Preparation and Characterization of ABS/HIPS Heterogeneous Anion Exchange Membrane Filled with Activated Carbon

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ABSTRACT: Acrylonitrile-butadiene-styrene (ABS)/high impact polystyrene (HIPS) blend heterogeneous anion exchange membranes were prepared by phase inversion method using tetrahydrofuran as solvent and anion exchange resin powder as functional group agent. Activated carbon was selected as inorganic filler additive. The additive concentration effect on properties of the prepared membranes was studied. Ultrasonic method was used to help appropriate dispersion of particles in the membrane's matrix. Scanning optical microscopy showed that sonication has a significant influence on distribution of resin particles in the membrane matrix and makes it possible to form more uniform phase. Moreover, images showed a relatively uniform surface for membranes. The increase of activated carbon concentration in casting solution led to a decline in membrane water content. The ion exchange capacity, membrane potential, permselectivity, transport number, ion permeability, ionic flux, and current efficiency of prepared membranes all were increased initially by the increase in additive concentration up to 1% wt and then they showed decrease trend with higher increase in additive concentration from 1 to 4% wt. Conversely, the electrical resistance and energy consumption showed opposite trends. In addition, with more additive loading, the oxidative stability of membranes was slightly decreased and their thermal stability was increased. Membrane with 1% wt additive loading exhibited higher efficiency and electrochemical properties in comparison with other prepared membranes in this research. Furthermore, prepared membranes exhibited suitable electrochemical properties compared to a commercial heterogeneous anion exchange membrane with the same experimental conditions. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3371–3383, 2010

Key words: heterogeneous anion exchange membrane; activated carbon; preparation; characterization; commercial membrane

INTRODUCTION

Nowadays, ion exchange membranes (IEMs) are widely utilized as active separators in diverse electrically driven processes such as electro-dialysis for desalting brackish waters, reconcentrating brine from seawater and production of table salt. They are also efficient tools in recovery of valuable metals from effluents industries and food and pharmacy processing as well as manufacturing basic chemical products. Moreover, the IEM play some important part in environmental protection, treating industrial, and biological effluents and many more processes.[1–10] In IEMs, the charged groups attached to polymer backbone are freely permeable to opposite sign ions under the influence of electrical field.[11–13] In such processes, ion interactions with membrane, water, and with each other occur in complex fashion.[7,14–16]

Power generation, energy saving, resource recovery and pollution control are the main reasons enumerated for the IEMs development and application.[3,17] However, preparing inexpensive membranes with special adapted selective characteristics such as suitable ionic conductivity and ionic selectivity, moderate swelling and appropriate mechanical and chemical stabilities may be vital step in future applications.[7,9,18–20] The variation of functional groups, selection of different polymeric matrices, use of various additives, alteration of cross-link density, nature of surface layer and more uniform distribution of functional groups are important ways to obtain superior membranes in IEM filed.[2,7,21] The ion-exchange membranes, both homogenous and heterogeneous, supersede each other.[15,22] Homogenous IEM usually show good electrochemical properties but are weak in their mechanical strength, whereas heterogeneous types have acceptable mechanical property but with inadequate electrochemical properties. Early reports on heterogeneous ion-exchange membranes revealed that these membranes can be prepared by calendaring ion exchange particles into an inert plastic film or dry moulding of inert film forming polymers and ion-exchange particles and then milling the mould stock in another way by

dispersion of resin particles in polymeric solution and casting technique.[9,15,21–23]

The preparation of heterogeneous anion exchange membranes with appropriate properties for using in electro-dialysis process in water recovery and waste water treatment in industrial plants was primary target of the current research. For this purpose, acrylonitrile-butadiene-styrene (ABS)/high impact polystyrene (HIPS) blend heterogeneous anion exchange membranes were prepared through solution casting techniques using anion exchange resin powder as functional group agents and tetrahydrofuran (THF) as solvent. The application of co- and terpolymers and polymers blending in process of membrane preparation provides the necessary potentials to improve the properties of the prepared membranes. Utilizing of ABS and HIPS and their blends as membrane binders can dedicate special selective characteristics in prepared membranes with respect to superior mechanical support of glassy polymers and high permeability of flexible rubbery ones.[24–27] Also, the activated carbon was employed as inorganic filler additive in the membrane matrix. The use of activated carbon in the matrix of membrane provides a very attractive alternative capitalizing on their superior separation properties.[28] Incorporation of inorganic particles or fillers into polymeric materials has been examined in many applications such as enhancing the mechanical and thermal properties of polymer matrixes and, more recently, improving the separation properties of membranes due to the synergism between organic-inorganic components properties.[10,24,28–32] Moreover, the ultrasonic method was employed to obtain better homogeneity and uniform dispersion and distribution of particles in the membrane matrix. Excessive homogeneity and uniform distribution of resin particles, i.e. functional groups on the membrane surface and in the bulk of membrane matrix, provide superior conducting regions for the prepared membrane and improve their electrochemical properties.

The effects of activated carbon concentration in the casting solution and sonication method during the preparation process on properties of prepared membranes were studied and evaluated.

During this experiment, potassium chloride was employed as ionic solutions for the membranes characterization. Eventually, the prepared membrane was compared with a commercial heterogeneous anion-exchange membrane.

MATERIALS AND METHODS

Materials

ABS, supplied by T.P.C, Iran and Polystyrene, high impact grade (HIPS), supplied by TAiRiReX, Taiwan,

were used as binders. THF was employed as solvent. The activated carbon (powder extra pure) as inorganic filler additive and Anion exchange resin (Amberlite® IRA-402, strongly basic anion exchanger, Cl⁻ form) by Merck were used to prepare the membranes. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used. The chemical structure of used polymers binder is shown in Table I.
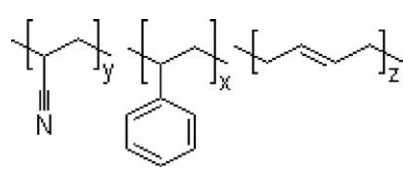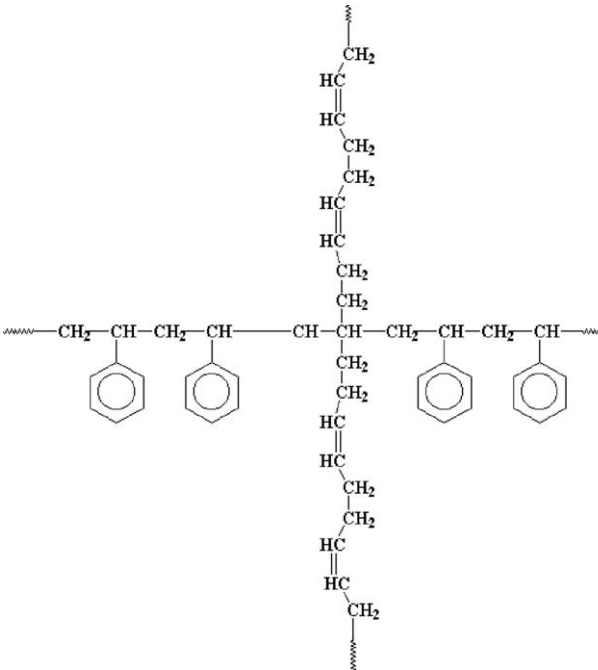
Commercial membrane

Commercial heterogeneous anion-exchange membrane (RALEX® AM), supplied by Mandressi Group Company, made by MEGA a.s., Czech Republic, was used in this study. The membrane contains quaternary ammonium as fixed groups. Polyethylene and polyester strings are employed as based binder and fabric in the membrane.

