



## Research Paper

# Electrochemical Properties and Antibacterial Activity of Polyvinyl Chloride Supported Silver Molybdate Ion-Exchange Composite Membrane

Mohammad Mujahid Ali Khan <sup>1,\*</sup>, Manoj Kumar <sup>2</sup>, Heba Abbas Keshmery <sup>3</sup>, Abdullah M. Asiri <sup>3,4</sup>

<sup>1</sup> Applied Science and Humanities Section, University Polytechnic, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh-202002, India

<sup>2</sup> Hans Raj College, University of Delhi-110007, India

<sup>3</sup> Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

<sup>4</sup> Centre of Excellence for Advanced Materials Research, King Abdulaziz University, Jeddah 21589, Saudi Arabia

## Article info

Received 2016-08-23

Revised 2016-12-29

Accepted 2017-02-12

Available online 2017-02-12

## Keywords

Polyvinyl chloride supported silver molybdate

Composite membrane

Solution casting

Instrumental analysis

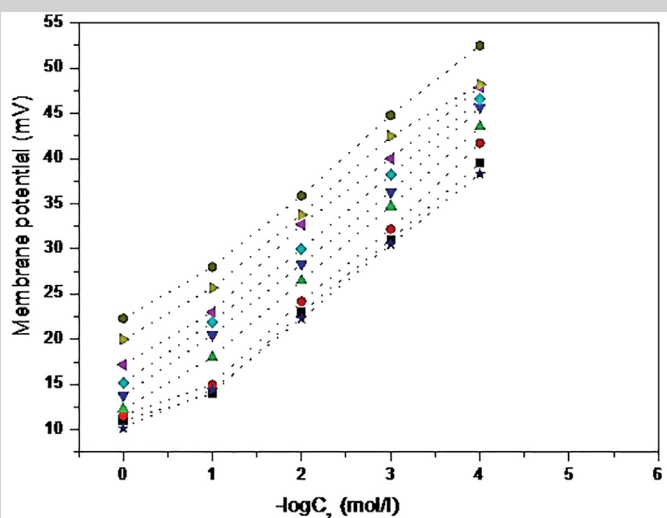
Antibacterial activity

Electrochemical properties

## Highlights

- The membrane is negatively charged.
- The membrane was found to be most stable in strong oxidant media.
- The membrane used in separation and desalination process.
- Surface charge density improves the performance of the membrane.
- The antibacterial activity of membrane shows good result against all the bacteria.

## Graphical abstract



## Abstract

Polyvinyl chloride supported silver molybdate composite material is used to develop by solution casting method. This membrane was characterized by various instrumental techniques such as Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and scanning electron microscopy (SEM) analyses. These characterizations are used to understand the functional groups, thermal stability, surface morphology, porosity, ion transportation, etc. The electrochemical study of the fabricated membrane showed that the ionic potentials decrease by increasing the concentration of electrolyte solutions while the surface charge density of membrane followed the reverse order. It indicated that the membrane is showing negative charge property. Electrochemical parameters of the fabricated membrane like surface charge density, transport number, mobility ratio, charge effectiveness and etc. are determined by TMS and Nernst theoretical equations.

© 2018 MPRL. All rights reserved.

## 1. Introduction

The organic-inorganic composite membranes have widely been used in food, drugs, wastewater treatment, beverages and dairy industries. These membranes have also been used for industrial applications such as electrodialysis, electrodeionization, fuel cells technology, energy saving, power generation and etc. [1-3].

The polymer based inorganic composite membranes are prepared by the

mixing of polymers and inorganic materials in a definite ratio of percentages to get the synergetic effects of both polymeric and inorganic materials. These composite membranes must have good chemical and mechanical stabilities and high conductivity as well as selectivity. The appropriate mechanical and chemical stabilities of the membranes supported their use in electrodialysis, heavy toxic metal separation and wastewater treatment. Electrodialysis is an

\* Corresponding author at: Phone: +919634325860

E-mail address: mujahidchemistry@gmail.com (M.M.A. Khan)

DOI: 10.22079/jmsr.2017.24343

important membrane based purification technology that can be easily processed and is much economical [4-8]. To examine the applicability of an ion-exchange membrane, it is very important to have a deep view of membrane's transport properties [9-13]. Material selection is one of the most important steps to prepare a well functional new composite membrane. PVC has been selected as a binder due to its polar nature and cheap price, and also it shows very good stability with inorganic SMB material. The electrochemical characterization of PVC-based SMB (silver molybdate) composite membrane that is included the complete electrochemical and physico-chemical properties such as ion-exchange capacity, water content nature, transport property, thickness, thermal plus chemical stability and lastly the structural properties have been considered. These above properties can easily be measured by various physical methods which have already reported by various authors [14-21].

