Research Paper

Fabrication and Electrochemical Characterization of Polyvinyl Chloride Based/Chitosan-co-Iron Nickel Oxide Nanoparticles Composite Heterogeneous Cation Exchange Membranes

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GRAPHICAL ABSTRACT

PVC/chitosan-co- Fe$_2$NiO$_4$ composite membrane

HIGHLIGHTS

• Polyvinyl chloride based/chitosan-co-iron nickel oxide nanoparticles composite heterogeneous cation exchange membrane
• Higher electrical conductivity compared to the unmodified membrane
• Uniform particle distribution and relatively uniform surfaces for the membranes

ABSTRACT

In this research, polyvinylchloride based composite heterogeneous cation exchange membranes were prepared by the solution casting technique. Chitosan-co-iron nickel oxide nanoparticles were utilized as membrane surface modifier to improve the membranes electrochemical properties. The effect of additive nanoparticle concentration in the modifier solution on the properties of composite membranes was studied. SOM images showed uniform particle distribution and relatively uniform surfaces for the membranes. Results showed that transport number, selectivity and surface charge density were improved slightly by composite layer formation on the membrane surface. Results showed that ionic permeability and flux was initially decreased by the CS-co-Fe$_2$NiO$_4$ layer introducing a membrane surface and increased again by a further increase in the iron-nickel oxide nanoparticles ratio from 2 to 4 wt% in the modifier solution. The PVC/CS-co-Fe$_2$NiO$_4$ nanoparticles composite membranes showed higher electrical conductivity compared to the unmodified membrane. The results are valuable for electro-membrane processes especially in electrodialysis for water recovery and waste water treatment.

1. Introduction

In recent years, ion exchange membranes have been utilized widely as active separators in various electrically driven processes such as electrodialysis for desalting brackish waters, reconcentrating brine from seawater and the production of table salt. Ion exchange membranes play an important role in environmental protection, treating industrial and biological effluents, resource recovery and food and pharmacy processing as well as the manufacturing of basic chemical products [1-14].

In ion exchange membranes, charged groups are attached to the polymer backbone and are freely permeable to opposite sign ions under the influence of an electrical field [13]. Knowledge of the electrochemical characteristics of ion exchange membranes is a major contributing factor behind decisions about their applicability in specific separation processes [1, 11, 15-17].

Preparing inexpensive ion exchange membranes with special adapted

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characteristics is a vital step in future chemical and waste treatment applications [3, 11, 18-20]. High performance may be obtained by membrane modifications [21]. A plethora of research has already been performed to improve the physico/chemical properties of ion exchange membranes which resulted in various modification techniques. Variation of functional groups, selection of different polymeric matrices, polymer blending, use of various additives, alteration of cross-link density and more uniform distribution of functional groups are important ways to obtain superior IEMs [1, 4, 5, 11, 22-27].

In recent years, the role of surface characteristics in determining the separation properties of the membrane is clear [28-30]. Different methods such as graft polymerization [31, 32], plasma modification [22], corona discharge, flame treatment [28, 33] have been utilized in membrane surface modification to alter the properties of membranes without affecting bulk properties.

In this study, surface modification of the PVC based heterogeneous cation exchange membrane was carried out to achieve efficient electrochemical properties useful in electrodialysis related to water recovery and treatment. For this purpose, polyvinylchloride (PVC) based heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional groups agent and tetrahydrofuran as solvent. *Chitosan-co-Fe$_2$NiO$_4$ nanoparticles* were employed as a membrane surface modifier by the casting technique. Currently, no research has considered the fabrication of *PVC/chitosan-co-Fe$_2$NiO$_4$ nanoparticles* composite cation exchange membrane and the literature is always silent on characteristics and functionality of electrodialysis ion exchange membranes coated with *PVC/chitosan-co-Fe$_2$NiO$_4$*.

Polyvinyl chloride (PVC) is a flexible and durable polymer with suitable biological and chemical resistance [34-36]. Chitosan (CS) is a cationic polymer with very interesting features such as hydrophilicity, biocompatibility, biodegradability, non-toxicity and adsorption properties which has been utilized widely in industrial waste treatment [37]. Iron-nickel oxide nanoparticles are a new class of advanced materials with very interesting capacity such as superior magnetic, electrical and adsorption characteristics which have been applied in water treatment. Utilizing inorganic particles especially nano-metal into polymeric membranes has been examined in many applications to enhance the separation properties of membranes based on the synergism between the organic-inorganic components properties [38, 39].

