



Research Paper

Synthesis and characterization of $\text{Co}_3(\text{PO}_4)_2$ and $\text{Ni}_3(\text{PO}_4)_2$ composite membranes based on PVC: A Comparative electrochemical studies through aqueous electrolyte solutions

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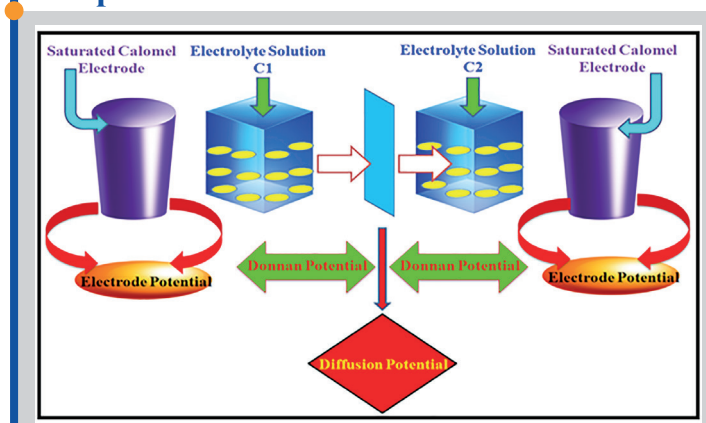
Highlights

- Mechanical strength of PVC based CP and NP composite ion exchange membranes.
- These membranes have lot of applications in different industrial field.
- These composite membranes have found to stable in acidic, basic and alkaline medium.
- The important parameters of membranes have been examined through the TMS theoretical equation.
- The order of membrane potential and surface charge density is $\text{KCl} < \text{NaCl} < \text{LiCl}$ and $\text{KCl} > \text{NaCl} > \text{LiCl}$.

Abstract

Mechanical stability is an important phenomenon that governs many application-based properties of membranes. The inorganic materials of a membrane have been synthesized by a qualitative sol-gel method of material synthesis. Membranes of cobalt (CP) and nickel (NP) composites were designed by mixing the polyvinyl chloride (PVC) with CP and NP materials separately into 1:1 ratio. These composite membranes were characterized by various sophisticated techniques like FTIR, XRD, TGA/DTA, SEM supported EDX, LCR studies, whereas antibacterial analysis and electrochemical studies have also been done by the TMS theoretical method. These prepared membranes have shown desired mechanical, chemical and thermal stabilities. The above characterization techniques indicate the functional groups, material nature, thermal stability, surface structure, porosity, elemental percentages, dielectric nature and ion transportation. The Teorell Meyer and Seviens (TMS) method was used to show the important membrane parameters like charge density, transport number, mobility ratio and charge effectiveness.

Graphical abstract



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1. Introduction

The organic-inorganic composite porous membranes and polymer-based inorganic precipitated composite porous membranes have many applications in the field of water separation and purification processes. Due to the strong mechanical stability in different environmental atmospheres, these membranes are utilized as a model to study the mechanism of transportation by using some strong electrolytes as well as heavy metal ions [1, 2]. For good mechanical stability, the material selection is one of the very important

steps in developing superior ion selective composite membranes. PVC is used as a binder due to its polar nature as well as economical point of views, which result in very good mechanical stability with CP and NP inorganic material. These types of membranes are prepared through mixing the organic polymer and inorganic ion exchange materials in 1:1 ratios. Therefore, the composite materials used to make the membranes revealed all properties of both the organic and inorganic components. The complete physicochemical

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characterizations are used to analyze the important parameters of membrane-like ion-exchange capacity, water content nature, structural and transport properties, thickness, thermal, mechanical and chemical stabilities [3-5].

The foremost importance of a membrane process mainly emphasizes the advantages as compared to the conventional processes, through which the precipitation, distillation, and stabilization may have studies and be accordingly modified. Nevertheless, the membrane processes remain somehow more expensive than the other conventional processes in terms of the investment and maintenance point of view, while it is acknowledged that membrane processes are more efficient, more economical, less destructive, have low electrical power consumption and are eco-friendly [6,7]. A neutral membrane can separate solutes according to the difference in their sizes or interaction of the ions with the membrane, while the charged membrane can easily transport the charged solutes according to their charges. The charged ion-exchange membrane (IEM) can easily separate the solution systems of unequal concentration due to containing fixed-charged groups, through which one dissolved ionic component from the aqueous, organic and electrolyte solution systems can easily permeate. Therefore, such types of IEM are indicated to show many applications for ion-selective electrodes and as chemical sensors, fuel cells, and electro-dialysis for brackish and seawater desalination [8-10].

The potential of membranes by using some strong electrolytes is an important and applicable observation which is used to analyze the transport phenomena of such pressure driven charged membranes like NF, MF and RO membranes. It has been theoretically recognized by the TMS equation, which is based on the Donnan equilibrium and Nernst-Planck consideration [11, 12]. To study the membrane process, it is necessary to know the transport phenomena of ions through the membrane when using some strong electrolyte solutions. Surface charge density is a prominent factor that has been a deciding factor for membrane applicability and performances and has been experimentally determined using observed and calculated potential values. The other important parameters of membranes such as transport number, mobility ratio and charge effectiveness have also been calculated by the TMS theoretical equation [13-15].

2. Theories

The theoretical approaches, which are normally used to calculate the fixed charge density of composite membranes, are TMS [16-18], Altug and Hair [19], Kobatake et al. [20, 21] and the most recent, that of Nagasawa et al. [22, 23]. In this paper, the TMS theory is used to calculate the fixed charge density of the composite membranes. This theory has several important points and postulates, which are illustrated as:

In the TMS approach, there must be an equilibrium development at all interfaces of the solution and membrane, which has proper connection with the Donnan equilibrium. The other important postulations are described as follows:

- The transfer of water from either side of the membrane may be ignored.
- The ionic movement and concentration of fixed charges are constant throughout the membrane matrix.
- The charge of the 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 the activities for salt concentration can only be approved through the Donnan potential, either by using Planck's or Henderson equation. The TMS graphical approach determines the fixed charge density and cation-to-anion mobility ratio [24].

