

PVC Based Ion-Exchange Membrane Blended with Magnesium Oxide Nanoparticles for Desalination: Fabrication, Characterization and Performance

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ABSTRACT

In this study, polyvinyl chloride (PVC) based nanocomposite cation exchange membranes incorporated with magnesium oxide (MgO) nanoparticles were fabricated by nonsolvent induced phase inversion method. The additive concentration and electrolyte conditions (concentrations/pH) were investigated. Morphology studies were done using SOM and SEM images exhibited uniform distribution of MgO nanoparticles in the membrane structure. FTIR analysis showed the chemical structure of prepared membrane that demonstrated MgO nanoparticles presence. The hydrophilicity of membranes increased when 0.5-4.0 wt.% of additive were embedded into the polymer matrix. The transport characteristics of prepared membrane were improved by increasing nanoparticle content from 0.5 to 1 wt.%. It was demonstrated that the ionic flux of developed cation exchange membranes improved with an increase in additive content up to 1 wt.%. A considerable reduction was observed in the values of electrical resistance for the prepared membrane containing MgO nanoparticles. Ionic selectivity was enhanced at the more concentrated solution and was slightly decreased at higher electrolyte concentration. Moreover, at the electrolyte solution of pH7 the optimal transport properties were achieved for the membranes.

Keywords: Desalination, ion exchange membrane, MgO nanoparticle, PVC, polymer matrix

1.0 INTRODUCTION

Ion exchange membranes (IEMs) have numerous applications in separation processes. The most important of these processes are electro-dialysis and membrane chloralkali cells. Nowadays, IEMs have been widely used in electrodialysis process for seawater desalination and extraction of valuable metals ions from industrial wastewater, etc. [1-16].

Based on preparation procedure and structures of ion-exchange membranes, they are classified into homogeneous and heterogeneous [17]. Moreover, according to functional groups of IEMs, they

are classified by anionic and cationic ones. Anion exchange membranes pass anions and repel cations, while cation exchange membranes allow the pass of cations, but reject anions [18]. Many studies have already been done on improving the physicochemical properties of IEMs. Some of the most important techniques to achieve superior ion exchange membranes include the use of different polymeric matrices, inorganic additives/fillers such as metal oxide and nano-materials, polymers blending, surface modification, difference in functional groups' form and alteration of cross-link density.

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Using inorganic nanoparticles, especially metal oxides in the structure of polymeric membranes could improve the physicochemical and separation properties due to desirable interaction between the organic and inorganic composition [13, 19-20].

With this respect, magnesium oxide (MgO) as a unique solid with high ionic character and electrical conductivity has found novel applications in electronics, adsorption, detection and remediation of chemical waste and other research areas. Magnesium oxide nanoparticles are odorless and non-toxic. They possess high hardness, high purity and a high melting point. MgO nanoparticle is an important material, which used in many applications like catalysis, toxic waste remediation, paint, superconducting products and anti-bacterial activities against food borne pathogens.

MgO is an interesting basic oxide that has many applications in analysis, adsorption and in the synthesis of refractory ceramics. It is a unique solid of high ionic character. It has been reported that the shape and size of nanocrystalline magnesium oxide particles endow them with high specific surface and reactivity, because of the high concentration of edge/corner sites and structural defects on their surface [1, 2, 10, 19-27]. So MgO nanoparticles can be considered to modify ion exchange membranes.

The aim of this research was to prepare a new heterogeneous cation exchange membrane based on the polyvinyl chloride (PVC) containing MgO nanoparticles by solution casting techniques which can be used in electro-dialysis process. Appropriate mechanical stability, excellent resistance to erosion, acids and

alkaline, and also low cost are reasons that PVC was used for this purpose [2, 28-34]. Therefore, at the next step of the present research, the modified ion exchange membranes were applied in electrolytes with different concentration and pH to examine their performance under diverse conditions [35]. The variations of membrane resistance, potential and ionic selectivity were investigated in NaCl solution with concentration range of 0.001-0.1 M and pH range of 2-12. The obtained results might have practical value in the field of water treatment using various electro-membrane processes especially electro-dialysis process.