PVC/chitosan-co-Fe$_2$NiO$_4$ nanoparticles composite cation exchange membranes were prepared. The effect of *chitosan-co-Fe$_2$NiO$_4$ nanoparticles* layer on the membrane surface and also nanoparticles concentration in modifier solution on electrochemical properties of membranes was studied. During the experiment, sodium chloride was employed for the preparation of ionic solutions in membrane characterization.

Table 1
Flow sheet of membrane preparation procedure.

The procedure for IEMs preparation	
Step 1	Resin particles draying (at 30 °C for 48 h)
Step 2	Resin particles pulverizing (-300 +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

2. Materials and methods

2.1. Materials

Polyvinylchloride (PVC, S-7054, density: 490 g/l, viscosity number: 105 Cm^3/g) supplied by Bandar Imam Petrochemical Company (BIPC), Iran, was used as polymeric based binder. Tetrahydrofuran (THF, Mw: 72.11, Density: 0.89 g/cm^3) was employed as solvent. Cation exchange resin (Ion exchanger Amberlyst® 15, strongly acidic cation exchanger, Hydrogen form- 4.7 meq/g)

by Supelco was used as functional group agents in membrane fabrication. Chitosan (CS, as cationic layer) by ACROSS, iron-nickel oxide nanoparticles (Fe$_2$NiO$_4$, <50 nm particle size, as inorganic filler additive) by Aldrich, poly ethylene glycol (EG, as pore former) and acetic acid by Merck were utilized in the preparation of modifier solution/composite membrane. All other chemicals were supplied by Merck Inc., Germany. Throughout the experiment, distilled water was used.

2.2. Preparation of the PVC based heterogeneous cation exchange membrane

The Polyvinylchloride (PVC) based heterogeneous cation exchange membrane was prepared by solution casting techniques using cation exchange resin powder as a functional group agent and tetrahydrofuran as solvent. In order to undertake the membranes preparation, 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 the desired particle size (-300 +400 mesh) was used in the membranes fabrication. The preparation proceeded by dissolving the polymer binder (PVC) into the solvent (THF: Polymer binder, (20: 1) (v/w)) in a glass reactor equipped with a mechanical stirrer (Model: Velp Sientifica Multi 6 stirrer) for more than 4 h. This was followed by dispersing a specific quantity of grinded resin particle (Resin: Polymer binder, (1: 1) (w/w)) as functional group agents in the polymeric solution. The mixture was mixed vigorously at room temperature to obtain uniform particle distribution in the polymeric solution. In addition, for better dispersion of particles and breaking up their aggregates, the solution was sonicated for 30 min using an ultrasonic instrument. After the sonication stage, the mixing process was repeated for another 10 min using 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 until the solvent evaporated and solidification was completely done. Then polymeric films were immersed in distilled water. As the final stage, the membranes were pretreated by immersing in 0.5 M NaCl solution. The membrane thickness was measured as 80 µm by a digital caliper device. A summary of the membrane preparation procedure is given in Table 1.

2.3. Fabrication of PVC/CS-co-Ir Ni oxide nanoparticles composite membrane

PVC/CS-co-Ir Ni oxide nanoparticles composite membrane was produced by the casting technique. Prior to modification, membranes were dipped in distilled water in order to remove any pollutant. The prepared heterogeneous cation exchange membrane was clamped between two glassy frames. An aqueous phase containing chitosan (cationic layer), acetic acid, poly ethylene glycol (pore former) and iron-nickel oxide nanoparticles (additive) was poured on top of the prepared membrane and rolled by a soft roller to eliminate any bubble and make a uniform area. It is worth mentioning that the modifier solution was mixed vigorously at room temperature and sonicated to obtain homogenously dispersed solution during the modifier preparation. After that, the membrane was dried at ambient temperature for 24 h until solidification was completely done. Then composite membranes were pretreated by immersing in 0.5 M NaCl solution. The composition of the used modifier solution in the fabrication of the composite membrane is shown in Table 2. The modifier film was deposited on the top surface of the prepared membrane.

2.4. Test cell

The electrochemical properties measurements for the prepared membranes were carried out using the test cell (Figure 1) as described elsewhere [22, 40]. The cell consists of two cylindrical compartments made of Pyrex glass which are 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 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 purposes. In order to minimize the effect of boundary layer during experiments and to establish the concentration polarization on the vicinity of the membrane's surface, both sections were stirred vigorously by magnetic stirrers (Model: Velp Sientifica Multi 6 stirrer).

