

Electrochemical Properties of Parchment Supported Iron Tungstate Ion Exchange Model Membrane



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Abstract

Parchment supported iron tungstate material is used to develop by ion interactren method. This membrane was characterized by various instrumental techniques such as Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy analysis (SEM). These characterizations are used to understand the functional groups. thermal stability, surface morphology, porosity, ion transportation etc. The Study of the fabricated membrane showed that the ionic potential 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 prepared membrane like charge density, transport number, mobility ratio, charge effectiveness etc. are determined by TMS and Nernst theoretical equations.

Keywords: Iron Tungstate Membrane, X-Ray diffraction, Membrane Potential, SEM and Thermogravimetric Analysis.

Introduction

The electrochemical property of model membranes have easily examined¹. Due to the ion exchange property, the synthesized model membrane show various possible applications like in food, drugs, and chemical, industries and in waste water treatment²⁻⁴. In the present investigation surface charge density, considered as the most effective parameter controlling membrane phenomena, has been determined by the TMS method using membrane potential measurements.

Objective of the study

The aim of the work is to prepare and physicochemical characterization of newly synthesized parchment supported inorganic precipitated iron tungstate membrane.

Review of Literature

Iron tungstate process occurring through synthetic membranes separating different solution have attracted the attention of chemical engineers and biologists. They want to understand the mechanism of transport so that they would be able to fabricate membrane of any desired properties. Biologists would like to use synthetic membranes as simple models for the physiological membranes in order to understand the behaviour of complex cell membranes in terms of established physicochemical principles.

The literature in journals describing membrane technology and application is very difficult to mention. The significant papers on membrane electrochemistry are by Siddique and Beg⁵, Matsumato⁶, Chaabane⁷, Chan and Tanioka⁸, Arfin and Rafiuddin⁹, Harmonic¹⁰, Mohammad Arsalan¹¹, Urfi Ishrat¹², Rafiuddin¹³ and M.M.A. Khan¹⁴. However some researchers have demonstrated that both parchment supported and polystyrene inorganic precipitate membranes possess small quantity of fixed charges^{1-5,9-14}.

Concepts and Hypothesis

The theoretical approche which is normally used to determine membrane potential of model membranes is TMS theory¹⁵⁻¹⁷. This theory has several inportant points and postulates, which are illustrated as in the TMS approach there must be an equiliberium developed at all interfaces of the solution and membrane, which has proper connection with the Donnan equiliberium. The other important postulations are described as follows:-

1. The transfer of water from either side of the membrane may be ignored.

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- The ionic movement and concentration of fixed charges are constant throughout the membrane matrix.
- The charge of membrane is independent of the salt concentration of the solutions.

Additional assumptions are that the activity coefficient of the salt is similar in both the solution and membrane phases. The introduction of activities for salt concentration can only be approved through the Donnan potential, either by using Planks or Henderson equation.

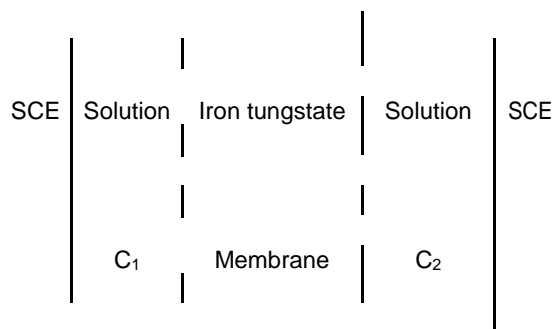
Materials and Methods

Preparation of membrane

Parchment supported inorganic precipitate Iron tungstate synthetic membrane has been prepared by the method of interaction as suggested by¹⁹. To precipitate these substances in the interstices of parchment paper, a 0.2M solution of sodium tungstate (S. D. Fine Ltd.) was placed inside glass tube, to one end of which was tied the parchment paper (Amul group of companies, Mumbai India) previously soaked in deionised water. The tube was suspended for 72 hours in a 0.2 M solution of Ferrous Ammonium Sulfate (Ranbaxy). The two solutions (fresh solution) were interchanged later and kept for another 72 hours. Thus parchment paper and inorganic precipitate as a whole acts as a synthetic membrane. The membrane thus prepared was washed with deionized water to remove free electrolytes.