3. Experimental protocols

3.1. Instrumentations

The SEM study was done by the equipment model LEO 435VP of SEM Tech Solutions by an accelerating voltage of 20 kV. In this microscope, the sample has been mounted on a copper stub and sputtered with gold to minimize the charging. The FTIR spectroscopic technique has been done by the "Interspec-2020" FTIR-spectrometer. The sample holder of this equipment is 200 mm wide, 290 mm deep and 255 mm high, the entrance and exit beam are sealed with a coated KBr window and there is a hinged cover used to seal it from the external environment. XRD analysis has been done by the "Miniflex-II X-Ray diffractometer" through CuK_α radiation. The TGA/DTA has been done by "Shimadzu DTG-60H" providing nitrogen atmosphere at a heating rate of $20\text{ }^\circ\text{C min}^{-1}$ in the temperature range of 25-800

$^\circ\text{C}$. The dielectric and impedance measurements have been performed in the 75 KHz-5MHz frequency ranges by using the "Agilent-4284A" LCR meter. The potentiometer "Electronic India-118" has been used to determine the potential of electrolyte solutions through the membrane system.

3.2. Materials and reagents

KCl, NaCl and LiCl electrolytes of unequal concentrations are required, 200 mesh size of PVC powder, 0.2M Na_3PO_4 , CoCl_2 and NiCl_2 solutions of 99.90% of purity were required to make the CP and NP precipitates. All the chemicals and reagents were from analytical grade and double distilled water was used to prepare the solutions [25].

3.3. Method

3.3.1. Sol gel method

By means of the sol-gel method of material preparation, the CP and NP inorganic materials have easily been synthesized by separately mixing the Na_3PO_4 solution with the CoCl_2 and NiCl_2 solutions. The mixing of metallic chloride with Na_3PO_4 solution gives a strong precipitation into the bottom of the beaker. Then a constant stirring with heating has been carried out until complete mixing. The heating process cannot be completed until the water of the precipitated solution has been vaporized and turned into gel form; while the pH of the solution must be kept constant. The gel was separated and washed nearly 4-5 times with deionized water to remove the free electrolytes and ions. Finally, both inorganic ion exchange materials have been placed into an oven for 2-3 h by maintaining 100°C temperature for the drying purpose [14].

3.4. Design the PVC based CP and NP composite membranes

To make both organic-inorganic composite membranes, the CP and NP materials are homogeneously mixed with PVC powder in the ratio of 1:1. The mixing of both materials with PVC binder has been done very cautiously through pestle and mortar until they are completely mixed with each other. Then the resulting composite materials are transferred separately into a special cast die of 2.45 cm diameter. Secondly the die must be placed into the advanced oven for 1-2 h by maintaining $100\text{ }^\circ\text{C}$ temperature to equilibrate the reaction mixture. Finally, it has been transferred into a pressure device of 'SL-89 UK' to apply 5 tons pressure, which results in good membrane fabrication. The 1:1 ratio of materials and binders indicated the very good morphological and stable mechanical nature of the membrane. If the ratio of both the members is exceeded or decreases, it never shows ideal stability and functions. At last, these stable membranes are subjected to inspect the microscopic and electrochemical examination to show the various important parameters of membrane technology [26, 27].

3.5. Potential observation of membranes

The potential of some strong electrolyte ions has been observed through the above-presented potentiometer. For this observation, the charged membrane was placed at the center of a special two chambered glass cell, which has the capacity of 35 ml each to be injected for the electrolyte solutions and the saturated calomel electrodes. It seems that the cations of electrolytes such as K^+ , Na^+ , and Li^+ are affecting the potentiometric response due to the nature of the charged membrane [24, 28]. The rough diagram of the electrochemical setup used for potential measurement is represented by Figure 1.

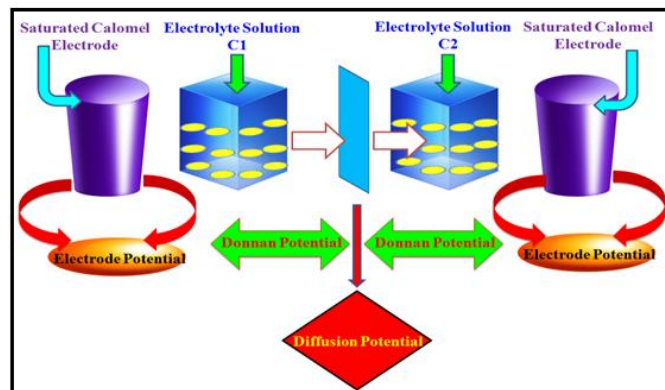


Fig. 1. Electrochemical setup used for ionic potential measurement.

3.6. Chemical stability

The chemical study of membranes has been carried out by means of the "ASTM D543-95" method, which analyzes the morphological changes and durability of the membrane which enlighten the change in color, surface, brightness, decomposition, splits, holes, deviation, etc. [29].

