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Elucidating the stability and electrochemical potential of PVP@ZP+Ze composite membrane with special reference to polymer and ion exchange materials concentration

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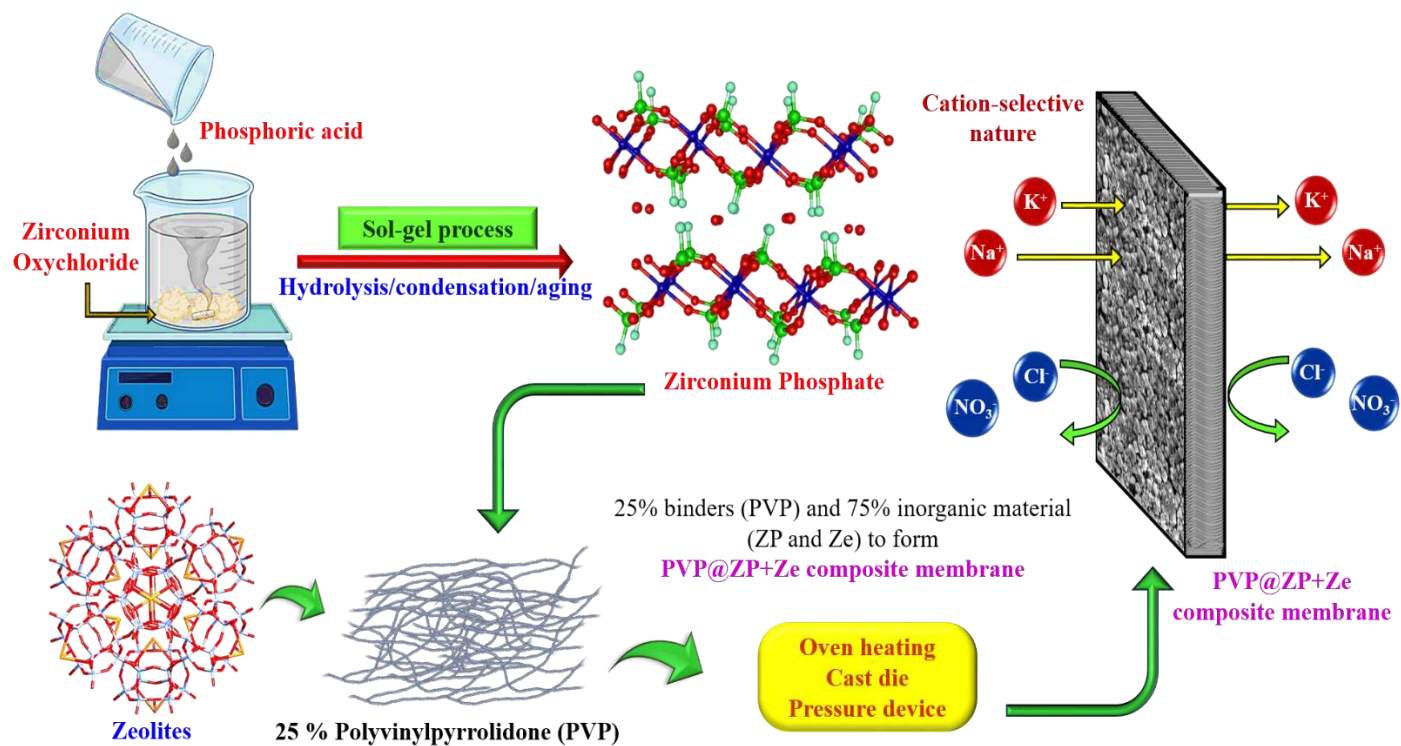
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Abstract

The chemical, mechanical, and electrochemical stabilities of composite membranes are pivotal to boost their filtering performance and application. This research is centered on the development of a composite membrane, from polyvinylpyrrolidone (25%) supported zirconium phosphate and zeolite (ZP+Ze). The membrane potential was evaluated using KCl, NaCl, NaNO₃, and KNO₃, electrolyte solutions to characterize the ion-transport phenomena over the charged membrane. The analysis showed that by transporting positive ions, the membrane manifests cation selectivity. For a given electrolyte, the sequence of potential values followed the trend $\text{KNO}_3 < \text{NaNO}_3 < \text{KCl} < \text{NaCl}$ reflecting the decreasing size of cations. Different factors of the developed membrane were assessed using the potential results, out of which the fixed charge density was found to be the significant factor affecting transport phenomena. The Teorell-Meyer-Sievers technique employed to measure the fixed charge density also considers ion adsorption, depending on the feed composition. The electrolytes' order of charge efficiency in the membrane was determined from the ionic radii of the counter-ions. Notably, the theoretical predictions and experimental findings regarding membrane potential were closely aligned. The membrane was further assessed using various analytical methods to determine its structural morphology and thermal stability. The engineered novel composite membrane could be a potential separation contrivance paving the way for the large-scale industrial application.

Keywords: Polyvinylpyrrolidone; Fixed charge density; Membrane potential; Composite membrane; Sol-gel process

Graphical Abstract



1. Introduction

The fast-paced industrialization and rising pollution pose serious threats to ecosystems and human populations, necessitating the treatment of industrial toxic effluents due to their harmful effects on human health before their release into the environment [1]. Scientists need materials that are environmentally safe, selective, highly repeatable, and effective in removing harmful metal ions in order to address these environmental issues [2,3]. When exposed to a variety of electrolytes with various ionic compositions, traditional filtration and separation frequently experience problems such chemical instability, limited mechanical strength, and poor selectivity. These limitations can be addressed using a membrane, which is a layer of selective permeability; that controls the passage of molecules, specific ions, and tiny particles, allowing certain substances to navigate while restricting others [4]. Membranes can have heterogeneous or homogeneous structures and a range of thicknesses. Particle transport can be either passive or active, and membranes can be charged or neutral.

Synthetic membranes are a category of membrane that are specifically designed and manufactured by human beings for industrial and laboratory applications. Hybrid membranes, a subset of synthetic membrane are designed and manufactured by combining different materials, typically an organic polymer with inorganic materials. The purpose of this combination is to maximize the advantages of each material, which can be challenging to accomplish with just one material. These advantages include improved mechanical strength, chemical stability, or certain permeability features. In addition, a hybrid membrane system improves process efficiency overall and lowers operating costs and environmental pollution [5,6]. A particular type of hybrid membrane, composite membranes, blends two or more materials, each contributing distinct functionalities that have been chosen to maximize the performance or characteristics of the membrane [7]. By balancing stability, selective permeability, and mechanical strength, composite membranes can be made to be very useful for intricate separation and filtration processes. They provide a special way to solve a variety of industrial, pharmaceutical, and environmental challenges, such as pollutant sensing, water and wastewater treatment, self-cleaning surfaces, food packaging, gas separation, and bioprocessing.

Recent studies have reported composite membranes using materials such as polyelectrolyte, hydrocarbon-based polymers, chitosan etc [8–10] which offer high chemical and thermal stability, good mechanical properties, and inherent selectivity for certain ions.

Nevertheless, these composite membranes frequently face constraints that impede their wider use. The low fixed charge concentrations of several of these membranes restrict their ability to transport ions selectively. Furthermore, when exposed to complicated electrolytic environments with a variety of ionic species, they might experience decreased selectivity or poor structural integrity. Scalability is also difficult since the ion-transport pathways have occasionally been poorly described, resulting in differences between theoretical expectations and actual performance. Due to its superior binding qualities and simplicity of manufacturing, polyvinylpyrrolidone (PVP), has become the most widely used binder (polymer) among the numerous polymers utilized today [11,12]. PVP is a versatile polymer known for its excellent film-forming properties, biocompatibility, and ability to enhance mechanical strength, making it an ideal matrix for supporting inorganic materials. Additionally, tetravalent metal phosphates are thought to be strong choices for having improved stability and selectivity when it comes to inorganic filler material. In membrane technology, the selection of materials is paramount, particularly the rationale behind choosing the appropriate fillers and polymers. Extensive experimentation with various ratios of polymer and inorganic compounds has demonstrated that certain composite formulations achieve enhanced chemical, mechanical, and thermal stability. These optimized compositions are essential for improving membrane performance, making them particularly suitable for practical applications across diverse fields [13].

