# Preparation and characterization of nanocomposite heterogeneous cation exchange membranes modified by silver nanoparticles

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**Abstract**–We prepared polyvinylchloride based nanocomposite heterogeneous cation exchange membranes by solution casting technique using cation exchange resin powder as functional groups agent and tetrahydrofuran as solvent. Silver nanoparticles were also used as fillers in membrane fabrication. The effect of silver nanoparticles concentration in casting solution on membrane physico/chemical and antibacterial characteristics was studied. The SEM images showed compact structure for the modified membranes. X-ray diffraction results also revealed that membrane crystallinity was clearly changed by increase of nanoparticle concentration. Membrane selectivity and transport number were enhanced initially by increase in nanoparticle content up to 4%wt in prepared membrane, and then showed decreasing trend by more increase in additive concentration from 4 to 8%wt. Selectivity and transport number were enhanced another time by further increase in nanoparticle loading ratio from 8 to 16%wt. Opposite trend was found for the membranes' average grain size by variation in additive content. Ionic flux was also clearly enhanced by using Ag nanoparticles in membrane matrix. Moreover, modified membranes showed good ability in decrease of *Escherichia coli* growth rate.

Keywords: Mixed Matrix Membrane, Ion Exchange, Silver Nanoparticles, Fabrication/Characterization, Antibacterial Property/*Escherichia coli* Growth Rate

## INTRODUCTION

Ion exchange membranes have gained considerable attention in diverse industries and also in daily human life [1,2]. In ion exchange membranes (IEMs), charged groups are attached to a polymer backbone and are freely permeable to opposite sign ions under an electrical field influence [2-5]. The industrial applications of ion exchange membranes for demineralizing and concentrating electrolyte solutions were developed in 1950 by producing high selective/low electrical resistance ion exchange membranes [6,7]. At the present time, IEMs are widely utilized as active separators in desalination, resource recovery and food and pharmacy processing as well as manufacturing of basic chemical products. Ion exchange membranes also can be employed in biological effluent processes. Preparing ion exchange membrane with special physico/chemical characteristics such as high ionic conductivity and selectivity, good permeability and suitable thermal, chemical and mechanical resistances may be a vital step in further IEMs' development and applications [2,8-15].

Preparing heterogeneous cation 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. PVC-based nanocomposite mixed matrix heterogeneous cation exchange membranes were prepared by solution casting techniques using cation exchange resin powder as functional group agent and tetrahydrofuran as solvent. Silver nanoparticles

were also employed as fillers in membrane fabrication. PVC is a flexible and durable polymer with suitable biological and chemical resistance [16-21]. The use of inorganic fillers, especially nano-materials into polymeric matrixes, has been examined in many applications to improve the physico/chemical characteristics of polymeric matrixes based on the synergism between the organic-inorganic components properties [21-24]. Silver nanoparticles are a new class of advanced material with very interesting features such as electrical conductivity, antimicrobial and adsorption characteristics. Ag nanoparticle also is one the the most interesting nano-metals in biomaterial applications [21,25-27].

Currently, a few researches have considered incorporating silver nanoparticles into ion exchange membranes but the literature is silent on characteristics and functionality of electrodialysis IEMs modified by Ag nanoparticles.

Moreover, knowledge of the electrokinetic and structural properties of IEMs is a major contributing factor behind the decision for the applicability of these membranes in a specific process [28, 29]. In earlier reported researches [21,30] Ag nanolayer has been utilized as surface modifier on ion exchange membranes. Because of weak adhesion of nanolayer on the polymeric substrates, release of nanoparticles may have occurred [31], which is harmful for biological cells [32,33]. In the current research, Ag nanoparticles were used as filler in casting solution during membrane fabrication. The effect of silver nanoparticle concentration on membrane physico/chemical and antibacterial characteristics was studied. Moreover, the correlation between the structure and electrochemical properties of membranes was investigated.

Obtained results are valuable for the electro-membrane processes especially electrodialysis in water recovery and treatment. During

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the experiments, sodium chloride was employed as ionic solution for membrane characterization.