Preparation of home-made membranes

Heterogeneous anion exchange membranes were prepared by casting solution technique and phase inversion method. To membranes preparation, resin particles were dried in oven (Behdad, Model: oven 5) at 30°C for 48 h and then pulverized into fine particles in a ball mill (Pulverisette 5, Fritisch) and sieved to the desired mesh size. The ion exchange resin with desired particles size (-300 $+400$ mesh) was used in membranes preparation. The membranes were prepared by dissolving the polymers binder in THF solvent in a glass reactor equipped with a mechanical stirrer (Model: Velp Sientifica Multi 6 stirrer) for more than 5 h. This was followed by dispersing a specific quantity of grinded resin particle as functional groups agents and activated carbon as inorganic filler additive in polymeric solution respectively. The mixture was mixed vigorously at room temperature to obtain a uniform particle distribution in the polymeric solution. In addition, for the better dispersion of particles and breaking up their aggregates, the solution was sonicated for 30 min using an ultrasonic instrument (Struers Metason 200 HT, by Struers, Copenhagen/Denmark). Then mixing was undertaken for more 15 min by mechanical stirrer. The mixture was then cast onto a clean and dry glass plate at 25°C. The membranes were dried at ambient temperature (25°C) and immersed in distilled water. As the final stage, the membranes were pretreated by immersing in NaCl solutions. The membrane thickness was measured by a digital caliper device (Electronic outside Micrometer, IP54 model OLR) to maintain the membrane thickness around 80–120 μm. The composition of casting solution is depicted in Table II.

TABLE I
Chemical Structures of Polymers Used

| Polymer	Chemical structure
Acrylonitrile-butadiene-styrene (ABS)	
High impact polystyrene (HIPS)	

Test cell

The test cell used in measuring transport number, specific electrical resistance, ion diffusion and other electrochemical properties is shown in Figure 1. The cell consists of two cylindrical compartments (vessel, each 150 cm^3) made of Pyrex glass separated by the membrane. The membrane was fixed between rubber rings. One side of each vessel was closed by Pt electrode supported with a piece of Teflon (Polytetrafluoroethylene) and the other side was equipped with a piece of porous medium to support the membrane. The top of each compartment contained two orifices for feeding and sampling. To minimize the effect of boundary layer during the experiments and establishment of concentration polarization on the vicinity of membrane's surface, both sections were stirred vigorously by

TABLE II
Compositions of Casting Solution for the Preparation of Home-Made Membranes*

Membrane	Activated carbon (Additive : Total solid) (w/w)
Sample 1	0.0 : 100
Sample 2	0.5 : 100
Sample 3	1.0 : 100
Sample 4	2.0 : 100
Sample 5	4.0 : 100

* Polymer binder (ABS: HIPS) (w/w), (1:1); Solvent (THF: Binder) (v/w), (20: 1); Resin particles (Resin: Binder) (w/w), (1:1)
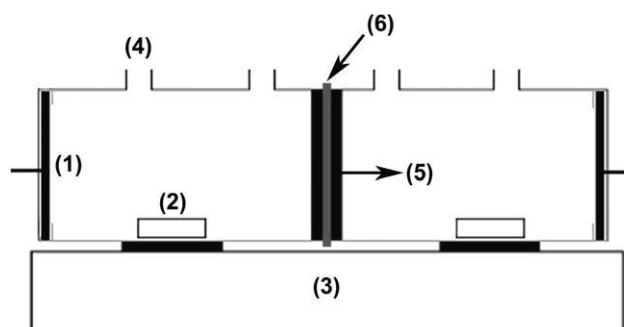
Figure 1 Schematic diagram of test cell: (1) Pt electrode, (2) Magnetic bar, (3) Stirrer, (4) Orifice, (5) Rubber ring, and (6) Membrane.

magnetic stirrers (Model: Velp Sientifica Multi 6 stirrer). The membrane area was 13.85 cm^2.

Membrane characterization

Morphological studies

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. For SOM by SOM device, the samples were cut in small pieces and after mounting between lamellas, observation was made by the optical microscope.

Water content

The water content was measured as the weight difference between the dried and swollen membranes. The membranes were immersed in distilled water for 24 h, following discharge, its surface wiped by filter paper and weighed (Mettler Toledo Group, Model: AL204). The wet membranes were dried at fixed temperature (50°C) for 4 h until constant weight was obtained known as dry-membrane. The following equation[4,19,23] can be used for water content calculation:

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

Ion exchange capacity (IEC)

The IEC determination was performed using titration method. To measure the ion exchange capacity, membranes were initially placed in 2 M NaCl solution to convert the exchange group to Cl type, and then they were washed and kept in water for 24 h. The sufficient washing time was obtained by not exhibiting white muddiness owing recognized by the reaction with AgNO$_3$. Subsequently, membranes were immersed in 2 M NaNO$_3$ solution for 24 h to liberate the Cl$^-$ ions (the Cl$^-$ ions in the membrane were replaced by NO$_3^-$ ions). The Cl$^-$ ions in the solution were then analyzed with 0.01 M AgNO$_3$ and K$_2$CrO$_4$ indicator (a meq). The IEC can be calculated from the following equation[13,23]:

$$\text{IEC} = \left(\frac{a}{W} \right) \qquad (2)$$

$$\text{F.I.C} = \left(\frac{\text{IEC}}{\text{Water content}} \right) \qquad (3)$$

Donnan equilibrium's Law

To evaluate the ions equilibrium condition in membrane matrix, the Donnan equilibrium law was con-

sidered in KCl solution. The ratio of entered counter to co ions in the membrane matrix can be used for the qualitative analysis representation of membrane's selectivity. For the purpose, membrane samples were kept in 0.5 M KCl solution.

According to the chemical potential equations and the mass conservation, the relations are established as follows[11,19]:

$$\bar{C}_{K^+} \times \bar{C}_{Cl^-} = K_0 C_{K^+} \times C_{Cl^-} \qquad (4)$$

where $\overline{C}$ is the ion concentration in membrane, C is the ion concentration in solution and K_o is the equilibrium constant. For anionic membrane:

$$\bar{C}_{Cl^-} = \bar{C}_{K^+} + (\text{F.I.C}) \qquad (5)$$

For the solution:

$$C_{K^+} = C_{Cl} = C_S \qquad (6)$$

where C_s is the concentration of KCl solution. By combining of equations:

$$(\bar{C}_{K^+} + (\text{F.I.C})) \times \bar{C}_{K^+} = K_0 C_S^2 \qquad (7)$$

$$\frac{\bar{C}_{K^+}}{\bar{C}_{Cl^-}} = K_0 \left[\frac{C_S^2}{(\bar{C}_{K^+} + (\text{F.I.C}))^2} \right] \qquad (8)$$

This quadratic equation can be used in the qualitative analysis of membrane selectivity.

