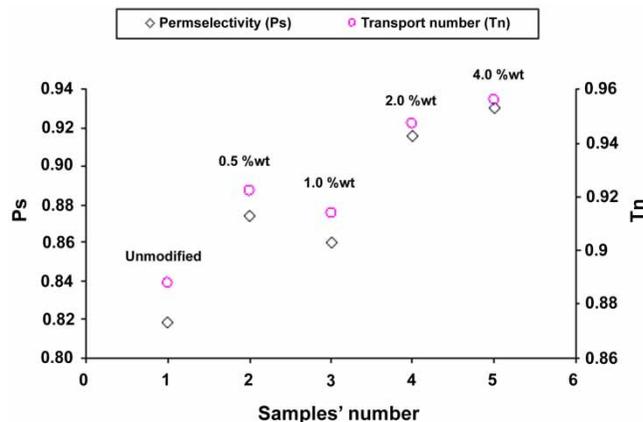

Figure 6 │ Comparison between the transport number and permselectivity of prepared membranes; unmodified membrane and composite membranes containing Cloisite.

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 Figure 7, utilizing clay nanoparticles in the casting solution up to 1%wt led to a sharp increase in ionic permeability and flux for sodium ions. This may be because of adsorptive characteristics and ionic transport properties of clay nanoparticles which in turn facilitates the ions transportation between the solution and membrane phase and increases the ionic permeability and flux. Also, an increase of membrane water content and IEC enhances the ionic flux.

The ionic permeability and flux were decreased again by a further increase in additive concentration from 1 to 4%wt in the prepared membranes. This may be due to the formation of narrow ionic transfer channels in the membrane matrix by the additive particles and the low amount of membrane water content and IEC for the prepared membrane which makes the ions transportation through the membrane difficult and so declines the ionic permeability and flux. The voids and cavities (free spaces) occupied by the nanoparticles in the membrane matrix also limits the pathways and restricts the transportation.

The barium flux for the unmodified membrane and modified membrane containing 1.0%wt NPs is also shown in Figure 8. A similar trend was found for bi-valent ions. The membranes exhibited lower flux for bivalent ions in comparison with monovalent type. This difference can be explained with respect to the stronger bonds of bivalent cations with
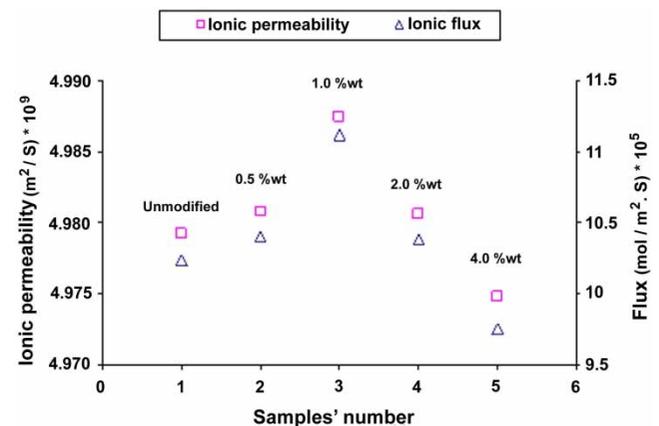

Figure 7 │ The ionic/sodium permeability and flux of prepared mixed matrix heterogeneous cation exchange membranes with various ratios of clay nanoparticles.
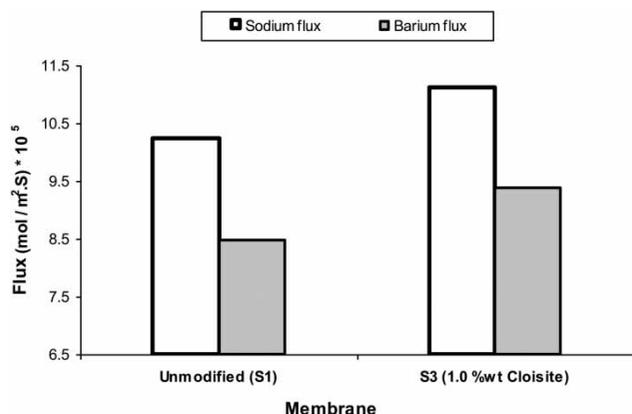
Figure 8 │ Comparison between the flux of prepared membranes in monovalent (Na$^+$) and bivalent (Ba^{2+}) ionic solution; unmodified membrane and modified membranes containing 1%wt Cloisite nanoparticles.

adsorptive characteristic/ionic properties of clay nanoparticles which in turn facilitates the ions transportation through the membrane and increases membrane electrical conductivity. Moreover, an increase of membrane water content and ion exchange capacity by utilizing clay nanoparticles up to 1%wt facilitates the ions transportation through the membrane matrix and improves the membrane electrical conductivity.