## MATERIALS AND METHODS

### 1. Materials

Polyvinylchloride (PVC, grade S-7054, bulk density: 490 (g/L), viscosity number (DIN-53726): 105 (cm³/g)) supplied by BIPC Company, Iran was used as binder. Tetrahydrofuran was used as solvent. Silver nanoparticle (US Research Nano materials, Inc., Houston, USA) with 30-50 nm average particle size and cation exchange resin (Ion exchanger Amberlyst® 15, strongly acidic cation exchanger, H+ form - more than 1.7 milli equivalent/g dry) by Merck Inc., Germany, were used in membrane fabrication. All other chemicals were supplied by Merck. Throughout the experiment, distilled water was used.

### 2. Preparation of Mixed Matrix Membrane

Heterogeneous cation exchange membranes were prepared by solution casting technique. Membranes were prepared by dissolving polyvinylchloride (PVC) as binder in THF as solvent (THF: polymer binder, (20 : 1) (v/w)) in a glass reactor equipped with a mechanical stirrer) for 1 h. This was followed by dispersing a specific quantity of grinded resin particle (resin: polymer binder, (1 : 1) w/w)) as functional groups agent and Ag nanoparticles as inorganic additive (0.0%wt, 1.0%wt, 2.0%wt, 4.0%wt, 8.0%wt and 16%wt) in polymeric solution. The mixture was mixed vigorously at room temperature to obtain a uniform particle distribution in the polymeric solution. Moreover, sonication was employed in membrane fabrication to achieve better homogeneity in the membrane matrix and also to obtain a balance between electrochemical properties and mechanical integrity. The mixture was then cast onto a clean and dry glass plate. The membranes were dried at ambient temperature and immersed in distilled water. As a final step, membranes were pretreated by immersing in NaCl solution. The membrane thickness was also measured by using a digital caliper device around 100-120 μm.

### 3. Test Cell

The membranes electrochemical properties were measured using the test cell (Fig. 1) as described earlier [21,23,30,34]. The cell consists of two cylindrical compartments made of Pyrex glass separated by the membrane. One side of each vessel was closed by Pt electrode supported with a piece of Teflon and the other side was equipped 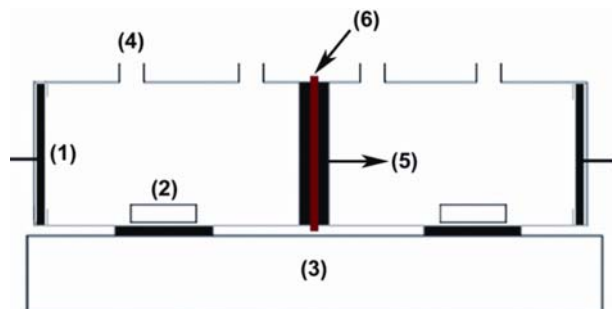with membrane. For feeding and sampling purposes, the top of each compartment contained two orifices. To minimize the effect of boundary layer during experiments and also concentration polarization, both sections were stirred vigorously by magnetic stirrers.

### 4. Morphological Characterization

The behavior of prepared membranes is closely related to their structure, especially the spatial distribution of ionic site and nanoparticles [35]. The structure of prepared membranes was examined by scanning electron microscope (SEM, Model EM-3200, KYKY, China) and X-ray diffraction (XRD, Philips PW 3373, $\lambda_{co}$=1.79 nm). The average grain size of crystals was also calculated using Scherrer's formula based on the X-ray results [36]:

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where D is the average grain size of the crystallite, $\lambda$=1.79 °A is the wavelength of used X-ray, B denotes the full width at half maximum (FWHM) for corresponding diffraction peak and $\theta$ is diffraction angle. K is equation constant (K=0.95).

### 5. FTIR Analysis

FTIR spectra measurement was carried out to provide information about the chemical structure of prepared membranes. FTIR spectra analysis was done using Galaxy series FTIR 5000 spectrometer. Scans were taken in spectral range of 400 and 4,000 cm⁻¹.

### 6. Antibacterial Property

The antibacterial property of prepared mixed matrix membranes was investigated by optical density (O.D) method using a single beam spectrophotometer (Elegant Thch.Cecil series 400, CE 4400) with wavelength 600 nm in a cell containing $10^6$ CFU/m.lit (Colony Forming Unit) of E-Coli. Three cells were prepared. A cell was applied as control unit without any membrane, which gives the growth rate of E-Coli with time. Other cells contained pristine membrane (unmodified one) and modified membrane containing 16%wt Ag nanoparticles, respectively. During the experiments test cells were stirred vigorously by magnetic stirrers.

