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Enhancing Electrochemical Performance of Heterogeneous Cation Exchange Membranes by Using Super Activated Carbon Nanoparticles

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ABSTRACT

Polyvinylchloride (PVC) based heterogeneous cation exchange membranes were prepared by the solution casting technique. The effect of super activated carbon nanoparticles concentration as filler additive in membrane matrix on ionic transfer behaviors of the membrane was studied. SOM images showed uniform particles distribution and relatively uniform surfaces for the membranes. The membrane water content was improved initially by using of super activated carbon nanoparticles up to 0.5 %wt in the casting solution and then began to decrease by more increase of nanoparticles content ratios from 0.5 to 4 %wt. Utilizing of activated carbon nanoparticles in the casting solution also led to increase of water contact angle, membrane ion exchange capacity, fixed ionic concentration, membrane potential, transport number and membrane selectivity obviously.An Opposite trend was observed for the membrane electrical resistance. The sodium flux/permeability was also enhanced initially by increase of nanoparticles concentration up to 0.5 %wt and then decreased slightly by more increase of nanoparticles loading ratios from 0.5 to 1 %wt. The sodium flux was sharply enhanced again by more increase of nanoparticles concentration form 1 to 4 %wt. The membrane transport number and selectivity were increased initially by increase of electrolyte concentration and then showed decreasing trend. The membranes showed higher transport number and selectivity at neutral pH compared to other pH values. The ED results showed that dialytic rate of lead ions was increased by utilizing of super activated carbon nanoparticles in the membrane matrix.

Keywords: Cation exchange membrane, Super activated carbon nanoparticles, Mixed matrix, Ionic transport property, Electrodialysis.

INTRODUCTION

Over half a century ago, ion exchange membranes (IEMs) have been developed from laboratory tools to industrial products as active separators. The classification of IEMs subjects to the type of ionic groups that they pass through them. Ion exchanger membranes which pass cations as counter ions and reject anions as co-ions are called cation exchange membranes. In this type of membranes, negative charged groups fixed to the membrane backbone whereas membranes with opposing behavior and positive functional groups are known as anion

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exchange membranes [1-4].

Different ion exchange membranes have been produced according to their requirements. IEMs are efficient tools as separators in various electrically driven processes such as electrodialysis for desalination of brackish waters, concentrating brine from seawater and production of table salt. Furthermore IEMs are used on a large scale in many commercial processes such as energy conversion or storage processes like fuel cells, electrical batteries and sensors. They also have important role in environmental protection for treating industrial and biological effluents. Additionally, IEMs have been widely used in resource recovery and food and pharmacy processing as well as manufacturing of basic chemical products [4-5,5-9].

In such processes, ion interactions with the membrane, water and each other occur in complex fashion. Therefore, knowledge about the electrochemical properties of ionic membrane is an important factor about their application in separation process [8-10].

Besides, demands for the superior ion exchange membranes are increased for the separation of dangerous pollutants soluble in water especially heavy metals are increasing which is due to an increase in reusing water and its quality. A number of researches have already been conducted to find ways for improving the physico-chemical and separation properties of the IEMs. Some important techniques are as follows: variation of functional group type, selection of different polymeric material, polymer blending, utilization of inorganic additives/filler, alteration of cross-link density and surface modification [8, 11-15]. Fabrication of adsorptive membranes by using adsorptive polymers or nanomaterials has also been studied to enhance the separation performance of the membranes especially for heavy metal elimination from water [16-18].

According to the reported studies, activated carbon particles have been used in waste treatment. Removal of endocrine disruptors and pharmaceuticals by using activated carbon particles have been examined by Snyder , et al [19]. In another research, Anisuzzaman et al. [20] studied the removal of 2, 4-dichlorophenol from wastewater by using activated carbon particles. Daifullah and the colleagues [21] worked on $KMnO_4$-modified activated carbon derived from steam pyrolysis of rice straw for waste treatment. Ramos and his colleagues [22] also used adsorptive activated carbon in fluoride removal from waste water. The application of activated carbon nano-fiber in capacitive deionization has also been studied elsewhere [23, 24]. Based on the literature survey, currently no reports have considered incorporating super activated carbon nanoparticles into IEMs and the literature is silent on characteristic and functionality of ion exchange membranes modified by super activated carbon nanoparticles.

Preparing the novel heterogeneous cation exchange membranes with appropriate physico-chemical properties for the application in electrodialysis processes relating to water recovery and treatment is the primary target of the current research. For this purpose, PVC based heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional group agent. Super activated carbon nanoparticles were also employed as inorganic filler additive in membrane fabrication in order to improve the IEMs properties. The super activated carbon nanoparticles are new class of advanced materials with very interesting features and capacity such as powerful specific surface area, superior selective adsorption characteristic and negative-ions concentration which make it usable in water desalination. PVC is also a flexible and durable polymer with suitable biological and chemical resistance [25].

The effects of super activated carbon nanoparticles concentration in the casting solution and electrolyte concentration/environment pH variation on the membrane electrochemical properties were also studied. Electrodialysis experiment was also carried out in a laboratory scale unit to evaluate the electrodialysis performance of modified membranes in Pb removal from waste water. The results are valuable for electro-membrane processes especially in electrodialysis process for water recovery and waste water treatment.

