Research Paper

Electrodialysis Heterogeneous Anion Exchange Membranes Filled with TiO_2 Nanoparticles: Membranes' Fabrication and Characterization

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HIGHLIGHTS

- PVC-co-TiO_2 NPs mixed matrix anion exchange membranes were prepared.
- Membrane transport number and selectivity were enhanced by TiO_2 ratio.
- Membrane ionic resistance was declined by using of TiO_2 NPs in membrane matrix.

GRAPHICAL ABSTRACT
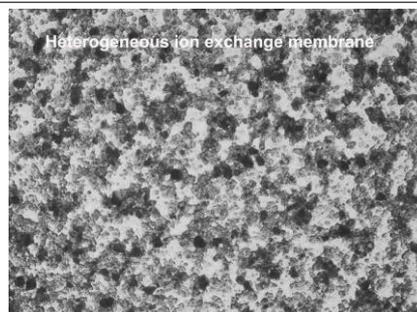
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ABSTRACT

In the current research, polyvinylchloride based mixed matrix heterogeneous anion exchange membranes were prepared by a solution casting technique. Titanium dioxide nanoparticles were also utilized as inorganic filler additive in the membrane fabrication. The effect of TiO2 nanoparticles concentration in the casting solution on the membrane physico-chemical properties was studied. Membrane water content was decreased by an increase of nanoparticle concentration. Ion exchange capacity was also improved initially by an increase of nanoparticle content ratio and then slightly decreased. The membrane fixed ionic concentration, membrane potential, transport number and permselectivity were all increased by an increase of additive loading ratio. The membrane ionic permeability was enhanced initially by an increase of nanoparticle concentration up to 0.5 %wt in the membrane matrix and then decreased by more additive content ratio from 0.5 to 4 %wt. Membrane ionic resistance was declined by using TiO2 nanoparticles in the membrane matrix. Membranes also exhibited lower permselectivity and transport number for bivalent ions in comparison to monovalent ones. An opposite trend was found for the membrane ionic permeability. The amount of swelling in the homemade membranes was also less than 5% in thickness and negligible in length and width. Among the prepared membranes, the modified membrane containing 0.5 %wt TiO2 nanoparticles concentration showed more appropriate performance compared to the others. The obtained results revealed that modified membranes in this study are comparable with commercial membranes.

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1. Introduction

Global demand for fresh water has had a great focus on utilization of the membrane based processes in water treatment. For many years membrane science has been cutting edge in a broad range of applications such as food and pharmaceutical industry, water treatment and sea or brackish water desalination. Although non-charged membranes are used in most applications, charged membranes have proven to be necessary prerequisites for electrically driven processes such as electrodialysis, electro-deionization and energy conversion [1-9].

In ion exchange membranes, the charged groups are attached to the polymer backbone and are freely permeable to opposite ions under an electrical field. In such processes, the ion interactions with membrane, water and with each other occur in complex fashions. Thus, knowledge of the physico-chemical properties of the ion exchange membrane is a major contributing factor behind decisions about their applicability in specific separation processes [9-14].

Preparing inexpensive membranes with special adapted physico-chemical characteristics such as high permselectivity and permeability, suitable water uptake, low ionic resistance and suitable mechanical and chemical stability may be a vital step in future chemical and waste treatment applications [4,9,10].

A lot of research has already been performed to improve the IEMs' properties which resulted in various modification techniques. Variation of membrane functional groups, utilizing different polymeric matrices, polymers blending, using different filler or additives, alteration of cross-link density, surface modifications and more uniform distribution of functional groups are important ways to obtain appropriate membranes [4,5,8,9,11-14]. Utilizing inorganic nanoparticles or fillers into polymeric materials has also been examined in many applications to enhance the mechanical, thermal and chemical stability of polymeric matrixes in severe conditions such as high temperature and strongly oxidizing the environment and also to improve the separation properties of membranes based on synergism between the organic-inorganic component properties [4,8,9,15,16]. Titanium dioxide (TiO_2) nanoparticles are one of the well-known metal oxide nanomaterials which have gained a great deal of attention because of their unique features. It is widely employed as an adsorbent agent for water contaminant removal in environmental based processes as suspended/beds adsorbent [17-20]. TiO_2 NPs were also utilized as filler additive in the membrane matrix (ultrafiltration, nanofiltration, osmosis, reverse osmosis and membrane distillation) due to its superior hydrophilicity, high adsorption capacity, large surface area, stable chemical properties and low cost [14-16,21-25]. Currently, no researches have considered the incorporation of TiO_2 nanoparticles into the anion exchange membrane and the literature is silent on characteristics and functionality of AEMs prepared using TiO_2 nanoparticles.