3.7. Ionic exchange capacity

The titration method was used to obtain the ion-exchange capacity of CP and NP ion exchange materials, in which the materials have initially been dipped in HNO₃ solution for 24 h and then washed more than two times by DMW. The materials have been titrated with 0.01M NaOH solution, which results in the release of H⁺ ions by Na⁺ ions in an ion-exchange reaction. Phenolphthalein is used as indicator for this titration. The equation used to determine the ion-exchange capacity of the composite materials of this work is as [30]:

$$IEC = \text{volume of consumed NaOH} \times \text{molarity of NaOH} / \text{weight of dried material} \quad (1)$$

3.8. Dielectric properties of the composite membrane

For the measurement of the dielectric and impedance properties, the composite samples have been made into circular pellets and coated with silver paste on adjacent faces, through which a parallel plate capacitor geometry is formed. Then, the values of Z , θ and C_p have been recorded. Using these recorded data, various dielectric parameters have been calculated very easily. The dielectric loss has been calculated by the following formula:

$$\tan\delta = 1/\tan\theta \quad (2)$$

where $\tan\delta$ is the dielectric loss tangent, which is proportional to the loss of energy from the applied field to the sample. This energy is dissipated as heat and therefore denoted as dielectric loss [31]. The real and imaginary part of impedance has been calculated by using the following formula:

$$Z' = Z\cos\theta \text{ and } Z'' = Z\sin\theta \quad (3)$$

3.9. Antibacterial activity of composite materials

The antibacterial activity of PVC based CP and NP composite materials has been tested in vitro condition by using the disc diffusion method against the two gram-positive and gram-negative bacteria *Staphylococcus aureus* (MSSA 22), *Bacillus subtilis*(ATCC 6051) and *Escherichia coli* (K12), *Streptococcus pneumonia* (ATCC, BAA-1705), respectively. The antifungal activity has also been done by *Candida albicans* (diploid fungus). The discs of 5 mm diameter have been prepared of Whatmann filter paper and sterilized by heating nearly 140 °C for at least 1–2 h and these discs were placed in a nutrient agar medium. The plates have been supplied in an incubator for 24 h at 37 °C and then measured afterwards. The screening was performed for 114.4 mg/ml concentration of the tested composite material and antibiotic disc, whereas the tetracycline (30 mg/disc, Hi-Media) was used to control it. The nutrient broth of logarithmiely serial took place by a two-fold diluted amount of tested composite material. It is controlled by inoculation within a range of 10⁷–10⁸ cfu/ml, however the highest dilution is required to capture the growth of bacteria. To spread the agar plates, each one has a 0.1 ml volume diameter zone and the number of colony forming units (cfu) has been counted after passing 24 h [32].

3.10. Measurement of water absorption

Water absorption or percentages of water into the membranes were calculated by the following equation.

$$\text{Water absorption (\%)} = \left[\frac{W_{wet} - W_{dry}}{W_{dry}} \right] \times 100 \quad (4)$$

where W_{wet} is the weight of swollen membrane that is obtained by soaking it into water for 5h, and W_{dry} is the weight of the dry membrane.

The porosity of the membrane can also be calculated very easily by the following equation.

$$\text{Porosity (\%)} = \left[\frac{W_{wet} - W_{dry}}{A \rho_w} \right] \times 100 \quad (5)$$

A is area of membrane, L is thickness of membrane, and ρ_w is density of water.

3.11. Measurements of diameter, thickness and swelling

With the help of the screw gauze, the diameter, thickness and swelling of membranes are calculated through making an average thickness of 4-5 replicates. The swelling can be measured by taking into account the difference between the average thickness of the membrane that has been equilibrated in 1 M NaCl solution and the dry membrane [24].

4. Results and discussion

SEM-EDX images are represented in Figure 2, which indicated the morphological structure of the porous composite membranes. It is illustrated that the mixing of materials has been done very uniformly and cautiously, through which the above figure illustrates that the examined membranes have a very porous surface and it helps the easy transportation of ions as well as charged species. EDX images show all the elemental percentages of used organic-inorganic composite materials. It is also indicated that there are no visible breakage or cracks on the surface of the membranes. Thus, it is concluded that the PVC has a very excellent binding nature with CP and NP inorganic materials [12].

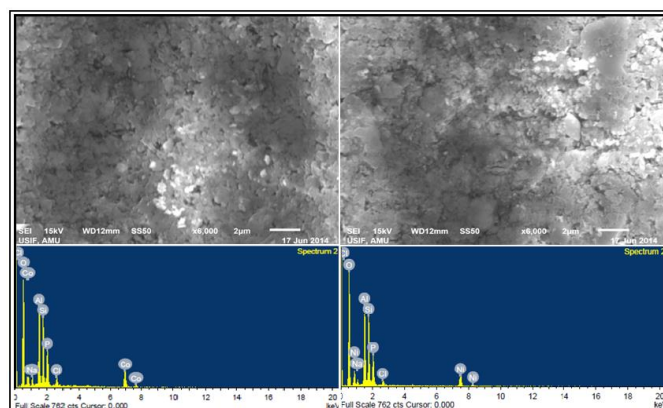
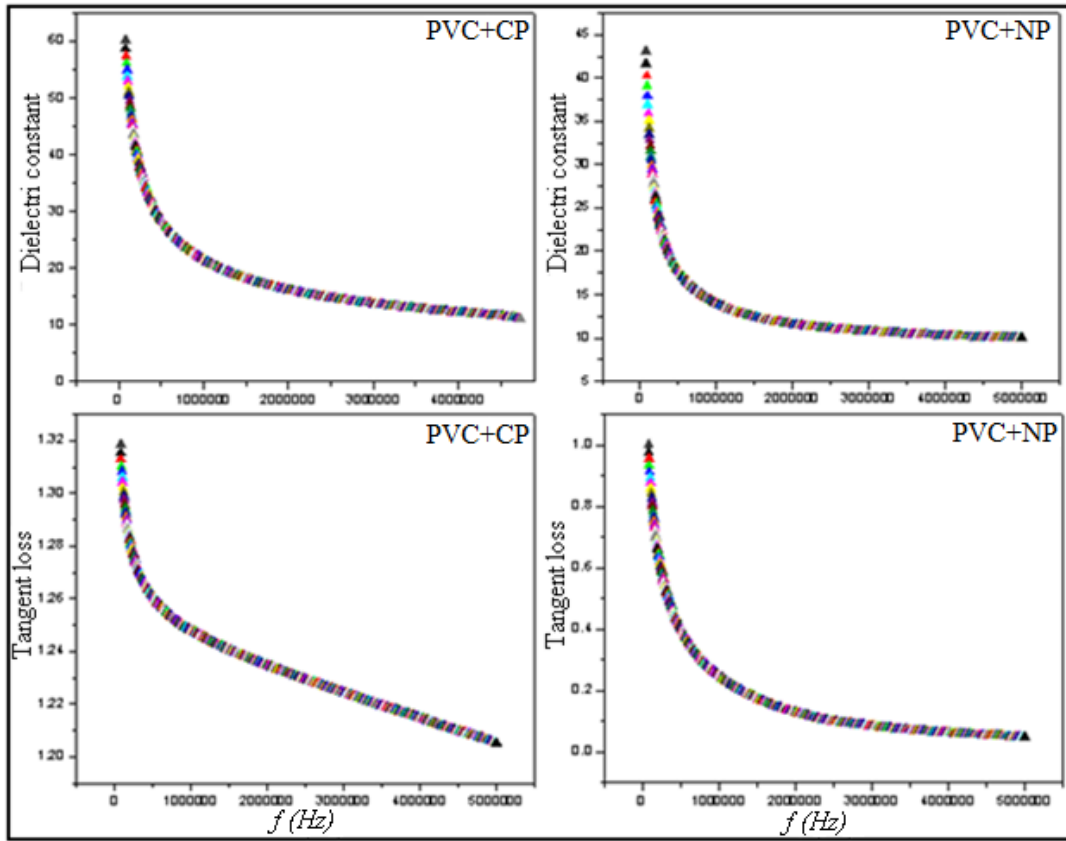