EXPERIMENTAL PROCEDURES

Materials and Methods

Polyvinylchloride (PVC, grade 7054, density: 490 g/L, viscosity: 105 cm^3/g) supplied by BIPC company, Iran, was used as binder. Tetrahydrofuran (THF, Merck Inc, Germany) was employed as solvent. Super activated carbon (black powder, average particle size <100nm) was used as inorganic filler additive and cation exchange resin (Ion exchanger Amberlyst® 15, acidic cation exchanger, H^+ form- more than 1.7 mEq/g dry, spec. density 0.6 g/cm^3, particle size (0.355- 1.18 mm) ≥ 90%) by Merck Inc., Germany, were also used in membrane fabrication. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used.

Preparation of Mixed Matrix Cation Exchange Membranes

The heterogeneous cation exchange membranes were prepared by solution casting technique and phase inversion method. Ion exchange resin with desired particles size (37<d≤44 μm) was used as functional group in membrane fabrication. For this purpose, they were pulverized into fine particles in a ball mall and sieved to the desired mesh size. The preparation was proceeded to dissolve the polymer binder into THF solvent in a glass reactor equipped with a mechanical stirrer. The preparation process was followed by dispersing resin particles and super activated carbon nanoparticles in polymeric solution, respectively. In addition, for better dispersion of particles and breaking up their aggregates, the solution was sonicated for 1 h using an ultrasonic instrument (30 °C, 28 KHz, PARS NAHAND ENG. CO). The homogeneity and uniform distribution of particles in the membrane matrix improves the membrane selectivity. Afterward, the mixing process was repeated for another 30 minute by using the mechanical stirrer. Then the mixture was casted onto a clean and dry glass plate at ambient temperature. The membranes were dried and immersed in distilled water. As final stage, the membranes were pretreated by immersing in 1M NaCl solution for 48 h. The membrane thickness was measured by a digital caliper device (Electronic outside micrometer, Ip54 model OLR) about 70μm. The composition of casting solution is given in Table 1.

Table 1: Compositions of casting solution used in preparation of cation exchange membranes.

Membrane	(Additive- super activated carbon) (%wt)
Sample 1 (S1)	0.0 (Unmodified/Pristine membrane)
Sample 2 (S2)	0.5
Sample 3 (S3)	1.0
Sample 4 (S4)	2.0
Sample 5 (S5)	4.0

(Polymer binder (PVC): Solvent (THF)) (w/v), (1: 20); ((Resin particle: Polymer binder) (w/w), (1:1))

Experimental Test Cell

The measurements of membrane electrochemical properties were carried out using the test cell as shown in Figure 1. In order to minimize the effect of boundary layer and to establish the concentration polarization on the vicinity of membrane surface, both sections were stirred vigorously by magnetic stirrers. The membrane area was 19.63 cm^2.

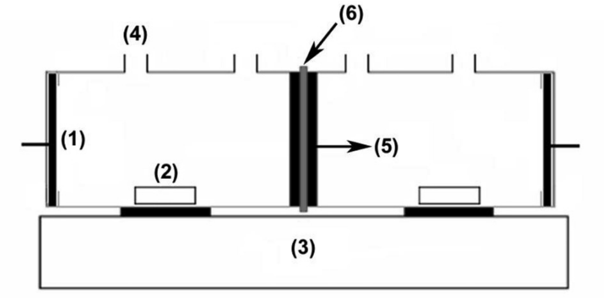


Figure 1: Schematic diagram of test cell: (1) Pt electrode, (2) Magnetic bar, (3) Stirrer, (4) Orifice, (5) Rubber ring, (6) Membrane.

Membrane Characterization

SOM Studies

The electrochemical behavior of prepared membranes is closely related to the spatial distribution of ionic site in membrane matrix. 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.

Water Contact Angle

The membrane contact angle measurement was carried out to evaluate the changes in surface hydrophilicity/hydrophobicity of the prepared membranes. The measurements were carried out at ambient condition using the water drop method on dry membranes. To minimize the experimental error, the contact angle was measured in five random locations for each sample and then their average was reported.

Water Content

The water content is described as the weight difference between the dried and swollen membranes. The wet membrane was weighed (OHAUS, Pioneer ™, Readability: 10^{-4} g, OHAUS Corp) at room temperature and then it dried in oven until the constant weight was obtained. Following equation [26-29] can be used for water content calculation:

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

Where W_{wet} is the weight of wet membrane and W_{dry} is the weight of dried membrane.

Ion Exchange Capacity (IEC) and Fixed Ion Concentration (FIC)

The IEC determination was performed using titration method. For the IEC measurements, the membranes in acid form (H^+) were converted to Na^+ form by immersing in 1 M NaCl solution to liberate the H+ ions. The H^+ ions in solution were then titrated with 0.01 M NaOH and phenolphthalein indicator. The IEC can be calculated from the following equation [28, 30-32]:

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

Where a, is the milli-equivalent of ion exchange group in membrane and W_{dry} is the weight of dry membrane (g). The fixed ion concentration also (F.I.C) can be calculated by:

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

Membrane Potential, Transport Number and Permselectivity

The membrane potential is 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 [15, 30, 31, 33]. This parameter was evaluated for the equilibrated membrane with unequal concentration of electrolyte solution (C_1= 0.1 M, C_2= 0.01 M) on either sides of the membrane used in the glass cell (Figure 1) at ambient temperature. During the experiment, electrolyte solution in each section was vigorously stirred to minimize the effect of boundary layers. The developed potential across the membrane was measured by connecting both compartments and using saturated calomel electrode (through KCl bridges) and digital auto multimeter (DEC, Model: DEC 330FC, Digital Multimeter, China). The membrane potential ($E_{Measure}$) is expressed using Nernst equation [26, 30, 32-35] as follows:

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

$$t_i^m = \frac{1}{2}[(E_{\text{Measure}})(\frac{nF}{RT})\text{In}(\frac{a_2}{a_1}) + 1] \tag{4}$$

where t_i^m is transport number of counter ions of membrane phase, R is gas constant, T is the temperature (K), n is the electrovalence of counter-ion and a_1 , a_2 are solutions electrolyte activities in contact membrane surfaces. The fraction of the total current carried by any particular ion is known as the transport number of that ion.