The charge density of membrane is another important parameter which elaborated the membrane model. It can be determined by using the calculation and theoretical potential values of different used electrolyte solutions. Related to the charge density, there are some other parameters including the transport numbers, mobility ratio, charge effectiveness, etc., which can be measured easily by using the TMS theoretical approaches that has already been discussed by Mujahid et al. [15]. The surface charge density which is a prominent parameter that controls the membrane concept and can easily determine by using the calculation and theoretical potential values of different used electrolytic solutions. So, the overall performances of PVC based SMB composite membrane totally depends on their physical, chemical and morphological, and transport features as well as thermal, chemical and mechanical stabilities [22, 23].

## 2. Materials and methods

### 2.1. Materials

CaCl<sub>2</sub>, MgCl<sub>2</sub> and BeCl<sub>2</sub> (Hi-Media Laboratories-India) were used to prepare the electrolytic solution samples of different concentrations. PVC powder (mesh size: 200), silver nitrate (E. Merck-India with purity of 99.90%), sodium molybdate (Otto-Kemi-India) were used to prepare the dope. The used reagents were of analytical reagent grade. The double distilled water was used to prepare the dope solutions [15].

## 3. Experimental

### 3.1. Synthesis of silver molybdate material

Silver molybdate material was prepared by the sol-gel method of mixing of 0.2 M silver nitrate and sodium molybdate solutions with a constant stirring of the solution for about 2 h. The resulting precipitate was filtered and this filtered material was then washed about 4-5 times by deionized water to remove the free electrolytes and ions. After that the above material has been dried at 100°C. Lastly, it was broken into powdered with the help of pestle and mortar until the size must be less than 200 meshes.

### 3.2. Preparation of PVC based silver molybdate composite membrane

The above precipitates were well mixed with PVC granules through the pestle and mortar and the mixture was then transferred into a cast-die of 2.45 cm diameter. After that, the die was transferred into a digital furnace maintained at 200°C for about 2 h to equilibrate the reaction mixture. Secondly, it was transferred into the pressure device of 'SL-89-UK' by applying 120 MPa pressure to equilibrate the fabrication of membrane. By embedding 25% of PVC the membrane was found to be more mechanically stable and gave a reproducible result. If the amount of polymer is (>25% or <25%), ideal stability and functions could be achieved. So, it is very clear that the amount of mixture utilized for the preparation of an ideal membrane is 0.125 and 0.375 g of PVC and of SMB material, respectively [24-26].

### 3.3. Physico-chemical characterization of composite membrane

#### 3.3.1. Chemical stability

Chemical stability was determined by 'ASTM D543-95' procedure. It was used to study the morphological changes such as alteration in color, texture, brightness, decomposition and splits of membrane. The above changes were analyzed by exposing it into the different acidic, basic and alkaline media for 24, 36, 48 and 60 hours [27].

#### 3.3.2. Scanning electron microscopy (SEM) analysis

Thanks to the SEM images, the morphology of membrane was investigated by 'Leo 4352' model at an accelerating voltage of 20 kV. The sample is mounted on a copper stub and sputter coated with gold to minimize the charging.

#### 3.3.3. FTIR spectra of composite membrane

The FTIR analysis of PVC-based SMB composite membrane was carried out by using 'Interspec 2020' FTIR spectrometer spectrolab-UK. The sample compartment is 200 mm wide, 290 mm deep and 255 mm high. The entrance and exit beam of sample chamber was sealed with a coated KBr window and there was a hinged cover present that was used to seal it from the external environment.

#### 3.3.4. The ion-exchange capacity and water uptake of the PVC-based SMB composite membrane

The ion-exchange capacity and the water uptake of the composite membrane were determined as described in previous study [25, 28].

#### 3.3.5. The antibacterial activity the PVC-based SMB composite membrane

The antibacterial activity of the PVC-based SMB composite membrane was tested in vitro condition by using the disc diffusion method. The discs sample of 5 mm in diameter were prepared from whatmann filter paper and sterilized by dry heat at 140 °C for 1 to 2 h. These sterile discs were placed in a nutrient agar medium and then supplied into an incubator for 24 h at 37 °C. After this time, the inhibition zone was measured. The screening was performed for 114.4 µg/ml concentration of tested composite membrane and antibiotic disc [28, 29].

### 3.4. Observation of membrane potential

The potential observation of ions was done by using a digital potentiometer 'Electronics India-118' as reported by Rafiuddin et al. [15]. The aqueous solutions of CaCl<sub>2</sub>, MgCl<sub>2</sub> and BeCl<sub>2</sub> are used to obtain the ionic potential. It was observed by using saturated calomel electrodes which were kept dipped into one of the collared chamber of glass cell that has unequal concentration of solutions.