Preparing heterogeneous anion exchange membranes with appropriate properties for the application in electrodialysis processes related to water recovery and treatment was the primary target of the current research. For this purpose, PVC/TiO_2 mixed matrix heterogeneous anion exchange membranes were prepared by the solution casting technique using anion exchange resin powder as functional group agents and tetrahydrofuran as solvent. Titanium dioxide nanoparticles were also employed as inorganic filler additive in membrane fabrication in order to improve the IEMs properties. The effect of TiO_2 nanoparticles concentration in the casting solution on membrane electrochemical properties was studied. The sodium chloride and sodium sulfate were employed as mono and bivalent ionic solutions for membrane characterization. The results are valuable for electro-membrane processes especially in the electrodialysis process for water recovery and desalination.
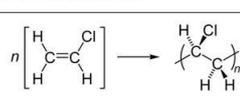
2. Materials and Methods

2.1. Materials

Polyvinylchloride (PVC, grade S-7054, density: 460 g/lit, viscosity number: 105 Cm^3/g) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as a membrane base binder. Tetrahydrofuran (THF, molar mass: 72.11 g/mol, density: 0.89 g/cm^3) was employed as solvent. Titanium dioxide nanoparticles (TiO_2, nano-powder, anatase crystal, and 15-25 nm particle size) were provided from US Research Nanomaterials, USA. Anion exchange resin (Amberlyst® IRA- 262, strongly basic anion exchanger, Cl− form) by Merck was used in membrane preparation. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used. The chemical structure of the used polymer and nanoparticles are shown in Table 1.

2.2. Preparation of composite anion exchange membranes

The heterogeneous anion exchange membranes were prepared by the solution casting technique through the phase inversion method [4]. The preparation proceeded by dissolving the polymer binder (PVC) into solvent (THF) in a glass reactor equipped with a mechanical stirrer (model: VELP Scientific-Multi stirrer) for more than 6 h. This was followed by dispersing resin particles (−300+400 mesh) as functional groups and TiO_2 nanoparticles as additive in the polymeric solution, respectively. In addition, for better dispersion of particles and breaking up their aggregations, the solution was sonicated for 1 h using an ultrasonic instrument. Then the mixing process was repeated for another 30 min using a mechanical stirrer. The mixture was then casted onto a clean and dry glass plate at ambient temperature. The membranes were dried at ambient temperature and immersed in distilled water, respectively. As a final step, the membranes were pretreated by immersing in 0.5 M NaCl solution for 48 h. The membrane thickness was measured by a digital caliper device (Electronic outside Micrometer, IP54 model OLR) at around 80 µm. The composition of casting solution is given in Table 2.

Table 2
Composition of casting solution used in preparation of mixed matrix anion exchange membranes[a].

Membrane	Titanium dioxide nanoparticles (TiO_2 nanoparticle: (PVC + resin)), (w/w)
Sample 1 (M1)	0.0 : 100
Sample 2 (M2)	0.5 : 100
Sample 3 (M3)	1.0 : 100
Sample 4 (M4)	2.0 : 100
Sample 5 (M5)	4.0 : 100

[a]*(Solvent to Polymer binder (THF: PVC) (v/w), (20:1); Resin particles (Resin: Polymer binder) (w/w), (1:1))*

2.3. Experimental test cell

The permselectivity, ionic flux and ionic resistance of prepared membranes were measured using the test cell as reported earlier (Figure 1) [4,5,8]. The cell consists of two cylindrical compartments (180 cm^3) made of Pyrex glass which are separated by the membrane. The membrane surface was 19.6 cm^2. One side of each vessel was closed by a Pt electrode supported with a piece of Teflon and the other side was equipped with the membrane. The top of each compartment contained two orifices for feeding and sampling purposes. In order to minimize the thickness of the boundary layer during experiments and to reduce the concentration polarization on the vicinity of the membrane surface, both sections were stirred vigorously by magnetic stirrers.