2.0 METHODS

2.1 Materials

Polyvinyl chloride (PVC, grade S-7054, density: 490 g/L, viscosity number: 105 cm³/g) was used as binder polymer obtained from Bandare Imam Petrochemical Co. (Iran). Tetrahydrofuran (THF, MW: 72.11, density: 0.89 g/cm³) and deionized water were used as solvent and non-solvent. The functional group agent was acidic cation exchanger resin (Amberlyst[®] 15, particle size of 0.355-1.18 mm, strongly acidic cation exchanger, H⁺ form with more than 1.7 meq/L, density 0.6 g/cm³) produced by Merck Inc. (Germany). Also MgO nanoparticle (MgO nano-white-powder, average particle size 20 nm, (MW: 40.30), (density: 3.58 g/cm³), BET area 50 m²/g) was used as inorganic modifier. The other chemical components were supplied by Merck.

2.2 Fabrication of PVC/ MgO Cation Exchange Membranes

PVC-based cation exchange membranes were fabricated by solution casting technique and phase inversion method [32, 33]. In order to dehumidify of the resin particles; they were put in oven (SANEE.V. S. Co.) at 30°C for 48 h and then were milled in a ball mill (Model: Pulverisette 5, Fritisch Co.). Then, by sieving the resin powder, the desired size (37–44 μm) was obtained for membrane fabrication. The polymer binder (PVC) was dissolved into the solvent (THF) (polymer: solvent (1: 20); (w/v)). Subsequently, a specific amount of the grinded resin particle and various percentages of MgO nanoparticles as additive were dispersed in the polymeric solution. Casting solution was mechanically stirred for 6 h to be uniform. The solutions were put in an ultrasonic bath for 1 h to achieve a desirable dispersion of nanoparticles and then, the mixture was stirred again using mechanical stirrer for half an hour. Afterward, the prepared solution was cast onto a glass with a knife and a gap of 400 μm at ambient temperature. The membranes were exposed to air for 60 s to dry and then immersed into coagulation bath containing DI water. The membrane thicknesses were measured by a digital caliper and their values were obtained around 70 μm . The prepared membranes were kept in a solution of sodium chloride for 24 h before testing.

2.3 Experimental Test Cell

The membranes characteristics were examined by means of home-made experimental cell as shown in Figure 1.

The cell was composed of two cylindrical sections made of Pyrex. Two compartments were separated by a membrane and at the end of each section a Pt electrode was placed.

2.4 Characterization of Cation Exchange Membrane

2.4.1 FTIR Analysis

In this study, the chemical structure of membrane was investigated using FTIR system (Fourier Transform Infrared Spectroscopy, Galaxy series 5000). Samples were scanned in the range of 4000–500 cm^{-1} .

2.4.2 Microstructure Analysis

The prepared membrane characteristics are depended on its structure, especially the distribution of its ionic site and dispersed nanoparticles [21]. The structure of prepared membrane was studied by SOM (scanning optical microscopy) images (Olympus, model IX 70) and SEM (scanning electron microscopy, Philips X-130) analysis.

2.4.3 Water Content

The difference between wet and dry weight of the membrane is defined as membrane water content (ϕ) as follows [2–4, 10]:

$$\phi = \left(\frac{M_{\text{wet}} - M_{\text{dry}}}{M_{\text{dry}}} \right) \times 100 \quad (1)$$

M_{wet} and M_{dry} represent the mass of the wet and dry membrane, respectively. M_{wet} was the weight of prepared membrane after immersing into the deionized water for sufficient time. After drying the membrane in

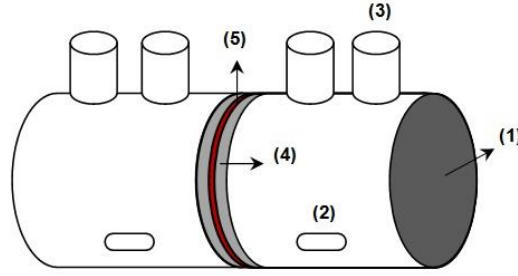


Figure 1 Schematic diagram of test cell. (1) Pt electrode, (2) Magnetic bar, (3) Orifice, (4) Rubber ring and (5) Membrane

oven at 60°C a constant weight was obtained as M_{dry} .