### 7. Membrane Potential, Transport Number and Permselectivity

Membrane potential, transport number and permselectivity of membranes were carried out using the test cell. Membrane potential was evaluated for the equilibrated membrane with unequal concentrations of sodium chloride ($C_1$=0.1 M, $C_2$=0.01 M @ ambient temperature) on either side of the membrane. The developed potential difference across the membrane was measured by connecting both compartments and using a saturated calomel electrode (through KCl bridges) and digital auto multimeter. The membrane potential ($E_{measure}$) generated is expressed using the Nernst equation [1,21,34, 35,37,38] as follows:

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

where $t^m$ is the transport number of counterions in the membrane phase, R is the gas constant, T is the temperature, n is the electrovalence of counterion and $a_1$, $a_2$ are solutions electrolyte activities in contact with both surfaces. The ionic permselectivity of membrane is expressed based on the migration of counterion through the ion exchange membrane [1,21,34,35,37,38].

$$P_S = \frac{t_i^m - t_0}{1 - t_0} \tag{3}$$



**Fig. 1. Schematic diagram of test cell.**

    (1) Pt electrode         (4) Orifice
    (2) Magnetic bar      (5) Rubber ring
    (3) Stirrer           (6) Membrane

Where $t_0$ is the transport number of the counterions in solution phase [39].

The concentration of fixed charge on the membrane surface (Y) also has been expressed in terms of permselectivity as follows [37,40]:

$$Y = \frac{2C_{Mean}P_s}{\sqrt{1-p_s^2}} \tag{4}$$

Where $C_{mean}$ is the mean concentration of electrolytes.

The existence of more conducting regions on the membrane surface can strengthen the intensity of the uniform electrical field around the membrane and decrease the concentration polarization phenomenon [41].

## 8. Ionic Flux

The ionic permeability and flux measurements were carried out using the test cell as reported earlier [21,23,30,34]. A 0.1 M NaCl solution was placed on one side of the cell and a 0.01 M solution on its other side. A DC electrical potential with an optimal constant voltage was applied across the cell with stable platinum electrodes. To ensure the equilibrium condition in two solution-membrane interfacial zones and to minimize the effect of boundary layers, both sections were stirred vigorously by magnetic stirrers.

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

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

According to the reactions that occurred, the produced hydroxide ions increase the pH of cathodic section. The amount of produced hydroxide ions in the cathodic section is equal to the sodium ions transported through the membrane. The pH changes were measured with a digital pH meter (Jenway, Model: 3510). According to first Fick's law, the flux of ions through the membrane can be expressed as follows [34,35,38]:

$$N = -P\frac{dC}{dx} = P\frac{C_1-C_2}{d} \tag{5}$$

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

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

$$C_1^0=0.1M,\ C_2^0=0.01M,\ C_1+C_2=C_1^0+C_2^0=0.11M \tag{7}$$

where, A is the membrane surface area. Integrating of Eq. (7) was as follows:

$$\ln\frac{(C_1^0+C_2^0-2C_2)}{(C_1^0-C_2^0)} = -\frac{2PAt}{Vd} \tag{8}$$

The diffusion coefficient and flux of cations in membrane phase are calculated from Eq. (8) considering pH changes in cathodic compartment.

## RESULTS AND DISCUSSION

### 1. Membrane Potential, Ionic Transport Number and Permselectivity

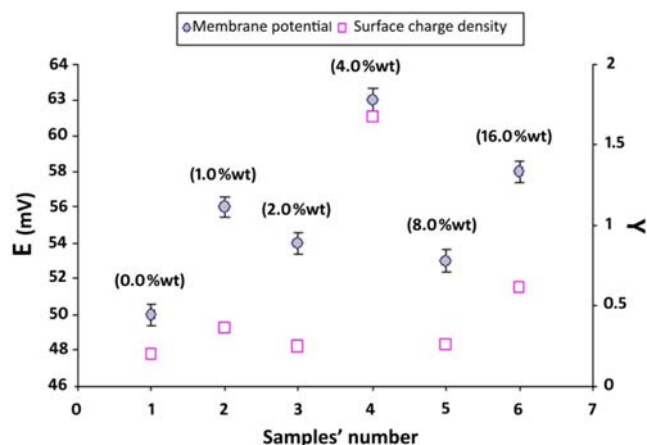Obtained results (Fig. 2) revealed that membrane potential was



