Bulgarian Chemical Communications, Volume 55, Issue 3 (pp. 250-255) 2023 DOI: 10.34049/bcc.55.3.NCNTC04

Pervaporative desalination by phosphomolybdic acid/PVA hybrid membrane

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Accepted: August 07, 2023

Water is indeed a precious natural resource and essential for all living organisms. Despite the Earth's abundant water resources, only a small portion is freshwater suitable for drinking and utilization. This accounts for approximately 0.3% of the Earth's total water capacity, equivalent to about 105 thousand km³. As a result, desalination has emerged as a viable solution to produce clean water by converting seawater, which is an almost limitless supply. Among the various desalination processes, pervaporation (PV) has attracted significant attention due to its numerous advantages, including low energy consumption, simplicity in operation, low cost, and high separation performance within a short period. The current study proposes the application of pervaporation for desalination purposes. Specifically, a hydrophilic polymer, polyvinyl alcohol (PVA), is chosen for membrane synthesis in the desalination process. Polymeric membranes are comparatively easier to produce and more cost-effective than other types of membranes. However, polymeric membranes tend to exhibit a swelling behavior, resulting in high flux and low selectivity. To address this challenge, recent advancements have led to the development of hybrid membranes, known as organic-inorganic composite membranes. In this study, phosphomolybdic acid (PMA) is chosen as an additive material. The effects of the amount of phosphomolybdic acid, salt concentration, and operation temperature on desalination performance are examined. Optimal operating conditions are determined, resulting in a salt rejection rate of 99.99% and a flux value of 2.45 kg/m² h. These findings demonstrate the potential of the proposed membrane system for efficient desalination applications.

Keywords: Desalination, membrane, pervaporation, phosphomolybdic acid, water

INTRODUCTION

The scarcity of freshwater resources and the increasing population, along with water contamination, pose significant threats to human livings sustainability. As a result, researchers have been actively searching for alternative sources of freshwater. In recent years, there has been a growing focus on obtaining freshwater from saline sources such as brackish water and seawater through a process known as desalination. Among the various technologies used in desalination, membrane technology has gained considerable attention due to its high separation efficiency, energy savings, environmental friendliness, ease of installation, and scalability [1].

Pervaporation, in particular, has emerged as a promising membrane technology for desalination. It offers cost efficiency and energy efficiency compared to traditional separation methods. Pervaporation can be operated under moderate process conditions, making it a viable option. It is also an environmentally friendly process and can be easily scaled up [2-4]. These advantages make pervaporation an attractive option in the field of desalination, providing a potential solution to the global water scarcity challenge. The transport mechanism in the pervaporation process is defined with a solution–diffusion model. According to this model, the membrane surface is contacted with the feed solution, the components in the feed solution are sorbed by the membrane selectively, this selective component is transported through the membrane and the sample is obtained in vapor phase by executing vacuum on the downside of the membrane. The pervaporation process is conducted by a chemical potential gradient [5-7].

The selection of a membrane plays a crucial role in the pervaporation process, and in recent years, hybrid membranes have been increasingly utilized to improve membrane properties [8, 9]. Hybrid membranes offer a smart approach to modify the membrane structure by incorporating both organic and inorganic phases. Typically, inorganic particles are dispersed within a polymeric matrix to create hybrid membranes. Commonly used inorganic fillers in hybrid membrane preparation include zeolites, silicas, metal oxides, heteropolyacids, carbon nanotubes, and graphene oxides. In the specific context of this study, phosphomolybdic acid is chosen as the inorganic filler material. Phosphomolybdic acid is classified as a heteropolyacid consisting of a heteroatom

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surrounded by four oxygen atoms in a tetrahedral structure. The bridging and terminal oxygen atoms on the periphery of the structure can associate with water molecules to form hydrates, thereby potentially enhancing selectivity to water. This property makes phosphomolybdic acid an attractive choice for improving the performance of the hybrid membrane in terms of water separation and selectivity. By incorporating phosphomolybdic acid as an inorganic filler material in the hybrid membrane, the researchers aim to foster its unique chemical characteristics to enhance the desalination performance of the pervaporation process [10, 11].