2.4.4 Potential and Transport Properties of IEMs

Differences in the concentrations of solutions in both sides of membrane develop an electrical potential which is affected by the properties of electrolyte solution.

The potential at the two sides of the membrane can be considered as the sum of Donnan potential plus diffusion potential in the membrane [20, 24]. The effect of boundary layers was eliminated by stirring both solutions using magnetic stirrers. To measure membrane potential, both sections were connected to pH meter electrodes and a digital auto-multimeter (Model: DEC 330FC, China) was used. The membrane potential ($E_{Measure}$) can be determined using the Nernst equation [2-4, 20]:

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

In this equation, a_1 , a_2 are the activities of solutions electrolyte in the both sides of the membrane as determined by the Debye-Huckel limiting law [36]. Also, t_i^m , R , T and n are the counter-ions' transport number in the membrane, gas constant, temperature and electrovalence of the counter-ion, respectively. The permselectivity (P_s)

of ion exchange membranes reflects the membrane ability to discriminate between counter- and co-ions [2, 5, 37-39]. This characteristic is developed based on counter-ion migration through the IEM according to [2-4, 7, 40-44]:

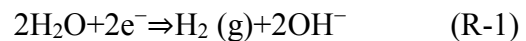
$$P_s = \frac{t_i^m - t_0}{1 - t_0} \quad (3)$$

where t_0 is the transport number of the [40].

2.4.5 Membrane Flux and Ionic Permeability

The flux and ionic permeability of the membranes were investigated, using the mentioned experimental cell which contains 0.01 M sodium chloride solution in the cathodic side. A direct constant electrical potential with an optimum voltage of 10 V was applied throughout the cell, using two connected platinum electrodes in two parts. Thus, the ions, with a positive charge, pass through the cation exchange membrane. Also, the pH of cathodic section is increased due to the production of hydroxide ions in this region by electrochemical reactions.

Cathodic reaction:



Anodic reaction:



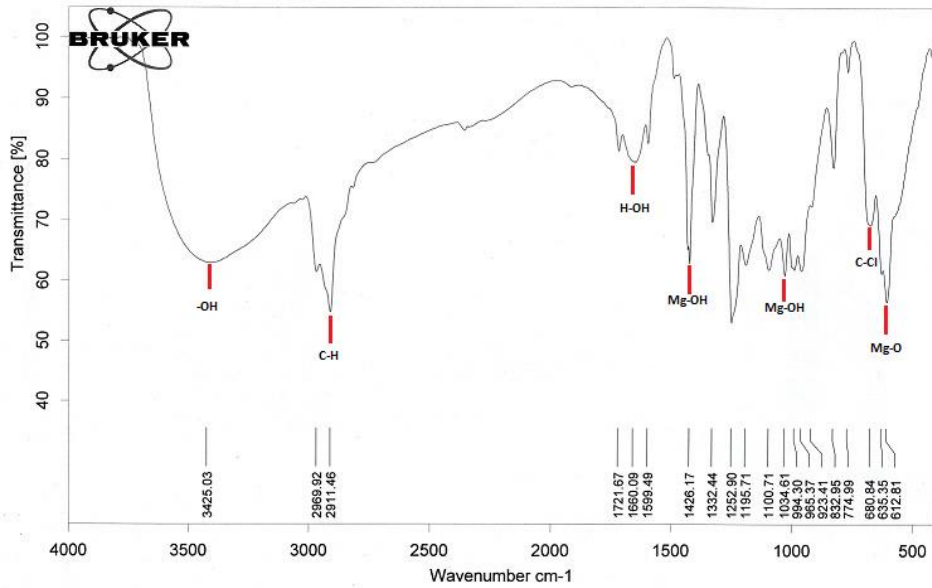


Figure 2 ATR-FTIR spectrums of PVC/Nano-MgO ion exchange membranes

The ionic flux can be determined using Fick's first law as follows [20, 21]:

$$N = -\frac{V}{A} \times \frac{dC_1}{dt} = P \frac{C_1 - C_2}{d} \quad (4)$$

In this equation, P, d, N, C and A are the ions diffusion coefficient, thickness of membrane, ionic flux, concentration of cations and the membrane surface area, respectively.