The ionic perm selectivity of membranes also is quantitatively expressed based on the migration of counter-ion through the IEMs [33-36]:

$$P_S = \frac{t_i^m - t_0}{1 - t_0} \tag{5}$$

Where, t_0 is the transport number of counter ions of the solution [37].

Ionic Permeability and Flux of Ions

Ionic permeability and flux measurements were carried out using the test cell. A 0.1 M solution was placed on anodic side of the cell and a 0.01 M solution on its cathodic side. A DC electrical potential (Dazheng, DC power supply, Model: PS-302D) with optimal constant (voltage 10 V) was applied across the cell with stable platinum electrodes. The cations pass through the membrane to cathodic section. During the experiment, both sections were recirculated and stirred vigorously to minimize the effect of boundary layers. The cations pass through the membrane to cathodic section and electrons pass through metals to this section. Also, according to anodic and cathodic reactions the produced hydroxide ions remain in cathodic section and increase the pH of this region.

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

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

According to the first Fick's law, the flux of ions through the membrane can be expressed as follows [32,38]:

$$N = -\frac{V}{A} \times \frac{dC_1}{dt} = P\frac{C_1 - C_2}{d} \tag{6}$$

Where, P is coefficient diffusion of ions, d is membrane thickness, N is ionic flux and C is the cations concentration in the compartments. The boundary conditions are:

$$C_1^0 = 0.1M \text{ , } C_2^0 = 0.01\text{M ,}$$
$$C_1 + C_2 = C_1^0 + C_2^0 = 0.1 \ M \tag{7}$$

Where, A is the membrane surface area. Integration of Equation 6 is as follows:

$$\text{In}\frac{(C_1^0 + C_2^0 - 2C_2)}{(C_1^0 - C_2^0)} = -\frac{2PAt}{vd} \tag{8}$$

Where V is the volume of each compartment in the used test cell and t is the time. The diffusion coefficient and the flux of cations of membrane phase were calculated from equation (8) considering pH changes measurements (Jenway, Model: 3510) in cathodic section.

Electrical Resistance

To measure the electrical resistance of membrane, 0.5 M NaCl solution was used on both sides of the cell at ambient temperature. Measurement was carried out by an alternating current bridge with 1500 Hz frequency (Audio signal generator, Electronic AfzarAzma Co. P. J. S). The membrane resistance is calculated using the different resistance between the cell (R_1) and electrolyte solution (R_2) ($R_m=R_1-R_2$) [14, 28, 29]. The membrane areal resistance was expressed as follows:

$$r=(R_mA) \quad (9)$$

Where, R_m is the membrane resistance and A is the membrane surface area.

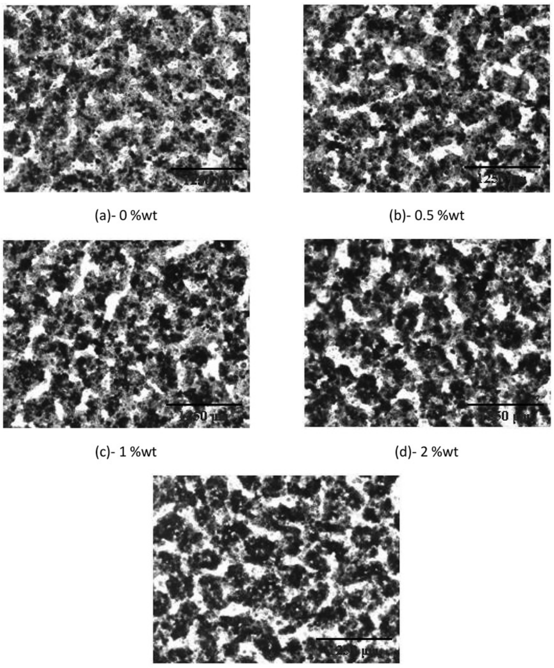
Electrodialysis for Pb Removal

The electrodialysis experiment was also carried out in a laboratory scale electrodialysis unit containing one cell pair of homemade cation exchange membrane and commercial anion exchange membrane with 19.63 cm^2 effective area to evaluate the electrodialytic performance of the modified membranes for water treating in Pb removal. Commercial heterogeneous anion-exchange membrane (RALEX® AMH-PES), made by MEGA a.s., Czech Republic, was used in this study. The anionic membrane contains fixed quaternary ammonium functional groups. Water content of the commercial membrane was measured as 63% (g absorbed water/g dry membrane). The ion exchange capacity (IEC) was also obtained as 1.85 (meq/g dry membrane). The Pb $(NO_3)_2$ electrolyte solution of known volume (180 cm^3) and concentration (0.01 M) was applied in the treated compartment, while 0.01 M NaCl solution was recirculated in the concentration compartments. The variation in concentration was determined by considering conductivity changes in treated compartment and also pH changes in cathodic region respectively.