Fig. 2. The effect of Ag nanoparticles concentration (%wt) on membrane potential (E) and surface charge density (Y) of prepared cation exchange membrane.

increased initially by increase of silver nanoparticle concentration up to 4%wt in prepared membranes. This may be attributed to the electrical property and adsorption characteristic of Ag nanoparticles [21,30] which increase the membrane charge density (Fig. 2). This causes superior interactions between ions and membrane surface and facilitates ions transport. This leads to enhanced Donnan exclusion that is responsible for the increment of membrane potential. The membrane potential was decreased again by further increase in additive content from 4 to 8%wt. This may be attributed to decrease in accessibility of ion exchange functional groups in membrane matrix by Ag nanoparticles which occupy the spaces around resin particles and so reduce the accessibility of them by their isolation. Moreover, decrease in fixed ionic concentration on membrane surface (Fig. 2) decreases the membrane potential. Membrane potential was increased another time by more increase in nanoparticle concentration from 8 to 16%wt in the casting solution. This may be attributed to the increment of nanoparticle density and also more uniform distribution of particles at high additive concentration, which can prevail upon the negative effect of inaccessibility of ion exchange
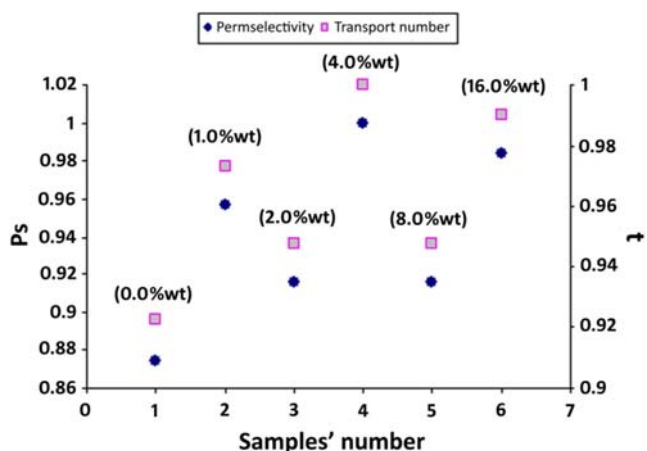


Fig. 3. The effect of Ag nanoparticles concentration (%wt) on permselectivity (Ps) and transport number (t) of membranes in NaCl ionic solution.

functional groups in membrane matrix and improve the membrane potential. Also, results showed higher membrane potential for the modified membranes compared to pristine type.

The permselectivity and transport number of prepared membranes in NaCl solution are also depicted in Fig. 3. At first, permselectivity and transport number were increased by increase of Ag nanoparticle content up to 4%wt in prepared membranes. This can be explained with respect to increase of membrane's fixed ionic concentration which provides suitable ionic pathways for the membranes.
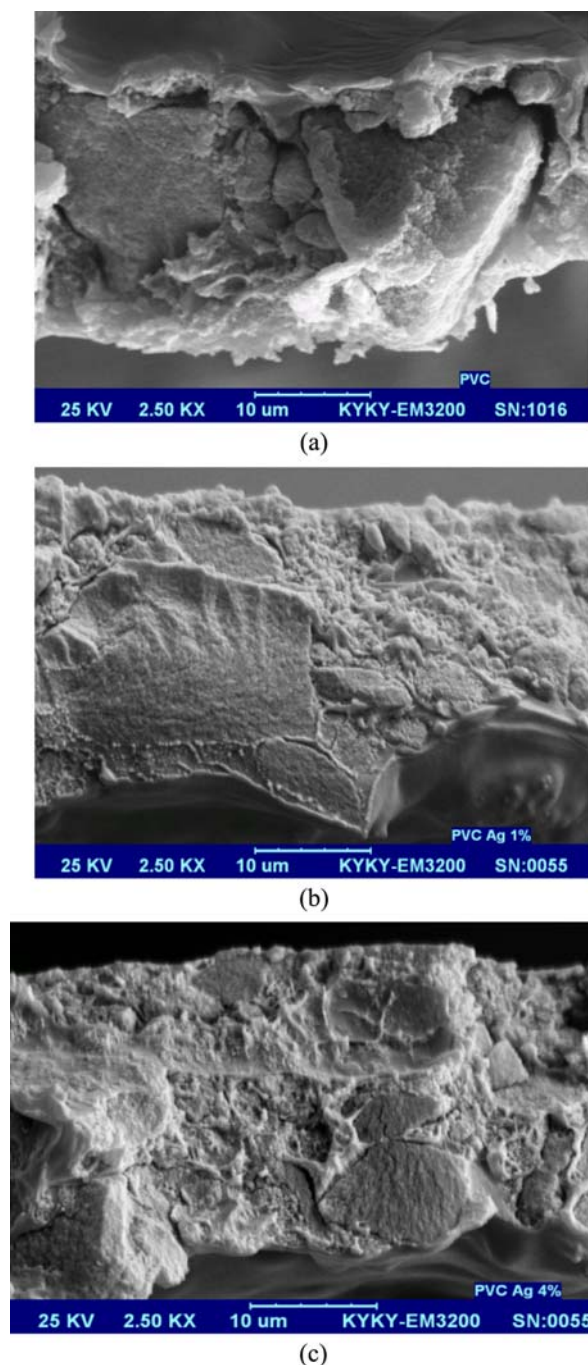