Measurement of membrane potential

The electrochemical cell of the type was used for measuring membrane potential (E_m) arising through the membrane by maintaining a tenfold difference in concentration (C₁ / C₂ = 10) and using a multimeter (Rishmulti^(R) 4^{3/4} digits 18S).



All the electrolyte solutions used in the investigation were prepared from analytical grade reagents and deionized water.

Membrane Characterization

The Iron tungstate model membrane for the electrochemical studies characterised as:

% total wet weight

The water uptake (total wet weight) was calculated as follows

$$\text{Water Uptake} = \left(\frac{W_w - W_d}{W_w} \right) \times 100$$

Where W_w is the weight of the soaked or wet model membrane and W_d the weight of the dry model membrane.

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Porosity (P)

Porosity was calculated as the volume of water incorporated in the cavities per unit membrane volume from the total wet weight data:

$$P = (W_w - W_d) / (A L \rho_w)$$

Where A is the area of the model membrane (cm²). L is the thickness of the membrane (cm) and ρ_w the density of water (g/cm³).

Thickness

The membrane thickness value was averaged from five measurements of different locations on the effective surface region of the model membrane.

Swelling

Swelling was measured as the difference between the average thickness of the model membrane equilibrated in one molar Sodium Chloride for twenty four hours and the dry membrane.

Electron Microscopy Studies

The SEM image of parchment supported Iron tungstate model membrane was analysed with scanning electron microscope (JEOL, FE-SEM).

Fourier Transformed Infra Red (FTIR) studies

The FTIR spectrum of parchment supported Iron tungstate model membrane was carried out by Perkin Elmer instrument (USA).

X-Ray Diffraction studies

X-ray diffraction pattern of the parchment supported Iron tungstate model membrane was recorded by Miniflex-II X-ray diffractometer (Rigaku Corporation) with CuKα radiation.

Thermogravimetric analysis studies

The degradation process and thermal stability of the membrane was investigated using thermogravimetric analyzer (Model STA 8000 Ltd), under nitrogen atmosphere (200 ml/min.)

Results and Discussion

The result of total wet weight, Porosity, thickness and swelling of parchment supported inorganic precipitate Iron tungstate membrane are summarized in Table 1.

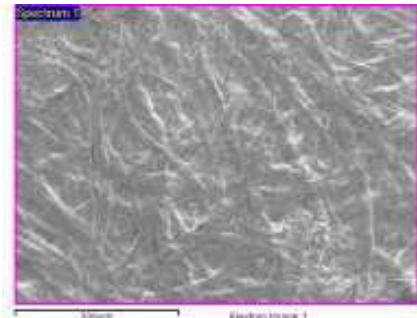
Table: 1

Thickness, Water Content, Porosity and Swelling Properties of Iron Tungstate Synthetic Membrane

| | |
|---|-------|
| Thickness of the membrane (cm) | 0.013 |
| Water content as % weight of wet membrane | 0.082 |
| Porosity | 0.769 |
| Swelling of % weight wet membrane | 0.08 |

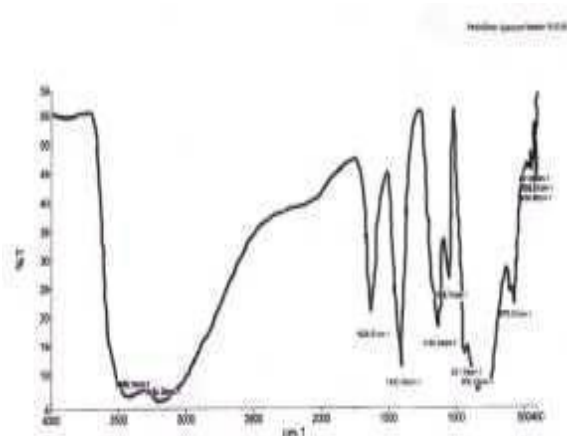
The SEM surface image of parchment supported Iron tungstate membrane is presented in Fig. 1. By the study of SEM micrograph the membrane is found heterogenous in nature and there is no visible cracks.