Fig. 2. SEM supported EDX images of PVC based CP and NP composite membrane.

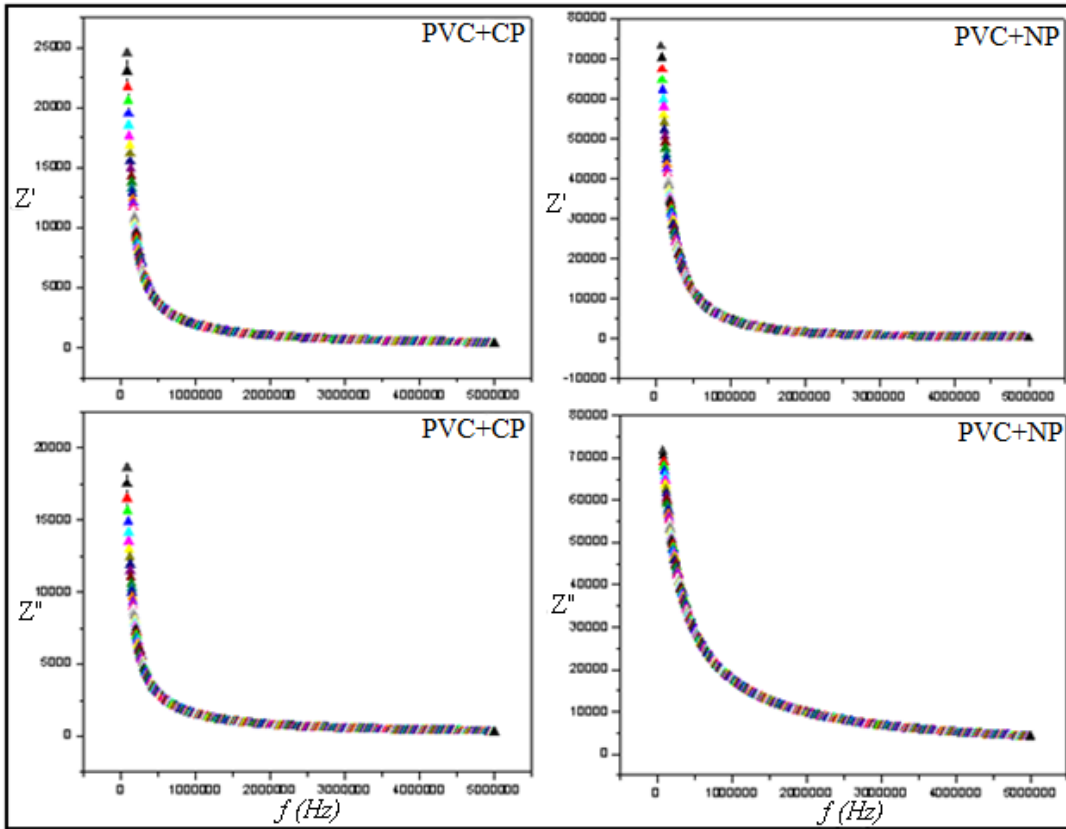
Figure 3 illustrated the FT-IR spectrum of only CP and PVC based CP, only NP and PVC based Ni-P materials, which indicated the presence of phosphate (PO₄³⁻) and hydroxyl (OH⁻) ions in the composite samples of the membranes. The band between 1000–1500 cm⁻¹ arises due to the P-O stretching vibrations, and the band at about 700-800 cm⁻¹ is assigned the characteristic vibrational mode of polymeric M_x(PO₄)_y, confirming their integrity in the final product. The band around 500 cm⁻¹ shows the presence of different groups at different ranges in the PVC based CP composite material. The broad peaks at about a range from 1500-1600 cm⁻¹ and about 3400 cm⁻¹ are assigned to -OH- bending and stretching vibrations, respectively [33]. The PVC based NP composite materials also show the band at around 1000–1500 cm⁻¹, which arises due to the stretching vibration of the phosphate group. The band at about 500-800 cm⁻¹ is assigned the presence of different groups at different ranges in the composite sample. The band at about 1500 and 3400-3500 cm⁻¹ shows the -OH- bending and stretching vibrations, respectively. This is while all the bands of the PVC based NP composite material show a somewhat broadened nature as compared to the PVC based CP material, which is due to the characteristic of the NP material [34].