Eq. (4) integration is as follows:

$$\ln \frac{(C_1^0 + C_2^0 - 2C_2)}{(C_1^0 - C_2^0)} = -\frac{2PA t}{Vd} \quad (5)$$

Regarding the pH changes in cathodic side, the diffusion coefficient of ions can be determined by Eq. (5).

2.4.6 Electrical Resistance

Measuring the membrane resistance is important in the evaluation of various functional groups contributions in the ion exchange task, and also it plays a vital role in the practical application of ion exchange membranes. The membrane electrical resistance was calculated, based on our previous works, using a test cell [2–4]. Electrical resistance was measured in

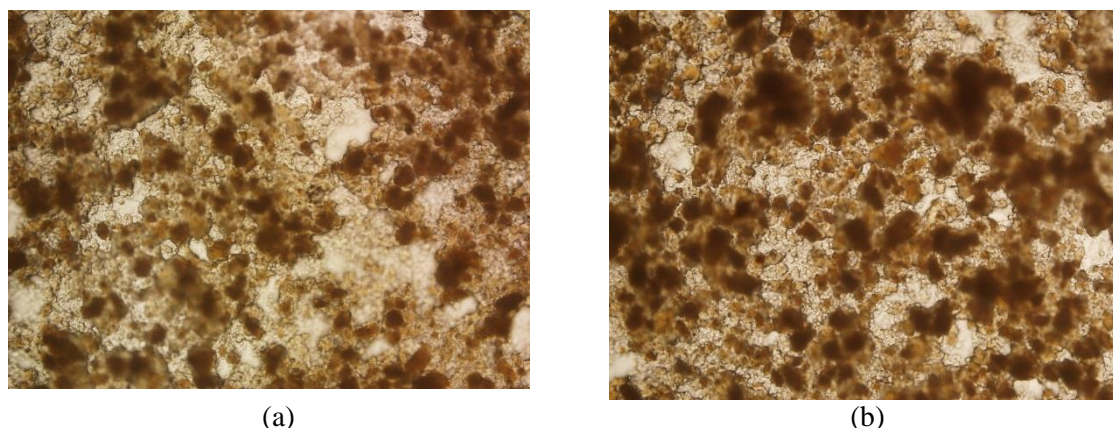
sodium chloride solution with the concentration of 0.5 M at 25°C, using 1000 Hz AC. The difference between the resistance of the cell (R_1) with the membrane and without the membrane (R_2) that ($R_m = R_1 - R_2$) is the electrical resistance of membrane [1, 24, 45–48]. Areal resistance (r) is obtained by multiplying R_m in the area of membrane surface (A) as follows:

$$r = (R_m A) \quad (6)$$

3.0 RESULTS AND DISCUSSION

3.1 Fourier Transform Infrared Spectroscopy (FTIR)

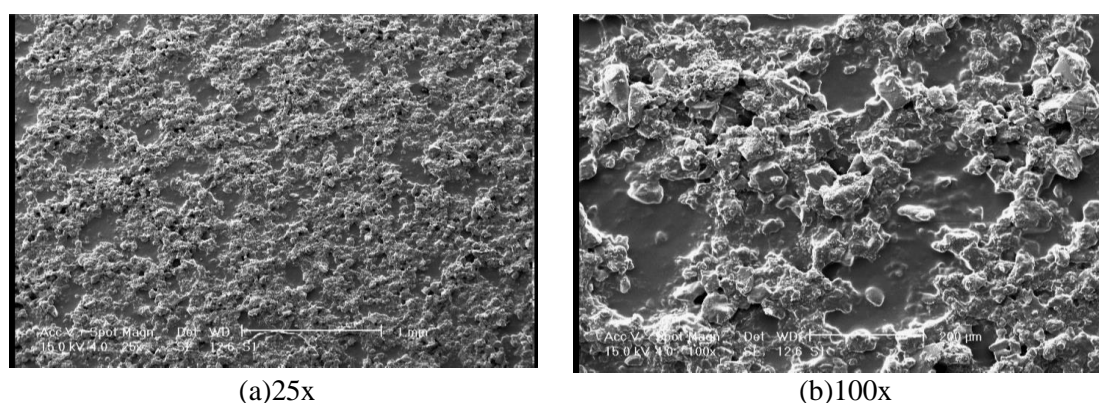
FTIR spectrum of prepared PVC/Nano-MgO ion exchange membrane is shown in Figure 2. The peak at 635 cm^{-1} is related to the Mg–O bonding [49]. Due to the interaction between MgO and presence moisture, absorption peaks at 1426 cm^{-1} and 1034 cm^{-1} were observed that show the Mg–OH stretching vibration.