The present study focuses on the synthesis, stability assessment, and electrochemical analyses of a novel composite ion exchange membrane produced from PVP-supported zirconium phosphate and zeolite (PVP@ZP+Ze). Zeolites are crystalline aluminosilicates characterized by their high surface area, tunable pore structures, and excellent ion-exchange capacities, which enhance ionic conductivity while providing thermal and chemical stability. Zirconium phosphate contributes exceptional ion-exchange properties and mechanical strength due to its layered structure, allowing efficient ion transport. By combining these materials, this study aims to develop a composite membrane that offers improved mechanical stability, ionic conductivity, and chemical resilience, addressing critical challenges in the field of ion-exchange membranes. The various polymer-to-filler ratios were developed and systematically evaluated to assess their influence on key performance characteristics of the composite membranes, including ion exchange capacity, porosity, and water absorption. This thorough examination aimed to identify the optimal ratio that enhances the stability and overall performance of the membrane, ensuring

improved ion transport and durability. Current research focuses on optimizing the pH-responsive membranes to enhance efficiency and versatility in separation technologies. The electrochemical properties such as mobility ratio, transport number, and membrane potential were determined for optimizing membrane design and enhancing separation processes. The fixed charge density of the membrane was calculated using the Teorell-Meyer-Sievers (TMS) model, a theoretical framework widely applied in electro membrane processes to compare membrane potential values. To further investigate the structural, thermal, and chemical stabilities of the membrane, various analytical methods were employed, providing a comprehensive understanding of its performance in ion transport applications. The experimental results were rigorously compared with theoretical predictions derived from the TMS model, enabling the validation of the model's applicability and the optimization of the membrane's design for enhanced efficiency in ion-selective applications. This thorough analysis underscores the significance of understanding charge dynamics and transport phenomena in the development of advanced membranes for water treatment and other separation technologies [14].

2. Experimental methodology

2.1. Chemicals and materials used

Phosphoric acid, zirconium oxychloride, and PVP were procured from Otto Kemi, Mumbai, India. Industrial-grade ZSM-5 MFI zeolite powder, synthesized via hydrothermal methods, was obtained from ACS Material. Stock electrolyte solutions, including potassium nitrate (KNO_3), sodium nitrate (NaNO_3), potassium chloride (KCl), and sodium chloride (NaCl), were purchased from E. Merck Limited, India. Analytical grade chemicals were used in this study ensuring the reliability and reproducibility of the experimental results.

2.2. Synthesis of zirconium phosphate

The sol-gel process, which involves hydrolysis, condensation and aging, was used to produce zirconium phosphate (ZP). Two solutions are prepared: 0.1 M zirconium oxychloride and 0.1 M phosphoric acid in distilled water. The mixing of two solutions was performed at room temperature by slowly adding the phosphoric acid solution to the zirconium oxychloride solution under continuous stirring. After stirring, the beaker was set aside for 24 hours to precipitate the

mixture. The resulting precipitate was filtered and then neutralized to reduce the pH to 7 by washing multiple times with distilled water to get the zirconium phosphate [15,16].

2.3. Fabrication of PVP@ZP+Ze composite membrane

Crushing and sieving PVP to a mesh size of 200 ensures a uniform particle size distribution, which is crucial for achieving consistent mechanical properties in the membrane. A finer particle size enhances the surface area for interactions between the binder and inorganic fillers, improving adhesion and structural integrity. The combination of PVP with zeolite and zirconium phosphate forms an inorganic-organic hybrid material that capitalizes on the beneficial properties of both components. The incorporation of zirconium phosphate and zeolite with PVP also enhances the electro transport capabilities of the composite membrane, making the choice and proportion of binder critical for optimal performance. A 25% PVP embedding was found to effectively balance mechanical stability and electrochemical properties. Concentrations above 25% can lead to reduced interconnectivity among the inorganic fillers, impairing ion transport, while concentrations below 5% may result in inadequate binding, compromising structural integrity. Thus, a 25% PVP proportion is essential for achieving a stable and high-performing membrane suitable for water treatment applications. After conducting a series of experiments to evaluate the chemical, mechanical, and thermal stability of various composite formulations, it was determined that a composition comprising 25% polymer and 75% inorganic material yields the most favorable results. This optimal ratio not only enhances the overall stability of the membranes but also ensures their suitability for practical applications in membrane technology. To achieve proper equilibration of the reaction mixture, the composite was oven-heated at 200 °C for one hour, then transferred to a cast die and subjected to 100 MPa of pressure using a pressure device (SL-89, UK) for membrane preparation. This process effectively ensured a strong morphology and mechanical stability in the final membrane, as the chosen ratio of binder to inorganic materials allows the PVP to provide flexibility and adhesion while the inorganic components (zirconium phosphate and zeolite) contribute enhanced mechanical strength and thermal stability. This balanced composition results in a durable membrane suitable for various applications [17].

2.4. Physicochemical characterisation of membrane

The membranes are comprehensively characterized to elucidate their intermolecular associations, gem structure, thermal stability, physicochemical properties, and morphology. This characterization is performed using different analytical techniques: Fourier transform infrared spectroscopy (FT-IR) assesses molecular interactions; X-ray diffraction (XRD) provides insights into crystallinity; energy dispersive X-ray analysis (EDAX) reveals elemental composition; zeta potential analysis evaluates surface charge properties; scanning electron microscopy (SEM) offers detailed morphological images; and thermogravimetric analysis (TG-DTA) examines thermal stability and decomposition behavior. Additionally, water uptake studies are conducted to assess the membrane's hydrophilicity and potential for water treatment applications. Together, these methods ensure a thorough understanding of the membranes' structural and functional characteristics.

2.4.1. Characterization of PVP@ZP+Ze

Several analytical techniques were used to elucidate the structural and compositional properties of PVP@ZP+Ze. Structural morphology of the membrane was analyzed using a JSM-6610, JEOL/EO Ltd scanning electron microscopy (SEM) instrument, whereas the surface components present in them were identified using energy dispersive X-Ray analysis (EDAX). A Philips' X'Pert Pro 3040/60, USA X-rays diffractometer that uses Cu-K α radiation was employed to study the structure, crystallinity, phase, and unit cell dimensions of synthesized membrane. Similarly, a Nicolet NEXUS 670 FT-IR spectrophotometer was used to perform fourier transform infrared (FTIR) spectroscopy for the determination of phase purity and functional groups in the membrane. Additionally, a Perkin-Elmer TGA-7, USA thermogravimetric analyzer performed the thermogravimetric analysis (TGA) and differential thermal analysis (DTA) which provided a brief idea about the thermal stability of the membrane.

2.4.2. Determination of zeta potential

Zeta potential is a key indicator of the surface charge at the solid-liquid interface, influencing the stability and interactions of particles, macromolecules, and materials in suspension. It is especially critical in colloidal dispersions, emulsions, and protein solutions, as it helps predict aggregation or dispersion tendencies. Higher absolute zeta potential values suggest stronger electrostatic repulsion between particles, which enhances stability and prevents coagulation.

Understanding zeta potential allows for the optimization of formulations, such as films and coatings, improving adhesion and performance in various applications, including drug delivery, water treatment, and material synthesis. Zeta potential was measured using a dynamic light scattering (DLS) instrument or zeta potential analyzer. In the analysis, a sample of the membrane or suspended particles is dispersed in a liquid medium, and an electric field is applied. Electrophoretic light scattering is used to quantify the particles' velocity as they approach the electrode with the opposite charge. This movement is converted into zeta potential values using the Smoluchowski equation, allowing researchers to quantify the surface charge of the particles or membrane, which correlates with its colloidal stability.

2.4.3. Swelling properties, water uptake percentage and porosity of PVP@ZP+Ze

The water percentage in the membrane voids/pores define its porosity. The film soaked in distilled water for 24h was gently dried with Whatman filter paper and then weighed. Reweighing and oven-drying the membrane at 80 °C ensured uniformity. Eq. (1) can be used to determine the porosity:

$$Porosity\ (\%) = \frac{W_{wet} - W_{dry}}{V_{dry} \times \rho_{water}} \quad (1)$$

Here ρ_{water} is the water density, W_{dry} and W_{wet} are the membrane's dry and wet masses, and V_{dry} is the dry membrane's volume. The average membrane thickness was measured using a micrometer screw gauge. The water take-up percentage was utilized to work out how much water was taken up by the pores or interstices of the film. The liquid weight absorbed by the membrane was the same as the increase in weight expressed by Eq. (2).

$$Water\ uptake\ (wt.\ \%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (2)$$

In order to prevent surface water inaccuracies, the measurements were made multiple times using various membrane samples. Swelling was also evaluated by comparing the thickness of the dry membrane with that of the membrane after being soaked in a 1 M NaCl solution for 24 hours, providing insight into its chemical stability. On the basis of this evaluation it can be evaluated the welling of the membrane. [18].

Following six hours of ambient temperature acclimatization for the composite membrane, its geometrical area was observed to change due to the effects of surface swelling. This swelling occurs as the membrane absorbs moisture or liquid from its surroundings, leading to an increase in its dimensions. To quantify this change and assess the extent of swelling, the swelling ratio (%) was determined using Equation (3). This equation provides a precise measure of the membrane's dimensional change by comparing its original dry state with its swollen state after equilibration, offering valuable insight into the membrane's physical properties and behavior under specific conditions.

$$Swelling\ (\%) = \frac{A_{wet} - A_{dry}}{A_{dry}} \times 100 \quad (3)$$

Where, the surface area (volume) of wet and dry membrane is showcased by A_{wet} and A_{dry} respectively.