2.5. Membrane characterization

2.5.1. Morphological studies

The behavior of prepared membranes is closely related to their structure, especially the spatial distribution of the ionic site [20]. 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 the SOM by SOM device, the samples were cut in small pieces and after mounting between lamellas, observations were made by the optical microscope.

Modifier aqueous Solution	Membrane [a]				
	S_1	S_2	S_3	S_4	S_5
Chitosan (%wt)	-	2	2	2	2
Acetic acid (%wt)	-	1	1	1	1
Poly ethylene glycol (%wt)	-	1	1	1	1
Fe$_2$NiO$_4$ nanoparticles to CS (%wt)	-	-	1	2	4

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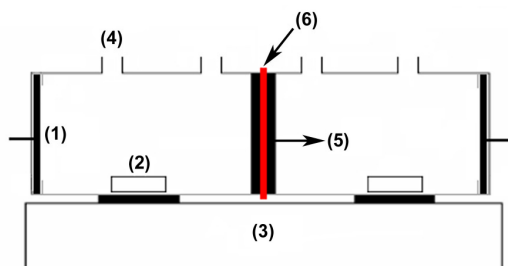

Fig. 1. Schematic diagram of test cell: (1) Pt electrode, (2) Magnetic bar, (3) Stirrer, (4) Orifice, (5) Rubber ring, (6) Membrane.

2.5.2. Membrane potential, transport number and permselectivity

The membrane potential is an 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 [4, 25, 41]. This parameter was evaluated for the equilibrated membrane with unequal concentrations of sodium chloride ionic solution (0.1 M/ 0.01 M) at ambient temperature on either sides of the membrane using a two-cell glassy apparatus (Figure 1). 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 the saturated calomel electrode (through KCl bridges) and digital auto multi-meter (DEC, Model: DEC 330FC, Digital Multimeter, China). The measurement was repeated until a constant value was obtained. The membrane potential ($E_{Measure}$) is expressed using Nernst equation [1, 27, 41-43] as follows:

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

where t_i^m is transport number of counter ions in the membrane phase, R is gas constant, T is the temperature, n is the electrovalence of counter-ion and a_1, a_2 are solution electrolyte activities in contact membrane surfaces. The ionic permselectivity of membranes is quantitatively expressed based on the migration of counter-ion through the IEMs [1, 4, 41, 43, 44]:

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

where, t_0 is the transport number of counter ions in the solution [45].

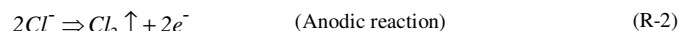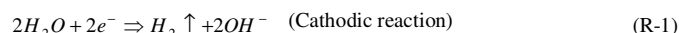### 2.5.3. Concentration of fixed charge on membrane surface

The homogeneity, concentration and uniform distribution of functional groups on the surface of the membranes provide more conducting regions and improve the membrane electrochemical properties. The concentration of fixed charge on the membrane surface (Y) has been expressed in terms of permselectivity as follows [15, 41, 43]:

$$Y = \frac{2C_{Mean}P_s}{\sqrt{1 - p_s^2}}$$
(3)

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

2.5.4. Ionic permeability and flux of ions

The measurements of ionic permeability and flux were carried out using the test cell. A 0.1 M ionic 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. During the experiment, both sections were recirculated and stirred vigorously to minimize the effect of boundary layers. The cations pass through the membrane to the cathodic section. According to anodic and cathodic reactions, the produced hydroxide ions remain in the cathodic section and increase the pH of this region.

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

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

According to Fick's first law, the flux of ions through the membrane can be expressed as follows [19, 20, 40]:

$$N = P\frac{C_1 - C_2}{d}$$
(4)

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

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

$$C_1^0 = 0.1M \; ; \; C_2^0 = 0.01M \; ; \; C_1 + C_2 = C_1^0 + C_2^0 = 0.11M$$
(6)

where, A is the membrane surface area. Integration of equation (5) was as follows:

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

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

2.5.5. Electrical resistance

The electrical resistance of the equilibrated membrane was measured in NaCl solution with 0.5 M concentration at ambient temperature [27, 40, 42]. Measurement was carried out by an alternating current bridge with 1500 Hz frequency (Audio signal generator, Electronic Afzar Azma Co. P.J.S).