2.4. Membrane characterization

2.4.1. 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 oven at 65 °C until the constant weight was obtained. The following equation [11-13,26-29] can be used to calculate the water content:

Table 1
Chemical structures of used polymer and nanoparticles.

Polymer	Chemical structure
Polyvinylchloride (PVC)	
Titanium dioxide nanoparticles (TiO_2)	

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

where W_{wet} is the weight of wet membrane and W_{dry} is the weight of dried membrane.
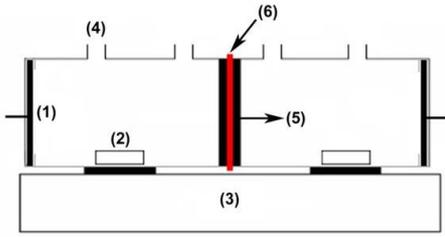
Fig. 1. Schematic diagram of test cell: (1) Pt electrode, (2) Magnetic bar, (3) Stirrer, (4) Orifice, (5) Rubber ring, (6) Membrane

2.4.2. Ion exchange capacity (IEC)

IEC is defined as the milli-equivalent of the ion exchange group included in 1 g of dry membrane. The IEC determination was performed using the titration method. In order 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 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 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. The IEC can be calculated from the following equation [4,13,29]:

$$IEC = (\frac{a}{W_{dry}}) \qquad (2)$$

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

The fixed membrane charge density or fixed ion concentration can also be calculated by:

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

2.4.3. Membrane potential, transport number and permselectivity

The membrane potential is the 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 [11-13,26,27]. This parameter was evaluated for the equilibrated membrane with unequal concentrations of electrolyte solution (NaCl/Na$_2$SO$_4$, C_1=0.1 M, C_2=0.01 M) at ambient temperature on either sides of the membrane using the test cell. 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 a saturated calomel electrode (through KCl bridges) and digital auto multi-meter (DEC, Model: DEC 330FC, Digital Multimeter, China). The membrane potential (EMeasure) is expressed using Nernst equation [11-13,26-30] as follows:

$$E_{Measure} = (2t_i^m - 1)(\frac{RT}{zF})\ln(\frac{a_1}{a_2}) \qquad (4)$$

where t_i^m is the transport number of counter ions in the membrane phase, R is gas constant, T is the temperature, z is the electrovalence of counter-ion, a_1, a_2 are the solutions electrolyte activities in contact membrane surfaces and F is the FARADAY constant. The ionic permselectivity of membranes is also quantitatively expressed based on the migration of counter-ions through the IEMs [4,13,29,30]:

$$P_s = \frac{t_i^m - t_0}{1 - t_0} \qquad (5)$$

where, t_0 is the transport number of counter ions in the solution [31].

2.4.4. Ionic permeability and flux

Ionic permeability and flux measurements were carried out using the test cell. A 0.1 M solution was placed on one side of the cell and a 0.01 M solution on its other side. A DC electrical potential (Dazheng, DC power supply, Model: PS-302D) 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 anions pass through the membrane to the anodic section. According to anodic and cathodic reactions, the produced hydroxide ions increase the pH of the cathodic section.