The XRD images of the PVC based CP and NP composite materials are represented in Figure 4, which indicated that very intense peaks of both the composite materials are found at the range of 20-30° values. Many other small and less intense peaks are also found at the range of 20-70° values, respectively. The PVC based CP material shows highly intense peaks compared to the NP material, which explains that both composite materials show a very crystalline nature. The intense peaks indicate that the used compound corresponds to the plane at different ranges. Thus, the peak resemblance at 2θ value indicated that the PVC based CP and NP composite materials have a very strong crystalline nature [11, 15].

TGA characterization is represented by Figure 5, which showed the weight loss of PVC based CP and NP composite materials at different temperature ranges. It shows the weight loss of only CP and PVC based CP, only NP and PVC based NP composite materials. It is stated that only the CP material shows two times weight loss of 26.14% and 12.69%, consecutively



(a)



(b)

Fig. 6. (a) Dielectric (constant and loss) of PVC based CP and NP composite membrane, (b) dielectric nature (real and imaginary part) of PVC based CP and NP composite membrane.

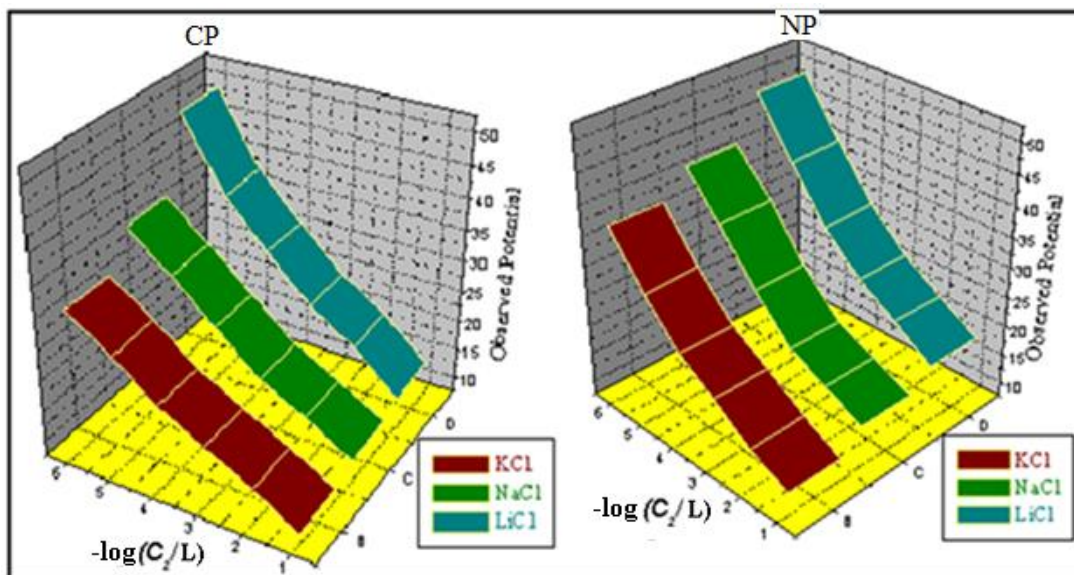


Fig. 7. The plots of observed membrane potentials against logarithm of concentration for PVC based CP and NP composite membrane.

Table 2

Thickness, porosity, swelling and diameter of PVC based CP and NP composite membranes.

Applied Pressure (Mpa)	Diameter (cm)		Thickness (cm)		Water content		Porosity		Swelling	
	CP	NP	CP	NP	CP	NP	CP	NP	CP	NP
100	2.45	2.45	0.072	0.064	0.030	0.036	0.014	0.018	No swelling	

The two gram-positive, two gram-negative bacteria and a diploid fungus were used to analyze the activity with the concentration range from 200 to 800 mg/ml. The tetracycline drug has been used as a standard for the comparison of bacterial results and examined data, which is also present in Table 1. Therefore, it is clear that the newly synthesized PVC based CP and NP materials have extraordinary inhibitory effects against the growth of bacterial strains. The data shows that the materials of the composite membrane illustrated evidences of activity against different types of used bacteria and fungus. Therefore, it is clear that the above composite material can be used as a potent antibacterial and antifungal agent.

It is analyzed that the membranes which were incubated in acidic, basic and alkaline medium to show the chemical stability and durability have lost their shape and structure after passing more time into the harsh pH solutions. Such morphological changes were seen after passing 12, 24, 36, 48 and lastly 60 h by putting the membrane into the solutions. As a result, the membrane is exhaustive in the above media after passing more than the examined time or it has also been affected by increasing the concentration of solutions. Thus, it is a very exclusive feature of the membrane that must have high chemical stability. The membranes diameter, porosity, water content percentage and swelling are clearly designated [24, 29] by Table 2.

PVC based CP and NP composite membranes have created ionic potentials due to the interphase present between two unequal concentrations of electrolyte solutions. The experimental ionic potential data shows the selectivity of some ions due to the charged membrane. The ions activity is more flourished in high concentration ranges, through which the membranes perform to behave as cations or anions selectively. In the above potential observations, anions did not broadly influence the potentiometer response. Figure 7 shows the positive potential order meaning that the potential has increased by decreasing the concentration of electrolyte solutions and this process follows the Nernst equation [36]. Thus, it is clear that both the membranes have perfectly cations selective nature, i.e. negatively charged.

In ordinary membranes, a very important electrochemical property is the difference in permeability of co-ions, counter ions and neutral molecules. However, charged membranes produce adsorption and transportation of ions, which depend on their nature and this shows less activity in the dilute region compared to the concentrated one. Charges are used to generate the potential that totally depends on the porosity of the membrane. If pores of the membranes are broad, many charges are required to generate good potential, whereas in a narrow one, a small quantity produces appropriate potential values. The cationic transportation has been completed after evaluating the thermodynamically effective fixed charge density. Through Figure 8, the

theoretical and observed potential has been designated by the dark and broken line, respectively and it is plotted as a function of $-\log C_2$.