The membrane resistance is calculated using difference resistance between the cell (R_1) and electrolyte solution (R_2) ($R_m = R_1 - R_2$). The areal resistance was expressed as follows:

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

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

3. Results and discussion

3.1. Morphological studies

The SOM studies have been carried out to evaluate the morphology and ionic/additive sites condition in the prepared membrane. The membranes SOM images in transmission mode with light going through them are depicted in Figure 2. The polymer binder, resin particles and additive nanoparticles used are clearly seen in the images. As it is observed, the brightness of the images were decreased and dark regions were increased by the chitosan-co-iron nickel oxide nanoparticles layer formation on the membrane surface which restricts the light transmission through the membranes. Moreover, images show a relatively uniform surface for the membranes. As shown, the particles (resin and additive) are uniformly distributed in the prepared membranes. It reveals that sonication has a

significant effect on the distribution of particles in the prepared composite membranes and results in formation of a more uniform phase. The excessive homogeneity and uniform distribution of particles (i.e. resin and Fe_2NiO_4) in the bulk and on the surface of the membrane provide superior conducting regions and generate easy flow channels for counter ion transportation. The presence of a more conducting region on the membrane surface can strengthen the intensity of the uniform electrical field around the membrane and decrease the concentration polarization phenomenon. Furthermore, uniform distribution of particles increases the viscosity of casting solution and reduces the evaporation rate of the casting solvent which improves the polymer chains relaxation as well as its conformation with the particles surfaces and enhances the membrane selectivity [46-48].
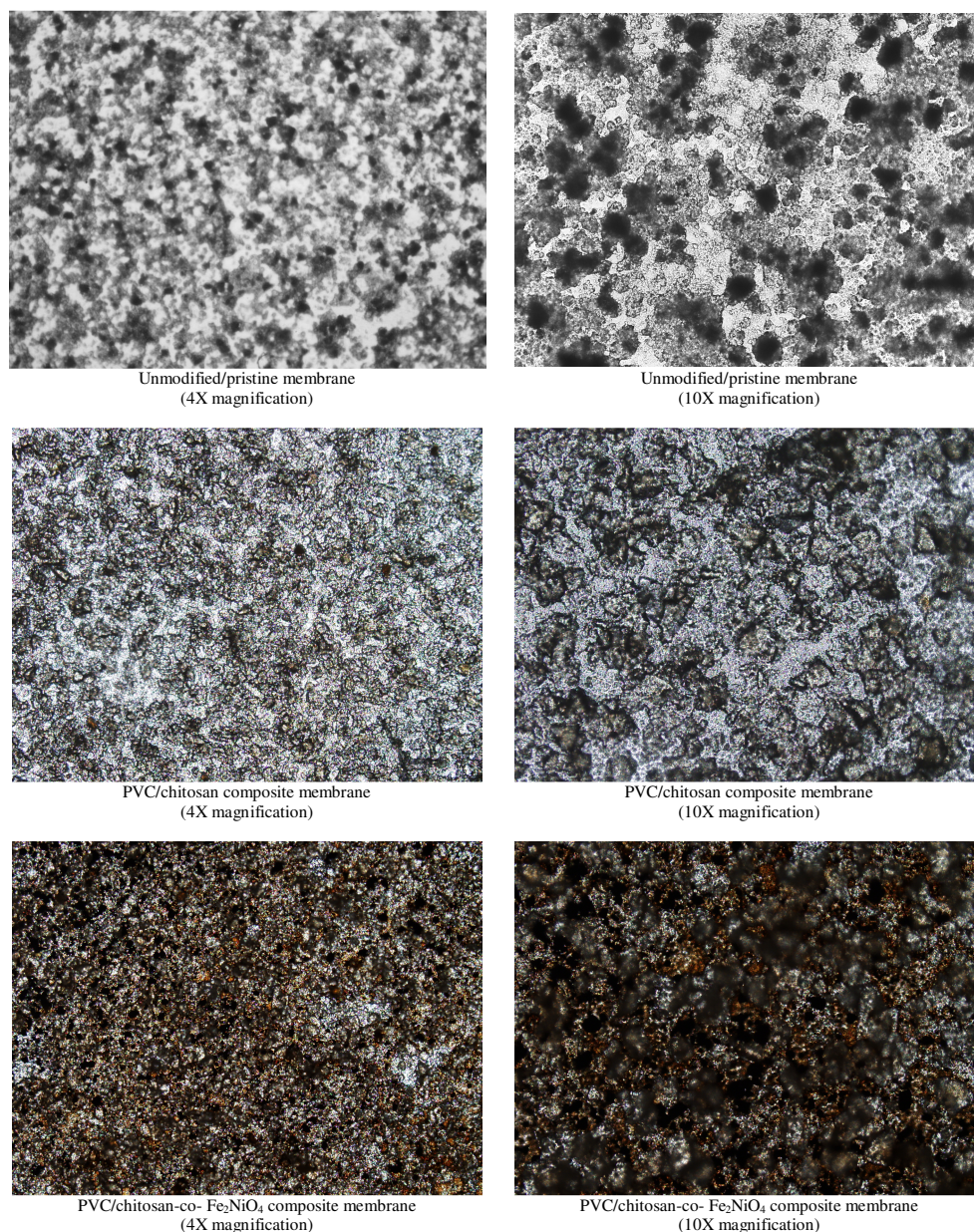