Membrane potential, transport number and permselectivity

When both surfaces of an ion exchange membrane are in contact with a solution in different concentration, an electrical potential would be developed across the membrane. Magnitude of this parameter depends on the electrical characteristic of the membrane along with the nature and concentration of the electrolyte solution. The membrane potential is algebraic sum of Donnan and diffusion potentials.[17,33,34] This parameter was evaluated for the equilibrated membrane with unequal concentrations of potassium chloride (KCl) ($C_1 = 0.1$ M, $C_2 = 0.01$ M @ ambient temperature) on either side of the membrane using a two-cell glassy apparatus (shown in Fig. 1). During the experiment, both sections were stirred vigorously by magnetic stirrers to minimize the effect of boundary layers on the measurement. The developed potential difference across the membrane was measured after 10 min 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 and meanwhile the potential was measured every 1 minute until a constant value

($E_{measure}$) was obtained. The membrane potential ($E_{Measure}$) generated is expressed using Nernst equation[17,19–21,23,30,33,35] as follows:

$$E_{Measure} = (2t_i^m - 1)\left(\frac{RT}{nF}\right)\ln\left(\frac{a_1}{a_2}\right) \qquad (9)$$

where t_i^m is the transport number of counter ions in the membrane phase, R is the gases constant, T is the temperature, n is the electrovalence of counterion and a_1, a_2 are solutions electrolyte activities in contact with both surfaces determined using the Debye-Huckel limiting law. The ionic permselectivity of membranes also is quantitatively expressed based on the migration of counter-ion through the ion-exchange membrane[17,30,33,35]:

$$P_S = \frac{t_i^m - t_0}{1 - t_0} \qquad (10)$$

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

The ionic permselectivity (P_s) is a real quantitative measure of characteristic difference between counter- and co-ions permeability through the membrane.

Concentration of fixed charge on membrane's surface

Excessive homogeneity, concentration and uniform distribution of functional groups on the surface of membranes provide more conducting regions in the prepared membranes and improve their electrochemical properties. Also, the existence of greater conducting regions on the membrane surface can strengthen the intensity of uniform electrical field around the membrane and decreases the concentration polarization phenomenon.[37] The concentration of fixed charge on the membrane surface (Y) has been expressed in terms of permselectivity as follows[14,17,30]:

$$Y = \frac{2C_{Mean}P_s}{\sqrt{1 - p_s^2}} \qquad (11)$$

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

Ionic permeability and flux of ions

The ionic permeability and flux of ions measurements were carried out using the test cell (Fig. 1). A 0.1 M KCl solution was placed on one side of the cell and a 0.01 M solution on its other side. A DC electrical potential (Dazheng, DC power supply, Model: PS-302D) with an optimal constant voltage was applied across the cell with stable platinum electrodes at the end of compartments. During the experiment, the ions

are passed through the membrane to the concentration section. To ensure the equilibrium condition in two solution-membrane interfacial zones and to minimize the effect of boundary layers, both sections were stirred vigorously by magnetic stirrers.

$$2Cl^- \Rightarrow Cl_2 \uparrow + 2e^- \quad \text{(Anodic reaction)} \qquad (12)$$

$$2H_2O + 2e^- \Rightarrow H_2 \uparrow + 2OH^- \quad \text{(Cathodic reaction)} \qquad (13)$$

Chloride ions pass through the membrane to anodic section and will be converted to chlorine gas. Also, according to occurred reactions, the produced hydroxide ions increase the pH of cathodic region. The amount of produced hydroxide ions in the cathodic section is equal to the chloride ions transported through the membrane. Therefore, the permeation of ions through the membrane phase is calculated based on the variations in pH measure in cathodic compartment. The pH changes were measured using digital pH-meter (Jenway, Model: 3510). According to first Fick's law, the flux of ions through the membrane can be expressed as follows[19,20]:

$$N = -P\frac{dC}{dx} = P\frac{C_1 - C_2}{d} \qquad (14)$$

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

$$N = -\frac{V}{A} \times \frac{dC_1}{dt} = P\frac{C_1 - C_2}{d}, \quad (C_2 = C_2^0) \qquad (15)$$

where A is the membrane surface area.

$$\int_{C_1^0}^{C_1} -\frac{dC_1}{(C_1 - C_2^0)} = \int_0^t P\frac{A}{Vd} \times dt \qquad (16)$$

$$\ln\left[\frac{(C_1 - C_2^0)}{(C_1^0 - C_2^0)}\right] = -\frac{PAt}{Vd} \qquad (17)$$

$$\ln\left[1 - \frac{C_1^0 - C_1}{C_1^0 - C_2^0}\right] = -\frac{PAt}{Vd}, \quad \left(\frac{C_1^0 - C_1}{C_1^0 - C_2^0}\right) << 1 \qquad (18)$$

$$-\left(\frac{C_1^0 - C_1}{C_1^0 - C_2^0}\right) = -\frac{PAt}{Vd} \qquad (19)$$

$$C_1 = -\frac{PAt(C_1^0 - C_2^0)}{Vd} + C_1^0 \qquad (20)$$

The diffusion coefficient (P) and flux of ions (N) in the membrane phase is calculated from these equations along with variations in pH measures.

Electrical resistance

The electrical resistance is practically important due to its relation with energy consumption in the process. The resistance was measured in the test cell (Fig. 1). An equilibrated membrane was incorporated into the cell. A 0.5 M KCl solution was supplied in cell compartments at 25°C. Electrical resistance (R_1) was measured by an alternating current bridge with frequency of 1500 Hz (Audio signal generator, Electronic Afzar Azma P.J.S). In the next step, the membrane sample was discharged; the apparatus was re-integrated without membrane, and electrical resistance (R_2) was measured. The membrane resistance can be calculated using the difference between the cell and electrolyte solution resistances ($R_m = R_1 - R_2$).[21,23] The areal resistance was expressed as follows:

$$r = (R_m A) \tag{21}$$

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

Current efficiency and energy consumption

The current efficiency (C.E) was calculated using following equation[20]:

$$C.E = \frac{F \times Z_i \times \Delta n}{\int_{t=0}^{t=t} I dt} \tag{22}$$

and for the energy consumption (E):

$$E = \frac{\int_{t=0}^{t=t} I \times V \times dt}{\Delta n \times M_w} \tag{23}$$

where Z_i is the valance of ion, Δn is transport number of moles, V is voltage, F is Faraday constant, I is the current intensity and M_w is the molecular weight of ions.

Membrane oxidative stability

The prepared heterogeneous membranes were immersed into 3% H_2O_2 aqueous solution containing 4 ppm Fe^{3+} at 25°C for up to 60 h. The weights of dried samples (drying at 50°C for 4 h) before and after the experiment were compared.

Thermal properties of prepared membranes

The thermal behavior analysis of prepared membranes with various ratios of additive (activated carbon) loading was investigated by Differential scanning calorimetry (DSC) test (METLER DSC 30 instrument) in a temperature range of 20–300°C at heating rate of 10°C min^{-1} under nitrogen.

## RESULTS AND DISCUSSION

Morphological studies

The behavior of prepared membranes is closely related to their structure, especially the spatial distribution of ionic site.[19] To evaluate the morphology and ionic sites condition (resin particles) in membrane matrix, SOM studies have been carried out.

The SOM images of membranes in transmission mode with light going through them are depicted in Figures 2 and 3. The non-conducting area (polymer binder) and conducting ion exchange areas (resin particles) are clearly seen in these images. The particles are observed as dark spots. As seen in these images, dark regions are increased with the higher of additive (activated carbon) concentration. Also, images show a relatively uniform surface for the membranes. Moreover, particles of resin and additive are uniformly distributed in the prepared membranes. Excessive homogeneity and uniform distribution of resin particles, i.e. functional groups, on the surface of membrane and in the bulk of membrane matrix, provide superior conducting regions in membrane and generate easy flow channels for the counter-ions transportation and therefore, they improve electrochemical properties. The existence of more conducting region on the membrane surface also can strengthen the intensity of uniform electrical field around the membrane and decreases the concentration polarization phenomenon.[37]

Figure 4 shows the effect of ultrasonic method on prepared membranes. As shown, the sonication has a significant effect on distribution of resin particles and provides more conducting regions for the prepared membranes. Moreover, sonication of solid particles can increase the viscosity of casting solution by reducing aggregation and sedimentation. The increase of casting solution's viscosity reduces the evaporation rate of casting solvent and therefore improves the polymer chains' relaxation and its conformation to the surface of resin particles. The conformation increases the polymer-particle interactions and promotes the compatibility of particles and binder.[28] This compatibility results in reduction of cracks and fissures between the binder and particles in the matrix of membrane and improves the membrane selectivity.