RESULTS AND DISCUSSION

Morphological Studies

SOM studies have been utilized to evaluate the ionic sites condition and filler nanoparticle spatial distribution in the membrane matrix. The SOM images are shown in Figures 2 and 3. The polymer binder and resin particles (conducting ionic area) are seen in the images clearly. The used particles (resin and additive) are observed as dark spots. As seen in the images, dark regions are increased at higher super activated carbon nanoparticles content ratio. Images also show a relative uniform surface for the prepared membranes. The images also show uniform distribution of particles for the prepared membranes.



(a)- 0 %wt

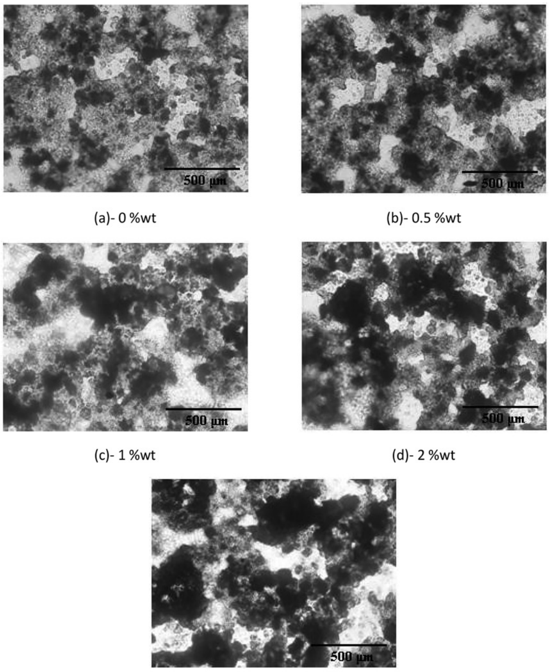
(b)- 0.5 %wt

(c)- 1 %wt

(d)- 2 %wt

(d)- 4 %wt

Figure 2: SOM images (4 X) of membranes with different concentration of super activated carbon nanoparticles: (a)0.0 %wt; (b)0.5 %wt; (c)1.0 %wt; (d)2.0 %wt; (e)4.0 %wt.



(a)- 0 %wt (b)- 0.5 %wt

(c)- 1 %wt (d)- 2 %wt

(d)- 4 %wt

Figure 3: SOM images (10 X) of home-made membranes with different nanoparticles content ratios: (a)0.0 %wt; (b)0.5 %wt; (c)1.0 %wt; (d)2.0 %wt; (e)4.0 %wt.

The homogeneity and uniform distribution of functional groups provide more conducting areas for the membrane which improve the membranes ionic transfer properties. This also can strengthen the intensity of uniform electrical field around the membrane and decreases the concentration polarization phenomenon [39]. Moreover, uniform distribution of solid particles in the membrane matrix improves the compatibility of particles and polymer binder which promotes the membrane selectivity [14, 40].

Membrane Water Content and Contact Angle

Obtained results (Figure 4) indicated that application of activated carbon nanoparticles up to 0.5 %wt in the casting solution led to increase water content for the prepared membranes. This may be due to an increase in membrane heterogeneity by the increase in additive loading ratio which enhances the amount of voids and cavities throughout the membrane matrix which subsequently improves the amount of water absorption and accommodation.

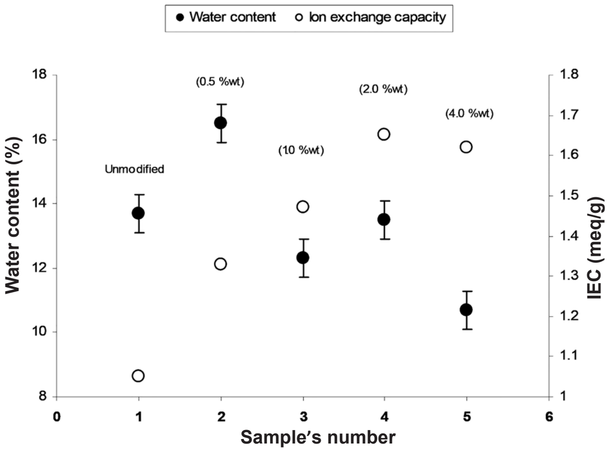


Figure 4: The water content and ion exchange capacity of prepared membranes with various ratios of super activated carbon nanoparticles (%wt).

The water content was decreased again by more enhancement of nanoparticle concentration in the casting solution. This is attributed to hydrophobic characteristic of used nanoparticles which reduces the membrane water content. Moreover, the pore filling/pore blockage phenomenon by the filler nanoparticles at high additive loading ratios reduces the amount of water molecules accommodation in the membrane matrix [41]. The swelling of the prepared membranes was less than 5% in thickness. Moreover this was negligible in length and width. This indicates that solvation does not change dimensions of the membrane manifestly. The suitable amount of membrane water content can take control the pathways of ions traffic and improves the membrane permselectivity.

The contact angle was measured 93°, 96°, 98°, 103°and 110° for the prepared samples (S1 to S5). The obtained results imply that by applying activated carbon nanoparticles in the casting solution a less hydrophilic surface is produced. This is attributed to hydrophobic characteristic of nanoparticles on the membrane surface which declines the surface hydrophilicity. Moreover, change in surface roughness by using of nanoparticles affects on membrane surface hydrophilicity.