Fig.1. SEM image of Iron Tungstate Membrane



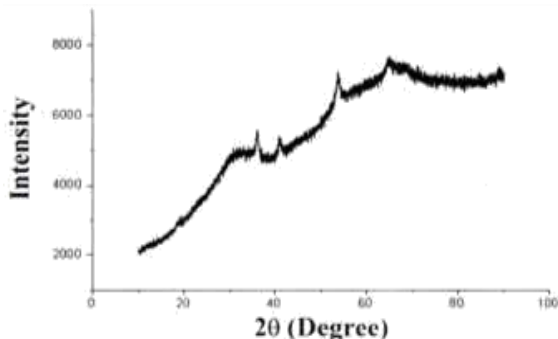
The FTIR spectra of the parchment supported Iron tungstate membrane is given in Fig. 2. The fabricated model membrane contains many important characteristic peaks.

Fig.2. FTIR spectra of Iron Tungstate Membrane



X-Ray scattering techniques are a family of non-destructive analytical technique which reveal information about the crystallographic structure, chemical composition and physical properties of materials. Fig. 3 shows X-ray diffraction spectrum of the Iron tungstate membrane. The material recorded in powdered sample exhibited some sharp peaks in the spectrum shows semi-crystalline nature of the material.

Fig.3. X-ray Pattern of Iron Tungstate Membrane

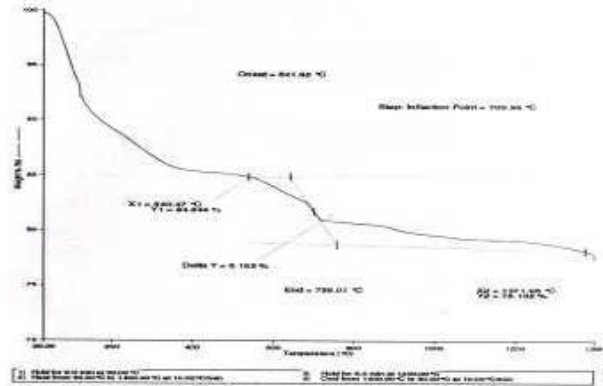


The thermal stability of the Iron tungstate membrane was analyzed by TGA. The TGA curve measured under flowing nitrogen is reported in Fig. 4 TGA of the membrane material showed gradual weight loss which may be due to the removal of

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external water molecules present at the surface of the membrane material. Further weight loss indicating the start of condensation due to the removal of the lattice water from the material.

Fig. 4-TGA curve of Iron Tungstate Membrane



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The membrane potential was used to measure the selectivity of different electrolyte solutions such as KNO_3 , $NaNO_3$ and NH_4Cl . The movement of ions by means of membrane potential is 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 experimentally observed membrane potential values are given in table 2. The potential data of composite membrane by using various electrolyte solutions are plotted as a function of $-\log C_2$, in Figure 5.