The coinciding point on both the graphs gives the value of charge density in the membrane process that always shows $\bar{D} \leq 1$ and always follows the $KCl > NaCl > LiCl$ order. Charge density always depends on the initial stage of material preparation as well as their nature, while the above order shows the size factor of the used electrolyte compounds [37, 38].

The used setup of the electrochemical parameter has developed two Donnan potentials at the two solution and membrane interfaces, whereas the membrane arises the diffusion potential due to different concentrations of electrolyte solutions. Thus, it must have an equilibrium development at both the solution and membrane interfaces, which has a proper similarity with the Donnan equilibrium. So, as a result, it should be an internal salt diffusion potential that has been represented by the Henderson equation and leads to the Planck expression. The TMS method is more applicable in high concentrated solutions because the low concentration of electrolyte solution created high deviation between the observed and calculated potential values. The TMS theoretical equation for the membrane potential is described as follows [37].

$$\Delta \bar{\psi}_m = 59.2 \left(\log \frac{C_2 \sqrt{4C_1^2 + \bar{D}^2} + \bar{D}}{C_1 \sqrt{4C_2^2 + \bar{D}^2}} + \bar{U} \log \frac{\sqrt{4C_2^2 + \bar{D}^2} + \bar{D}\bar{U}}{\sqrt{4C_1^2 + \bar{D}^2} + \bar{D}\bar{U}} \right) \quad (6)$$

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

where \bar{u} and \bar{v} are the mobility of cations and anions, respectively, C_1 and C_2 are solution concentration of chamber 1 and 2, and \bar{D} is charge density of the membrane. Eq.6 can also be expressed by the sum of Donnan ($\Delta \Psi_{Don}$) and diffusion potential ($\Delta \Psi_{Diff}$).

$$\Delta \bar{\psi}_{m,e} = \Delta \bar{\psi}_{Don} + \Delta \bar{\psi}_{diff} \quad (7)$$

$$\Delta \bar{\psi}_{Don} = - \frac{RT}{V_k F} \ln \left(\frac{\gamma_{2\pm} C_2 \bar{C}_{1\pm}}{\gamma_{1\pm} C_1 \bar{C}_{2\pm}} \right) \quad (8)$$

F , R and T have their standard values, $\gamma_{1\pm}$ and $\gamma_{2\pm}$ are mean ionic activity coefficients and $C_{1\pm}$, $C_{2\pm}$ are the cation concentration on both chambers of the membrane.

$$\bar{C}_{\pm} = \sqrt{\left(\frac{V_x \bar{D}}{2V_k} \right)^2 + \left(\frac{\gamma_{\pm} C}{q} \right)^2} - \frac{V_x \bar{D}}{2V_k} \quad (9)$$

Here V_k and V_x are valance of cations and fixed-charge groups on the membrane, respectively and q is the charge effectiveness of the membrane.

$$q = \sqrt{\frac{\gamma_{\pm}}{K_{\pm}}} \quad (10)$$

Here K_{\pm} is the distribution coefficient expressed as:

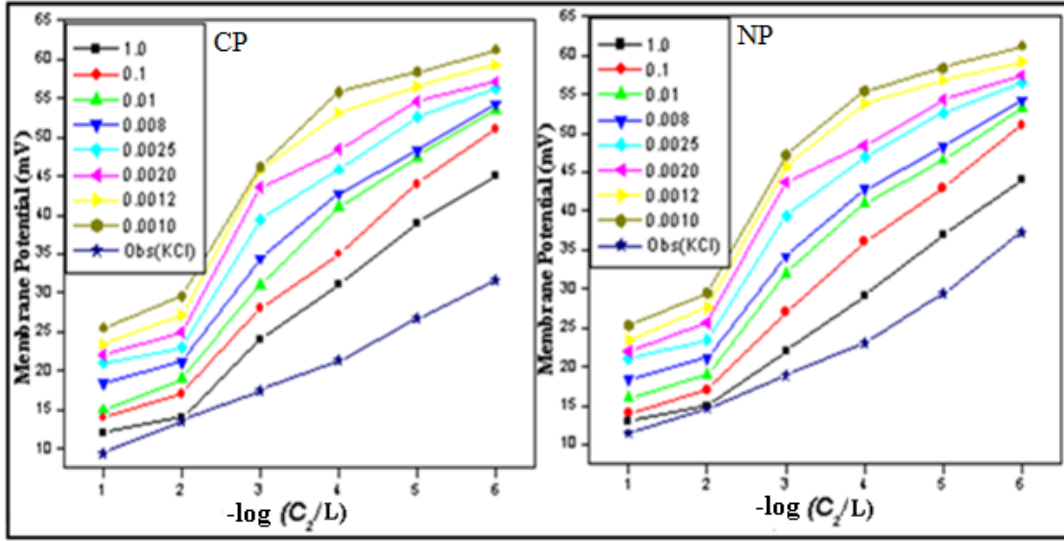


Fig. 8. The plots of membrane potential (theoretical and observed) against logarithm of concentration of KCl electrolyte solution for PVC based CP and NP composite membrane.