2.4.4. Membrane potential measurement

A digital potentiometer (Electronics India model 118) was used to detect the membrane potential. The potentiometer has a measurement cell featuring two glass chambers with collars. The developed membrane was positioned vertically and firmly clamped at the centre of a measurement cell. To minimize the concentration polarization, two electrodes (SCE) were dipped into the collar chamber and the cell was filled with continuously stirred electrolyte solution. Magnetic stirrers were used in each chamber. The concentration of electrolytes ranged from 0.001 M to 1 M [19]. Four different electrolytes namely KNO_3 , KCl , $NaCl$, and $NaNO_3$ was used to evaluate the membrane potential of various membranes that were developed. The electrolyte concentrations in the two measuring cell compartments were kept at a tenfold difference. Fig. 1 shows the electrochemical setup needed to measure the membrane potential.

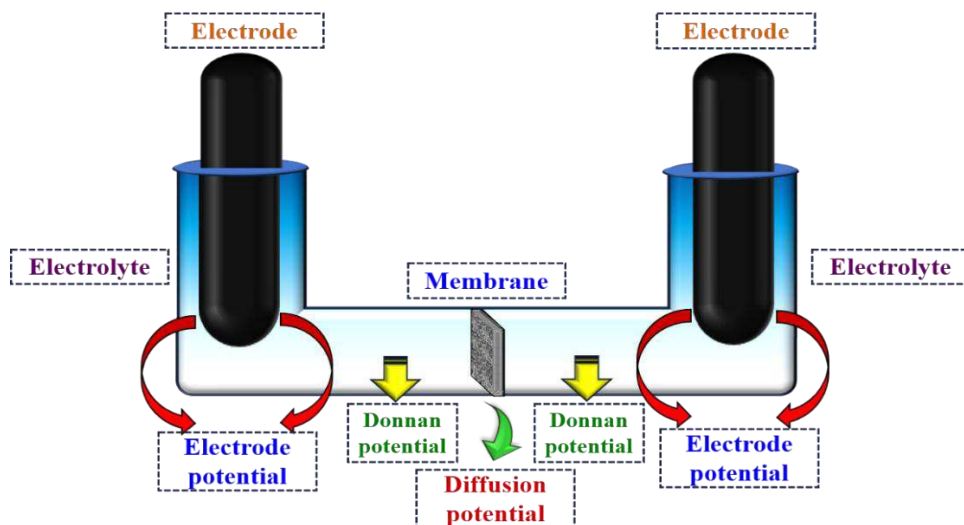


Fig. 1: Electrochemical configuration for assessing the membrane potential

3. Results and outcomes

3.1. Characterization of PVP@ZP+Ze

Fig. 2a and b clearly indicates the homogeneity of the membrane, with a consistent distribution of voids throughout the membrane surface. The SEM offers insights into the surface morphology of different materials synthesized under various applied pressures. It also verified that there are no visible breakages or cracks, in addition to establishing the material's homogenous and porous nature [20]. Particle aggregations, both dense and loose, make up the membrane surface. The SEM image further demonstrated that pores are smaller as applied pressure increases. Thus, the membrane designed at a pressure of 70 MPa has the biggest pore size, while the membrane fabricated under a pressure of 160 MPa exhibits smallest pore size. The remaining membranes exhibit a similar pattern. Ion transport and electrolyte diffusion are facilitated by surface pores on the membrane. While the nanopores in ion-exchange membranes play a crucial role by providing pathways for selective ion transport, enhancing ion diffusion and separation efficiency [11,21]. EDAX analysis (Fig. 2c) was used to perform the chemical analysis which showed that the developed membrane contains oxygen, sodium, aluminum, silicon, phosphorous and zirconium in it.

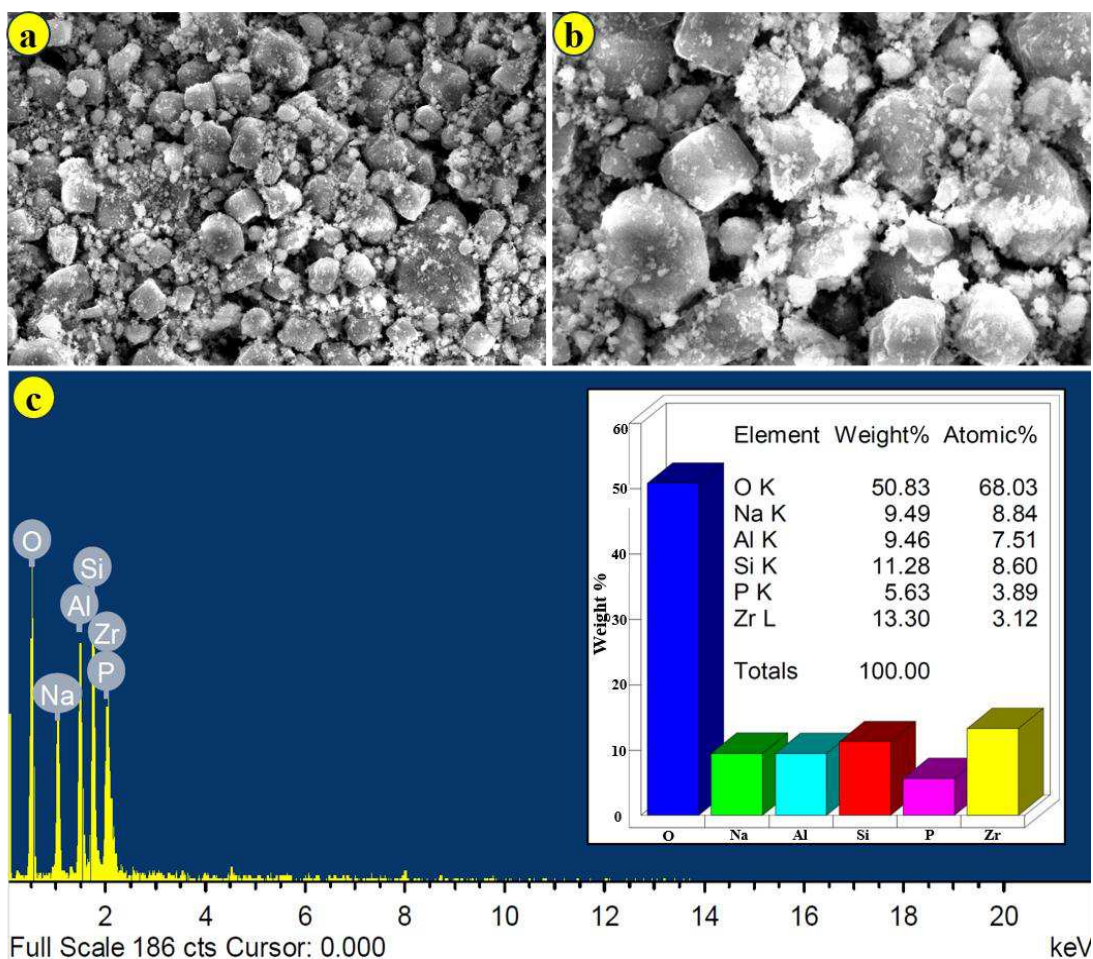


Fig. 2: SEM and EDX micrograph for the PVP@ZP+Ze composite membrane

A Rigaku miniflex x-ray diffractometer was employed to perform the XRD analysis to determine the synthesized membrane's crystalline structure. Fig.3 illustrates the XRD spectrum of inorganic material (Zirconium phosphate + Zeolite) and PVP@ZP+Ze composite membranes. The sharp and intense diffraction peak observed for the PVP@ZP+Ze membrane in the 15–25° two-theta (2θ) range strongly indicates the presence of a dominant crystalline phase within the membrane. The additional, smaller peaks observed in the 10–80° 2θ range suggest the existence of secondary crystalline regions or less ordered phases. This combination of prominent and subtle diffraction peaks highlights a heterogeneous crystalline structure, suggesting that the membrane's crystallinity likely plays a significant role in enhancing its mechanical strength, stability, and overall performance. The presence of these crystalline characteristics is crucial for the membrane's functionality in applications requiring high

structural integrity.