The present study focuses on the synthesis and application of phosphomolybdic acid (PMA)-loaded polyvinyl alcohol (PVA) membrane for desalination using the pervaporation (PV) process. PVA has been widely used in pervaporation desalination due to its favorable properties. It is relatively easy to obtain PVA films, and they exhibit good hydrophilic properties, as well as chemical and mechanical resistance [12, 13]. The novelty of this study proceeds from the preparation and usage of PMA-incorporated PVA membranes specifically for pervaporative desalination. The membranes were characterized using techniques such as FTIR, TGA, and SEM. The effects of feed salt concentration, temperature, and PMA loading ratio on salt rejection and flux were investigated. This study contributes valuable insights for the development of high-performance PMA/PVA hybrid membranes in pervaporation-based desalination. By exploring the influence of various parameters on the membrane's desalination efficiency, it paves the way for further improvements in membrane design and performance in the field of desalination.

EXPERIMENTAL

Materials

In this study, the materials used for the membrane synthesis and experimental procedures were purchased from specific suppliers. Polyvinyl alcohol, phosphomolybdic acid, and glutaraldehyde were acquired from Sigma-Aldrich. Sodium chloride and acetone were obtained from Merck Chemicals.

Membrane preparation

5 wt.% of PVA was dissolved in deionized water to create a homogeneous polymeric membrane solution. A certain amount of PMA particles (ranging from 5 wt.% to 20 wt.%), based on the mass of the polymer, were added to the PVA solution. The PMA particles were mixed thoroughly with the PVA solution to ensure homogeneity and dispersion of the additive within the membrane material. The solution casting method, also known as the solvent evaporation method, was utilized for membrane fabrication. The PVA-PMA mixture was cast as a thin film onto a suitable surface. The cast membrane was then subjected to a drying process to remove the solvent (water in this case) and obtain a solid membrane structure. After drying, the membrane was crosslinked to improve its stability and mechanical properties. A 1 wt.% solution of glutaraldehyde was prepared in a 50% v/v aqueous acetone solution. The dried membrane was immersed in the glutaraldehyde solution for crosslinking.

Membrane characterization

In this study, the synthesized membranes were subjected to characterization using three techniques: FTIR, TGA, and SEM. These characterization methods provide valuable insights into the chemical structure, thermal stability, and structural morphology of the membranes.

FTIR analysis was performed to examine changes in the chemical structure of the PVA membrane as a result of the addition of PMA. FTIR allows for the identification of functional groups and chemical bonds, thus providing information on the molecular changes occurring in the membrane due to the presence of PMA.

TGA was employed to evaluate the thermal stability of the membranes. TGA measures the weight loss of membranes as a function of temperature. The thermal behavior of the membranes is analyzed, including factors such as decomposition temperature, degradation profile, and thermal stability, which are crucial for their application in desalination.

SEM was utilized to examine the structural morphology of the membranes at a microscopic level. SEM imaging helps visualize the dispersion of PMA particles within the PVA matrix and assess the interfacial interactions between the components, contributing to a better understanding of the membrane structure.

Pervaporative desalination experiments

Water desalination tests were performed in the pervaporation system which is represented in Fig. 1.

In the desalination setup, the hybrid membrane with an active surface area of 9.62 cm^2 was placed inside the membrane chamber. The volume of the membrane chamber was filled with NaCl-water solution.

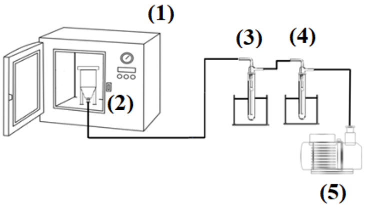

Fig. 1. Pervaporation system: (1) oven, (2) membrane chamber, (3-4) cold trap, (5) vacuum pump

The feed mixture in the membrane chamber was kept at atmospheric pressure and the downstream side of the membrane chamber was kept at 5 mbar. The permeate fresh water, which is the desalinated water passing through the membrane, was condensed using cold traps. The permeate samples were collected on an hourly basis. The collected samples were then subjected to analysis using the conductivity method. To evaluate the performance of the water desalination tests using the hybrid membrane, two metrics were used: flux (Eq. 1) and salt rejection (Eq. 2).