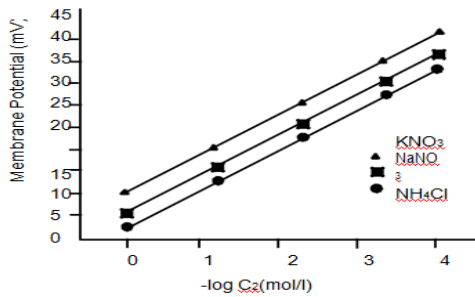
Table-2

Experimentally observed values of membrane potential E_m (mv) across parchment supported iron tungstate membrane at $25 \pm 0.1^\circ C$

| Concentration (Mol/l) C_2/C_1 | Electrolytes | | |
|------------------------------------|--------------|----------|----------|
| | KNO_3 | $NaNO_3$ | NH_4Cl |
| 1.0/0.1 | 1 | 4 | 5 |
| 0.5/0.05 | 4 | 8 | 9 |
| 0.2/0.02 | 13 | 15 | 17 |
| 0.1/0.01 | 23 | 24 | 25 |
| 0.05/0.005 | 33 | 35 | 32 |
| 0.02/0.002 | 38 | 43 | 38 |
| 0.01/0.001 | 41 | 44 | 40 |
| 0.005/0.0005 | 43 | 45 | 41 |

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Fig. 5 Plots of observed membrane potentials against $-\log C_2$ for iron tungstate membrane using various electrolytes at $25 \pm 0.1^\circ\text{C}$.



According to TMS theory¹⁵⁻¹⁷ the membrane potential is given by the following equation at 25°C :

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

Where, \bar{u} and \bar{v} are the ionic mobility's of cation and anion ($\text{m}^2/\text{v}\cdot\text{s}$), respectively, in the membrane phase, C_1 and C_2 are concentrations of electrolytes; and \bar{D} is the charge on membrane which is expressed in equivalent per liter. The graphical method of TMS determines the fixed charge \bar{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 charged density of the membrane is determined through plotting the observed and theoretical membrane potential data as a function of $-\log C_2$, as is shown in Fig 6. The coinciding point in the graphical curves of above figure gave the value of charge density \bar{D} as is presented in Table 3.

Table 3
Derived Values of Membrane Charge Density (eq/l) of Iron Tungstate Membrane for Various Electrolyte System using TMS Equations

| Electrolytes | KNO ₃ | NaNO ₃ | NH ₄ Cl |
|-----------------------|------------------|-------------------|--------------------|
| Charge Density (eq/l) | 0.061 | 0.052 | 0.047 |

The order of surface charge density was found to be $\text{KNO}_3 > \text{NaNO}_3 > \text{NH}_4\text{Cl}$. The 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 phase¹⁸⁻¹⁹.

$$\Delta\Psi_{m,e} = \Delta\Psi_{Don} + \Delta\Psi_{diff} \quad (2)$$

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

R, T and F have their usual significance; $\gamma_{1\pm}$ and $\gamma_{2\pm}$ are the mean ionic activity coefficients. $\bar{C}_{1\pm}$ and $\bar{C}_{2\pm}$ are the cation concentrations in the first and

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second membrane phases, respectively. The cation concentration is given by the following equation.

$$\bar{C}_{+} = \sqrt{\left(\frac{V_2 \bar{D}}{2V_k} \right)^2 + \left(\frac{\gamma_{\pm} C}{q} \right)^2} - \frac{V_2 \bar{D}}{2V_k} \quad (4)$$

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 follows:

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

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

$$K_{\pm} = \frac{\bar{C}_i}{C_i}$$

$C_i = C_i - D$

Where, \bar{C}_i is the i^{th} ion concentration in membrane phase and C_i is the i^{th} ion concentration of external solution.

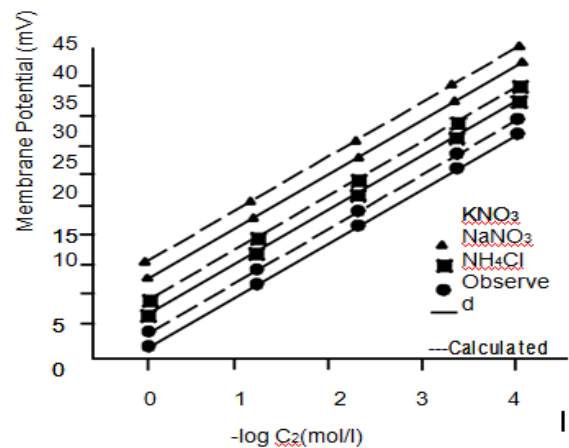


Fig. 6 Plots of membrane potential (theoretical and observed) versus $-\log C_2$ (mol/l) at different concentration of electrolytes solution for iron tungstate membrane.