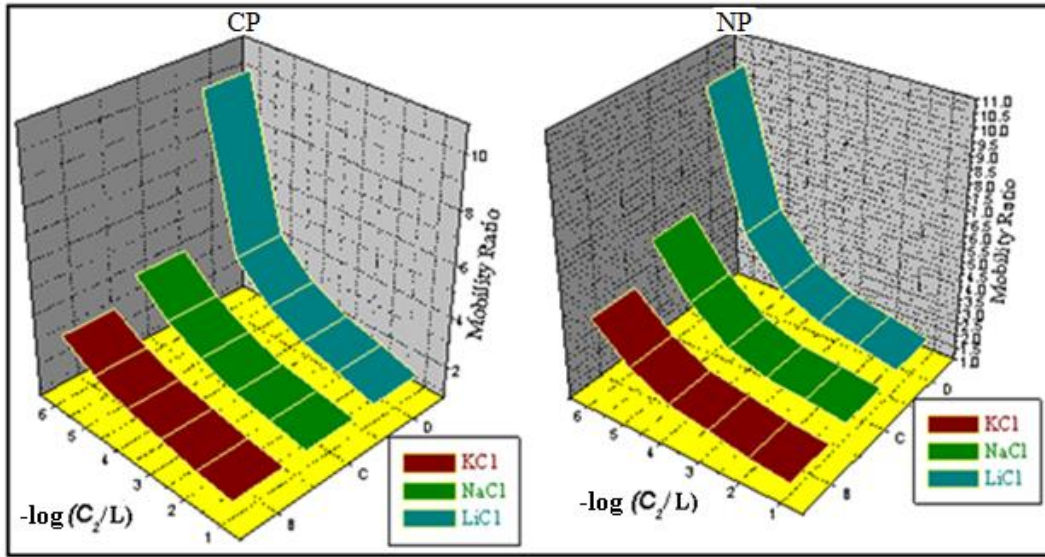


Fig. 9. The plots of transport number against logarithm of concentration of PVC based CP and NP composite membrane.

$$K_{\pm} = \frac{\bar{C}_i}{C_i}, \bar{C}_i = C_i - \bar{D} \quad (11)$$

C_i^- and C_i is the i th ion concentration in the membrane and external solutions. The diffusion potential is as follows:

$$\Delta\bar{\psi}_{diff} = -\frac{RT\bar{\omega}-1}{V_k F \bar{\omega}+1} \times \ln \left(\frac{(\bar{\omega}+1)\bar{C}_2 + (V_x/V_k)\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_x/V_k)\bar{D}} \right) \quad (12)$$

Here, $\bar{\omega}^- = u/v$ is the mobility ratio of the cation to anion through the membrane phase. Thus, the overall membrane potential can be obtained with the addition of $\Delta\bar{\psi}_{Don}$ and $\Delta\bar{\psi}_{diff}$.

$$\Delta\bar{\psi}_{m.e} = -\frac{RT}{V_k F} \ln \left(\frac{\gamma_{2\pm} C_2 \bar{C}_{1+}}{\gamma_{1\pm} C_1 \bar{C}_{2+}} \right) - \frac{RT\bar{\omega}-1}{V_k F \bar{\omega}+1} \times \ln \left(\frac{(\bar{\omega}+1)\bar{C}_2 + (V_x/V_k)\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_x/V_k)\bar{D}} \right) \quad (13)$$

$$\Delta\bar{\psi}_m = -\frac{RT}{F} (t_+ - t_-) \ln \frac{C_2}{C_1} \quad (14)$$

where

$$\frac{t_+}{t_-} = \frac{\bar{u}}{\bar{v}} \quad (15)$$

The values of t_+ and $\bar{\omega}^-$ can easily be obtained by Eq. (9) and (10). To show the applicability of the TMS equation, the diffusion and Donnan potential have been easily calculated through the observed potential values. The equation parameters such as $\gamma_{1\pm}$, $\gamma_{2\pm}$, \bar{C}_{1+} , \bar{C}_{2+} , $\bar{\omega}$, V_x , V_k , and γ_{\pm} have the usual charted values. It is clear that the higher transport number follows the high mobility ratio of ions that increases by decreasing the concentration of electrolyte solutions. Thus, the ionic mobility ratios and transport number through the above used composite membrane follow the LiCl>NaCl>KCl order which is represented by Figure 9 and Figure 10, respectively [28, 29]. It is also an important property that the distribution coefficient of ionic solutions decreases by increasing the concentration of solutions and the values of U^- are also represented by Figure 11. A very important parameter, charge density, has been calculated by equations (3) and (7) [39, 40] and is presented in Table 3.

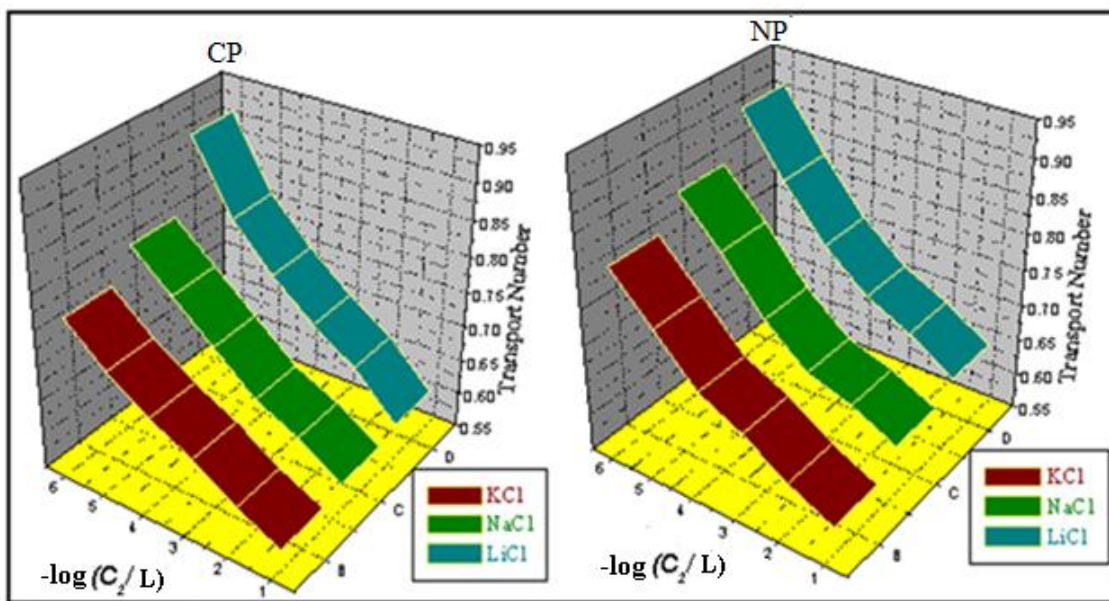


Fig. 10. The plots of mobility ratio against logarithm of concentration of PVC based CP and NP composite membrane.