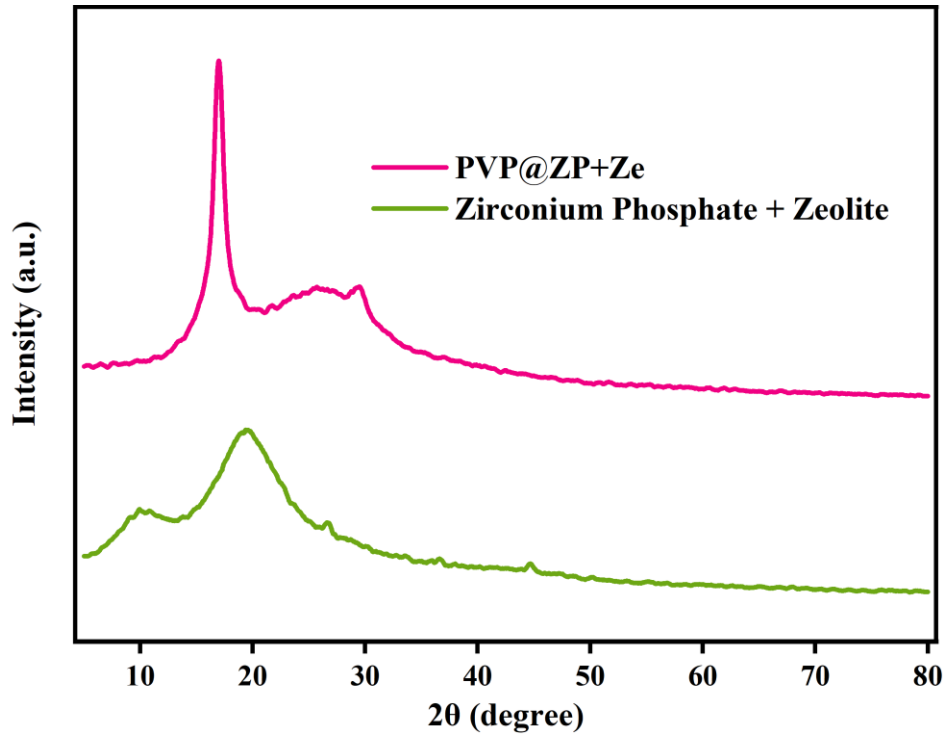


Fig. 3: XRD spectrum of the inorganic material and PVP@ZP+Ze composite membrane

FTIR spectroscopy was used to identify the functional groups that were present in the materials, with spectra recorded for the PVP@ZP+Ze composite, pure PVP, and pure zirconium phosphate (ZP) using KBr pellets, as illustrated in Fig. 4. A broad absorption band between 2900 cm^{-1} and 3436 cm^{-1} corresponds to O–H stretching vibrations, representing the presence of water molecules during crystallization, which is further supported by the broadening of these bands, confirming intermolecular hydrogen bonding. Peaks at approximately 1500 cm^{-1} and 1650 cm^{-1} are associated with the bending vibrations of absorbed water. Phosphate groups are identified by a sharp band at 1100 cm^{-1} , representing P–O stretching, and smaller bands between 800 cm^{-1} and 900 cm^{-1} , indicating P–O–P bending vibrations. For pure PVP, characteristic peaks appear at 1650 cm^{-1} , corresponding to C=O stretching of the amide group, and around 1290 cm^{-1} , indicating C–N stretching. Zeolite is characterized by absorption bands in the 1050 cm^{-1} to 1150 cm^{-1} region, assigned to Si–O–Si and Al–O–Si stretching vibrations. These peaks confirm the structural integrity and interaction of the PVP, zeolite, and zirconium phosphate in the composite membrane [22,23].

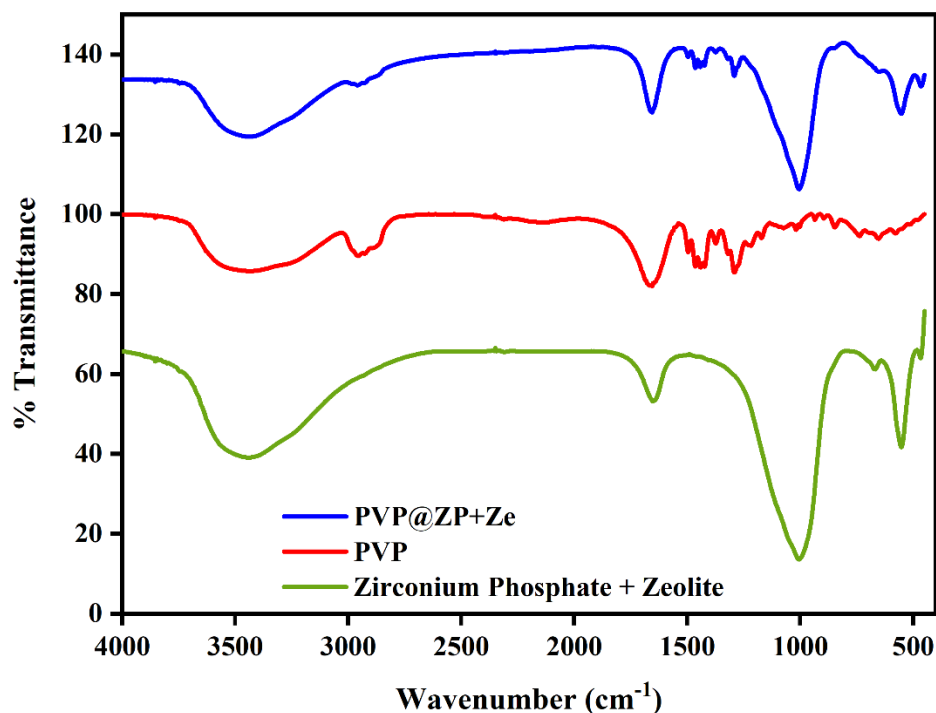


Fig. 4: FTIR spectrum of the inorganic materials and PVP@ZP+Ze composite membrane

As shown in figure 5, the developed membrane's thermal stability was studied using TGA-DTA analysis. Approximately 8% weight loss up to 200°C can be observed in TGA, which is ascribed to the elimination of water molecules on the surface. A gradual loss of mass observed between 200 and 500°C is ascribed to the removal of water molecules as a result of condensation of hydroxyl groups [24]. Additionally, the condensation of the organic counterpart, PVP, appears from 500°C forward. According to the results, the synthetic composite membrane has strong thermal stability, making it suitable for use in water separation processes. Plotting the difference in temperature (ΔT) against the reference temperature (T) is known as the DTA curve. The DTA curve, which is an endothermic descending plot, indicates that the sample temperature is lower in comparison to the reference materials. The endothermic peak, or peak at 100 °C on the DTA curve, is caused by the elimination of water molecules as a result of the reduction of atmospheric moisture-derived water content [25].

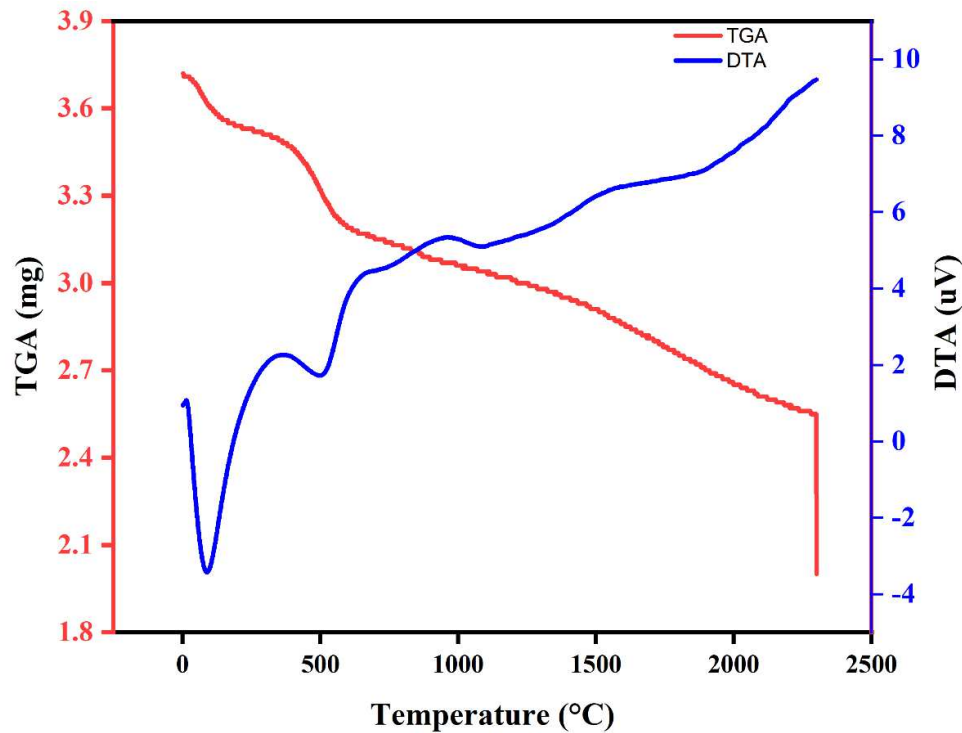


Fig. 5: TGA and DTA curves of the PVP@ZP+Ze composite membrane

3.2 Measurement of zeta potential, swelling properties, water uptake percentage and porosity of PVP@ZP+Ze

Nanocomposite materials having zeta potentials of more than +30 mV or less than -30 mV are regarded as strongly cationic, whereas nanocomposite materials with zeta potentials between -10 and +10 mV are regarded as about neutral. Fig. 6 shows the zeta potential value of PVP@ZP+Ze composite material which demonstrates the apparent zeta potential peaks around 0 mV for all recorded measurements, with total counts reaching approximately 3,000,000 for the most prominent peak (Record 54). This suggests that the membrane exhibits a near-neutral surface charge, which is consistent across multiple tests (Records 51, 52, 53, and 54), with minor variations in the distribution width and peak height. The slight shifts in zeta potential between -50 mV and +50 mV suggest a stable membrane surface charge, which can be attributed to the uniform distribution of charge within the composite structure. This near-neutral zeta potential is beneficial for minimizing fouling in water treatment applications, as it reduces the likelihood of strong electrostatic interactions with contaminants.