(a)

(b)

Figure 3 The SOM images (10x magnifications) of home-made membranes with different concentration of MgO nanoparticle: (a) 0.0 wt% and (b) 4wt%



(a)25x

(b)100x

Figure 4 SEM images of prepared membranes

Absorption peak for C–H stretching was observed at 2911 cm^{-1} . Also the peak at 680 cm^{-1} corresponds to C–Cl functional group of PVC [50]. The broad peak at 3425 cm^{-1} was demonstrated to the present of OH functional group [51] of PVA structure. Whereas water has been used during membrane preparation an absorption peak was appeared at 1660 cm^{-1} [49].

3.2 Microstructure Analysis

To study the morphological changes associated with the additive and ionic site condition, SOM images of the prepared membranes surface were taken as shown in Figure 3. As shown

in these figures with increasing the additive, the image brightness was decreased. Also SEM images at 25x and 100x magnifications of surfaces of prepared membrane are shown in Figure 4.

In general, uniformed distribution of nanoparticles on the membrane surface was observed that has been affected by sonication. The uniformed dispersion of particles creates regions with higher conductivity that facilitates counter ion transportation.

3.3 Water Content

Figure 5 shows the measured quantities of water contained in the prepared membranes. By an increase in

nanoparticles concentration up to 0.5 wt%, the water content of membrane decreased. This is due to the pores filling by the magnesium oxide nanoparticle in this loading ratio.

However, with the more adding of nanoparticles in the range of 0.5 to 4

wt%, the membrane water content increased. This can be observed that hydrophilicity affinity of MgO nanoparticles to the water make more hydrophilic membrane.

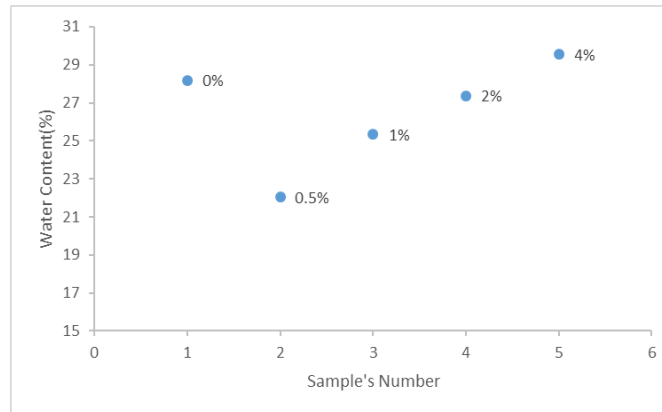


Figure 5 The effect of MgO nanoparticle loading on membrane water content

The appropriate quantity of water content, leads to a better control over the ions pathways and so enhances the selectivity of membrane [43]. While the large amounts of water content causes to loose the membrane structure.

3.4 Potential and Transport Properties of IEMs

In Figure 6 (a) and (b), the potential, transport number and permselectivity of the fabricated membranes are presented. Results indicate the membranes' properties are dependent on MgO nanoparticle concentration. By adding nano-MgO up to 0.5 wt%, the membrane potential decreases. This is because of nanoparticles' agglomeration and so decreasing the active sites effective surface areas and reducing the adsorption properties of membranes. However, the membrane potential increased with increasing MgO concentration from 0.5 to 1 wt%. The reason is that nanoparticles provide more conducting areas and

create suitable flow channels throughout the membranes which facilitate the counter-ions passage. Thus, the Donnan exclusion responsible for the membrane potential increment is enhanced [4, 19, 39-42].