(a)



(b)



(c)

**Fig. 4. SEM cross section images of membranes with various ratios of additive loading: (a) Pristine membrane (0%wt); (b) Modified membrane (1 %wt); (c) Modified membrane (4%wt).**

As shown in SEM images (Fig. 4) by increase of nanoparticles concentration, the pathways and channels in the membrane matrix are occupied by the additive particles and so they are narrowed by them as space limiting factor [21,23,34]. This strengthens the ionic site domination on ion traffic and improves the membrane permselectivity and transport number. Furthermore, XRD results (Fig. 5) showed that membrane average grain size (Fig. 6) decreased from 32 to 29 nm by increase of nanoparticle loading ratio up to 4%wt. Decrease of average grain size makes a compact structure for the membranes (see SEM images, Fig. 4) and so strengthens the ionic site domination on ion traffic, which improves the selectivity. Permselectivity and transport number decreased again by further increase in Ag nanoparticle concentration from 4 to 8%wt due to lower amount of fixed ionic concentration for the membranes. This is because of ionic site isolation by the additive particles, which facilitates the co ions percolation through the membrane and reduces the selectivity. Also as shown in Fig. 6, increase in membrane average grain (from 29 to 40 nm) by increase in nanoparticle content (from 4 to 8%wt) produces more free spaces throughout the membrane matrix and diminishes the ionic site domination on ion traffic and so reduces the membrane selectivity. The membrane permselectivity and transport number were increased another time by further increase in silver nanoparticle content from 8 to 16%wt, which was attributed to increase of membrane surface charge density. Additionally, decrease of mem-
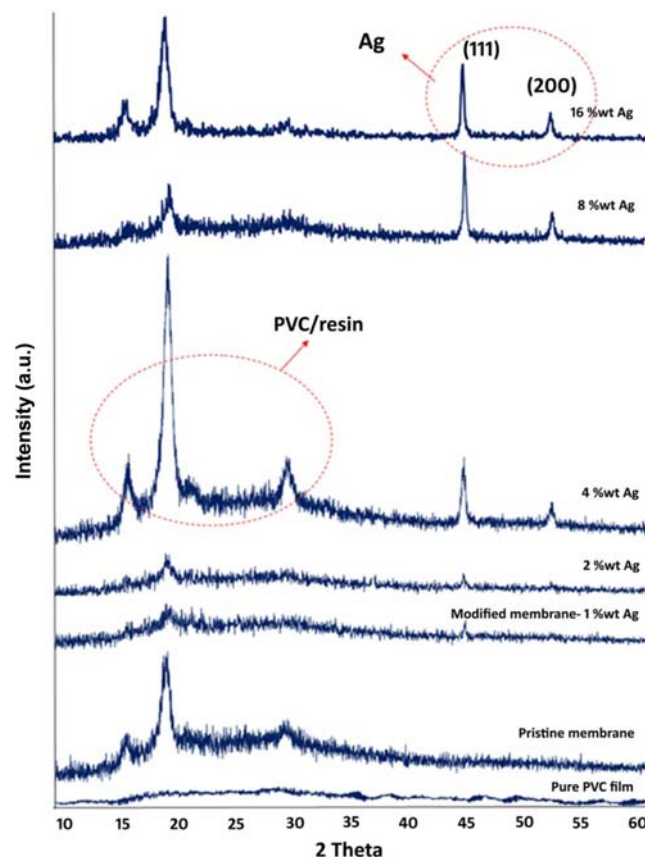