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

$$\Delta\Psi_{diff} = \frac{RT}{v_1 F} \frac{\omega - 1}{\omega + 1} \times \ln \left(\frac{(\omega + 1) \bar{C}_2 + (V_x/V_k) \bar{D}}{(\omega + 1) \bar{C}_1 + (V_x/V_k) \bar{D}} \right) \quad (7)$$

Where \bar{u}/\bar{v} is the mobility ratio of cation towards the anion in membrane phase. Therefore, the total membrane potential $\Delta\Psi$ has obtained by the following equation

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

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

Where,

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

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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 obtained from the experimental membrane potential data. The mobility ratio $\omega = \bar{u} / \bar{v}$ 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 $\text{KNO}_3 > \text{NaNO}_3 > \text{NH}_4\text{Cl}$ order as is shown in Figure 7. 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 $\text{KNO}_3 > \text{NaNO}_3 > \text{NH}_4\text{Cl}$ and is graphically shown in Figure 8.

Fig. 7 The Plot of Mobility Ratio of Iron Tungstate Membrane For Electrolytes Versus Concentrations

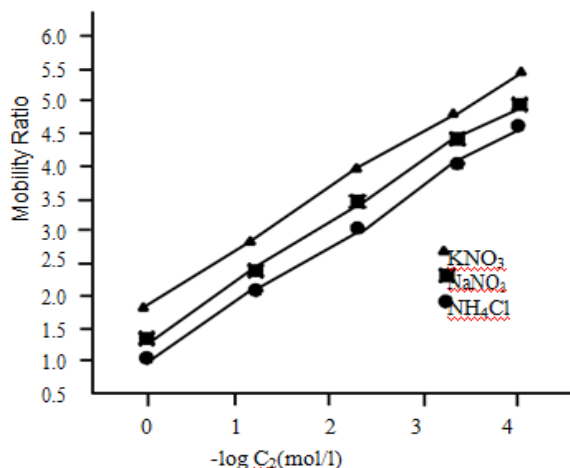
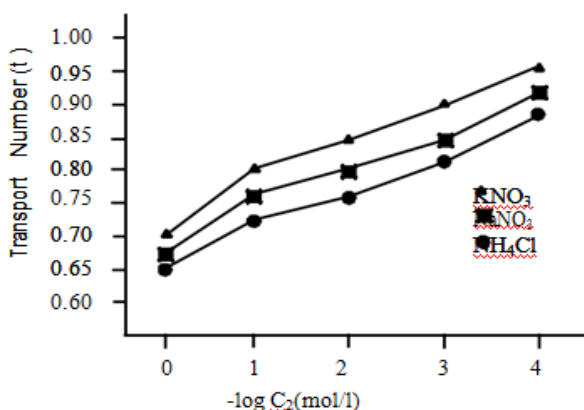


Fig. 8 The Plot of Transport Number of Cation of Iron Tungstate Membrane for Electrolytes



Conclusion

The parchment supported inorganic precipitated iron tungstate membrane was successfully prepared by interaction method. The membrane has found to be stable. The fixed charge density is the most effective parameter that governs the transport phenomena of the membrane. The

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membrane potential for different used electrolytes was found to follow the order as $\text{KNO}_3 > \text{NaNO}_3 > \text{NH}_4\text{Cl}$ whereas the surface charge density follows the reverse order of the above one. The membrane was found to be cation selective and have a many applications in waste water treatment.