## 4. Results and discussion

Figure 1 shows the spectra of the PVC-based SMB composite material. A broad peak at 3418.67 cm<sup>-1</sup> clearly indicated the presence of H<sub>2</sub>O molecules. The sharp peaks at the range of 830.03-567.16 cm<sup>-1</sup> and 1635-1092 cm<sup>-1</sup> showed the presence of C-Cl and C-H bond of the PVC polymer, respectively. Lastly, the peak found at the range of 472.10 cm<sup>-1</sup> showed the presence of metallic phosphate group in the composite material of synthesized membrane [30, 31].

The surface morphology of the composite membrane is investigated by the SEM analysis as is shown in Figure 2. It is clear from the SEM images that the particles of SMB and PVC are uniformly distributed throughout the membrane matrix. Therefore, the composite membrane was considered homogeneous in nature and also was possessed cracks or breakage free surface which is very important property to use the membrane for separation purposes [32, 33].

The chemical stability was determined by soaking the membrane in acidic, alkaline and strongly oxidant media such as 1M HNO<sub>3</sub>, NaOH and KMnO<sub>4</sub> solutions for 15, 30, 45, 55 and 60 h. So it is clear that the membrane was destabilized in above media after passing more than the proposed time. So, the high chemical and mechanical stabilities and the specificity for ions are the important features for such type of composite membrane [34-36].

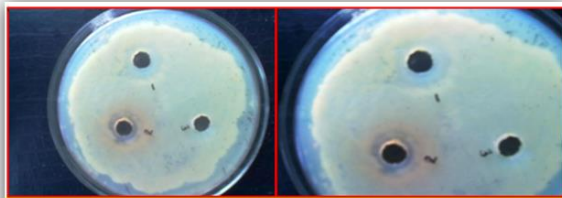
The antibacterial activity of above composite material was tested in vitro condition against the one gram-positive bacteria (i.e., *Bacillus subtilis* (ATCC 6051)) as well as two gram-negative bacteria (i.e., *Escherichia Coli* (K12) and *Pseudomonas aeruginosa* (MTCC 2488)) through using disc diffusion method. Tetracycline drug was used as a standard for the comparison of bacterial results and the results are given in Table 1.

The tetracycline data (20,23,21 µg/disc, Hi-Media) follows less activity than the examined one gram positive and two gram negative bacterium (27.5, 24.2, 21.6 µg/disc), So, it is clear that the newly synthesized PVC-based SMB composite material has extraordinary inhibitory effects against the growth of bacterial strains. The above data shows that the material was more active against *B. subtilis* as compared to *E. coli* and *P. aeruginosa*. Therefore, it is clear that the gram-positive bacteria show high activity than the gram-negative bacteria which leads that the composite material can be used as a potent antibacterial agent [28].

The membrane potential was used to measure the selectivity of different electrolyte solutions such as CaCl<sub>2</sub>, MgCl<sub>2</sub> and BeCl<sub>2</sub>. The movement of ions

by means of membrane potential is more victorious in the concentration range through which the membrane behaves as an ideal selective nature. It is clear from the observation data that the membrane potential decreases with an increase in external electrolyte concentrations which results that the membrane is cation selective in nature. The potential data of composite membrane by using various electrolyte solutions are plotted as a function of  $-\log C_2$  in Figure 3.

**Table 1**  
Antibacterial activity of PVC based SMB composite membrane.



Diameter of zone of inhibition in mm at 100 µg/ml and DMSO as control

Bacteria	NP composite membrane	Tetracycline
<i>Bacillus subtilis</i>	27.5 (±1.30)	20 (± 0.35)
<i>Escherichia coli</i>	24.2 (±0.74)	23 (± 0.55)
<i>Pseudomonas aeruginosa</i>	21.6 (±0.86)	21 (± 0.46)

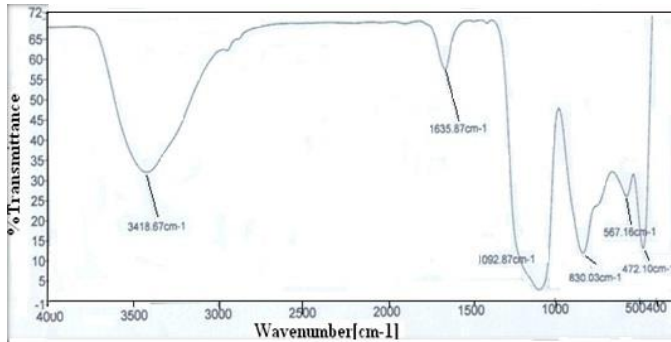


Fig. 1. FTIR Spectra of PVC based SMB composite membrane.