Water absorption was defined as the proportion of the soaked membrane's weight increase over its initial weight. It was found that the surrounding vapor pressure had an impact on the

membrane's ability to absorb water. In this experiment, the water absorption characteristics and low order water uptake% of all the membranes are similar. This demonstrates that the membrane's ion exchange sites are primarily in charge of allowing diffusion to occur, confirming the extremely low levels of interstices. Water absorption and swelling should be kept to a minimum to ensure that the membrane has sufficient mechanical properties. If they are, the membrane may become more fragile and alter in size. In severe situations, the membrane may even begin to dissolve at high temperatures [26].

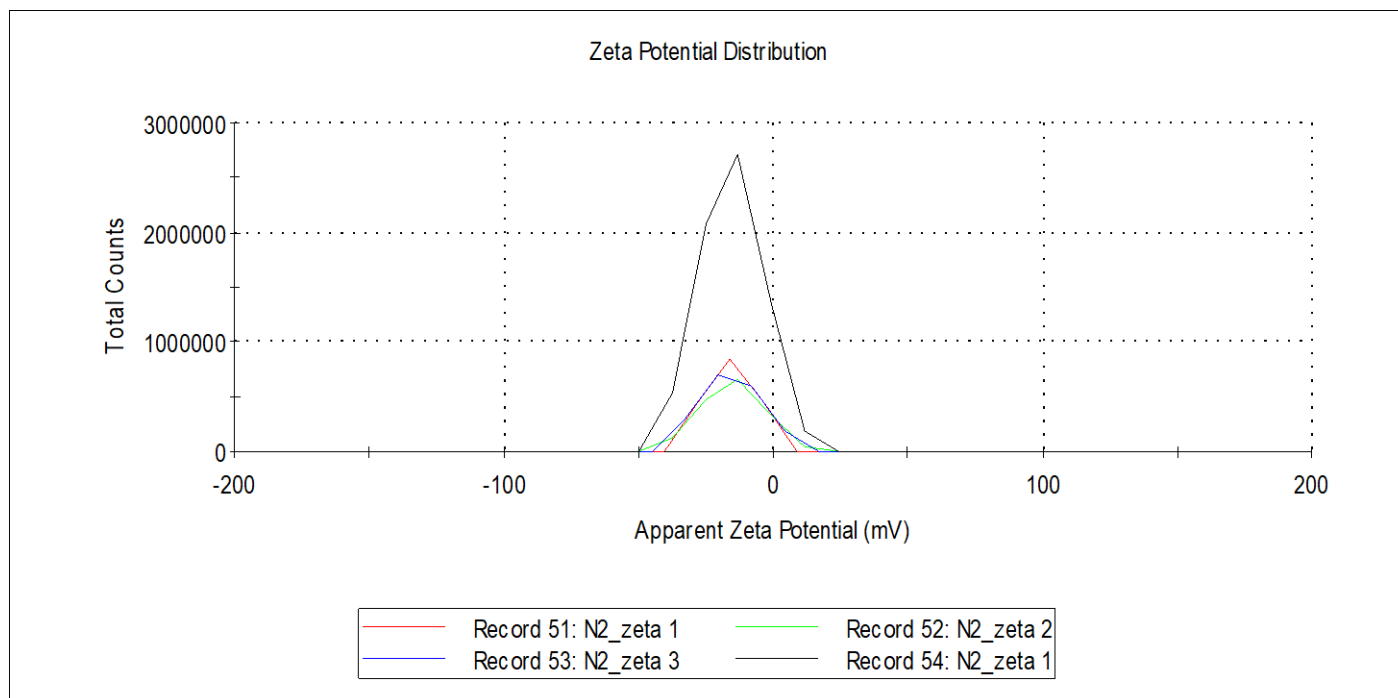


Fig. 6: Values of zeta potential for the PVP@ZP+Ze composite membrane

One important factor in assessing the mechanical stability of membranes is swelling. The swelling ratio was defined as the percentage of the original membrane's area gained by the soaked membrane. Because of the force that results from the polymer's elastic nature and internal osmotic pressure, the ion exchange membrane may swell. Since all of the membranes have been shown to have very little swelling, ions are transported through pores or ion exchange sites rather than interstices [27]. Table 1 summarizes the values in numbers for water uptake percentage, swelling characteristics, and membrane thickness, at various applied pressures.

Table 1. Swelling %, water uptake %, and thickness of PVP@ZP+Ze

Membrane thickness (cm)	Water uptake % of membrane	Applied pressure (MPa) of membrane	Swelling % of membrane
0.089	0.075	70	No swelling

3.3 Determination of membrane potential

Determining the electrochemical properties of the membrane is essential for predicting its performance in practical applications. When a membrane interacts with an electrolyte at varying concentrations, the variation in ion flow causes a potential difference to form across the membrane. The generated electrical potential accelerates the slow-moving ions and impedes the fast-moving ions to preserve the electron neutrality condition. Ion dispersion is driven by both diffusion and electro migration processes. As a result, an electrical double layer formed, giving the other solutions a charged surface and an excess of counter ions that balanced them properly. TMS Theory states that an equilibrium process that is very similar to Donnan equilibrium arises at each solution-membrane contact [14,28]. Here, through the application of theory, the theoretical membrane potential values have been determined. This theory is also employed to examine the transport characteristics and fixed charge density of the membrane. The following assumptions support the TMS theory:

- Equilibrium must be reached at the interface between feed solution, and membrane and it should possess similarity with Donnan equilibrium.
- Both the solution and membrane phases should possess same activity coefficient for the salt, while the ion's activity coefficient is considered as unity.
- The mobilities of cations and anions, along with fixed charge concentrations and other properties, are assumed to remain constant within the membrane phase and are unaffected by the electrolyte concentration.
- There is minimal influence of the water transference and diffusion boundary layer from both sides at the membrane solution interface.
- Throughout the membrane matrix, the fixed charge groups are evenly and consistently distributed.

Membrane potential refers to the voltage contrast between the exterior and interior of the cell membrane. Ions moving across the membrane cause this change in electrical potential or voltage difference. Membranes often react to various gradients present across their two sides. Assuming the angle is fixation, the dialysis process results. When the electrolyte solutions of the same salt at different concentrations are separated by the charged membrane in this dialysis system, a contact area called 'junctions for the same electrolyte' forms across the membranes. The membrane secures an electrical charge because of inconsistent electrolyte fixation. Adsorption of charged species or dissociation of functional groups from the solution onto the walls of pores are two potential sources of this electric charge [29]. These outcomes in the advancement of electrical distinction across the membrane are expected because of the inconsistent progression of particles. As a result, by measuring membrane potential across a charged membrane, its transport phenomena can be defined. The membrane potential can be viewed as the combined contributions from two Donnan possibilities at the right and left surfaces of the layer along with the dissemination expected across the film, which is based on Donnan equilibrium theory and the Nernst-Planck equation [30].

Depending on their nature charged membranes produce absorption or adsorption properties and indicate less activity in diluted solutions over the more concentrated region, the important electrochemical property of membranes generally shows differences in the permeability of neutral molecules, counter-ions, as well as co-ions. The potential that charges can produce is dependent on the porosity of the membrane. Broad and narrow pores require a large and small number of charges, respectively to produce the ideal potential of ions. It is not possible to complete the transference of both cations and anions by calculating the membrane's thermodynamically effective fixed charge density [31].

The value of membrane potential using various concentrations of NaCl, KNO₃, KCl, and NaNO₃ solutions across the PVP@ZP+Ze (observed at 25°C) was plotted against $-\log C_2$ as given in Table 2 as well as represented in Fig. 7a. As the electrolyte concentration decreased, the membrane potential values increased, showing a positive correlation. This confirmed that the composite membrane exhibits cation selectivity, due to the change in double layer structure at the interface between membrane and solution [37]. These differences in potential depend on the concentration, electrolyte nature, cation charge, or valence of the ions. The dispersion potential emerges from the distinction in movement rates

of anions and cations. The transport is influenced by the varying mobilities of the electrolyte's ions. In order to maintain electro neutrality, the fast-moving ions diffuse quickly from the side of high-concentration to that of low-concentration through junctions. On the higher concentration side, the less mobile ions remain behind. The charge separation would result in an electrical potential, and this type of ion distribution is solely caused by electro migration and diffusion [38][32]. These differences in potential depend on the concentration, electrolyte nature, cation charge or the valence of ions. The dispersion potential emerges due to the distinction in anion and cation mobilities. The transport is influenced by the varying mobilities of the electrolyte's ions[33].