Ion Exchange Capacity and Fixed Ion Concentration

The IEC results (Figure 4) indicated that increasing of activated carbon nanoparticles content ratio up to 2 %wt in the casting solution led to an improvement in ion exchange capacity in prepared membranes from 1.05 to 1.65 (mEq/g). This may be attributed to adsorption characteristic of carbon activated nanoparticles which caused superior interaction between ions and surface of membrane and facilitates the ion transportation between the solution and membrane phase. The high surface area to volume ratios of the nanoparticles was also favorable for diffusion of ions from solution onto the active sites of particles surface which improves the accessibility of ion exchange functional groups in membrane matrix. Also the carboxyl and hydroxyl groups of super activated carbon nanoparticles enhance the ionic functional groups of the membrane. The ion exchange capacity was decreased again slightly by more increase of additive concentration from 2 to 4 wt%. This may be due to decrease of ion exchange functional groups' accessibility in the membrane matrix at high nanoparticles loading ratio which occupy the channels and spaces around the resin and reduce the ion exchange possibility by the resin particles isolation.

In addition, there is a relationship between the IEC and water content which optimizes their effects during the process. The membrane FIC results are shown in Figure 5. As shown in the figure, increase of activated carbon nanoparticles concentration in the casting solution led to increase of membrane FIC. The high fixed ion concentration can have better control on the pathway of counter ions traffic in the matrix and increases the ionic selectivity.

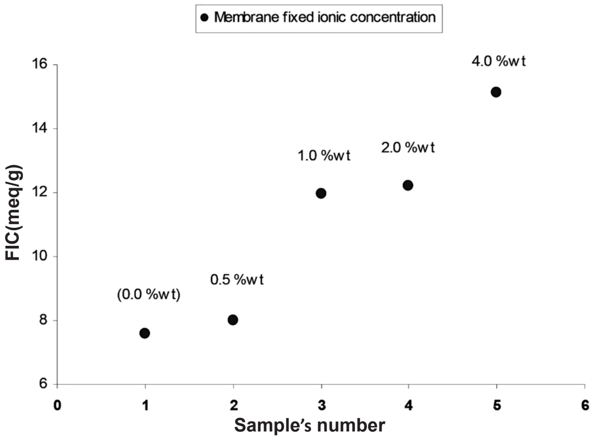


Figure 5: The effect of nanoparticles concentration (%wt) on fixed ionic concentration of home-made membranes.

Membrane Potential, Permselectivity and Transport Number

Obtained results revealed that the membrane potential, transport number and permselectivity (Figures 6, 7) were improved in sodium chloride ionic solution by inclusion super activated carbon nanoparticles in the membrane matrix. This behavior may be attributed to the increase in fixed ionic concentration (FIC) which provides more conducting regions/suitable flow channels for the membrane with improved control for the ions traffic. This leads to enhanced Donnan exclusion that is responsible for the enhancement of the membrane potential, transport number and selectivity [33, 35, 42]. Moreover, occupation of the ionic pathways by the used nanoparticles limits the spaces and makes narrow the channels which strengthens the ionic sites dominations on ions traffic and improves the selectivity.

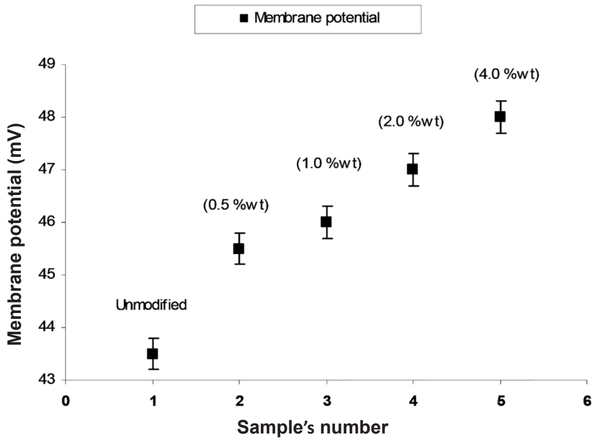


Figure 6: Membrane potential of fabricated membranes in NaCl ionic solution.

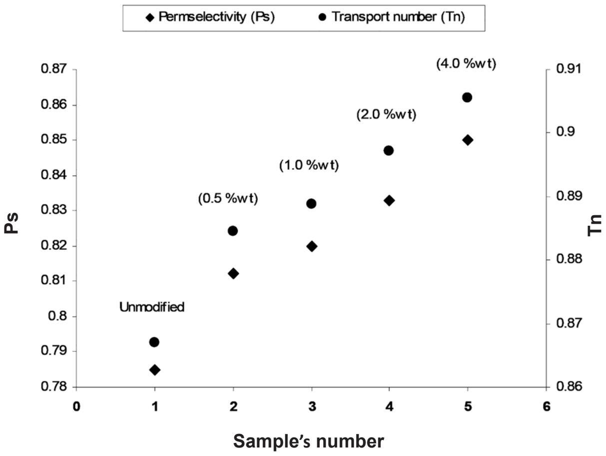


Figure 7: Transport number and permselectivity of cation exchange membranes with various concentration of SAC nanoparticles in NaCl ionic solution.