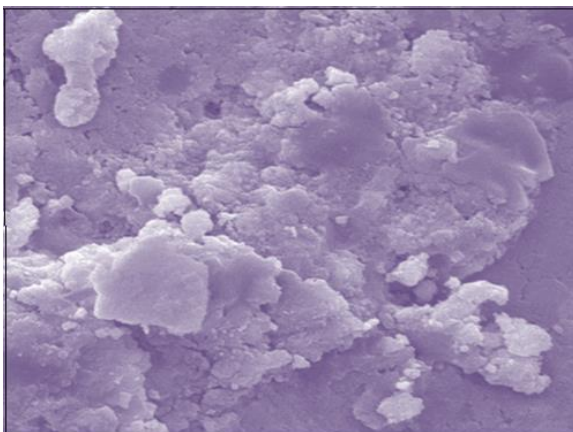


Fig. 2. SEM image of PVC based SMB composite membrane.

According to TMS theory [22, 23, 37-39], the membrane potential is given by the following equation at 25 °C:

$$\Delta \bar{\psi}_m = 59.2 \left( \log \frac{C_2}{C_1} \frac{\sqrt{4C_1^2 + \bar{D}^2} + \bar{D}}{\sqrt{4C_2^2 + \bar{D}^2} + \bar{D}} + \bar{U} \log \frac{\sqrt{4C_2^2 + \bar{D}^2} + \bar{D}U}{\sqrt{4C_1^2 + \bar{D}^2} + \bar{D}U} \right) \quad (1)$$

$$\bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v})$$

where  $u^-$  and  $v^-$  are the ionic mobility's of cation and anion ( $m^2/v/s$ ), respectively, in the membrane phase;  $C_1$  and  $C_2$  are concentrations of electrolytes; and  $D^-$  is the charge on membrane which is expressed in equivalent per liter. The graphical method of TMS determines the fixed charge  $D^-$  in eq/L as well as the cation-to-anion mobility ratio in membrane phase.

The charge on membrane played a major role for the transportation of electrolyte ions in membrane process. Therefore, without the evaluation of thermodynamically effective fixed charge density the transport mechanism of electrolytes solution within the membrane cannot be completed. The surface charge density of the PVC-based SMB composite membrane is determined through plotting the observed and theoretical membrane potential data as a function of  $-\log C_2$ , as is shown in Figure 4. The coinciding point in the graphical curves of above figure gave the value of charge density  $D^-$  as is presented in Table 2. The order of surface charge density was found to be  $CaCl_2 > MgCl_2 > BeCl_2$ . The charge density is higher in case of  $CaCl_2$  than that of  $MgCl_2$  and  $BeCl_2$  due to the size factor. The TMS Eq.1 can also be expressed by the sum of the Donnan potential ( $\Delta \psi_{Don}$ ) and the diffusion potential ( $\Delta \psi_{Diff}$ ) within the membrane phase [22, 40,41]:

$$\Delta \bar{\psi}_{m,e} = \Delta \psi_{Don} + \Delta \bar{\psi}_{diff} \quad (2)$$

$$\Delta \psi_{Don} = - \frac{RT}{V_k F} \ln \left( \frac{\gamma_{2\pm} C_2 \bar{C}_{1+}}{\gamma_{1\pm} C_1 \bar{C}_{2+}} \right) \quad (3)$$

$R$ ,  $T$  and  $F$  have their usual significance;  $\gamma_{1\pm}$  and  $\gamma_{2\pm}$  are the mean ionic activity coefficients.  $C_{-1\pm}$  and  $C_{-2\pm}$  are the cation concentrations in the first and second membrane phases, respectively. The cation concentration is given by the following equation.

$$\bar{C}_+ = \sqrt{\left( \frac{V_x \bar{D}}{2V_k} \right)^2 \left( \frac{\gamma_{\pm} C}{q} \right)^2} - \frac{V_x \bar{D}}{2V_k} \quad (4)$$

where  $V_k$  and  $V_x$  denoted the valency of cation and fixed-charge groups on membrane matrix, respectively, and  $q$  is the charge effectiveness of membrane and it is defined as follow:

$$q = \sqrt{\frac{\gamma_{\pm}}{K_{\pm}}} \quad (5)$$

where  $K_{\pm}$  is distribution coefficient and it has expressed by the following equation.

$$K_{\pm} = \frac{\bar{C}_i}{C_i}, \bar{C}_i = C_i - \bar{D} \quad (6)$$

where  $C_i^-$  is the  $i^{th}$  ion concentration in membrane phase and  $C^i$  is the  $i^{th}$  ion concentration of external solution.