Water content

The increase of additive (activated carbon) concentration in the casting solution led to decrease in water content from 50.19% to 44.5% in the prepared membranes (Table III) due to hydrophobic characteristic of activated carbon. This indicates that a more hydrophobic membrane is produced by increase of the percentage of activated carbon in the casting solution.
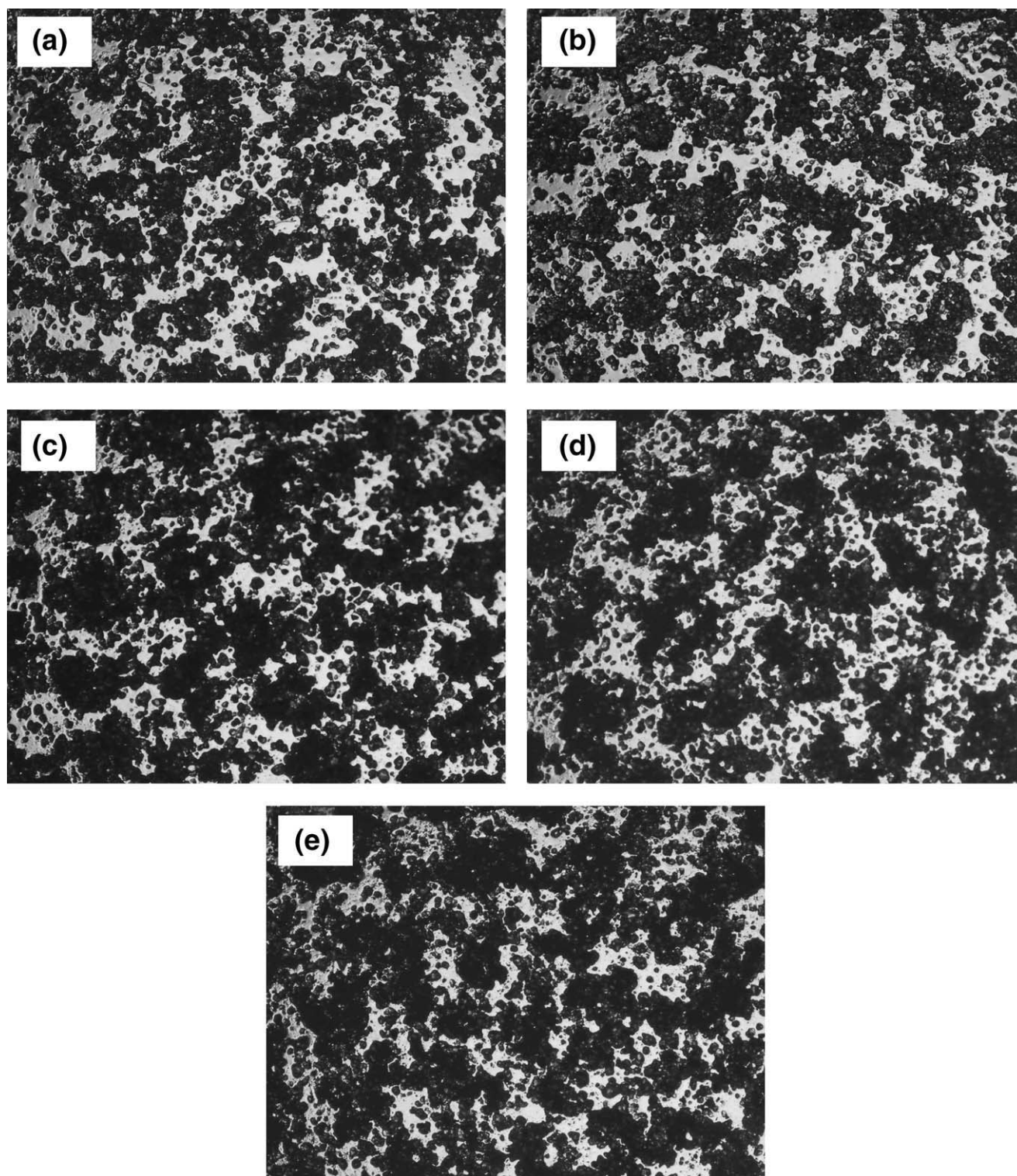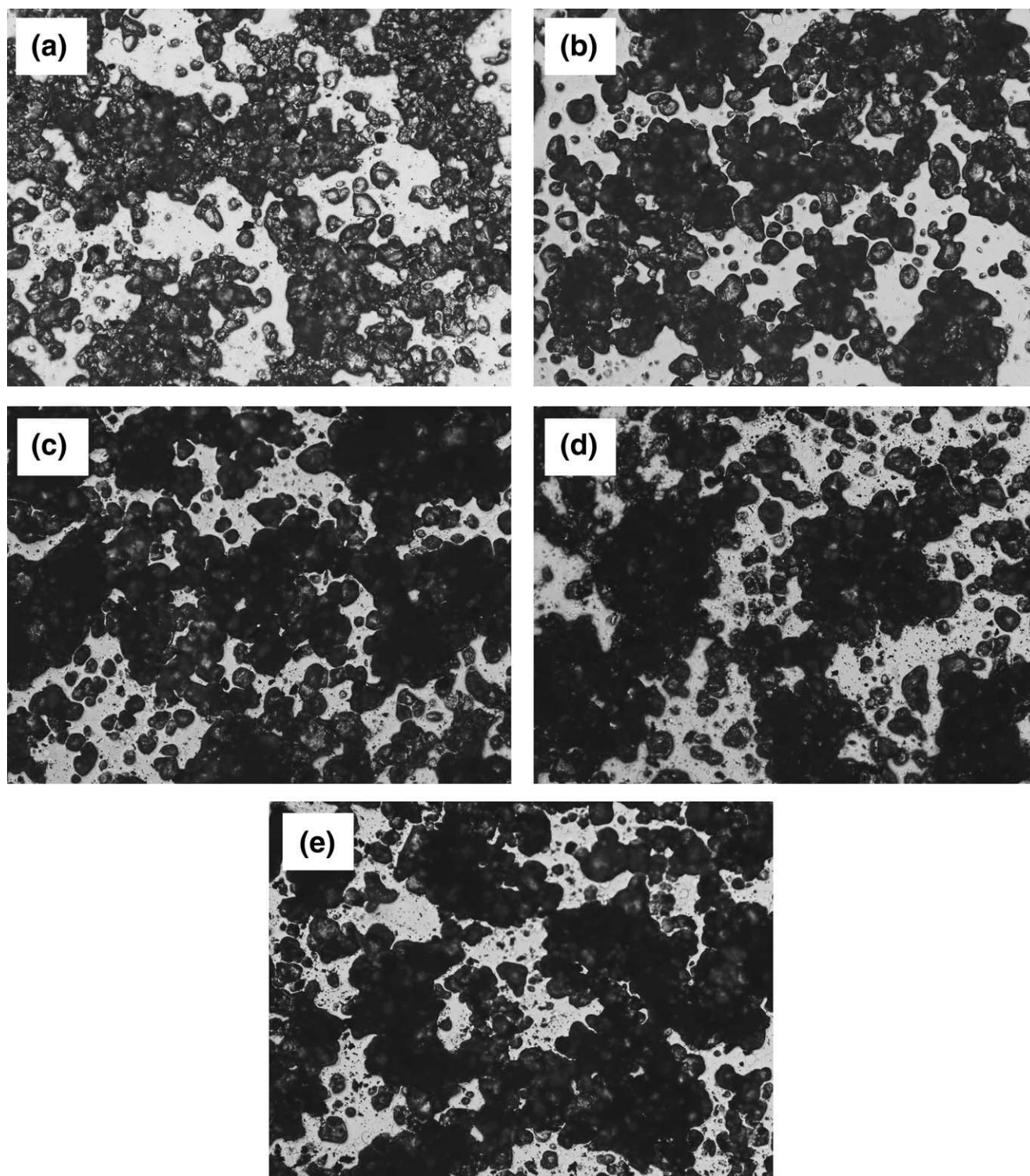
Figure 2 SOM images (with 4× magnifications) of home-made membranes with various concentrations of activated carbon: (a) 0% wt; (b) 0.5% wt; (c) 1% wt; (d) 2% wt; and (e) 4% wt.