Ionic Permeability and Flux

The modified membranes showed a higher ionic permeability and flux in comparison with the unmodified ones generally. The obtained results (Figure8) revealed that the membrane ionic permeability and flux were enhanced initially by increasing nanoparticles concentration up to 0.5%wt in the casting solution. This may be attributed to the adsorption characteristic of activated carbon nanoparticles which in turn enhances the ions interactions with membrane surface and strengthens the intensity of electrical field around the membrane. These improve the counter ions transportation through the membrane matrix. Moreover, increase of membrane water content by using additive nanoparticles up to 0.5 %wt causes formation of appropriate ionic transfer pathways in the membrane matrix and facilitates the ions traffic.

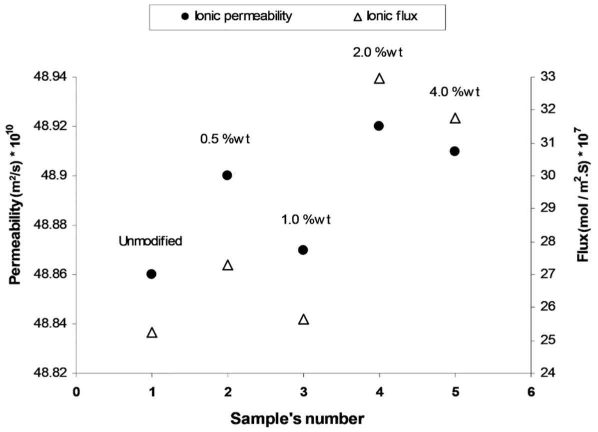


Figure 8: The sodium permeability and flux for the home-made membranes at various loading ratios of super activated carbon nanoparticles.

The ionic permeability and flux were decreased slightly by further nanoparticles loading ratios from 0.5 to 1 wt% in the casting solution. This may be attributed to pores filling/blockage phenomenon by the nanoparticles and consequent reduction of membrane water content, which in turn, makes the ions transportation thorough the membrane matrix more difficult leading to a decline in the flux. Again, the ionic permeability and flux were enhanced sharply by nanoparticles concentration form 1 to 4 wt%. This may be due to discontinuity of polymer chains in the binder at high additive concentration, which enhances the membrane permeability. Moreover, the superior adsorption characteristic of super activated carbon nanoparticles at high nanoparticle content ratios can be prevailed upon the negative effect of filling phenomenon of pores increasing the membrane ionic permeability/flux.

Electrical Resistance

The electrical resistance is practically important due to its relation with energy consumption in the process. The areal electrical resistance of the unmodified membrane (sample 1) and the modified membranes (samples 4 and 5) are shown in Figure 9.

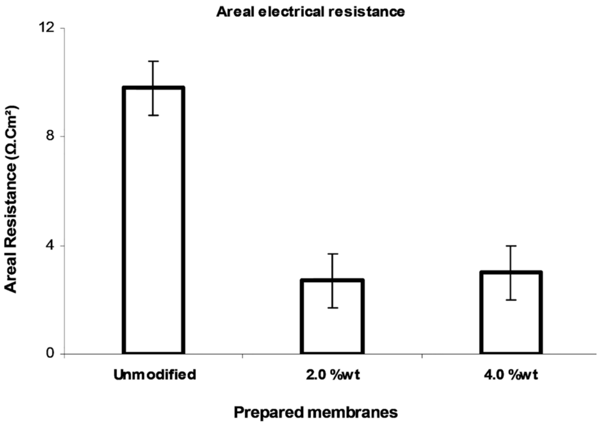


Figure 9: The effect of super activated carbon nanoparticles concentration (%wt) in the casting solution on membrane areal electrical resistance.

It was found that the real electrical resistance was declined sharply by utilizing super activated carbon nanoparticles in the membrane matrix. This is due to adsorption property of the used additive, which facilitates the ion transportation between the solution and the membrane. Generally, less selective membranes have lower membrane resistances, but this is not always true and it depends on the membrane structure and properties [43].

Tables 2 and 3 also compare the electrochemical properties of prepared membranes in this study with some commercial membranes and the current state-of-the-art membranes, respectively. The obtained results for membrane selectivity, electrical resistance and ion exchange capacity show that the modified membranes (S4, S5) in this study is comparable with that of other reported ones.

Table 2: Comparison between the electrochemical properties of prepared membrane in this study and some commercial membranes [1, 6, 43].

Membrane	Permselectivity [a] (%)	Electrical resistance [b] (Ω cm²)	IEC (meq/g)
Un-modified membrane (S1) (HCEM) [c]	> 78	9 – 10	1.05
Modified membrane (S4) (HCEM)	> 83	2 – 3	1.65
Modified membrane (S5) (HCEM)	> 85	3 – 4	1.62
Fumasep® FKD	> 95	< 3	-
Tokuyama Soda Co. Ltd. Japan (Neosepta CMX)	97	1.8 – 3.8	-
CSMCRI, India (HCEM)	87	4 – 6	0.67 - 0.77
Ralex® CMH-PES (HCEM)	> 92	< 10	2.2
Ionics Inc., USA (61CZL386) (HCEM)	_	9	-
RAI Research Corp., USA R-5010-H	95	8 – 12	-
FuMA-Tech GmbH, Germany FKB	_	5 – 10	-
Ionics Inc., USA, CR61-CMP (HCEM)	_	11	-

[a] (Measured in 0.1/ 0.01M NaCl solution)

[b] (Measured in 0.5 M NaCl solution)

[c] (Heterogeneous cation exchange membrane)

Table 3: Comparison of the performance characteristics of modified ion exchange membrane reported in this study with that of the some earlier reported researches [8, 45-49].