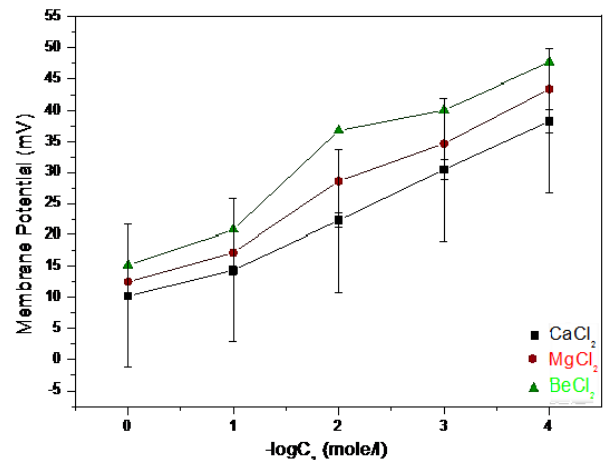


Fig. 3. Plots of observed membrane potentials against logarithm of concentration for PVC based SMB composite membrane using various electrolytes at 25 °C.

**Table 2**

Derived values of membrane charge density (eq/l) of PVC based SMB composite membrane for various electrolyte system using TMS equation.

Electrolytes	Charge density (eq/l)
CaCl <sub>2</sub>	0.055
MgCl <sub>2</sub>	0.047
BeCl <sub>2</sub>	0.039

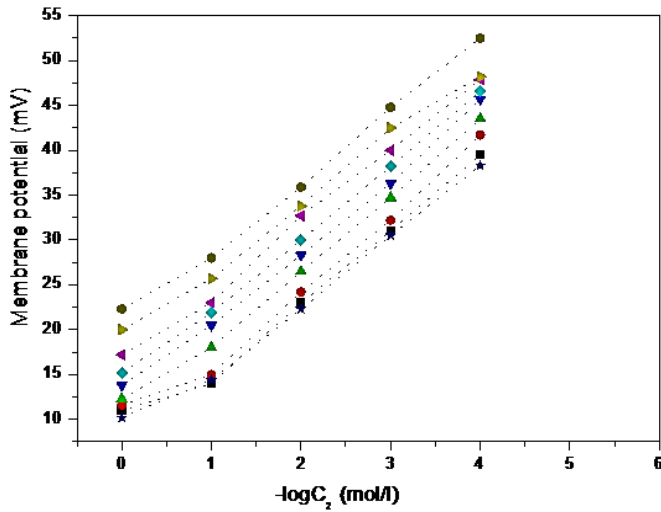


Fig. 4. Plots of membrane potential (theoretical and observed) (mV) versus  $-\log C_2$  (mol/l) at different concentrations of CaCl<sub>2</sub> electrolyte solution for PVC based SMB composite membrane.

The diffusion potential,  $\Delta\psi_{diff}$  was expressed as follow:

$$\Delta\bar{\psi}_{diff} = -\frac{RT\bar{\omega}-1}{V_k F \bar{\omega}+1} \times \ln \left( \frac{(\bar{\omega}+1)\bar{C}_2 + (V_X/V_k)\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_X/V_k)\bar{D}} \right) \quad (7)$$

where  $\bar{\omega} = u^+/v^-$  is the mobility ratio of cation towards the anion in membrane phase. Therefore, the total membrane potential  $\Delta\psi^{me}$  has obtained by the following equation.

$$\Delta\bar{\psi}_{m,e} = -\frac{RT}{V_k F} \ln \left( \frac{\gamma_{2\pm} C_2 \bar{C}_{1\pm}}{\gamma_{1\pm} C_1 \bar{C}_{2\pm}} \right) - \frac{RT\bar{\omega}-1}{V_k F \bar{\omega}+1} \times \ln \left( \frac{(\bar{\omega}+1)\bar{C}_2 + (V_X/V_k)\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_X/V_k)\bar{D}} \right) \quad (8)$$

$$\Delta\bar{\psi}_m = -\frac{RT}{F} (t_+ - t_-) \ln \frac{C_2}{C_1} \quad (9)$$

where

$$\frac{t_+}{t_-} = \frac{\bar{u}}{\bar{v}} \quad (10)$$

For the applicability of these theoretical equations, the diffusion and the Donnan potential were separately calculated from the membrane potential observations. To determine the values of transport number ( $t_+$ ), Eq. (9) can be used and  $t_+$  is also obtains from the experimental membrane potential data. The mobility ratio  $\bar{\omega} = u^+/v^-$  has calculated very easily with the help of transport number. The mobility of electrolytes in the membrane phase was found to be high and it follows the BeCl<sub>2</sub>>MgCl<sub>2</sub>>CaCl<sub>2</sub> order as is shown in Figure 5. The high mobility is due to the higher transport number of comparatively free ions of electrolytes. The similar trend of mobility was also observed in the least concentrated solutions. The transport number of cation for the various used electrolytes increases by decreasing the concentration of electrolyte solution which follows the increasing order BeCl<sub>2</sub>>MgCl<sub>2</sub>>CaCl<sub>2</sub> and is graphically shown in Figure 6.