Also, with more increment of additive concentration, it is possible that cavities and voids in the matrix of membrane be surrounded and isolated more by carbon particles and then results in less water absorption. The water content of prepared membranes is comparable, but lower than, to the water content of the tested commercial membrane. This is attributed to the type of polymer binder and its type and functional groups concentration and distribution.

The high water content provides more and wider transfer channels for transportation of co- and counter-ions and decreases the ion selectivity and also

Figure 3 SOM images (with $10\times$ magnifications) of home-made membranes with various activated carbon loadings: (a) 0% wt; (b) 0.5% wt; (c) 1% wt; (d) 2% wt; and (e) 4% wt.

leads to formation of a loose membrane structure. The lower water content of prepared membranes compared to its commercial counterpart can dominate better on ions paths and so it improves the membrane's permselectivity.

Ion exchange capacity (IEC) and fixed ion concentration (F.I.C)

The prepared heterogeneous anion exchange membranes possess appropriate IEC in comparison with tested commercial membrane (Fig. 5). The results
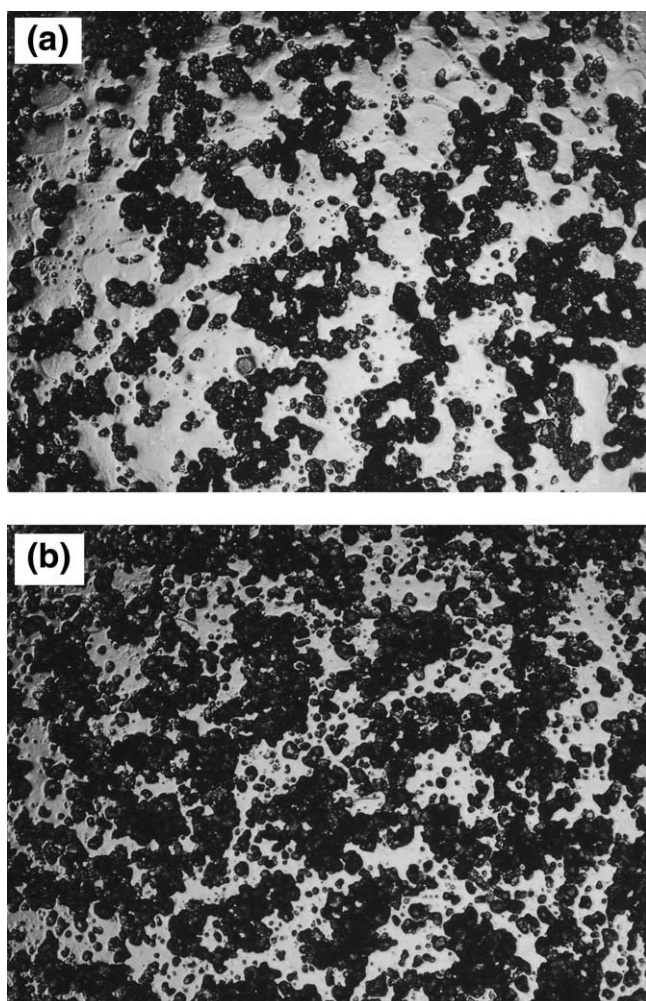
Figure 4 The effect of sonication on distribution of particles (resin and additive) in prepared membranes: (a) before sonication; (b) after sonication.

indicated that the increment of activated carbon concentration (additive: total solids) to 1% wt in the casting solution led to an improvement in ion exchange capacity from 1.810 to 1.935 (meq/gr) in prepared membranes. This is attributed to adsorption property of activated carbon which causes superior interaction between ions and surface of membrane which in turn facilitates the ions transportation between the solution and membrane phase. This enhances the ion exchange

TABLE III
Water Content of Home-Made Membranes with Various Additive Loadings and Commercial Type (with 1-2.1% Standard Deviation)

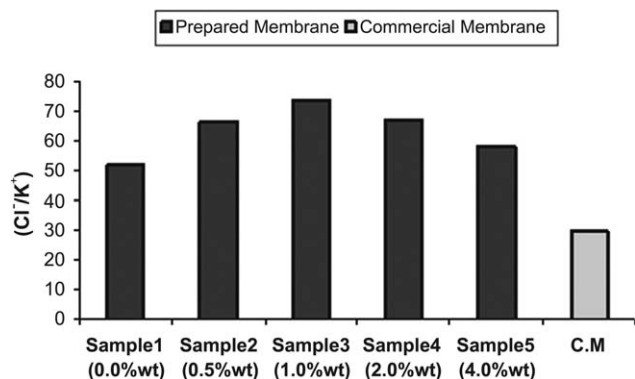| Membrane	Water content (%)
Sample 1, (0.0% wt activated carbon)	50.19
Sample 2, (0.5% wt activated carbon)	47.11
Sample 3, (1.0% wt activated carbon)	45.41
Sample 4, (2.0% wt activated carbon)	45.00
Sample 5, (4.0% wt activated carbon)	44.50
Commercial membrane	65.02
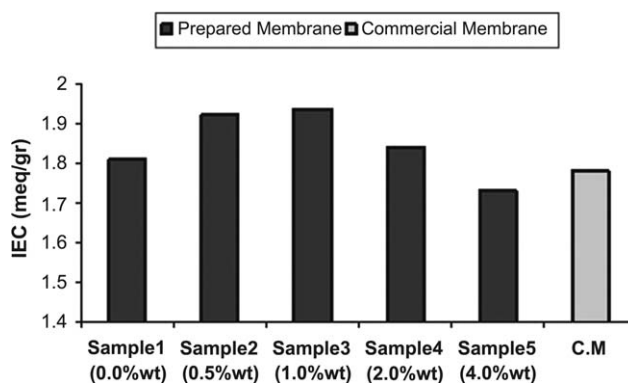
Figure 5 Ion exchange capacity of prepared membranes with various ratios of additive loading and commercial membrane.

possibilities. The ion exchange capacity was decreased again from 1.935 to 1.730 (meq/gr) with higher increase of activated carbon loading from 1 to 4% wt. This may be attributed to decrease in accessibility of ion exchange groups in the membrane matrix due to the increase of additive particles which can occupy the spaces around the resin particles and so reduces the accessibility of ion exchange functional groups by their isolation. In fact, higher additive concentration from 1 to 4%wt in the casting solution, more the functional groups in the membrane matrix are surrounded and isolated by the activated carbon particles; so they are not partially accessible to ion exchange which in turn leads to IEC decrease.