Membrane	Permselectivity [a] (%)	Electrical resistance [b] (Ω cm^2)
(S4) (2 %wt AC NPs)	> 83	2 – 3
(S5) (4 %wt AC NPs)	> 85	3 – 4
HCEM (2.0 %wt- Zeolite NPs) [8]	> 88	6 - 7
HCEM (2.0 %wt- AMAH) [45]	> 95	14 - 15
HCEM (2.0 %wt- SiO_2 NPs) [46]	> 90	6 – 7
HCEM (0.5 %wt- Fe_3O_4/PAA NPs) [47]	> 84	11 - 12
HCEM (8.0 %wt- Al_2O_3 NPs) [48]	> 80	6 - 7
HCEM (1.0 %wt- Clay NPs) [49]	> 89	9 - 10

[a] (Measured in 0.1/ 0.01M NaCl solution)
[b] (Measured in 0.5 M NaCl solution)

Effects of Concentration/pH on Transport Number and Selectivity

Results showed that (Figures 10-12) membrane potential, transport number and permselectivity all were improved initially by increasing electrolyte concentration. This may be attributed to the increase of counter ions concentration in the electrolyte environment, which increases the possibility of ionic interaction with the membrane surface. This leads to enhanced Donnan exclusion. The results are significantly in contrast with Donnan equilibrium theory [33, 35, 43, and 44]. The membrane potential, transport number and permselectivity were declined again by further increase in electrolyte concentration. This may be assigned to concentration polarization phenomenon and membrane swelling at high salt concentration which increases the possibility of co-ions percolation through the membrane matrix.

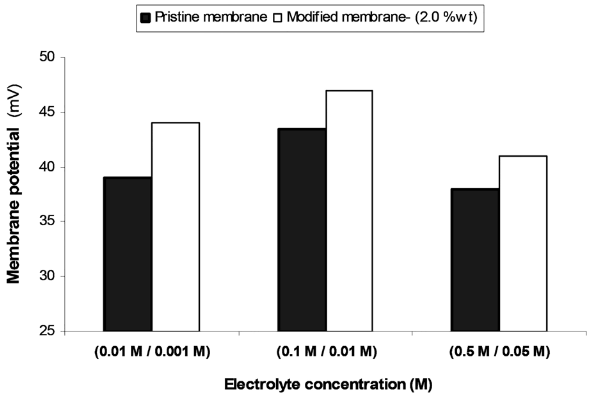


Figure 10: The effect of electrolyte concentration on membrane potential of prepared cation exchange membranes.

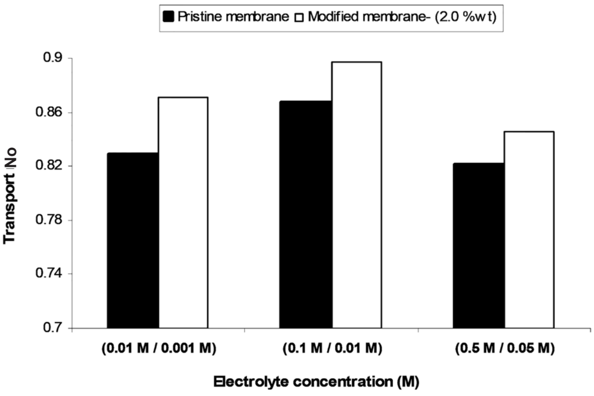


Figure 11: The transport number of prepared membranes at different electrolyte concentration; (NaCl ionic solution, neutral pH).

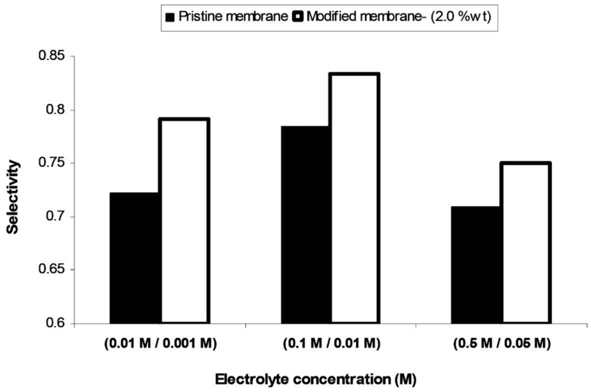


Figure 12: The effect of electrolyte concentration on membrane permselectivity.

The achieved results also (Figures 13-15) showed higher potential, transport number and selectivity at pH=7 compared to other pH values. This is because of the difference in functional groups dissociation at various pH values, which has important impact on the charge nature of the membrane matrix [15].

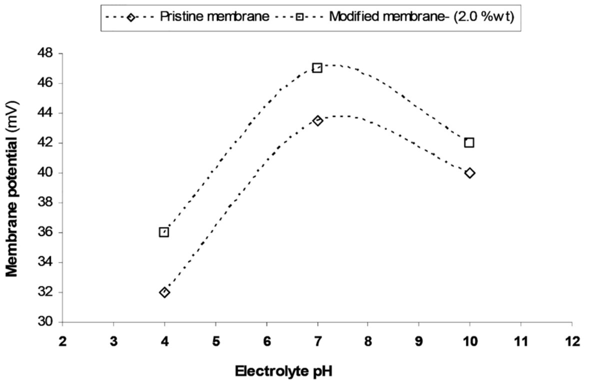


Figure 13: The effect of electrolyte pH on membrane potential of prepared membranes (NaCl ionic solution, 0.1 M/ 0.01 M).