$$J = \frac{m}{A.t} \qquad (1)$$

$$R = \frac{C_f - C_p}{C_f} x100 \qquad (2)$$

J represents the flux, which is the rate of water permeation through the membrane. V is the volume of permeate water collected (in liters). A is the active surface area of the membrane (in square meters). t is the time taken to collect the permeate (in hours). R represents the salt rejection, which indicates the percentage of salt removed from the feed mixture. C_p is the concentration of salt in the permeate (in mg/L or ppm). C_f is the concentration of salt in the feed mixture (in mg/L or ppm).

RESULTS AND DISCUSSION

Characterization results

FTIR analysis. By using FTIR, it was possible to compare the chemical bonds in the membranes. The FTIR spectra of the membranes are displayed in Figure 2.

For the pristine PVA membrane, the OH group is observed at a characteristic band around 3278 cm^{-1}. The C-H (carbon-hydrogen) bonds are identified by the band at approximately 2924 cm^{-1}. The C=O (carbonyl) group is indicated by the band at around 1710 cm^{-1}. The presence of phosphomolybdic acid is revealed by the characteristic bands at 807, 957, 1079, 1420, 1653, 1740, 2926, and 2975 cm^{-1} in the FTIR spectra. The intensity of the -OH band around 3288 cm^{-1}, representing the hydroxyl bonds in the PVA membrane, shows a reduced intensity compared to the pristine PVA film.

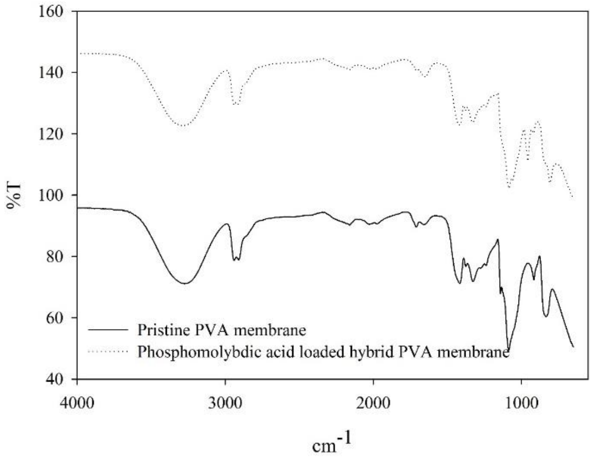

Fig. 2. FTIR spectra of the membranes: (a) pristine PVA membrane, (b) phosphomolybdic acid-loaded hybrid PVA membrane

The reduced intensity suggests an interaction between the phosphomolybdic acid and the hydroxyl bonds in the PVA membrane through various possible interactions, such as (Mo-Ot), (Mo-Oc-Mo), and (Mo-Oe-Mo) [14-16]. These observations indicate that the hybrid membrane with phosphomolybdic acid exhibits modifications and new chemical bonds compared to the pristine PVA film. The presence of phosphomolybdic acid in the hybrid membrane introduces additional functional groups and potentially influences the membrane's properties and performance in the desalination process.

TGA analysis. The thermal stability of the film was tested by TGA. Figure 3 shows the TGA curves of the membrane. The TGA of the hybrid membrane loaded with phosphomolybdic acid showed mass loss between 180 and 200°C. The mass loss occurring in this temperature range is attributed to the evaporation of water molecules. From 250 to 420◦C, the mass loss in this temperature range is likely due to the decomposition or oxidation of side chains and main chains present in the hybrid membrane. This indicates that the membrane undergoes chemical changes or degradation under the influence of heat, resulting in the release of volatile components. The mass loss in the temperature range from 420 °C to 500 °C is associated with a chemical reaction involving phosphomolybdic acid. The reaction is described as $H_3PMo_{12}O_{40} \rightarrow (1/2)\ P_2O_5 + 12MoO_3 + (3/2)H_2O$ (Mo=W). This reaction indicates the decomposition of phosphomolybdic acid into various products such as phosphorus pentoxide (P_2O_5), molybdenum trioxide (MoO_3), and water (H_2O) [14, 15].