There is a relationship between the IEC and water content [eq. (3)] and so their effects during the process are open to optimization. For the purpose, fixed ion concentration or equivalent of functional group per absorbed water content can be used. The prepared membranes exhibited a good fixed ion concentration (F.I.C) in comparison with commercial membrane (Fig. 6). The high fixed ion concentration can have better control on the pathways of counter ions traffic in the matrix of membrane and therefore, it increases the ion selectivity. This factor indicates appropriate ion
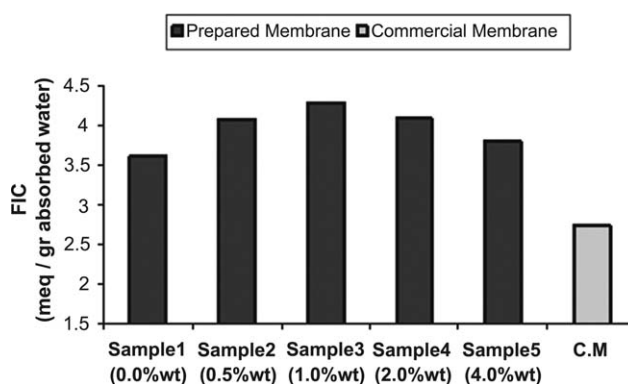
Figure 6 Comparison between the fixed ion concentration (F.I.C) of prepared membranes and commercial ones.

Figure 7 Donnan equilibrium condition for the home-made membranes with various additive loadings and commercial membrane.

Figure 8 Membrane potential of prepared membranes with various concentrations of additive and commercial type.

selectivity for the prepared membranes compared to commercial type due to suitable amount of water content and IEC for the prepared membranes.

Donnan equilibrium's law

To evaluate the equilibrium condition of anions against cations in the prepared membranes matrix as a function of activated carbon concentration, the Donnan equilibrium law was considered using 0.5 M KCl solution. The ratio of entered counter to co-ions in the membrane matrix can be used only for the qualitative evaluation of membrane selectivity (not quantitative evaluation). Results show that selectivity to Cl^- is initially enhanced with the increase of additive concentration to 1% wt in prepared membranes (Fig. 7). This result is partly attributed to the formation of more suitable transfer pathways by improved IEC and fixed ion concentration which prevent co-ions diffusion. The selectivity is decreased again with higher increase in activated carbon concentration from 1 to 4% wt due to the decrease in fixed ion concentration as was shown in F.I.C results.

High fixed ion concentration can dominate the ions pathway traffic which result in improvement of membrane selectivity. Moreover, the home-made heterogeneous anion exchange membranes exhibited superior ion permselectivity in comparison with commercial ones. This clear difference can be explained by the higher fixed ion concentration for the home-made membranes due to lower amount of water content and appropriate IEC compared to commercial type.

Membrane potential, surface charge density, permselectivity and transport number

The membranes potential was measured between 55 and 57 mV (Fig. 8) which is comparable with commercial ones (54.5 mV). The membrane potential initially was improved with the increase of activated
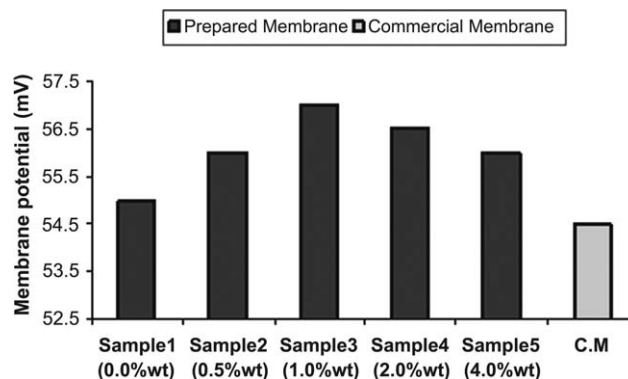
carbon concentration (up to 1% wt) in the prepared membranes. This may be attributed to the increment of fixed ion concentration and membrane surface charge density (Fig. 9) which provide additional conducting regions for membrane and generate suitable flow channels for easy passage of the counter ions and lead to enhanced Donnan exclusion that is responsible for the increment of membrane potential. The membrane potential is decreased again with more increase in additive concentration from 1 to 4% wt due to lower fixed ion concentration and membrane surface charge density.

The permselectivity and transport number of membranes are depicted in Figures 10 and 11, respectively. At first, both increased with the increment of activated carbon concentration to 1% wt in the casting solution. This happening can be explained with respect to the increase in fixed ion concentration with improved control of pathways for ions traffic due to the existence of adequate ionic functional groups and appropriate quantity of water content. Permselectivity and transport number are decreased again with more increment of additive loading from 1 to 4% wt due to lower membrane
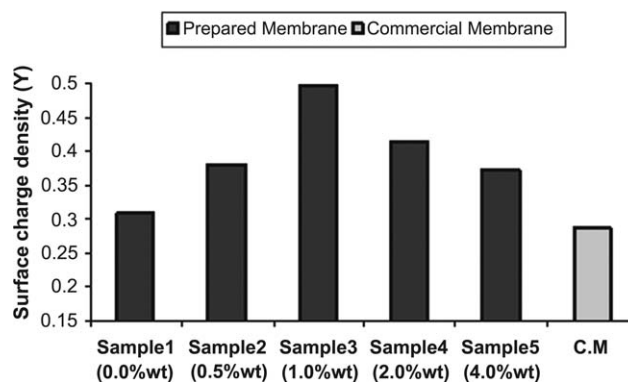
Figure 9 Comparison between the surface charge density of prepared membranes with different ratios of additive loading and commercial membrane.
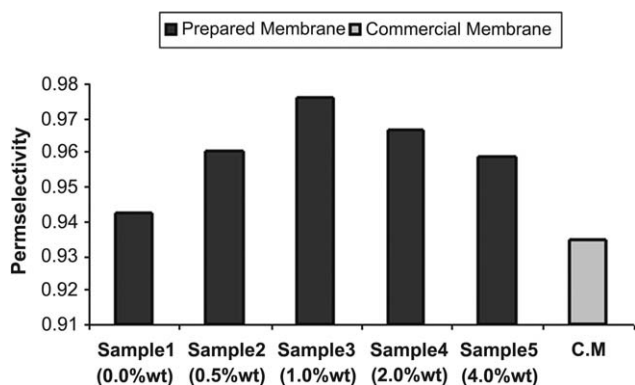
Figure 10 The permselectivity of prepared membranes with various concentrations of additive and commercial membrane.

fixed ion concentration. Also, the home-made membranes exhibited appropriate selectivity and transport number in comparison with commercial one because of higher F.I.C and suitable compatibility of particles with binder which latter is happened due to sonication.[28] Moreover, the lower transport number and permselectivity of commercial membrane can be explained by the higher swelling rate which facilitates the diffusion of co ions through the membrane.[20]