**Fig. 5. X-ray diffraction analysis of membranes with different nanoparticles concentration (%wt); preferred orientations: 2* Theta=19.5° for membranes and 2* Theta=44.4° for Ag nanoparticles (111).**
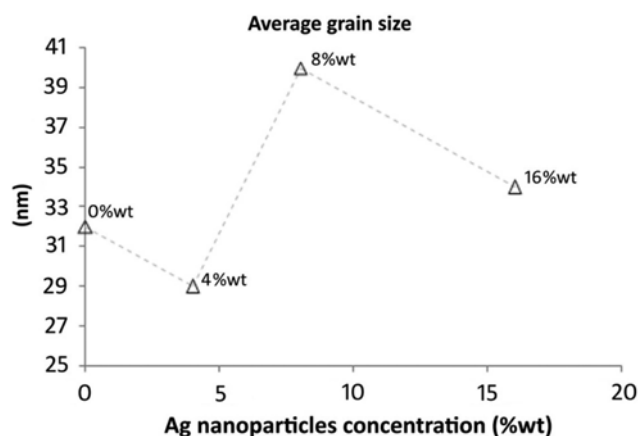
Fig. 6. The effect of Ag nanoparticles concentration on average grain size of membrane structure.
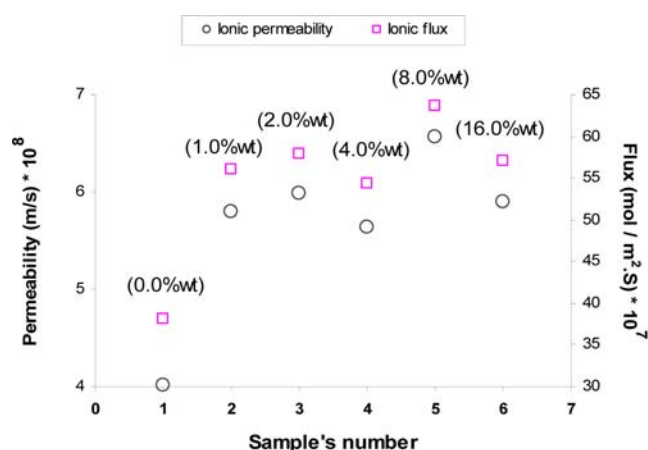


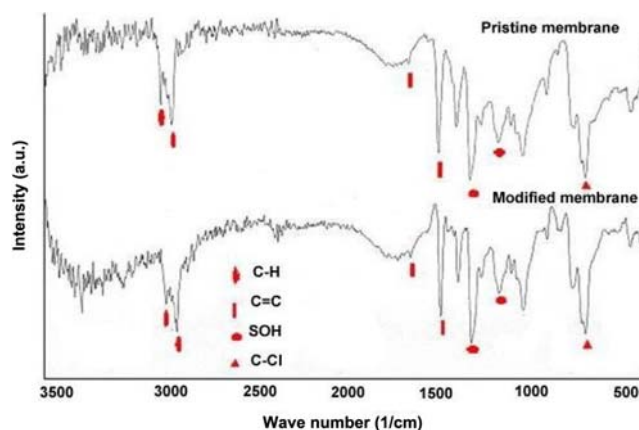Fig. 7. Effect of Ag nanoparticles loading ratio (%wt) on ionic permeability and flux.



Fig. 8. Infrared spectroscopy for (a) pristine membrane and (b) modified membrane containing 2%wt nanoparticles.

and also narrow ionic transfer channels in membrane matrix at 4%wt Ag nanoparticle concentration reduces the ionic transport.

The permeability and flux were increased another time by further increase in nanoparticle content from 4 to 8%wt and then showed decreasing trend by more additive concentration. This may be attributed to variation in membrane crystallinity as was discussed before (XRD results).

The modified membranes containing Ag nanoparticles showed higher ionic permeability and flux compared to pristine membrane. This is because of the electrical property and adsorption characteristic of silver nanoparticles, which makes superior electrostatic interactions between ions and membrane surface and so improves the permeability and flux.

### 3. FTIR Analysis of Modified Membrane

FT-IR spectrum of the modified membrane also is shown in Fig. 8. The spectrum results show stretching bands for C-H at 2,970-2,920 $cm^{-1}$ and C=C at 1,590-1,430 $cm^{-1}$ and $SO_3^-$ at 1,250-1,100 $cm^{-1}$, respectively. Also the band around 615 $cm^{-1}$ is attributed to C-Cl (corresponding to PVC). Moreover, no chemical binding was observed between Ag nanoparticles and polymer binder/resin particles.