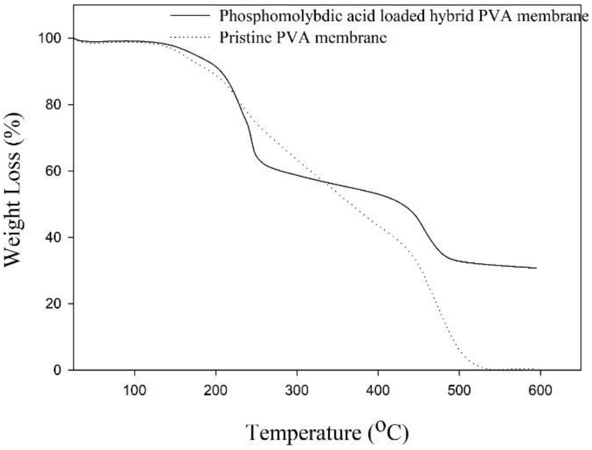

Fig. 3. TGA curve of membranes: (a) pristine PVA membrane (b) phosphomolybdic acid-loaded hybrid membrane

SEM analysis. The surface images of pristine and hybrid membranes are shown in Figure 4. While Fig. 4(a) shows the surface image of the pristine membrane, Fig. 4 (b) shows the surface image and SEM-EDX analysis of the hybrid membranes.

The surface image of the pristine PVA membrane (Fig. 4(a)) shows a dense structure. This suggests a compact and smooth surface without significant visible features or particles. The surface image of the hybrid membrane (Fig. 4(b)) reveals the presence of small white particles on the surface of the membrane. These particles are identified as phosphomolybdic acid, as mentioned. The particles appear to be evenly distributed throughout the membrane.

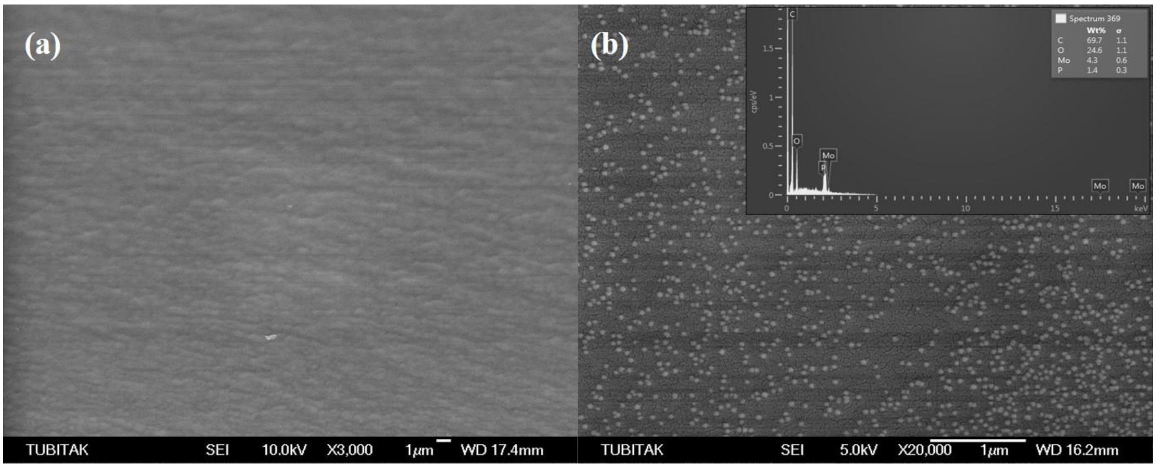

Fig. 4. SEM surface images of the membranes: (a) pristine PVA membrane (b) PMA/PVA hybrid membrane and SEM-EDX analysis

The SEM-EDX analysis conducted on the hybrid membrane (Fig. 4(b)) confirms the presence of phosphomolybdic acid. The elements phosphorus (P), molybdenum (Mo), and oxygen (O) are clearly visible in the EDX spectrum, indicating their presence in the membrane. This further confirms the successful incorporation of phosphomolybdic acid particles into the hybrid membrane.