Ionic permeability and flux of ions

During the experiment, the ions pass through the membrane and reach to concentration section. With respect to occurred reactions in anodic and cathodic sections, the amount of transported chloride ions through the membrane to concentration section is equal to the produced hydroxide ions in the cathodic section. The permeation of ions through the membrane phase is calculated based on the pH variations in cathodic section which is indicator of ions passage through the membrane. The pH of cathodic
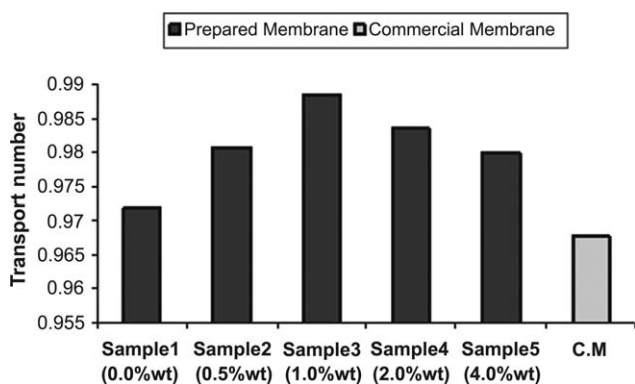
Figure 11 Transport number of home-made membranes with different activated carbon loadings and commercial ones.
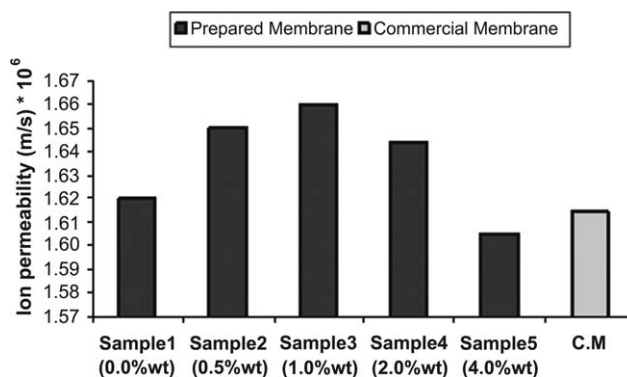

Figure 12 The ion permeability of prepared heterogeneous anion exchange membranes with various weight ratios of additive loadings and commercial membrane.

compartment was improved over time for all of the membranes.

Results showed that the ionic permeability (Fig. 12) and flux of ions (Fig. 13) were enhanced initially with variation in additive loading to 1% wt due to improvement in ion exchange capacity and ionic concentration for the prepared membranes which provide suitable channels in membrane matrix for ions passage. The ion permeability and flux were decreased again with more increase in additive loading from 1 to 4% wt due to decline in membrane IEC and water content. The obtained data are comparable with the characteristics of the commercial membrane.

Electrical resistance

The areal electrical resistance of prepared membranes was initially decreased with increase in additive loadings to 1% wt (Table IV). This is attributed to the formation of suitable ion conducting pathways throughout the membrane which resulted from the increase in accessibility of ion exchange functional groups, surface charge density and also fixed ion concentration. These provide higher membrane conductivity. Areal electrical resistance was increased
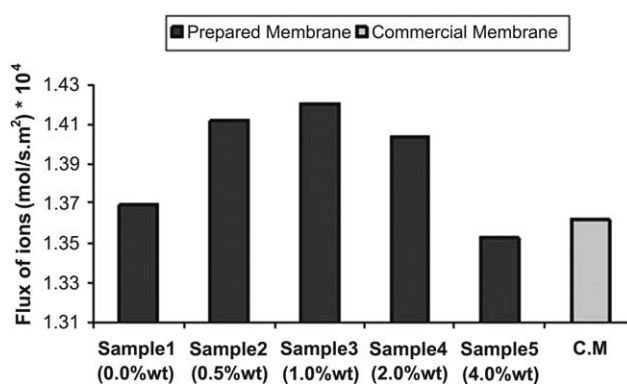
Figure 13 Flux of ions for prepared heterogeneous anion exchange membranes with various amounts of additive loading and commercial type.

TABLE IV
Areal Electrical Resistance of Prepared Anion Exchange Membranes and Commercial Type

Membrane	Resistance (ohm. Cm^2)
Sample 1, (0.0% wt activated carbon)	3.577
Sample 2, (0.5% wt activated carbon)	3.215
Sample 3, (1.0% wt activated carbon)	2.866
Sample 4, (2.0% wt activated carbon)	3.367
Sample 5, (4.0% wt activated carbon)	3.718
Commercial membrane	3.621

TABLE V
Swelling Evaluation of Home-Made Anion Exchange Membranes and Commercial Type

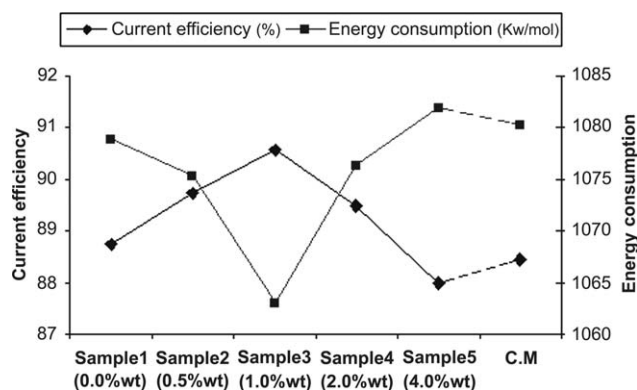| Membrane	Thickness (Δx %)	Length (Δl %)	Width (Δw %)
Home-made membranes	Less than 5	Negligible	Negligible
Commercial membrane	About 55%	About 4%	About 4%

again with more increment of additive loading from 1 to 4% wt due to decline in surface charge density, ionic concentration and accessibility of ionic functional groups. The obtained data for home-made membranes are comparable with the characteristics of commercial type.

Current efficiency and energy consumption

The obtained data indicated that current efficiency was slightly increased and energy consumption (Fig. 14) was marginally decreased with increase in activated carbon loadings to 1% wt in prepared membranes because of improvement in ionic flux and ionic permeability according to eqs. (22) and (23). Again, the current efficiency was decreased and energy consumption was increased with higher additive concentration from 1 to 4% wt. Moreover, results show that prepared membranes are efficient in comparison with commercial ones.

Dimensional and oxidative stability

During the preparation process, due to evaporation, the loss of molecules solvent introduces cavities and voids between the resin particles and polymer binder region. These micro voids are sufficient to accommodate the solvent molecules for the solvation

of ionic groups in the resin particles. Therefore, the solvation does not change membranes dimensions manifestly.[9,18] Moreover, it was found that the swelling of prepared membrane is negligible compared to the commercial ones (Table V).
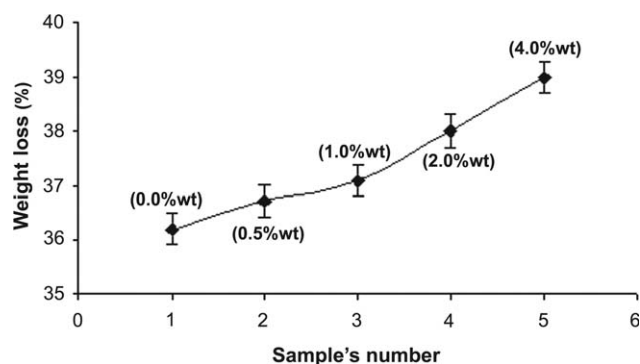
Prepared membranes also were immersed in an oxidant aqueous solution for oxidative stability measurements. The results (Fig. 15) show that oxidative stability of prepared membranes is slightly decreased with higher additive loading. This may be attributed to the adsorption characteristic of activated carbon which increases the possibility of oxidant diffusion in the matrix of membrane.

Thermal analysis of prepared membranes

The effect of additive loading on thermal behavior of prepared membranes was studied by differential scanning calorimetry (DSC). Obtained results (Table VI) showed that thermal stability of prepared membranes was slightly improved by the increase in additive loading. This is due to the local heterogeneity in prepared membranes with well dispersed carbon particles which make favorable molecular interactions between the additive particles and binder and create an interfacial zone of polymer segments.[38]

Superior membrane

The home-made membranes exhibited superior electrochemical properties in comparison with tested commercial membrane. Among the prepared membranes,

Figure 14 Current efficiency and energy consumption of home-made membranes with different concentrations of activated carbon and commercial membrane (at applied potential).