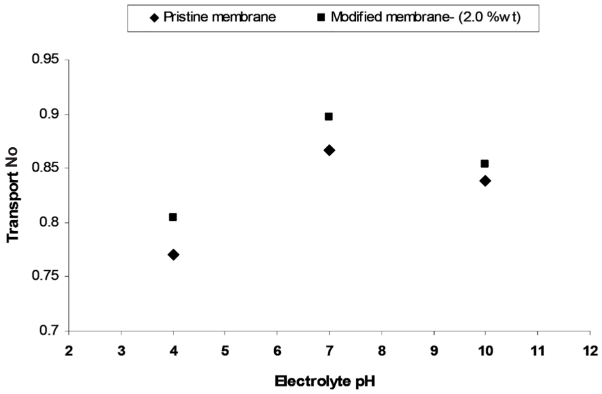


Figure 14: Effect of electrolyte pH on membrane transport number of prepared ion exchange membranes (NaCl ionic solution, 0.1 M/ 0.01 M).

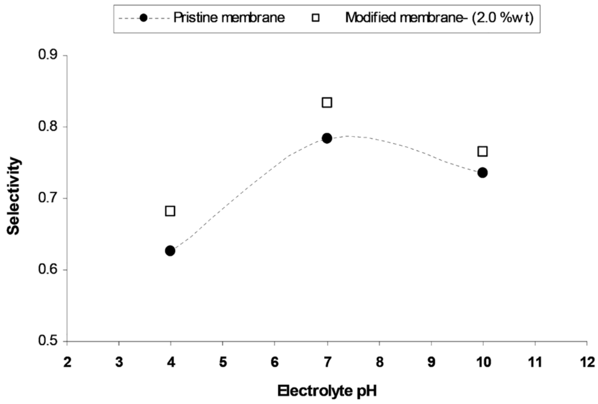


Figure 15: The permselectivity of prepared membranes at various electrolytes' pH in sodium chloride ionic solution (0.1 M/ 0.01 M).

Electrodialysis for Lead Removal

The electrodialysis experiment was carried out in a laboratory scale unit to evaluate the electrodialytic performance of the modified membranes for Pb removal from waste water. The dialytic rate for lead (Pb^{+2}) ions are shown in Figure 16. Results showed that dialytic rate was increased sharply for Pb^{+2} ions removal by increasing additive concentration in the prepared membranes. This is due to the superior and unique adsorptive characteristic of super activated carbon nanoparticles in lead metal ions adsorption, which enhances the permeability for Pb^{+2} ions obviously in water treatment process.

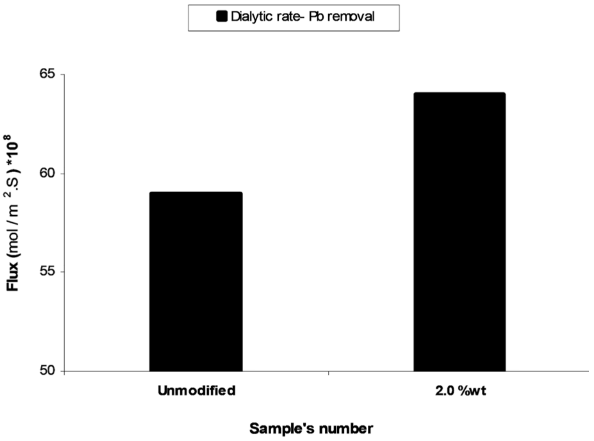


Figure 16: The ionic flux of membranes (S1 , S4) for lead ions removal (dialytic rate) in water treating process (laboratory scale unit containing one cell pair).

CONCLUSIONS

The scanning optical microscopy images illustrated uniform particle distribution and relatively uniform surfaces for the prepared membranes. It was found that membrane water content was enhanced initially by utilizing super activated carbon nanoparticles up to 0.5 %wt in the casting solution and then began to decrease by more increase of nanoparticle concentration from 0.5 to 4 wt%. Water contact angle, membrane ion exchange capacity, fixed ionic concentration, membrane potential; transport number and membrane selectivity all were increased by using super activated carbon nanoparticles in the membrane matrix. The membrane areal electrical resistance was also declined by employment of super activated carbon nanoparticles in the casting solution. The sodium flux was enhanced initially by increase of nanoparticles concentration up to 0.5 wt% and then decreased slightly by more increase of nanoparticle content ratios from 0.5 to 1 wt%. Again, the sodium flux was enhanced sharply by further increase in nanoparticle concentration form 1 to 4 %wt. The membrane transport number and selectivity were also enhanced initially by increase of electrolyte concentration and then showed a decreasing trend by further increase of environment concentration. The membranes showed higher transport number and selectivity at neutral pH compared to other pH values. The electrodialysis results showed that dialytic rate of lead ions was amplified by utilization of super activated carbon nanoparticles in the membrane matrix. Among the prepared membranes, the modified ones (S2) containing 2 wt% of activated carbon nanoparticles showed more appropriate performance compared to other modified membranes and the unmodified membrane. The obtained results are also valuable for electro-membrane processes especially electrodialysis for water recover and treatment.

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