A comparison between the selectivity and areal electrical resistance of prepared membranes in this study and some commercial membranes is given in Table 2.

ion exchange functional groups (Nagarale *et al.* 2004a) which poison the membranes. 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 make lower flux for the bivalent cation (Nagarale *et al.* 2004a; Tanaka 2007).

Electrical resistance

The membrane areal electrical resistance (Figure 9) was declined by an increase of clay nanoparticles concentration in the casting solution. This may be due to
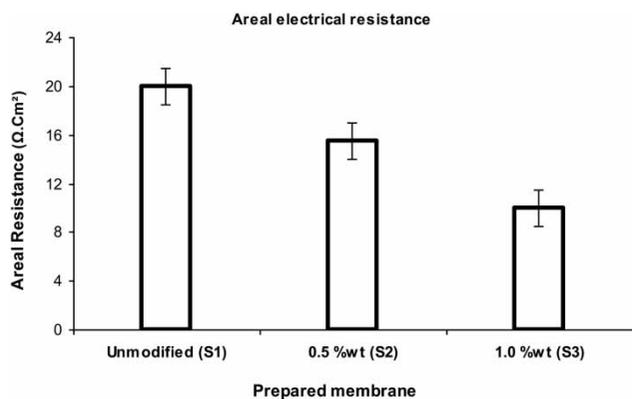
Mechanical property and dimensional stability

During the preparation process, the loss of molecules solvent introduces cavities and voids between the particles and polymer binder region due to evaporation. These micro-voids are sufficient to accommodate the solvent molecules for the solvation. Therefore, solvation did not change membranes dimensions manifestly. The amount of swelling in prepared membranes was less than 5% in thickness. Also, their swelling was negligible in length and width.

Obtained results (Figure 10) also revealed that the membrane mechanical strength improved by an increase of NPs content ratio which is due to the presence of strong interfacial bonding between the polymers and nanoparticles (Cadek *et al.* 2002; Kim *et al.* 2007).

Figure 9 │ The areal electrical resistance of prepared membranes: unmodified membrane and modified membranes containing clay nanoparticles.

Table 2 │ Comparison between the electrochemical properties of prepared membranes in this research and some commercial membranes (Xu 2005; Nagarale *et al.* 2006; Dlugolecki *et al.* 2008)

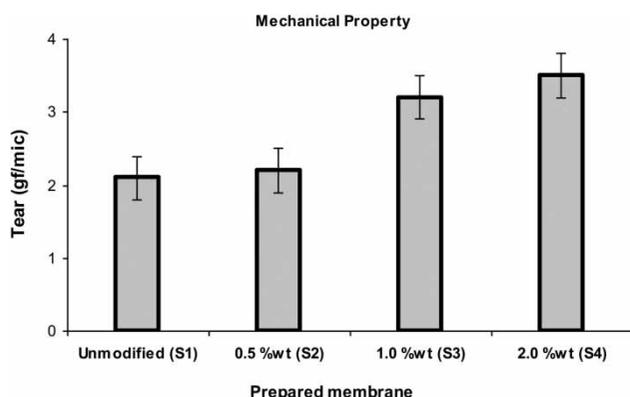| Membrane	Permselectivity[a] (%)	Electrical resistance[a] (Ω cm^2)
Modified membrane (S1-1.0%wt NPs)	>89	< 10
RAI Research Corp., USA R-5010-H	95	8–12
FuMA-Tech GmbH, Germany FKB	–	5–10
Ralex® CMH-PES	>92	<10
CSMCRI, India (HGC)	87	4–6
Neosepta® CMX	>96	1.8–3.8

Figure 10 | The effect of clay nanoparticles loading ratio on mechanical property of prepared membranes.