Table 2. Membrane potential observed across PVP@ZP+Ze with different 1:1 electrolyte solution at varying concentrations

Concentration of electrolyte $C_2/C_1(\text{molL}^{-1})$	Membrane potential (mV)			
	NaCl	KCl	KNO ₃	NaNO ₃
1/0.1	13.3	9.9	2.6	4.4
0.1/0.01	16.9	14.8	10.7	11.9
0.05/0.005	22.8	18.7	15.9	17.7
0.02/0.002	26.7	24.2	17.1	20.2
0.01/0.001	32.8	29.2	22.5	28.8

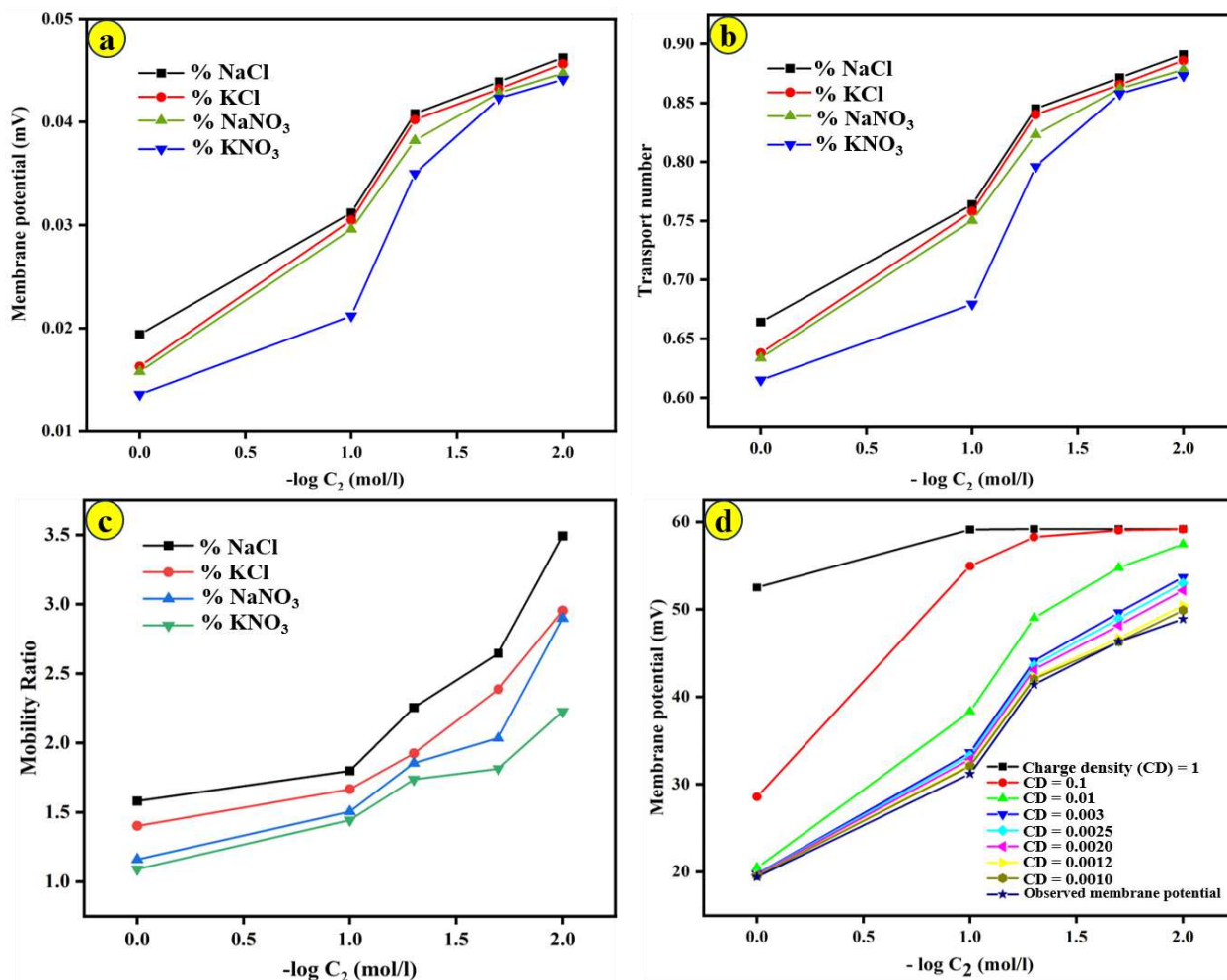


Fig. 7: (a) Membrane potential measurement plots of different 1:1 electrolyte in contact to the PVP@ZP+Ze, (b) Transport number plot for various electrolytes of the PVP@ZP+Ze, (c) Mobility ratio plot for the PVP@ZP+Ze, (d) $-\log C_2$ (mol/l) vs membrane potential (mV) plot at various electrolyte concentrations for PVP@ZP+Ze by TMS method. The theoretical membrane potential values for various densities, starting with $D < 1$, are represented by each smooth curve.

3.4 Measurement of mobility ratio and transport number

For a given electrolyte, the sequence of potential values is $\text{KNO}_3 < \text{NaNO}_3 < \text{KCl} < \text{NaCl}$ reflecting the decreasing size of cations. The percentage of the total current that counter-ions conduct across the membrane is known as the transport number. The transport number of a membrane can be determined from its potential value when it is separated by different electrolytes. The transport number of the membrane is influenced by variables such as pore size, thickness,

surface charge, characteristic electrical charge, and the ion's electrical mobility. Higher mobility corresponds to a higher transport number[34]. The effective charge on the membrane has an effect on the transport number as well. Equation (9), when applied, yields the expression to calculate the transport number and, subsequently, the mobility ratio. Both the parameters rise and follow the pattern $\text{KNO}_3 < \text{NaNO}_3 < \text{KCl} < \text{NaCl}$ with decrease in electrolyte concentration, as demonstrated in plots provided by Fig. 7b and Fig. 7c, respectively. Hence, the transport number and mobility ratio are dependent on concentration of electrolyte. This tendency is maintained since lithium ions have a smaller size in comparison to potassium and smaller ions are more mobile than larger ions. Smaller particles also account for higher transport numbers and mobility ratios. Additionally, a high mobility ratio value is obtained, which is explained by the electrolyte's increased transportation number of free cations. The membrane potential measurements are employed to compute the membrane's fixed charge density, taking into account that for every 1:1 electrolyte system, $D \leq 1$. Figure 7d shows the membrane potential values that were determined both theoretically and experimentally plotted against the inverse logarithm of electrolyte concentration ($-\log C_2$). The fixed charge density values for different electrolyte systems, were assessed using the above curve's intersection point. Charge density is dependent on the characteristics of the early stages of material synthesis and can also suggest the above relationship because of the size factor of the electrolyte solutions that are utilized [35].

According to the electrochemical setup used to measure the ionic potential, two Donnan potentials occur at the solution-membrane interfaces, and the incubated membrane develops a diffusion potential as a result of the electrolyte solutions' dissimilar concentrations. Thus, it is suggested that equilibrium development exhibiting appropriate resemblance to Donnan equilibrium must occur at both the membrane and solution interfaces. An internal salt diffusion potential should be discovered, which the Henderson equation represents and which also leads to the Planck expression. The TMS theoretical approach is more useful in the range of highly concentrated solutions as there are large differences between the measured and estimated potential values of the utilized electrolyte ions at low concentrations. The theoretical membrane potential (TMS) is defined by Eq. (4) as follows [36].