## 5. Conclusions

The PVC-based SMB composite membrane was successfully prepared by sol-gel method of material preparation. The membrane has found to be stable in acidic, alkaline as well as strongly oxidant media but it is most stable in oxidant medium. The fixed-charge density is the most effective parameter that governs the transport phenomena of the composite membrane. The membrane potential for different used electrolytes was found to follows the CaCl<sub>2</sub><MgCl<sub>2</sub><BeCl<sub>2</sub> order whereas the surface charge density follows the reverse order of the above one. The membrane was found to be negatively charged and it also shows a lot of applications, especially in wastewater treatment.

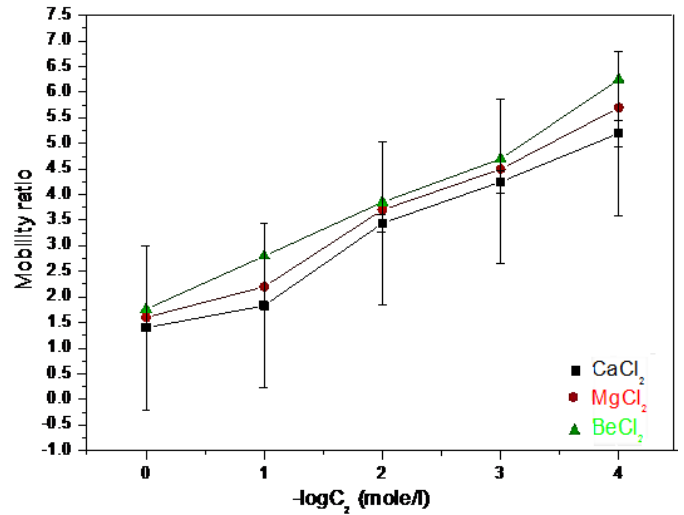


Fig. 5. The plot of mobility ratio of PVC based SMB composite membrane for electrolytes (CaCl<sub>2</sub>, MgCl<sub>2</sub>, BeCl<sub>2</sub>) versus concentrations.

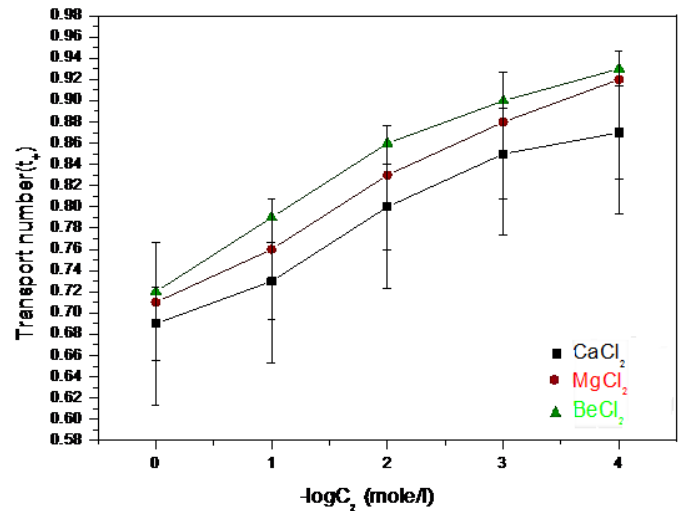


Fig. 6. The plot of transport number of cation of PVC based SMB composite membrane for 1:1 electrolytes (CaCl<sub>2</sub>, MgCl<sub>2</sub>, BeCl<sub>2</sub>) versus concentrations.

## Acknowledgement

The authors gratefully acknowledge Principal, University Polytechnic, Faculty of Eng. and Technology and the Chairman, Department of Chemistry, Aligarh Muslim University, Aligarh, India for providing necessary research facilities. We are also thankful to the UGC for providing financial assistance and USIF, AMU Aligarh for scanning electron microscopy facility.

## References

- [1] T.J Chou, A.Tanioka, Ionic behavior across charged membranes in methanol water solutions. I: Membrane potential, J. Membr. Sci. 144 (1998) 275-284.