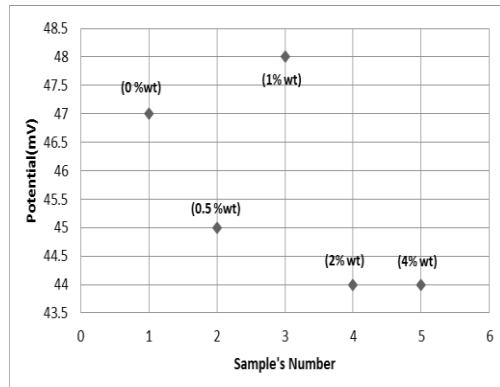
The transport properties of membrane declined by adding the nanoparticles more from 1 to 4 wt%. This can be due to increase in particle density that cause reduces the effect of active sites.

Figure 6 (b) illustrates that the increase of MgO nanoparticles percentage (up to 0.5 wt.%) in casting solution is associated with the reduction of transport number and permselectivity. It happened because of the accumulation of nanoparticles that led to decline in charge density of the membrane and affected the cation percolation.

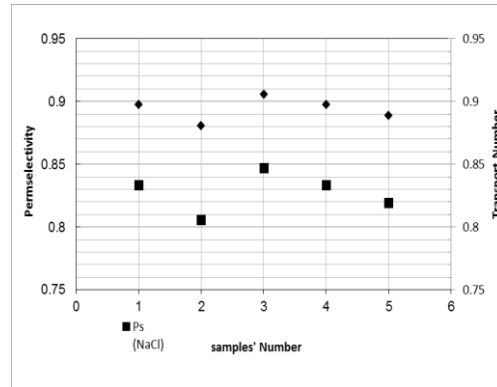
Increasing the nanoparticles in the range of 0.5 to 1 wt. % led to the improvement of transport properties of membranes. It may be due to the adsorptive ability of MgO nanoparticle which facilitates the ion transfer. Also,

adding the nanoparticle causes the occupation of the ionic pathways and so the ion passage becomes narrow in the membrane structure. Therefore, the ions transportation is intensified and the permselectivity of membrane is improved. However, with further increase in nanoparticles concentration

from 1 to 4 wt.%, the selectivity of membranes is declined. This declining could be as a result of the existence of higher density of nanoparticle in the polymeric solution that causes the discontinuity of polymer chain binder.



(a)



(b)

Figure 6 The potential, transport number and permselectivity of prepared membranes with various additive loading

3.5 Membrane Flux and Ionic Permeability

According to the amount of hydroxide ions produced at the cathodic side, the transfer of sodium ions occurs. As shown in Figure 7, with the increasing of MgO nanoparticles up to 1 wt.%, the flux and ionic permeability of the membranes were enhanced.

The possible cause of this event is the improved interaction between the counter ions and the membrane surface, which is caused by the adsorption capability of MgO nanoparticles and facilitated ion transportation. Moreover, the surface of volume ratios of MgO nanoparticles is relatively high that aid to the ion diffusion from solution to particle surface. The ionic permeability and

flux declined by increasing the concentration of nanoparticle from 1 to 4 wt.%. This may be due to the pore filling phenomenon by nanoparticles which causes ion transition to be more difficult [38, 40].

3.6 Electrical Resistance

Figure 8 illustrates that the adding MgO nanoparticles led to reduce the areal electrical resistance of ion exchange membrane. It can be influenced by the adsorption properties of nanoparticles which assist the ion transport between the electrolyte and membrane, thereby the membrane conductivity improves.