$$2H_2O + 2e^- \Rightarrow H_2 \uparrow + 2OH^- \text{ (Cathodic reaction) (R-1)}$$

$$2Cl^- \Rightarrow Cl_2 \uparrow + 2e^- \text{ (Anodic reaction)-NaCl solution (R-2)}$$

$$2H_2O \Rightarrow O_2 \uparrow + 4H^+ + 4e^- \text{ (Anodic reaction)- Na}_2\text{SO}_4\text{ solution (R-3)}$$
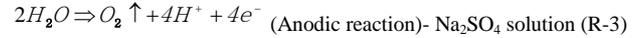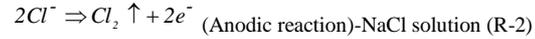
According to Fick's first law, the flux of ions through the membrane can be expressed as follows [4,30,32]:

$$N = -\frac{V}{A} \times \frac{dC}{dt} = P\frac{C_1 - C_2}{d} \qquad (6)$$

where, A is the membrane surface area, t is time, V is the volume of the cell's compartment, P is the coefficient diffusion of ions, d is membrane thickness, N is ionic flux and C_1, C_2 are concentration of electrolyte solutions on either sides of the membrane.

The boundary conditions are as follows:

NaCl solution: $C_1^0 = 0.1M$, $C_2^0 = 0.01M$, $C_2 = C_2^0$ (7)

Na$_2$SO$_4$ solution: $C_1^0 = 0.1M$, $C_2^0 = 0.01M$, $C_1 + C_2 = C_1^0 + C_2^0 = 0.11M$ (8)

Integrating equation (6) was as follows:

$$\ln\frac{(C_1 - C_2^0)}{(C_1^0 - C_2^0)} = -\frac{PAt}{Vd} \text{ (NaCl solution)}, \quad \ln\frac{(C_1^0 + C_2^0 - 2C_2)}{(C_1^0 - C_2^0)} = -\frac{2PAt}{Vd} \text{ (Na}_2\text{SO}_4\text{ solution) (9)}$$

The diffusion coefficient of ions in the membrane phase is calculated from equation 9, considering PH changes measurements (Digital pH-meter, Jenway, Model: 3510).

2.4.5. Ionic resistance

The ionic resistance of the membrane was measured in NaCl solution with 0.5 M concentration at ambient temperature. For this purpose, an equilibrated membrane with 19.6 cm^2 was incorporated into the test cell. 0.5 M NaCl solution was supplied in the cell compartments. Ionic resistance (R_1) was measured by an alternating current bridge with a frequency of 1500 Hz (Audio signal generator, Electronic Afzar Azma Co. P.J.S). In the next step, the membrane sample was discharged; the apparatus was re-integrated without the membrane, and ionic resistance (R_2) was measured. The membrane resistance is calculated using a different resistance between the cell (R_1) and electrolyte solution (R_2); ($R_m = R_1 - R_2$). The areal resistance was expressed as follows [29,30,33]:

$$r = (R_m A) \qquad (10)$$

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

3. Results and discussion

3.1. Water content

The obtained results (Figure 2) revealed that increases of titanium dioxide nanoparticle concentration in the casting solution led to a decrease of water content. This indicates that a more hydrophobic membrane is produced by an increase of nanoparticle percentage in the casting solution which is in contrast with super hydrophilic characteristics of TiO$_2$ nanoparticles [25,34]. This is due to voids and cavities occupying the used nanoparticles in the membrane matrix which result in less water molecules accommodation (Figure 3). Moreover, the amount of swelling in the homemade membranes was less than 5% in thickness and negligible in length and width. This