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References

1. Beg, M.N. Matin, M.A., (2002) Studies with nickel phosphat membrane evaluation of charge density and test of recently developed theory of membrane potential, *J. Membr Sci*, 196, 95-102
2. Arfin, T., Rafiuddin (2011) An Electrochemical and theoretical comparison of ionic transport through a polystyrene based cobalt aeseenate membrane, *Electrothematica Acta*, 56, 7476-7483.
3. Khan, A.A., Habiba, U., Shaheen. S., Khalid M. (2013) Ion exchange and humidity sensing properties of poly-o-anisiding Sn(IV) aeseenophosphate nano composite cation exchanger, *J. Environ, Chem. Eng.* 1, 310-319.
4. Khan, M.R. Rafiuddin, (2013) synthesis, characterization and properties of polystyrene incorporated calcium tungstate membrane and studies of its physicochemical and transport behaviour, *J. Mol. Struct*, 103, 145-153
5. Siddiqi F.A., Beg M.N., Singh S.P. (1979) Studies with model membranes. X. Evaluation of the thermodynamically effective fixed charge density and perm selectivity of mercuric and cupri iodide parchment-supported membranes, *J. Polym, Sci.* 15, 959-972.
6. Matsumoto H., Chen Y.C., Yamamoto R., Konosu Y., Minagnwa M., Tanioka A. (2005) Membrane potentials across nanofiltration membrane: effect of manoscalded cavity structure, *J. Mol. Struct.* 739 99-104.
7. Chaabane L, Bulvestre G., Innocent C., Pourcelly G., Auclair B. (2006) Physicochemical characterization of ion-exchange membranes in water-methanol mixtures, *Eur. Polym. J.* 42 1403-1416.
8. Chou I.J., Tanioka A. (1998) Ionic behavior across charged membranes in methanol-water solutions, I: Membrane potential, *J. Member. Sci.* 144 275-284
9. Arfin T., Rafiuddin (2009), Transport studies of nickel arsenate membrane, *J. Electrical. Chem.* 636 113-122.
10. Moya A.A., Harmonic Y. (2013) Analysis in ideal ion-exchange membrane system, *Electro. Acta.* 90 1-11.
11. Arsalan M., Khan M.M.A. Rafiuddin (2013) A comparative study of theoretical, electrochemical and ionic transport through PVC based $\text{Cu}_3(\text{PO}_4)_2$ composite ion exchange porous membranes, *Desalination* 318, 97-106.
12. Ishrat U., Rafiuddin (2012) Synthesis characterization and electrical properties of Titanium molybdate composite membrane, *Desalination* 286, 8-12.

13. Arsalan M., Rafiuddin (2014) *Synthesi, structural characterization, electrochemical and electrical study of polystyrene based manganous tungstate composite cation exchange membrane*, 52, 7531-7542
14. Arsalan M., Rafiuddin (2014) *Synthesi, structural characterization, electrochemical and electrical study of polystyrene based manganous tungstate composite cation exchange membrane*, 52, 7531-7542.
15. Teorell T. (1935) *An attempt to formulate a quantative theory of membrane permeability* *Poc. Soc. Exp. Biol. Med.* 33, 282-285.
16. Meyer K.H., Sievers J.F. (1936) *La permeabilite des membranes I. Theorie de 1a permeabilite ionique*, *Helv. Chim Acta.* 19, 649-664.
17. Meyer K.H., Sievers J.F. (1936) *La permeabilite des membranes. II Essais avec des membranes selectives artificielles*, *Helv. Chim Acta.* 19, 665-677.
18. Jabeen F. Jabeen, Rafiuddin (2010) *Transport studies with composite membrane by sol-gel method*, *J. Disp. Sci. Technol.* 31, 1708-1713.
19. Siddiqi F.A., Lakshminarayanaiah, N, Beg M.N. (1971) *Studies with inorganic precipitate membranes. IV. Evaluation of apparent fixed charge on membranes*, *J. Polym. Sci.* 9, 2869-2875.