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

$$\text{Here, we put, } \bar{U} = \frac{(\bar{u} - \bar{v})}{(\bar{u} + \bar{v})}$$

Where C_2 and C_1 represents concentration of solutions in chambers 2 and 1, D^- is the charge density of the membrane, and $\bar{v}$ and $\bar{u}$, respectively, are the mobility of anions and cations. The sum of the diffusion potential ($\Delta\Psi_{\text{Diff}}$) and Donnan ($\Delta\Psi_{\text{Don}}$) can also be used to express Eq. (5) and Eq. (6) as:

$$\Delta\bar{\Psi}_{m,e} = \Delta\Psi_{\text{Don}} + \Delta\bar{\Psi}_{\text{diff}} \quad (5)$$

$$\Delta\bar{\Psi}_{\text{Don}} = -\frac{RT}{V_k F} \ln \left[\frac{\gamma_{2\pm} C_2 \bar{C}_{1+}}{\gamma_{1\pm} C_1 \bar{C}_{2+}} \right] \quad (6)$$

F , R and T have their standard values, C_{1+} , C_{2+} are the cation concentration and $\gamma_{1\pm}$, $\gamma_{2\pm}$ are mean ionic activity coefficients on both the chamber of membrane following Eq. (7).

$$\bar{C}_+ = \sqrt{\left[\frac{V_x \bar{D}}{2V_k} \right]^2 \left[\frac{\gamma_{\pm} C}{q} \right]^2} - \frac{V_x \bar{D}}{2V_k} \quad (7)$$

Here, q is the membrane's charge effectiveness, while V_x and V_k are the valency of the fixed-charge groups and cations on the membrane, respectively. The equation 8, in which $K_{\pm}$ represents the charge distribution coefficient, can be used to determine the charge effectiveness (q). In contrast to K values for different monovalent electrolyte concentrations, the charge efficiency (q) values exhibit a consistent pattern; that is, they rise as the electrolyte concentration decreases. The concentration of counter ions and the concentration of fixed charged groups in the membrane phase change with decreasing and increasing external electrolyte concentrations. Because of the binding attraction between the polymer's counter-ions, and fixed charge groups several counters reach into the membrane phase as a result, which lowers the charge effectiveness value.

$$q = \sqrt{\frac{\gamma_{\pm}}{K_{\pm}}} \quad (8)$$

Here $K_{\pm}$ is the distribution coefficient expressed as shown in Eq. 9:

$$K_{\pm} = \frac{\bar{C}_i}{C_i}, \bar{C}_i = C_i - \bar{D} \quad (9)$$

C_i and $\bar{C}_i$ is the i^{th} ion concentration in external and membrane solutions. The diffusion potential (Eq. 10) is as follows:

$$\Delta\bar{\psi}_{diff} = -\frac{RT}{V_k F} \frac{\bar{\omega}-1}{\bar{\omega}+1} \times \ln \left(\frac{(\bar{\omega}+1)\bar{C}_2 + (V_X/V_k)\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_X/V_k)\bar{D}} \right) \quad (10)$$

Here $\bar{\omega} = u/v$ is the mobility ratio of cation to anion through membrane phase. So, by the addition of $\Delta\Psi_{Don}$ and $\Delta\Psi_{diff}$, the total membrane potential can be obtained as shown in Eq. 11:

$$\Delta\bar{\psi}_{m,e} = -\frac{RT}{V_k F} \ln \left(\frac{\gamma_{2\pm} C_2 \bar{C}_{1+}}{\gamma_{1\pm} C_1 \bar{C}_{2+}} \right) - \frac{RT\bar{\omega}-1}{V_k F \bar{\omega}+1} \times \ln \left(\frac{(\bar{\omega}+1)\bar{C}_2 + (V_X/V_k)\bar{D}}{(\bar{\omega}+1)\bar{C}_1 + (V_X/V_k)\bar{D}} \right) \quad (11)$$

Equation 12 is used to calculate the membrane transport properties in various feed solutions.

$$\Delta\bar{\psi}_m = -\frac{RT}{F} (t_+ - t_-) \ln \frac{C_2}{C_1} \quad (12)$$

The transport number (t_+) can be determined using Eq. (13):

$$t_+/t_- = \bar{u}/\bar{v} \quad (13)$$

In addition, the Donnan and diffusion potentials can be calculated from the measured potential values to show the applicability of the TMS equation. The symbols of all the equations, like, $\gamma_{1\pm}$, $\gamma_{2\pm}$, $\bar{C}_{1+}$, $\bar{C}_{2+}$, $\bar{\omega}$, V_X , V_k , and $\gamma_{\pm}$ have the usual charted values. In TMS theory, the mobility ratio refers to the relative speed of cations and anions moving through the membrane, which influences the diffusion potential. A higher mobility ratio means cations move faster than anions, contributing more to the membrane potential. The transport number, on the other hand, represents the fraction of total ion transport carried by a specific ion. It reflects the ion's role in the overall ionic current, with higher transport numbers indicating greater ion contribution to the membrane's electrical properties. Together, these factors help explain ion movement and membrane potential in charged systems. It is clear from the analysis that the higher transport number consistently corresponds to a high ion mobility ratio, which increases with decrease in the solution concentration, and these values are represented by Table 3. As a result, we can learn more about the mobility ratio from the transport number [37]. The membrane's electrical charge is another factor influencing its transport property. In charged membranes, the impact of the Donnan effect on co-ions can be disregarded because of the

differing mobilities of co-ions and counter-ions; instead, the membrane potential is mostly determined by the diffusion potential.

Table 3. The mobility ratios and transport numbers of different concentrations of electrolyte solutions

Electrolyte Concentration (log C ₂)	KNO ₃		KCl		NaCl		NaNO ₃	
	$\bar{\omega}$	t_+	$\bar{\omega}$	t_+	$\bar{\omega}$	t_+	$\bar{\omega}$	t_+
1.0	1.0899	0.5215	1.40096	0.5835	1.5806	0.6125	1.1598	0.537
0.1	1.4425	0.590	1.666	0.625	1.798	0.6425	1.5037	0.6005
0.05	1.7369	0.644	1.9239	0.658	2.254	0.692	1.8542	0.649
0.02	1.814	0.634	2.3864	0.704	2.6459	0.725	2.0349	0.6705
0.001	2.2258	0.69	2.95256	0.747	3.492	0.777	2.8986	0.7435

4. Conclusion

The cross-linked framework of polymer (PVP) used in the synthesis of the membrane provides structural flexibility and mechanical stability, while the inorganic material (a zirconium phosphate and zeolite composite) offers thermal stability. According to the structural characterization, the membrane was found to be homogenous and have a smooth surface with a uniform pore distribution within its surface, which facilitated the phenomena of exchange and transport. The TMS Theory described the electrochemical characteristics and derived values for transport parameters, membrane potential, and fixed charge density. It was found that the experimental findings and theoretical predictions regarding membrane potential were closely aligned. The most crucial factor influencing transport and exchange characteristics, as well as separation effectiveness and fouling behavior, was found to be charge density. The dependent characteristics of electrolyte concentration and applied pressure on mobility ratio, transport number, fixed charge density, charge effectiveness, and membrane potential have been demonstrated by electrochemical and transport properties. Membrane potential increased as electrolyte concentration decreased and exhibited greater values, indicating the cation selectivity of the synthesized membrane. Except for charge effectiveness, and charge density which followed the opposite order, all parameters followed the pattern NaCl>KCl>NaNO₃>KNO₃.

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References

- [1] M. Ilyas, W. Ahmad, H. Khan, S. Yousaf, M. Yasir, A. Khan, Environmental and health impacts of industrial wastewater effluents in Pakistan: A review, *Rev. Environ. Health*. 34 (2019) 171–186. <https://doi.org/10.1515/reveh-2018-0078>.
- [2] L.A. Malik, A. Bashir, A. Qureashi, A.H. Pandith, Detection and removal of heavy metal ions: a review, *Environ. Chem. Lett.* 17 (2019) 1495–1521. <https://doi.org/10.1007/s10311-019-00891-z>.
- [3] A. Waheed, N. Baig, N. Ullah, W. Falath, Removal of hazardous dyes, toxic metal ions and organic pollutants from wastewater by using porous hyper-cross-linked polymeric materials: A review of recent advances, *J. Environ. Manage.* 287 (2021) 112360. <https://doi.org/10.1016/j.jenvman.2021.112360>.
- [4] C. Charcosset, Ultrafiltration, Microfiltration, Nanofiltration and Reverse Osmosis in Integrated Membrane Processes, *Integr. Membr. Syst. Process.* (2016) 1–22. <https://doi.org/10.1002/9781118739167.ch1>.
- [5] W.L. Ang, A.W. Mohammad, N. Hilal, C.P. Leo, A review on the applicability of integrated/hybrid membrane processes in water treatment and desalination plants, *Desalination*. 363 (2015) 2–18. <https://doi.org/10.1016/j.desal.2014.03.008>.
- [6] N. Ghaffour, S. Soukane, J.G. Lee, Y. Kim, A. Alpatova, Membrane distillation hybrids for water production and energy efficiency enhancement: A critical review, *Appl. Energy*. 254 (2019) 113698. <https://doi.org/10.1016/j.apenergy.2019.113698>.
- [7] C.Z. Liang, T.S. Chung, J.Y. Lai, A review of polymeric composite membranes for gas separation and energy production, *Prog. Polym. Sci.* 97 (2019) 101141. <https://doi.org/10.1016/j.progpolymsci.2019.06.001>.
- [8] * and Mingdong Dong* Jing Hu,* Pengfei Wang, Jianbo Hu, Menglian Zheng, Advanced

Science - 2024 - Hu - Chitosan Composite Membrane with Efficient Hydroxide Ion Transport via Nano-Confined.pdf, (n.d.).