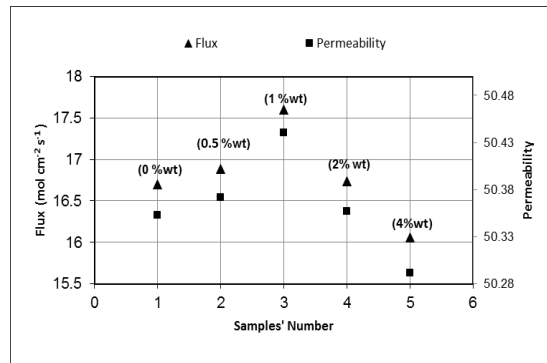


Figure 7 The effect MgO nanoparticles concentration on the ionic flux and permeability of sodium ions for the home-made cation exchange membranes

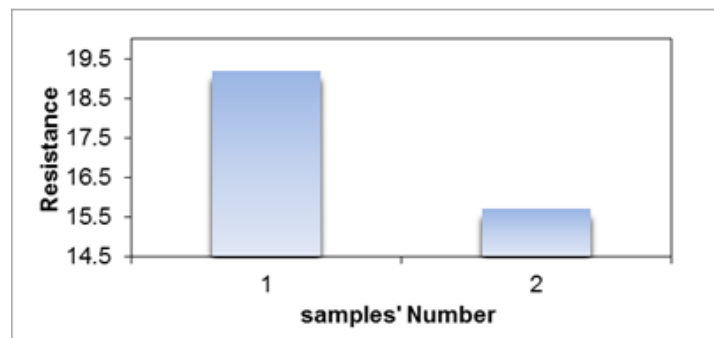


Figure 8 The areal electrical resistance of prepared membranes with various zinc oxide nanoparticle concentrations

3.7 Effect of pH and Concentration

Figures. 9 (a)–(c) indicate an increase in concentration of solution from (0.001-0.01) to (0.01-0.1), and the transport properties of membranes were initially improved. It is due to more presence of counter-ions in the electrolyte environment which causes more interaction between counter-ions and membrane surface [24]. Therefore, Donnan exclusion is enhanced as responsible for the improvement of membrane potential and selectivity. A considerable contrast exists between the obtained results and Donnan equilibrium theory [40].

A slight decrease in all of the mentioned parameters will take place with higher increase in ionic solution concentration from (0.01-0.1) to (0.05-0.5). The reason is the more osmotic pressure difference between the

external and internal salt solution in the membrane phase at high solution concentration [39]. Besides, at high concentration of sodium chloride solution the membrane swelling may decline the transport properties of membranes [40-44].

As shown in Figures 10 (a)–(c), the modified membrane showed better performance at pH 7 in comparison with other pH values. One possible explanation for happening this event could be the difference in dissociation of ionic functional groups ($-\text{SO}_3\text{H}$) and charge density of filler additives in various pH values which influences the charge nature of membrane matrix [40]. In a suitable electrolyte pH, more dissociation of sulfonic groups and higher charge nature of membrane matrix will facilitate ion transportation from solution to membrane.