indicates that solvation does not change the membrane's dimensions manifestly.
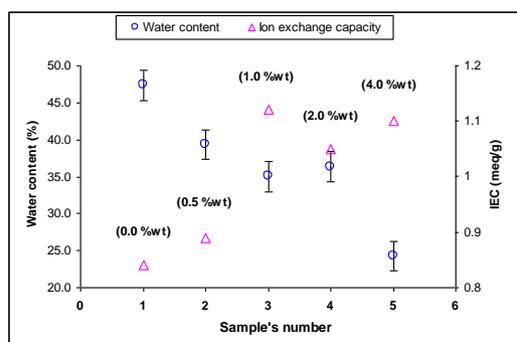
Fig. 2. The effect of titanium dioxide nanoparticles concentration (%wt) on water content and ion exchange capacity of prepared anion exchange membranes.
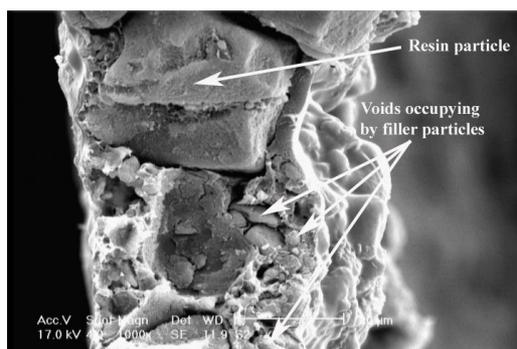
Fig. 3. The voids and cavities occupying by the used nanoparticles in membrane matrix.
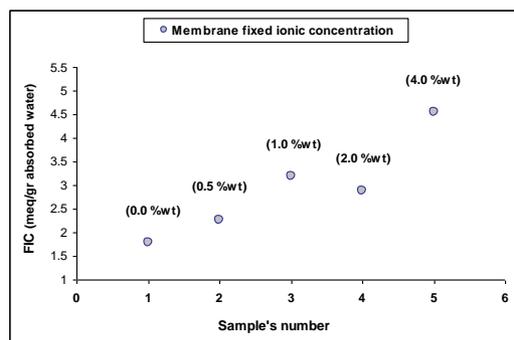
Fig. 4. The effect of TiO$_2$ nanoparticles loading ratio (%wt) on fixed ion concentration of prepared membranes.
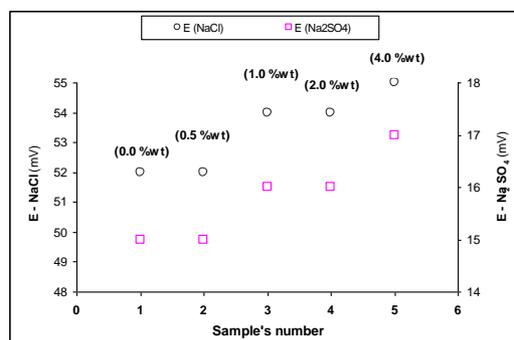
Fig. 5. Membrane potential of prepared anion exchange membrane with various ratios of TiO$_2$ nanoparticles content in sodium chloride and sodium sulfate ionic solutions.

3.2. Ion exchange capacity and fixed ionic concentration

The obtained results (Figure 2) indicated that an increase of TiO$_2$ nanoparticle concentration up to 1 %wt in the casting solution led to an increase of ion exchange capacity in the prepared membranes. This may be

attributed to the adsorption characteristic of the titanium dioxide nanoparticle which causes superior interaction between ions and the membrane surface. This facilitates the ions transportation between the solution and membrane phase and thus enhances the ion exchange possibilities. The ion exchange capacity was slightly decreased once more by a greater increase in additive content ratio from 1 to 4 %wt. This may be due to a decrease of accessibility of ion exchange functional groups in the membrane matrix due to an increase of nanoparticle concentration which occupies the spaces around the resin particles and reduces the accessibility of ion exchange functional groups by their isolation. Thus, they are not partially accessible to the ion exchange which in turn leads to a decrease in IEC. There is a relationship between the IEC and water content and so their effects during the process are open to optimization. For this purpose, the fixed ion concentration or equivalent of the functional group per absorbed water content can be used. As shown in Figure 4, an increase of TiO$_2$ nanoparticle concentration in the casting solution led to an increase of the membrane FIC. The high fixed ion concentration can have better control on the pathways of the counter ion traffic in the matrix of the membrane and increase the ionic permselectivity. It is worth mentioning that the measurements were carried out three times for each sample and then their average value was reported.