Overall, the comparison of the surface images and SEM-EDX analysis between the pristine PVA membrane and hybrid membrane provides evidence of the modification and incorporation of phosphomolybdic acid particles onto the surface of the membrane. These observations indicate the successful synthesis and loading of phosphomolybdic acid in the hybrid membrane, which can potentially impact its properties and performance in various applications.

DESALINATION RESULTS

Effect of feed salt concentration

Figure 5 shows the effect of feed salt concentration on water flux and salt rejection values of hybrid films loaded with 5% PMA by weight.

As the NaCl concentration in the feed stream increases from 250 ppm to 1000 ppm, the water flux decreases from 5.98 to 2.87 kg/m^2 h. This suggests that the presence of higher salt concentration has a negative impact on the water permeability of the membrane. With an increase in the feed concentration of NaCl, the mole fraction of water decreases. This indicates that the proportion of water molecules in the feed stream decreases as the NaCl concentration increases.

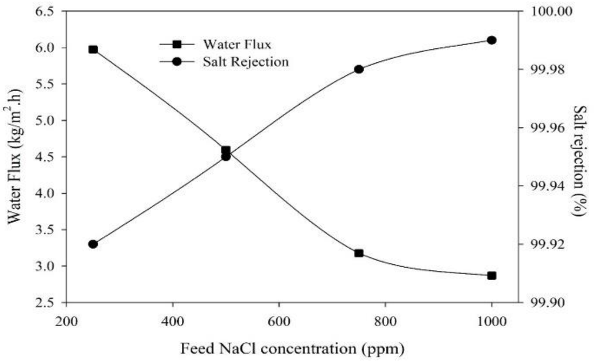

Fig. 5. Effect of feed salt concentration on salt rejection and flux

Despite the decrease in water flux, the salt rejection remains consistently high, around 99.99% and 99.92%. This demonstrates that the hybrid membrane loaded with 5 wt% of PMA effectively removes the salt ions from the feed stream, regardless of the increasing NaCl concentration. With a higher concentration of salt in the feed stream, water molecules form stronger interactions with salt ions, reducing the amount of free water molecules available for transport through the membrane. According to Fick's law, the decrease in the thermodynamic activity of water due to increased salt concentration reduces the solubility of water in the membrane. This reduction in solubility is a primary factor contributing to the decrease in water flux observed [17].

Effect of temperature

Fig. 6 presents the variations in flux and salt rejection *versus* operating temperature by the membrane loaded with 5 wt.% of phosphomolybdic acid and with constant NaCl concentration (250 ppm).

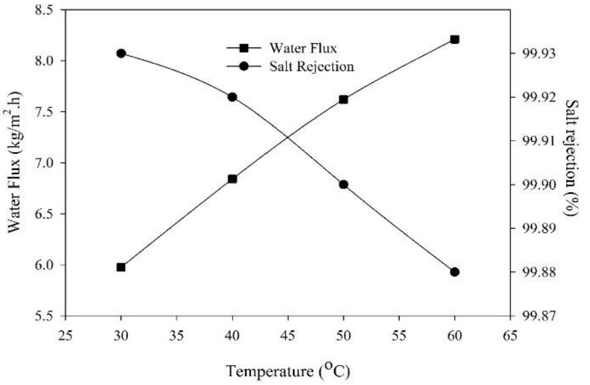

Fig. 6. Effect of temperature on salt rejection and flux

Increasing the temperature leads to an increase in water flux. This is because the vapor pressure of the feed mixture rises with temperature, creating a higher driving force for diffusion of components across the membrane. The constant vapor pressure on the permeate side maintains a concentration gradient that further enhances the driving force and increases the water flux. The mobility of the PVA chains within the membrane increases as the process temperature rises. This increased mobility results in the creation of additional free volume in the membrane. The increase in membrane mobility and the associated increase in free volume have an impact on salt rejection. As the width of the polymer diffusion channel widens due to increased mobility, the dimensional separation effect becomes less pronounced. This means that dissolved ions with larger kinetic diameters can more easily pass through the membrane. Consequently, the salt rejection of the membrane decreases. Due to the reduced dimensional separation effect and increased mobility of the PVA chains, the flux increases while salt retention decreases. This allows for the transportation of dissolved ions through the membrane, resulting in increased water flux and lower salt rejection. In summary, the increase in water flux with temperature is attributed to the increased vapor pressure of the feed mixture. The mobility of PVA chains also increases with temperature, leading to additional free volume in the membrane. However, this increase in mobility negatively affects the dimensional separation effect, resulting in decreased salt rejection and increased water flux [18].