CONCLUSIONS

SOM images showed a relatively uniform surface for the membranes. Also, particles are uniformly distributed in the prepared membranes. It was found that membrane water content was increased initially by using clay nanoparticles up to 1%wt in the casting solution and then began to decrease by a further increase in additive concentration from 1 to 4%wt which is in contrast with the hydrophilic characteristic of Cloisite. Moreover, the amount of swelling in prepared membranes was less than 5% in thickness and negligible in length and width. It was found that membrane potential, transport number and permselectivity were all improved in sodium chloride ionic solution by using clay nanoparticles in the casting solution. Utilizing clay nanoparticles in the casting solution up to 1%wt also led to a sharp increase in sodium permeability and flux in prepared membranes. Results revealed that sodium permeability and flux were decreased again by a further increase in additive concentration from 1 to 4%wt. Also, membranes exhibited lower permeability and flux for bivalent ions in comparison with monovalent ones. The membrane areal electrical resistance was decreased by an increase of clay nanoparticles concentration in the casting solution. The opposite trend was found for the membrane mechanical property. Also, the amount of swelling in prepared membranes was less than 5% in thickness. Their swelling was also negligible with respect to length and width measurements. Among the prepared membranes, modified membrane containing 1%wt clay

nanoparticles showed more suitable electrochemical properties compared to others. The obtained results are valuable for electro-membrane processes, especially electrodialysis for water recovery and treatment.

REFERENCES

Baker, R. W. 2004 *Membrane Technology and Applications*, 2nd edn. John Wiley & Sons Ltd, UK.

Cadek, M., Coleman, J. N., Barron, V., Hedicke, K. & Blau, W. J. 2002 Morphological and mechanical properties of carbon-nanotube-reinforced semicrystalline and amorphous polymer composites. *App. Phys. Lett.* **81**, 5123–5126.

Daraei, P., Madaeni, S. S., Salehi, E., Ghaemi, N., Ghari, H. S., Khadivi, M. A. & Rostami, E. 2013 Novel thin film composite membrane fabricated by mixed matrix nanoclay/chitosan on PVDF micro filtration support: preparation, characterization and performance in dye removal. *J. Memb. Sci.* **436**, 97–108.

Długolecki, P., Nymeijer, K., Metz, S. & Wessling, M. 2008 Current status of ion exchange membranes for power generation from salinity gradients. *J. Memb. Sci.* **319**, 214–222.

Dlugolecki, P., Anet, B., Metz, S. J., Nijmeijer, K. & Wessling, M. 2010 Transport limitations in ion exchange membranes at low salt concentrations. *J. Memb. Sci.* **346**, 163–171.

Fathizadeh, M., Aroujalian, A. & Raisi, A. 2011 Effect of added NaX nano-zeolite into polyamide as a top thin layer of membrane on water flux and salt rejection in a reverse osmosis process. *J. Memb. Sci.* **375**, 88–95.

Ghaemi, N., Madaeni, S. S., Alizadeh, A., Rajabi, H. & Daraei, P. 2011 Preparation, characterization and performance of polyethersulfone/organically modified montmorillonite nanocomposite membranes in removal of pesticides. *J. Memb. Sci.* **382**, 135–147.

Gohil, G. S., Binsu, V. V. & Shahi, V. K. 2006 Preparation and characterization of mono-valent ion selective polypyrrole composite ion-exchange membranes. *J. Memb. Sci.* **280**, 210–218.

Harper, C. A. 1975 *Handbook of Plastic and Elastomers*. McGraw-Hill, New York.

Hosseini, S. M., Madaeni, S. S., Zendehnam, A., Moghadassi, A. R., Khodabakhshi, A. R. & Sanaeepur, H. 2013 Preparation and characterization of PVC based heterogeneous ion exchange membrane coated with Ag nanoparticles by (thermal-plasma) treatment assisted surface modification. *J. Ind. Eng. Chem.* **19**, 854–862.

Hosseini, S. M., Gholami, A., Koranian, P., Nemati, M., Madaeni, S. S. & Moghadassi, A. R. 2014 Electrochemical characterization of mixed matrix heterogeneous cation exchange membrane modified by aluminum oxide nanoparticles: mono/bivalent ionic transportation. *J. Taiwan Inst. Chem. Eng.* **45** (4), 1241–1248.

Kang, M. S., Choi, Y. J., Choi, I. J., Yoon, T. H. & Moon, S. H. 2003 Electrochemical characterization of sulfonated poly (arylene ether sulphone) (S-PES) cation-exchange membranes. *J. Memb. Sci.* **216**, 39–53.