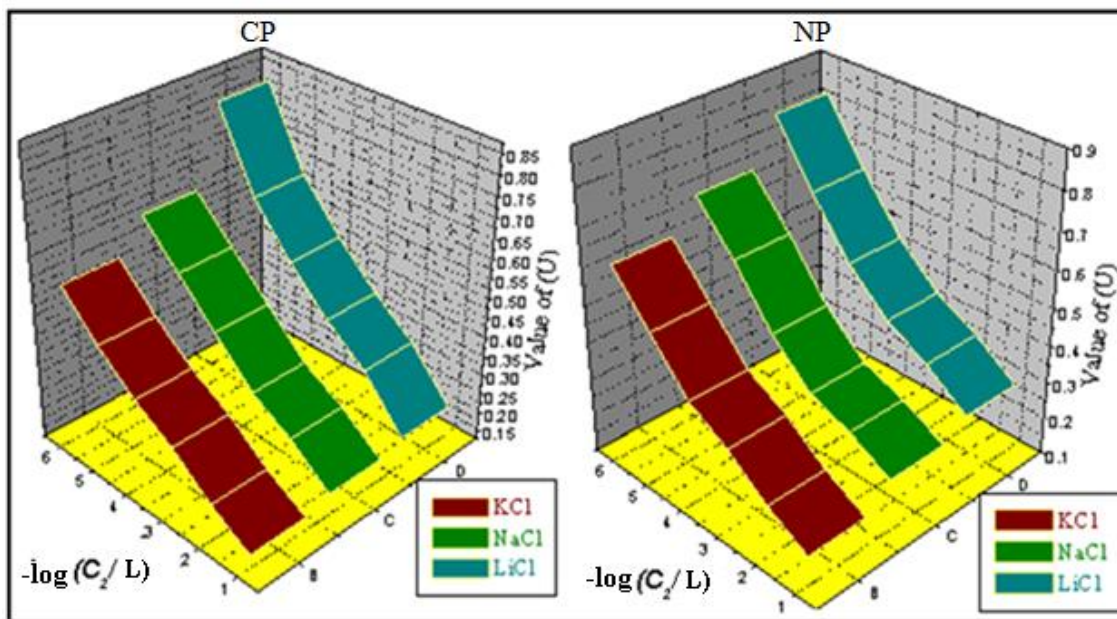


Fig. 11. The plots of (U) value against logarithm of concentration of PVC based CP and NP composite membrane.

Table 3

Observed membrane potential and charge densities across the PVC based CP and NP composite membranes in contact with various 1:1 electrolytes solutions at different concentrations.

Membrane Potential Conc.	KCl		NaCl		LiCl	
	CP	NP	CP	NP	CP	NP
1.0	9.4	11.4	11.4	14.5	12.5	17.3
0.1	13.6	14.6	15.6	17.5	18.8	21.5
0.01	17.5	18.9	19.4	20.3	23.4	25.5
0.001	21.3	23.0	25.4	26.6	30.2	31.4
0.0001	26.7	29.4	31.5	34.9	37.2	39.5
0.00001	31.6	37.3	37.0	41.4	48.5	48.6
Charge Densities(Dx10 ⁻³ eq/l)	1.99	2.10	1.74	1.83	1.58	1.70

5. Conclusions

The PVC-based CP and NP composite membranes have shown appropriate mechanical and thermal stability due to the good polymer binding with inorganic materials. The CP and NP have been successfully prepared by

the sol-gel method of material synthesis. The characterization techniques assigned good results that categorize the membranes to accordingly show the idealized functions and applications. The IEC confirmed that the composite materials of both the membranes have a cation selective nature. The morphology of the membrane such as thickness, diameter, porosity and water incorporation are clearly shown in the manuscript. The TMS theoretical approach and experimental results agree well by obtaining satisfied values of charge density. The potential of ions and charge density are the important parameters that govern the transport phenomena of the membrane, which is dependent on the feed composition and applied pressure. The univalent electrolyte potential for both the membranes shows the KCl<NaCl<LiCl order, while the charge density follows its reverse order. Therefore, this membrane model would be easily acceptable for commercial purposes and withstand upcoming research.

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Nomenclatures

AR	Analytical reagent
C_1, C_2	Concentrations of electrolyte solution on either side of the membrane (mol/L)
\bar{C}_{2+}	Cation concentration in membrane phase 2 (mol/L)
C_i	i^{th} ion concentration of external solution (mol/L)
\bar{C}_i	i^{th} ion concentration in membrane phase (mol/L)
\bar{D}	Charge density in membrane (Eq/L)
F	Faraday constant (C/mol)
MPa	Mega pascal
Q	Charge effectiveness of the membrane
R	Gas constant (J/K/mol)
IEM	Ion exchange membrane
SCE	Saturated calomel electrode
TMS	Teorell, Meyer and Sievers
t_+	Transport number of cation
t_-	Transport number of anion
\bar{u}	Mobility of cations in the membrane phase ($\text{m}^2/\text{v/s}$)
\bar{v}	Mobility of anions in the membrane phase ($\text{m}^2/\text{v/s}$)
V _k	Valency of cation
V _x	Valency of fixed-charge group
\bar{U}	$\bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v})$
EDX	X-ray dispersive analysis
SEM	Scanning electron microscopy
FTIR	Fourier transform infrared spectroscopy
XRD	X-ray diffraction
TGA	Thermo gravimetric analysis
PVC	Polyvinyl chloride
CP	Cobalt phosphate
NP	Nickel phosphate
NF	Nano filtration
MF	Micro filtration
RO	Reverse osmosis

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