Fig. 2. The SOM images of prepared membranes with 4 X and 10 X magnifications; unmodified membrane, CS coated membrane and CS-co-Fe$_2$NiO$_4$ coated composite membranes.

3.2. Membrane potential, permselectivity and transport number

The membrane potential (Figure 3) was improved slightly by formation of the CS-co-Ir Ni nanoparticles layer on the membrane surface in sodium chloride ionic solution. This may be attributed to the increase of membrane charge density (Figure 3) because of amino functional groups of CS and unique adsorptive characteristic of chitosan and iron oxide nanoparticles which provide additional conducting regions for the membranes and generate suitable flow channels for easy passage of counter ions. This leads to enhanced Donnan exclusion that is responsible for increment of membrane potential [1, 4, 41, 49].

The permselectivity and transport number of membranes in NaCl solution are depicted in Figure 4. The composite membranes showed better selectivity and transport number compared to the unmodified membrane. This occurrence can be explained with respect to the increase of membrane charge density with improved control of pathways for ion traffic. Moreover, the diffusion of chitosan and nanoparticles into the membrane matrix occupy the cracks, voids and cavities in the membrane. This makes the ionic pathways narrow in the membrane matrix as space limiting factors and strengthens the ionic site dominations on ion traffic and improves the membrane selectivity.

3.3. Ionic permeability and flux of ions

During the experiment, ions pass through the membrane and reach the concentration section. The obtained results (Figure 5) showed that ionic permeability and flux were decreased initially by the CS-co-Ir Ni nanoparticle layer formation on the membrane surface. This may be attributed to formation of a rigid layer on the membrane surface and narrow ionic pathway in the membrane matrix which makes the ions transportation difficult. This reduces the permeability and flux. The ionic permeability and flux was enhanced

again by a further increase in the iron-nickel oxide nanoparticles ratio from 2 to 4 %wt in the modifier solution. This may be due to an increase of layer porosity on the membrane surface by more additives loading ratios which enhances the heterogeneity and increases the accessibility of ion exchange functional groups in this layer. Also, the unique adsorptive characteristic of Fe_2NiO_4 nanoparticles improve the electrostatic interactions of ions with the membrane surface and so facilitate the ions transportation between the solution and membrane phase which enhances the ion traffic.
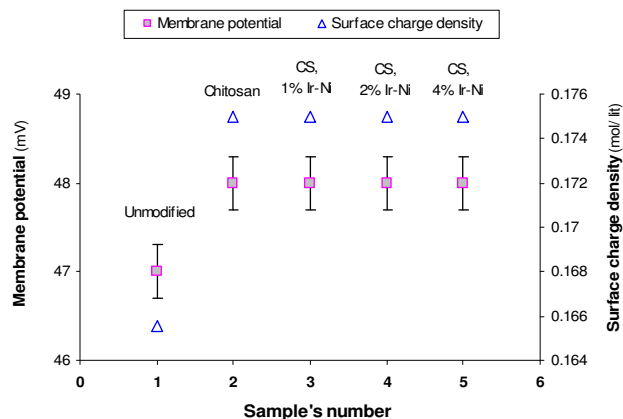
3.4. Electrical resistance

The PVC/CS-co-Fe_2NiO_4 nanoparticles composite membranes showed higher electrical conductivity compared to the unmodified ones in 0.5 M NaCl solutions (Figure 6). This is due to an increase of charge density for the composite membranes which in turn enhances the ions transportation. This decreases the membrane electrical resistance. Introducing the CS-co-Fe_2NiO_4 nanoparticles layer on the membrane surface provides more functional groups (amino groups of chitosan) and unique adsorptive sites (CS and Fe_2NiO_4) for the modified membrane which improves the ionic transportation between the solution and membrane and thus declines the membrane areal resistance.