Effect of PMA loading ratio

Effect of PMA loading ratio on separation performance of membrane was analyzed by the water-NaCl mixture containing 250 ppm NaCl at 30^{o}C. Fig. 7 shows the change in flux and salt rejection values by PMA ratio.

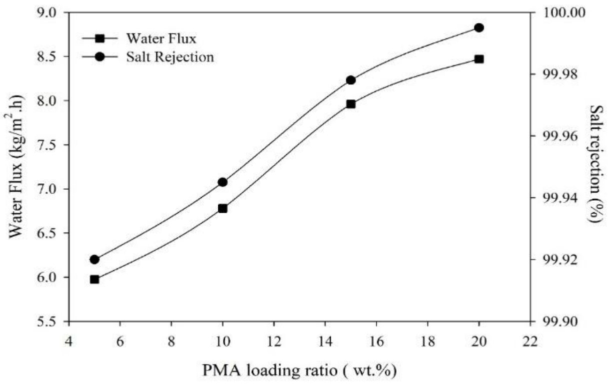

Fig. 7. Effect of PMA loading ratio on salt rejection and flux

According to Fig. 7, the addition of PMA to the membrane increases salt rejection. This indicates that PMA contributes to the membrane's ability to effectively remove salt ions from the feed solution.

PMA is described as a heteropolyacid with a specific molecular structure. It contains a central heteroatom surrounded by four oxygen atoms, forming a tetrahedral arrangement. Additionally, there are 12 octahedral moieties (MO_6 units) linked to each other by neighboring oxygen atoms, resulting in the presence of 24 bridging oxygen atoms. The peripheral oxygen atoms, both terminal and bridging, in the PMA structure are available to bind with water molecules, forming hydrates. These hydrates are believed to improve the selectivity of water transport through the membrane. The interaction between PMA and water molecules potentially contributes to enhanced water selectivity and salt rejection. A high loading ratio of PMA in the hybrid membrane results in a higher absorption of water molecules by the membrane. This increased hydration can lead to improved selectivity and enhanced flux values compared to a pristine PVA membrane [19]. Overall, the addition of PMA to the hybrid membrane is shown to increase salt rejection and water flux. The unique molecular structure of PMA allows for interactions with water molecules, forming hydrates, which potentially improve the selectivity of water transport. Moreover, higher loading ratios of PMA can result in greater water absorption and improved membrane performance compared to a pristine PVA membrane.

CONCLUSION

This study focuses on the development of a novel hybrid membrane for water desalination through pervaporation. The hybrid membrane is composed of PMA particles and PVA, and its performance was characterized and evaluated. The hydrophilic structure of PMA plays a significant role in enhancing water purification. This implies that the presence of PMA in the hybrid membrane improves its ability to remove salt and impurities from water during the desalination process. The membranes were characterized using FTIR, TGA, and SEM. These techniques are commonly used to analyze the chemical composition, thermal stability, and surface morphology of membranes. The study investigated the effects of feed salt concentration, PMA loading ratio, and process temperature on the performance of the hybrid membrane for desalination. A higher PMA loading ratio in the hybrid membrane resulted in increased salt rejection percentage and flux value. This indicates that a greater amount of PMA in the membrane improves its desalination performance. The optimum process temperature for the hybrid membrane was found to be 30°C. At temperatures higher than 30°C, the salt rejection value decreased, suggesting that the membrane's performance in salt removal was less effective at elevated temperatures. The hybrid membrane, comprised of PMA particles and PVA, demonstrated excellent separation performance for water desalination. The highest salt rejection achieved was around 99.99%, while the permeate flux reached 8.47 kg/(m^2 h) under the conditions of 30°C process temperature and 20 wt.% PMA loading ratio. A hybrid phosphomolybdic acid/PVA membrane has shown a great separation performance for use in water desalination.

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