- [2] H. Matsumoto, Y.C. Chen, R. Yamamoto, Y. Konosu, M. Minagawa, A. Tanioka, Membrane potentials across nanofiltration membranes: effect of nanoscaled cavity structure, *J. Mol. Struct.* 739 (2005) 99–104.
- [3] S. Weqar, A. Khan, A. Shakeel, Inamuddin, Synthesis, characterization and ion-exchange properties of a new and novel 'organic-inorganic' hybrid cation-exchanger: Poly(methyl methacrylate) Zr(IV) phosphate, *Colloid. Surf.* 295 (2007) 193–199.
- [4] R.K. Nagarale, V.K. Shahi, S.K. Thampy, R. Rangarajan, Studies on electrochemical characterization of polycarbonate and polysulfone based heterogeneous cation-exchange membranes *Reac. Func. Polym.* 61 (2004) 131–138.
- [5] M.N. Beg, M.A. Matin, Studies with nickel phosphate membranes: evaluation of charge density and test of recently developed theory of membrane potential, *J. Membr. Sci.* 196 (2002) 95–102.
- [6] T. Arfin, Rafiuddin, An electrochemical and theoretical comparison of ionic transport through a polystyrene-based cobalt arsenate membrane, *Electro. Acta* 56 (2011) 7476–7483.
- [7] Z.A. Al-Othman, Mu. Naushad, Inamuddin, Organic-inorganic type composite cation exchanger poly-o-toluidine Zr(IV) tungstate: Preparation, physicochemical characterization and its analytical application in separation of heavy metals, *Chem. Eng. J.* 172 (2011) 369–375.
- [8] M.K. Ramir, Rafiuddin, Synthesis, characterization and properties of polystyrene incorporated calcium tungstate membrane and studies of its physicochemical and transport behavior, *J. Mol. Struct.* 1033 (2013) 145–153.
- [9] T.J. Chou, A. Tanioka, Ionic behavior across charged membranes in methanol-water solutions. I: Membrane potential, *J. Membr. Sci.* 144 (1998) 275–284.
- [10] M.M.A. Khan, Rafiuddin, Inamuddin, Electrochemical characterization and transport properties of polyvinyl chloride based carboxy methyl cellulose Ce(IV) molybdophosphate composite cation exchange membrane, *J. Ind. Eng. Chem.* 18 (2012) 1391–1397.
- [11] G.S. Gohil, R.K. Nagarale, V.V. Binsu, V.K. Shahi, Preparation and characterization of monovalent cation selective sulfonated poly (ether ether ketone) and poly (ether sulfone) composite membranes, *J. Colloids Interf. Sci.* 298 (2006) 845–853.
- [12] A.A. Moya, Harmonic analysis in ideal ion-exchange membrane systems, *Electro. Acta* 90 (2013) 1–11.
- [13] M.M.A. Khan, Rafiuddin, Synthesis, electrochemical characterization, antibacterial study and evaluation of fixed charge density of polystyrene based calcium-strontium phosphate composite membrane, *Desalination* 284 (2012) 200–206.
- [14] Z.A. Al-Othman, Mu. Naushad, Determination of ion-exchange kinetic parameters for the poly-o-methoxyaniline Zr (IV) molybdate composite cation-exchanger, *Chem. Eng. J.* 166 (2011) 639–645.
- [15] M.M.A. Khan, Rafiuddin, Preparation, electrochemical characterization and antibacterial study of polystyrene-based magnesium-strontium phosphate composite membrane, *Mater. Sci. Eng. C* 32 (2012) 1210–1217.
- [16] Z.A. Al-Othman, Inamuddin, Mu. Naushad, Recent developments in synthesis, characterization and applications of zirconium(IV) based composite ion exchangers -A review, *J. Inorg. Organomet. Polym.* 23 (2013) 257–269.
- [17] N. Hilal, H. Al-Zoubi, N.A. Darwish, A.W. Mohammad, M. Abu Arabi, A comprehensive review of nanofiltration membranes: treatment, pretreatment, modeling, and atomic force microscopy, *Desalination* 170 (2004) 281–308.
- [18] G.S. Gohil, V.V. Binsu, V.K. Shahi, Preparation and characterization of monovalent ion selective polypyrrole composite ion-exchange membranes. *J. Membr. Sci.* 280 (2006) 210–218.
- [19] R.K. Nagarale, V.K. Shahi, R. Schubert, R. Rangarajan, R. Mehnert, Development of urethane acrylate composite ion-exchange membranes and their electrochemical characterization. *J. Colloids Interf. Sci.* 270 (2004) 446–454.
- [20] M. Zarrinkhameh, A. Zandehnam, S.M. Hosseini, Electrochemical, morphological and antibacterial characterization of PVC based cation exchange membrane modified by zinc oxide nanoparticles. *J. Polym. Res.* 20 (2013) 1–9.