- [9] D.W. Shin, M.D. Guiver, Y.M. Lee, Hydrocarbon-Based Polymer Electrolyte Membranes: Importance of Morphology on Ion Transport and Membrane Stability, *Chem. Rev.* 117 (2017) 4759–4805. <https://doi.org/10.1021/acs.chemrev.6b00586>.
- [10] E. Evdochenko, J. Kamp, R. Femmer, Y. Xu, V. V. Nikonenko, M. Wessling, Unraveling the effect of charge distribution in a polyelectrolyte multilayer nanofiltration membrane on its ion transport properties, *J. Memb. Sci.* 611 (2020). <https://doi.org/10.1016/j.memsci.2020.118045>.
- [11] M. Arsalan, Rafiuddin, Synthesis, structural characterization, electrochemical, and electrical study of polystyrene-based manganous tungstate composite cation exchange membrane, *Desalin. Water Treat.* 52 (2014) 7531–7542. <https://doi.org/10.1080/19443994.2013.831793>.
- [12] K. Abu-Shandi, F. Al-Wedian, Estimation of composition, coordination model, and stability constant of some metal/phosphate complexes using spectral and potentiometric measurements, *Chem. Pap.* 63 (2009) 420–425. <https://doi.org/10.2478/s11696-009-0027-5>.
- [13] M. Arsalan, Rafiuddin, Binding nature of polystyrene and PVC 50:50% with CP and NP 50:50% ion exchangeable, mechanically and thermally stable membrane, *J. Ind. Eng. Chem.* 20 (2014) 3283–3291. <https://doi.org/10.1016/j.jiec.2013.11.068>.
- [14] M.M.A. Khan, Rafiuddin, Inamuddin, Electrochemical characterization and transport properties of polyvinyl chloride based carboxymethyl cellulose Ce(IV) molybdophosphate composite cation exchange membrane, *J. Ind. Eng. Chem.* 18 (2012) 1391–1397. <https://doi.org/10.1016/j.jiec.2012.01.042>.
- [15] M.R. Khan, 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. <https://doi.org/10.1016/j.molstruc.2012.07.057>.
- [16] A.A. Khan, U. Habiba, S. Shaheen, M. Khalid, Ion-exchange and humidity sensing properties of poly-o-anisidine Sn(IV) arsenophosphate nano-composite cation-exchanger, *J. Environ. Chem. Eng.* 1 (2013) 310–319. <https://doi.org/10.1016/j.jece.2013.05.010>.

- [17] L. Chaabane, G. Bulvestre, C. Innocent, G. Pourcelly, B. Auclair, Physicochemical characterization of ion-exchange membranes in water-methanol mixtures, *Eur. Polym. J.* 42 (2006) 1403–1416. <https://doi.org/10.1016/j.eurpolymj.2005.12.019>.
- [18] T. Arfin, Rafiuddin, Transport studies of nickel arsenate membrane, *J. Electroanal. Chem.* 636 (2009) 113–122. <https://doi.org/10.1016/j.jelechem.2009.09.019>.
- [19] A.A. Moya, Harmonic analysis in ideal ion-exchange membrane systems, *Electrochim. Acta.* 90 (2013) 1–11. <https://doi.org/10.1016/j.electacta.2012.12.031>.
- [20] M. Arsalan, M.M.A. 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. <https://doi.org/10.1016/j.desal.2013.03.014>.
- [21] U. Ishrat, Rafiuddin, Synthesis, characterization and electrical properties of Titanium molybdate composite membrane, *Desalination.* 286 (2012) 8–15. <https://doi.org/10.1016/j.desal.2011.11.059>.
- [22] A. Zehra, M.M.A. Khan, Rafiuddin, Mathematical modelling of cobalt based composite membrane using TMS method; confirming its efficiency and selectivity, *J. Polym. Res.* 25 (2018). <https://doi.org/10.1007/s10965-018-1611-6>.
- [23] S.N.S. Nor Mahiran, N.H. Abd Kadir, M. Maulidiani, T.R. Tengku Mohamad, N.J. Gooderham, M. Alam, Multivariate modelling analysis for prediction of glycidyl esters and 3-monochloropropane-1,2-diol (3-MCPD) formation in periodically heated palm oil, *Heliyon.* 9 (2023) e20413. <https://doi.org/10.1016/j.heliyon.2023.e20413>.
- [24] J.H. Jo, C.H. Jo, H. Yashiro, S.J. Kim, S.T. Myung, Re-heating effect of Ni-rich cathode material on structure and electrochemical properties, *J. Power Sources.* 313 (2016) 1–8. <https://doi.org/10.1016/j.jpowsour.2016.02.015>.
- [25] E.E. Çakırca, A.N. Akin, Study on heterogeneous catalysts from calcined Ca riched hydrotalcite like compounds for biodiesel production, *Sustain. Chem. Pharm.* 20 (2021). <https://doi.org/10.1016/j.scp.2021.100378>.
- [26] M.M.A. Khan, Rafiuddin, Synthesis, characterization and electrochemical study of calcium phosphate ion-exchange membrane, *Desalination.* 272 (2011) 306–312. <https://doi.org/10.1016/j.desal.2011.01.041>.
- [27] 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. <https://doi.org/10.1016/j.desal.2011.08.059>.
- [28] R.S. and I.A. M. NASIM BEG, FASIH A. SIDDIQI, EVALUATION OF MEMBRANE SELECTIVITY FROM ELECTRIC POTENTIAL AND CONDUCTIVITY MEASUREMENTS M., *Biochem. Biophys. Res. Commun.* 91 (1979) 498–501.
- [29] A.A. Khan, S. Shaheen, U. Habiba, Synthesis and characterization of poly-o-anisidine Sn(IV) tungstate: A new and novel “organic-inorganic” nano-composite material and its electro-analytical applications as Hg(II) ion-selective membrane electrode, *J. Adv. Res.* 3 (2012) 269–278. <https://doi.org/10.1016/j.jare.2011.09.002>.
- [30] M. Arsalan, Rafiuddin, Fabrication, characterization, transportation of ions and antibacterial potential of polystyrene based $\text{Cu}_3(\text{PO}_4)_2/\text{Ni}_3(\text{PO}_4)_2$ composite membrane, *J. Ind. Eng. Chem.* 20 (2014) 3568–3577. <https://doi.org/10.1016/j.jiec.2013.12.050>.
- [31] 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, *Eur. J. Med. Chem.* 45 (2010) 264–269. <https://doi.org/10.1016/j.ejmech.2009.10.005>.
- [32] A. Cahil, M. Najdoski, V. Stefov, Infrared and Raman spectra of magnesium ammonium phosphate hexahydrate (struvite) and its isomorphous analogues. IV. FTIR spectra of protiated and partially deuterated nickel ammonium phosphate hexahydrate and nickel potassium phosphate hexahydrate, *J. Mol. Struct.* 834–836 (2007) 408–413. <https://doi.org/10.1016/j.molstruc.2006.11.049>.
- [33] 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. Memb. Sci.* 196 (2002) 95–102. [https://doi.org/10.1016/S0376-7388\(01\)00582-8](https://doi.org/10.1016/S0376-7388(01)00582-8).
- [34] F.A. Siddiqi, M.N. Beg, P. Prakash, Studies with model membranes. Part IX. Evaluation of the thermodynamic effective fixed charge density and permselectivity of parchment supported cobalt tungstate and mercuric chromate membranes, *J. Electroanal. Chem.* 80 (1977) 223–238. [https://doi.org/10.1016/S0022-0728\(77\)80045-4](https://doi.org/10.1016/S0022-0728(77)80045-4).
- [35] A. Pottier, S. Cassaignon, C. Chanéac, F. Villain, E. Tronc, J.P. Jolivet, Size tailoring of

- TiO₂ anatase nanoparticles in aqueous medium and synthesis of nanocomposites. Characterization by Raman spectroscopy, *J. Mater. Chem.* 13 (2003) 877–882. <https://doi.org/10.1039/b211271j>.
- [36] A.H. Galama, J.W. Post, H.V.M. Hamelers, V. V. Nikonenko, P.M. Biesheuvel, On the origin of the membrane potential arising across densely charged ion exchange membranes: How well does the teorell-meyer-sievers theory work?, *J. Membr. Sci. Res.* 2 (2016) 128–140.
- [37] M. Arsalan, F. Alam, I. Khan, M. Oves, Synthesis and characterization of Co₃(Po₄)₂ and Ni₃(Po₄)₂ composite membranes based on PVC: A Comparative electrochemical studies through aqueous electrolyte solutions, *J. Membr. Sci. Res.* 4 (2018) 41–50. <https://doi.org/10.22079/jmsr.2017.60443.1129>.