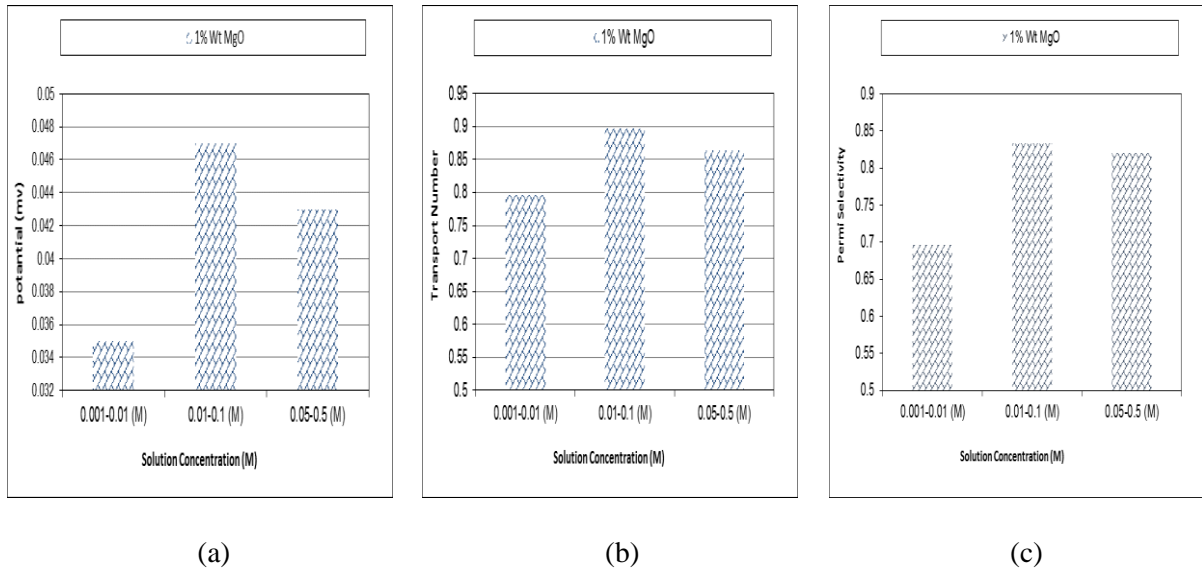


Figure 9 The effect of solution (NaCl) concentration variations on (a) membrane potential, (b) transport number and (c) permselectivity

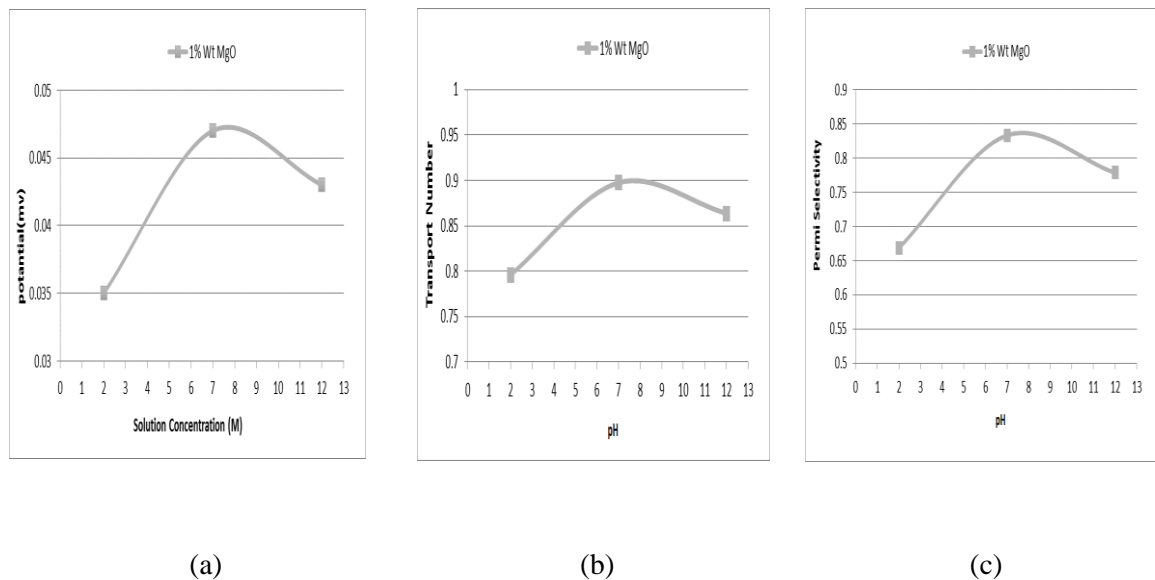


Figure 10 The effect of pH variations on (a) membrane potential, (b) transport number and (c) permselectivity

4.0 CONCLUSION

SOM images and SEM analysis showed the morphology of membranes and distribution of particles on the membrane surface. FTIR analysis demonstrated the presence of MgO nanoparticles in the structure of prepared membrane.

Results illustrated an initial decrease in water content of membranes by increasing the additive up to 0.5 wt% and then increased by more additive content. A declining trend was achieved for transport properties of membranes by adding nanoparticle up to 0.5 wt.%. After that by a more additive content from 0.5 to 1 wt.%, the membranes' properties enhanced.

As the MgO nanoparticles increased to 4 wt.%, the modified membranes presents the lower potential, transport number and selectivity. By adding nanoparticles up to 1 wt. %, the prepared membrane exhibit a higher ionic permeability and flux and then were decreased by more increasing in additive content to 4%. The electrical resistance of fabricated membrane containing nanoparticles decreased. Investigation of modified membranes performance in different electrolytic environments exhibited that by increasing electrolyte concentration. The transport properties of IEMs were enhanced and then declined slightly at high solution concentration. Also at pH 7 the optimized values of membranes characteristics were achieved.

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