Figure 15 The effect of additive loading ratio on oxidative stability of prepared membranes.

TABLE VI
The Effect of Activated Carbon Loading Ratio on the Thermal Properties of Home-Made Membranes

Membrane	Melting temperature (T_m), K	Destroying temperature (T_d), K
Sample 1, (0.0% wt)	344.25	538.05
Sample 3, (1.0% wt)	357.55	539.05
Sample 5, (4.0% wt)	363.15	542.25

heterogeneous anion exchange membrane with 1% wt activated carbon (sample 3), with highest ionic flux, permeability, selectivity and current efficiency and suitable oxidative and thermal stability and lowest energy consumption showed more appropriate performance compared to other prepared membranes in this research and commercial ones. Also obtained results are comparable with other reported heterogeneous anion exchange membranes.[10,13,21,23]

CONCLUSION

The SOM images showed that ultrasonic method has a significant effect on distribution of resin particles in prepared membranes and makes highly uniform phase to form. Also images showed a relatively uniform surface for membranes. Results revealed that the increase of activated carbon concentration in the casting solution led to decline in membranes water content. It was found that increment of additive concentration to 1% wt in casting solution led to an improvement in ion exchange capacity in prepared membranes. The ion exchange capacity was decreased with higher increase in activated carbon concentration from 1 to 4% wt. The membrane potential, permselectivity, transport number, ionic permeability, ionic flux and current efficiency initially were enhanced with variations in activated carbon concentration to 1% wt. All of them decreased again with more increase in additive loading from 1 to 4% wt. The areal electrical resistance and energy consumption of home-made membranes were declined initially with higher additive loadings and then it began to increase. Also oxidative stability of prepared membranes was slightly decreased and their thermal stability was increased with increase in additive concentration. The swelling of the prepared membranes was negligible compared to commercial ones. The prepared membranes possessed appropriate properties and higher efficiency compared to commercial membrane.

References

1. Nagarale, R. K.; Gohil, G. S.; Shahi, V. K.; Trivedi, G. S.; Rangarajan, R. J Colloid Interface Sci 2004, 277, 162.
2. Vyas, P. V.; Ray, P.; Adhikary, S. K.; Shah, B. G.; Rangarajan, R. J Colloid Interface Sci 2003, 257, 127.
3. Nagarale, R. K.; Shahi, V. K.; Schubert, R.; Rangarajan, R.; Mehnert, R. J Colloid Interface Sci 2004, 270, 446.
4. Hwang, G. J.; Ohya, H.; Nagai, T. J Membr Sci 1999, 156, 61.
5. Volodina, E.; Pismenskaya, N.; Nikonenko, V.; Larchet, C.; Pourcelly, G. J Colloid Interface Sci 2005, 285, 247.
6. M' Bareck, C. O.; Nguyen, Q. T.; Alexandre, S.; Zimmerlin, I. J Membr Sci 2006, 278, 10.
7. Elattar, A.; Elmidaoui, A.; Pismenskaia, N.; Gavach, C.; Pourcelly, G. J Membr Sci 1998, 143, 249.
8. Schauer, J.; Brozova, L. J Membr Sci 2005, 250, 151.
9. Kariduraganavar, M. Y.; Nagarale, R. K.; Kittur, A. A.; Kulkarni, S. S. Desalination 2006, 197, 225.
10. Xu, T. J Membr Sci 2005, 263, 1.
11. Baker, R. W. Membrane Technology and Applications, 2nd ed.; Wiley: England, 2004; Chapter 1, p 398.
12. Koter, S.; Warszawski, A. Pol J Environ Stud 2000, 9/1, 45.
13. Xu, T.; Yang, W. J Membr Sci 2001, 190, 159.
14. Shahi, V. K.; Trivedi, G. S.; Thampy, S. K.; Rangarajan, R. J Colloid Interface Sci 2003, 262, 566.
15. Gohil, G. S.; Shahi, V. K.; Rangarajan, R. J Membr Sci 2004, 240, 211.
16. Dlugolecki, P.; Anet, B.; Metz, S. J.; Nijmeijer, K.; Wessling, M. J Membr Sci 2010, 346, 163.
17. Nagarale, R. K.; Shahi, V. K.; Thampy, S. K.; Rangarajan, R. React Funct Polym 2004, 61, 131.
18. Nagarale, R. K.; Gohil, G. S.; Shahi, V. K. Adv Colloid Interface Sci 2006, 119, 97.
19. Li, X.; Wang, Z.; Lu, H.; Zhao, C.; Na, H.; Zhao, C. J Membr Sci 2005, 254, 147.
20. Kerres, J.; Cui, W.; Disson, R.; Neubrand, W. J Membr Sci 1998, 139, 211.
21. Sata, T. Ion Exchange Membranes: Preparation, Characterization, Modification and Application; The Royal Society of Chemistry: Cambridge, UK, 2004; Chapter 3, 4, 5.
22. Vyas, P. V.; Shah, B. G.; Trivedi, G. S.; Ray, P.; Adhikary, S. K.; Rangarajan, R. J Membr Sci 2001, 187, 39.
23. Tanaka, Y. Ion Exchange Membranes: Fundamentals and Applications; Membrane Science and Technology Series 12; Elsevier: Netherlands, 2007; Chapters 1, 2, 3.
24. Marchese, J.; Anson, M.; Ochoa, N. A.; Pradanos, P.; Hernandez, A. Chem Eng Sci 2006, 61, 5448.
25. Harper, C. A. Handbook of Plastic and Elastomers, 2nd ed.; McGraw-Hill: New York, 1975; p 1–62, 2–42, 3–1.
26. Wiks, E. S. Industrial Polymers Handbook: Products, Processes, Application; Wiley-VCH Press: Germany, 2001.
27. Mark, E. J. Polymer Data Handbook; Oxford University Press, Inc.: New York, 1999; p 829, 980, 983.
28. Vu, D. Q.; Koros, W. J.; Miller, S. J. J Membr Sci 2003, 211, 311.
29. Kim, D. S.; Yun, T. I.; Seo, M. Y.; Cho, H. I.; Lee, Y. M.; Nam, S. Y.; Rhim, J. W. Desalination 2006, 200, 634.
30. Nagarale, R. K.; Shahi, V. K.; Rangarajan, R. J Membr Sci 2005, 248, 37.
31. Luo, J.; Wu, C.; Wu, Y.; Xu, T. J Membr Sci 2010, 347, 240.
32. Wu, Y.; Wu, C.; Li, Y.; Xu, T.; Fu, Y. J Membr Sci 2010, 350, 322.
33. Shahi, V. K.; Thampy, S. K.; Rangarajan, R. J Membr Sci 1999, 158, 77.
34. Nagarale, R. K.; Gohil, G. S.; Shahi, V. K.; Rangarajan, R. Colloids Surf A 2004, 251, 133.
35. Gohil, G. S.; Binsu, V. V.; Shahi, V. K. J Membr Sci 2006, 280, 210.
36. Lide, D. R. CRC Handbook of Chemistry and Physics, 87th ed.; CRC press, Taylor & Francis Group: Florida, 2006–2007; p 5–78.
37. Kang, M. S.; Choi, Y. J.; Choi, I. J.; Yoon, T. H.; Moon, S. H. J Membr Sci 2003, 216, 39.
38. Kim, S.; Chen, L.; Johnson, J. K.; Marand, E. J Membr Sci 2007, 294, 147.