Fig. 3. The effect of CS-co-Ir-Ni oxide nanoparticles layer on membrane potential and surface charge density of prepared composite membranes in sodium chloride ionic solution.
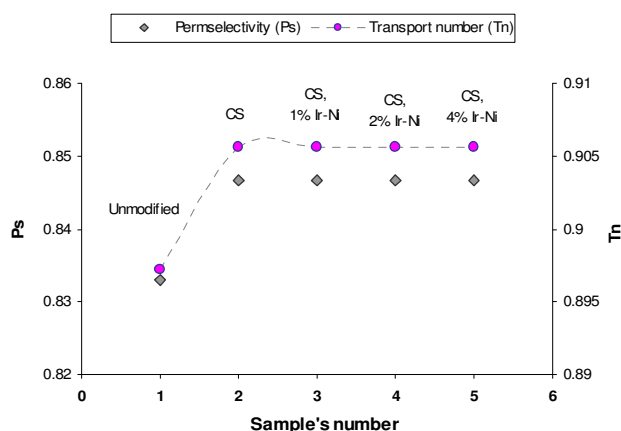

Fig. 6. The effect of CS-co- Fe_2NiO_4 coated layer on the areal electrical resistance of prepared composite ion exchange membranes.

4. Conclusions

SOM images showed that particles are uniformly distributed in the prepared membranes. SOM images showed uniform particle distribution and relatively uniform surfaces for the membranes. The brightness of images was decreased and dark regions were increased by CS-co-Fe_2NiO_4 layer formation on the membrane surface. It was found that membrane potential, transport number, selectivity and surface charge density were improved slightly by composite layer formation on the membrane surface. Also, results showed that membrane ionic permeability and flux was decreased initially by CS-co-Fe_2NiO_4 nanoparticle layer fabrication on the membrane surface. The ionic permeability and flux was increased again by further increase in iron-nickel oxide nanoparticles concentration from 2 to 4 %wt in the modifier solution. The PVC/CS-co-Fe_2NiO_4 nanoparticles composite membranes showed higher electrical conductivity compared to the unmodified membrane. The results are valuable for electro-membrane processes especially in the electro-dialysis process for water recovery and waste water treatment.

Fig. 4. Comparison between the transport number and selectivity of prepared membranes; Un-modified membrane and PVC/CS-co-Ir Ni oxide nanoparticles composite membranes.
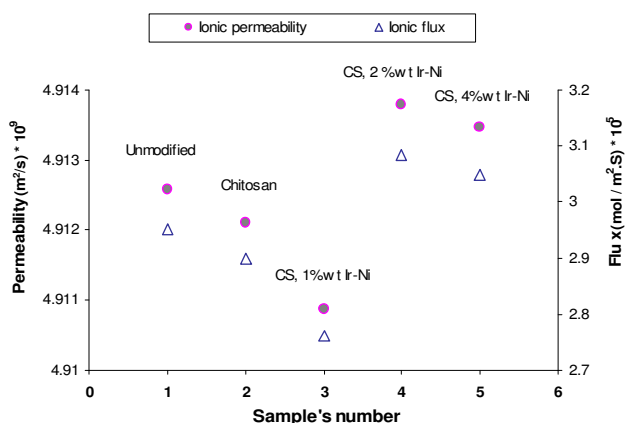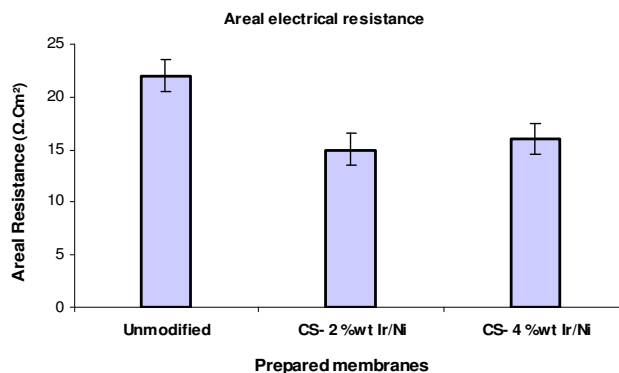
Fig. 5. The effect of CS-co-Ir Ni oxide nanoparticles layer on ionic permeability and flux of cation exchange membranes in sodium chloride ionic solution.

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