3.3. Membrane potential, permselectivity and transport number

The obtained results revealed that membrane potential, transport number and permselectivity (Figures 5 to 7) were all increased in sodium chloride (monovalent) and sodium sulfate (bivalent) ionic solutions by an increase of nanoparticle concentration. This may be attributed to the increment of membrane fixed ionic concentration which provides more suitable ionic transfer channels for the membranes. This leads to enhanced Donnan exclusion [4,30]. Moreover, the ionic pathways occupying the nanoparticles narrow the channels and strengthen the ionic site dominations on ionic traffic and hence improve the permselectivity. The prepared membranes also exhibited lower potential, permselectivity and transport number for the bivalent ion compared to the monovalent ones. This different behavior can be explained with respect to the stronger bonds for bivalent ions with ion exchange functional groups which poison the membranes and decrease the membrane transport number and permselectivity [26]. Furthermore, the larger radius of sulfate ions and their hydrated size in comparison with chlorine ions makes a lower potential, transport number and permselectivity for the bivalent ions. Also, the adsorption property of TiO$_2$ nanoparticles is more considerable for bivalent ions compared to monovalent ones which make possible the co-ions percolation.
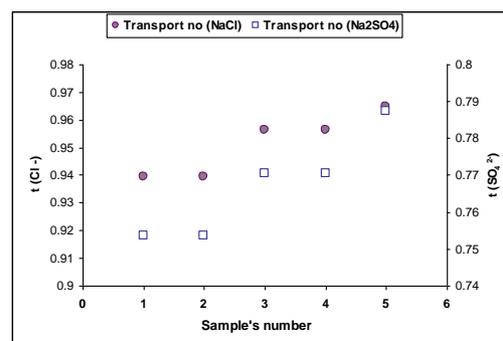
Fig. 6. The transport number of prepared membranes with various ratios of additive loadings in NaCl and Na$_2$SO$_4$ ionic solutions.
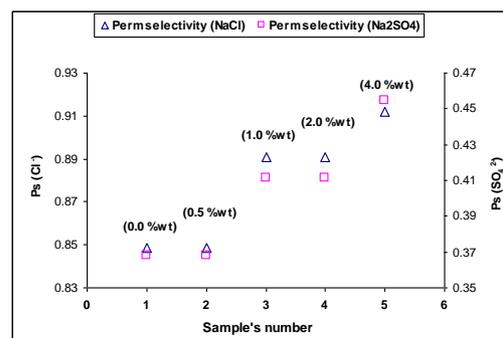
Fig. 7. Permselectivity of prepared anion exchange membranes with various ratios of titanium dioxide nanoparticles concentration in mono and bivalent ionic solutions.
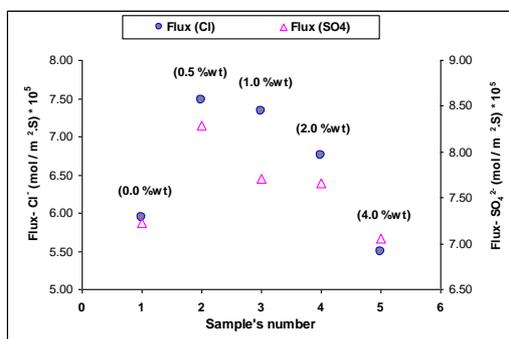
Fig. 8. Comparison between the ionic fluxes of prepared membranes with various ratios of additive concentration in sodium chloride and sodium sulfate ionic solutions.