### 4. Antibacterial Property

It was found that silver nanoparticles incorporate into the bacterial cells' membrane and damage it significantly by formation of pits in cell walls. The mechanism of inhibitory action of silver nanoparticles on microorganisms is partially known. It is believed that DNA loses its replication ability and cellular proteins become inactivated during the Ag treatment. In addition, the silver binds to functional groups of bacteria and damages it by interfering with membrane receptors and participating with bacterial electron transport, which results in protein denaturation [44-46]. Optical density (O.D) was used to investigate the anti-bacterial property of prepared mixed matrix membranes in a cell containing $10^6$ CFU/m.lit (Colony Forming Unit) of E-Coli. Fig. 9 shows the variation of optical density versus time in all cells. As seen, modified membranes containing Ag nanoparticles showed good ability in decrease of *Escherichia coli* growth rate.

### CONCLUSIONS

The SEM images show a compact structure for the modified mem-

brane average grain size (from 40 to 34 nm) by more additive loading (from 8 to 16%wt) improved the membrane selectivity.

Results showed better membrane selectivity and transport number for the modified membranes compared to pristine ones.

### 2. Membrane Ionic Permeability and Flux

Obtained results revealed that ionic permeability and flux (Fig. 7) were increased initially by increase of silver nanoparticle concentration up to 2%wt in prepared membranes. This may be attributed to increase of membrane electrical conductivity, which enhances the intensity of the uniform electrical field around the membrane and increases the ionic permeability and flux. Moreover, decrease of membrane crystallinity (XRD results) by increase of additive content up to 2%wt in prepared membranes can improve the ionic permeability and flux. Ionic permeability and flux decreased again by further increase in nanoparticle loading ratio from 2 to 4%wt. This may be due to increase of membrane crystallinity, which decreases the ion transport through the membrane. Increase in membrane crystallinity makes difficult the ion traffic and decreases the ionic permeability and flux significantly. Increase in membrane crystallinity hinders the moieties and segments moving in membrane matrix, which in turn decreases ion transport [42,43]. Moreover, formation of a compact structure for the membrane (see SEM images)
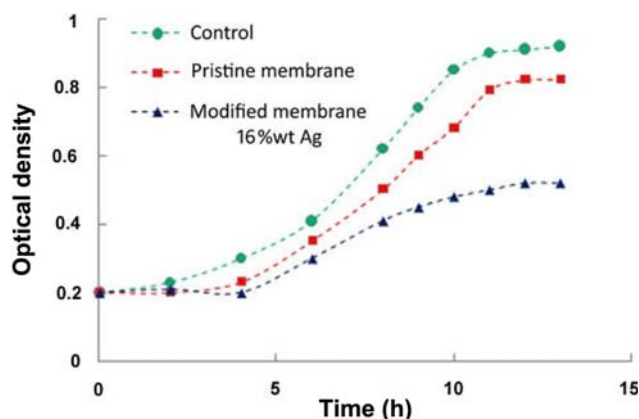
**Fig. 9. Variation of optical density (O.D) with time: (a) control cell, (b) pristine membrane, (c) modified membrane containing 16%wt Ag nanoparticles.**

branes. X-ray diffraction results also reveal that membrane crystallinity was changed by increase in nanoparticle concentration in the casting solution. Membrane potential, selectivity and transport number were enhanced initially by increase of additive concentration up to 4%wt in prepared membrane and then showed decreasing trend by further increase in additive content from 4 to 8%wt. All mentioned parameters increased another time by further increase of nanoparticle concentration from 8 to 16%wt. The opposite trend was found for the average grain size of membrane structure by variation in additive concentration. Ionic permeability and flux were also enhanced initially by increase of nanoparticle concentration up to 8%wt in prepared membranes and then showed decreasing trend by further increase in additive content. The modified membranes containing silver nanoparticles showed better performance compared to pristine ones. Moreover, modified membranes containing Ag nanoparticles showed good ability in decrease of *Escherichia coli* growth rate. The results are valuable for electro-membrane processes, especially in electrodialysis for water recovery and treatment.

## ACKNOWLEDGEMENT

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