- [21] A. Zandehnam, M. Arabzadegan, S.M. Hosseini, N. Robatmili, S.S. Madaeni, Fabrication and modification of polyvinylchloride based heterogeneous cation exchange membranes by simultaneously using Fe-Ni oxide nanoparticles and Ag nanolayer: Physico-chemical and antibacterial characteristics. *Korean J. Chem. Eng.* 30 (2013) 1265–1271.
- [22] M. Arsalan, MMA Khan, Rafiuddin, A comparative study of theoretical, electrochemical and ionic transport through PVC based  $\text{Cu}_3(\text{PO}_4)_2$  and polystyrene supported  $\text{Ni}_3(\text{PO}_4)_2$  composite ion exchange porous membranes, *Desalination* 318 (2013) 97–106.
- [23] U. Ishrat, Rafiuddin, Synthesis characterization and electrical properties of titanium molybdate composite membrane, *Desalination* 286 (2012) 8–15.
- [24] M.M.A. Khan and Rafiuddin, Synthesis, characterization and antibacterial activity of polystyrene based  $\text{Mg}_3(\text{PO}_4)_2/\text{Ca}_3(\text{PO}_4)_2$  composite membrane, *Desalination* 294 (2012) 74–81.
- [25] M.M.A. Khan, Rafiuddin, Inamuddin, Synthesis, characterization, thermal behaviour and transport properties of polyvinyl chloride based zirconium phosphate composite membrane, *J. Environ. Chem. Eng.* 2 (2014) 471–476.
- [26] A.M. Hollman, N.T. Scherrer, A.C. Goodwin, D. Bhattacharyya, Separation of dilute electrolytes in poly(amino acid) functionalized microporous membranes: model evaluation and experimental results, *J. Membr. Sci.* 239 (2004) 65–79.
- [27] ASTM D543-95, Standard particles for evaluating the resistance of plastics to chemical reagents, 1998.
- [28] M.M.A. Khan, Rafiuddin, Synthesis, characterization and electrochemical study of calcium phosphate ion exchange membrane, *Desalination*, 272 (2011) 306–312.
- [29] M.N. Beg, F.A. Siddiqi, R. Shyam, I. Altaf, Studies with inorganic precipitate membranes: Part XXVI. Evaluation of membrane selectivity from electric potential and conductivity measurements, *J. Electroanal. Chem.* 98 (1978) 231–240.
- [30] Mu. Naushad, Inamuddin, T.A. Rangreez, Z.A. AlOthman, A mercury ion selective electrode based on poly-o-toluidine Zr(IV) tungstate composite membrane, *J. Electroanal. Chem.* 713 (2014) 125–130.
- [31] F. Jabeen, Rafiuddin, Membrane potential and fixed charge density across  $\text{TiPO}_4\text{-VPO}_4$  composite membranes for univalent electrolyte solution, *J. Por. Mat.* 16 (2009) 257–265.
- [32] X. Zhang, X. Shiyu, H. Gaorong, Fabrication and photo catalytic activity of  $\text{TiO}_2$  nanofiber membrane, *Mat. Lett.* 63 (2009) 1761–1763.
- [33] Z.A. Siddiqi, M. Khalid, S. Kumar, M. Shahid, S. Noor, Antimicrobial and SOD activities of novel transition metal complexes of pyridine-2,6-dicarboxylic acid containing 4-picoline as auxiliary ligand, *E. J. Med. Chem.* 45 (2010) 264–9.
- [34] R. Niwas, A.A. Khan, K.G. Varshney, Synthesis and ion exchange behaviour of polyaniline Sn(IV) arsenophosphate: a polymeric inorganic ion exchanger, *Coll. Surf. A* 150 (1999) 7–14.
- [35] A.A. Khan, Inamuddin, M.M. Alam, Determination and separation of  $\text{Pb}^{2+}$  from aqueous solutions using a fibrous type organic-inorganic hybrid cation-exchange material: polypyrrole thorium(IV) phosphate, *React. Func. Polym.* 63 (2005) 119–133.
- [36] T.J. Chou, A. Tanioka, Membrane potential of composite bipolar membrane in ethanol-water solutions- the role of the membrane interface, *J. Colloids Interf. Sci.* 212 (1999) 293–300.
- [37] M.A. Ansari, M. Kumar, N. Singh, K.S. Dadoriya, R.S. Kushwaha, S. Ayub, Ion transport studies through polystyrene based model membrane: Conductance data and absolute reaction rate theory, *Adv. Appl. Sci. Res.* 3 (2012) 251–260.
- [38] H. Haibo, G. Bin, C. Feng, Effect of membrane surface characterization on salt and water transport through aromatic polyamide membranes, *Adv. Sci. Lett.* 12 (2012) 218–222.
- [39] A. Kruissink, Bergsma, Ion-exchange membranes, *Adv. Polym. Sci.* 2/1 (1960) 307–362.
- [40] F. Jabeen, Rafiuddin, Transport studies with composite membrane by sol-gel method, *J. Disp. Sci. Technol.* 31 (2010) 1708–1713.
- [41] F.A. Siddiqi, N. Lakshminarayanaiah, M.N. Beg, Studies with inorganic precipitate membranes. IV. Evaluation of apparent fixed charge on membranes, *J. Polym. Sci.* 9 (1971) 2869–2875.