3.4. Ionic permeability and flux

It was found that membrane ionic flux and permeability (Figures 8 and 9) were enhanced for chloride and sulfate ions by an increase of nanoparticle loading ratio up to 0.5 %wt in the casting solution. This may be attributed to the adsorption characteristic of TiO_2 nanoparticles which improves the ionic interactions with membrane surface and thus improves the counter ion transportation. Moreover, an increase of IEC and suitable amount of water content for the membranes cause formation of appropriate ionic transfer pathways in the membrane matrix and facilitates the ion traffic. The permeability and flux were decreased again by a further increase in additive content ratio from 0.5 to 4 %wt. This may be attributed to the formation of narrow ionic transfer channels in the membrane matrix and low amount of water content for the prepared membranes which makes the ions traffic difficult and thus declines the flux. Modified membranes showed lower permeability/flux for bivalent ions compared to the monovalent type.
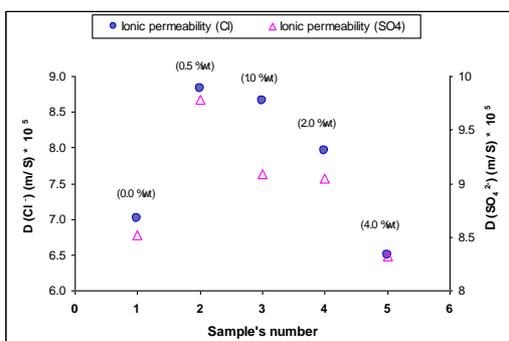
Fig. 9. Ionic permeability (mono- or bivalent ions) for the prepared membranes with various blend ratios of TiO_2 nanoparticles.
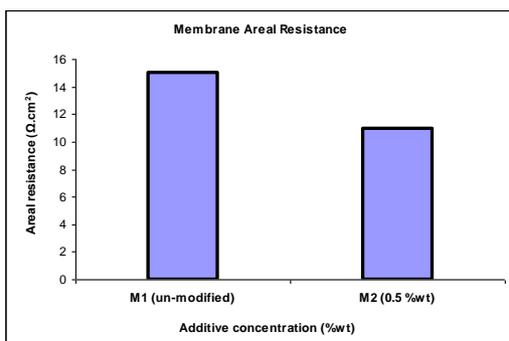
Fig. 10. The areal electrical resistance of prepared membranes with various ratios of TiO_2 nanoparticles concentration.

3.5. Ionic resistance

The ionic resistance of the pristine membrane (M1) and superior membrane (M2) was measured in 0.5 M NaCl solution at ambient temperature. Results (Figure 10) revealed that membrane areal ionic resistance was declined by using TiO_2 nanoparticles in the membrane matrix. This can be explained with respect to adsorption characteristics of titanium dioxide nanoparticles, an increase of ion exchange capacity and a suitable amount of water content for the membranes which improves the membrane

conductivity. In general, less selective membranes have lower membrane resistances. But this is not always true and depends on the membrane structure and properties [35]. A comparison between electrochemical properties of the prepared membrane in this research and some commercial membranes [35-37] is given in Table 3. Results showed that the modified membrane in this study is comparable with that of other commercial ones.

4. Conclusion

An increase of titanium oxide nanoparticles concentration led to a decline in water content in the prepared membranes. The amount of swelling in the homemade membranes was also negligible in length and width. The membrane ion exchange capacity was improved initially by an increase of TiO_2 nanoparticle content in the membrane matrices and then decreased slightly. The membrane potential, transport number and permselectivity showed an increasing trend in both monovalent and bivalent ionic solutions by an increase in titanium dioxide nanoparticles. Also, the membranes exhibited a lower potential, permselectivity and transport number for bivalent ions in comparison to monovalent ones. An increase of TiO_2 nanoparticles loading ratio up to 0.5 %wt in the casting solution led to an increase of ionic permeability. The ionic permeability was declined again by more additive concentration. Furthermore, membrane ionic conductivity was improved by using TiO_2 nanoparticles in the membrane matrix. The results are valuable for electro-membrane processes especially in the electrodialysis process for water recovery and desalination which is a major contributing factor behind decisions about the IEMs applicability in specific separation processes at different operating conditions.

Table 3
Comparison between the electrochemical properties of prepared membrane in this research and some commercial membranes [35-37].

Membrane	Permselectivity [a] (%)	Electrical resistance [a] (Ω cm^2)
Modified membrane (M2)	> 86	< 11
Ionics Inc., USA AR103QDP	-	14.5
Ralex® AMH-PES	> 90	< 8
RAI Research Corp., USA (R-5030-L Anion LDPF)	83	4.0 - 7.0
CSMCRI, Bhavnagar India (HGA Anion, PVC Heterogeneous)	82	5.0–7.0
CSMCRI, Bhavnagar India (IPA Anion LDPE/HDPE)	92	2.0 - 4.0
Ionics Inc., USA AR204SZRA	-	6.2 – 9.3
Asahi Glass Co. Ltd. Japan (AMV Anion PS/butadiene)	92	2.0 - 4.5

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