Kariduraganavar, M. Y., Nagarale, R. K., Kittur, A. A. & Kulkarni, S. S. 2006 Ion-exchange membranes: preparative methods for electro-dialysis and fuel cell application. *Desalination* **197**, 225–246.

Kerres, J., Cui, W., Disson, R. & Neubrand, W. 1998 Development and characterization of crosslinked ionomer membranes based upon sulfinated and sulfonated PSU crosslinked PSU blend membranes by disproportionation of sulfinic acid groups. *J. Memb. Sci.* **139**, 211–225.

Kim, S., Chen, L., Johnson, J. K. & Marand, E. 2007 Polysulfone and functionalized carbon nanotube mixed matrix membranes for gas separation: theory and experiment. *J. Memb. Sci.* **294**, 147–158.

Li, X., Wang, Z., Lu, H., Zhao, C., Na, H. & Zhao, C. 2005 Electrochemical properties of sulfonated PEEK used for ion exchange membranes. *J. Memb. Sci.* **254**, 147–155.

Lide, D. R. 2006 *CRC Handbook of Chemistry and Physics*, 87th edn. CRC Press, Boca Raton, USA.

Lin, R. Y., Chen, B. S., Chen, G. L., Wu, J. Y., Chiu, H. C. & Suen, S. Y. 2009 Preparation of porous PMMA/Na^+-montmorillonite cation-exchange membranes for cationic dye adsorption. *J. Memb. Sci.* **326**, 117–129.

Mark, J. E. 1999 *Polymer Data Handbook*. Oxford University Press Inc., New York.

Nagarale, R. K., Gohil, G. S., Shahi, V. K. & Rangarajan, R. 2004a Preparation and electrochemical characterization of cation-exchange membranes with different functional groups. *Colloids Surf. A* **251**, 133–140.

Nagarale, R. K., Shahi, V. K., Thampy, S. K. & Rangarajan, R. 2004b Studies on electrochemical characterization of polycarbonate and polysulfone based heterogeneous cation-exchange membranes. *React. Funct. Polym.* **61**, 131–138.

Nagarale, R. K., Shahi, V. K. & Rangarajan, R. 2005 Preparation of polyvinyl alcohol-silica hybrid heterogeneous anion-exchange membranes by sol-gel method and their characterization. *J. Memb. Sci.* **248**, 37–44.

Nagarale, R. K., Gohil, G. S. & Shahi, V. K. 2006 Recent developments on ion-exchange membranes and electro-membrane processes. *Adv. Colloid Interface Sci.* **119**, 97–130.

Powell, C. E. & Qiao, G. G. 2006 Polymeric CO_2/N_2 gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J. Memb. Sci.* **279**, 1–49.

Rajabi, H., Ghaemi, N., Madaeni, S. S., Daraei, P., Khadivi, M. A. & Falsafi, M. 2014 Nanoclay embedded mixed matrix PVDF nanocomposite membrane: preparation, characterization and biofouling resistance. *App. Sur. Sci.* **313**, 207–214.

Sata, T. 2004 *Ion Exchange Membranes: Preparation, Characterization, Modification and Application*. The Royal Society of Chemistry, Cambridge, UK.

Shahi, V. K., Trivedi, G. S., Thampy, S. K. & Rangarajan, R. 2003 Studies on the electrochemical and permeation characteristic of asymmetric charged porous membranes. *J. Colloid Interface Sci.* **262**, 566–573.

Tanaka, Y. 2007 *Ion Exchange Membranes: Fundamentals and Applications*. Membrane Science and Technology Series. Elsevier, The Netherlands.

Xu, T. 2005 Ion exchange membrane: state of their development and perspective. *J. Memb. Sci.* **263**, 1–29.

Zarrinkhameh, M., Zendehnam, A. & Hosseini, S. M. 2014 Preparation and characterization of nanocomposite heterogeneous cation exchange membranes modified by silver nanoparticles. *Korean J. Chem. Eng.* **31** (7), 1187–1193.

Zendehnam, A., Arabzadegan, M., Hosseini, S. M., Robatmili, N. & Madaeni, S. S. 2013 Fabrication and modification of polyvinylchloride based heterogeneous cation exchange membranes by simultaneous using Fe-Ni oxide nanoparticles and Ag nanolayer: physico-chemical and antibacterial characteristics. *Korean J. Chem. Eng.* **30** (6), 1265–1271.