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Tailoring Nanocomposite Membranes of Cellulose of Acetate/Silica Nanoparticles for Desalination

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Abstract

Herein, fabrication of cellulose acetate (CA) silica-based nanocomposite membranes via the dry-wet phase inversion procedure for the water desalination was investigated. The modified and unmodified silica nanoparticles (SNPs and MSNPs) were prepared by the sol-gel technique. The addition effect of the SNPs and MSNPs was investigated on the CA membranes properties and their performance for water separation. The CA nanocomposite membranes were characterized to study their structure, hydrophilicity, and morphology. The fabricated nanocomposite membranes showed hydrophilic surface properties. The performance of reverse osmosis (RO) membranes was measured using a crossflow RO unit. At 10 bar, The membrane with 10 mg of SNPs showed enhanced permeate water flux compared to the pristine CA membrane by 1.6 L/m².hr. Increasing the SNPs in the nanocomposite membrane showed enhancement in the permeate water flux all over the operating pressure. The effect of MSNPs on the nanocomposites' performance was lower than their counterpart in the case of adding SNPs. The membrane with 30 mg of MSNPs showed the highest permeate water flux among other nanocomposite membranes with a value of 35.7 L/m².hr at 24 bar.

Keywords: Silica nanoparticles, Amino-modified silica, APTES, Cellulose acetate, Nanocomposite membrane, Water desalination.

1. Introduction

Desalination is now utilized to resolve freshwater shortages in many parts of the world ¹. It is a feasible opportunity that can reduce the gap between the accelerating demands and the available capacities. That has been used for quite in many rural, deserted areas and coastal regions to provide clean drinking water ². The traditional solutions are being demonstrated by the most recent commercial technologies such as reverse osmosis (RO), multi-stage flash desalination, and multi-effect distillation ¹. RO is widely accepted and applied as an environmentally friendly and effective method for desalting numerous types water; for example, groundwater, rivers, lakes, brackish water, and seawater ³.

Polymeric membranes either as a support or an active material are used widely in RO applications ⁴. Different methods to produce efficient and low-cost biopolymers for water desalination have recently been investigated. CA is one of the most promising biopolymers which increased the hydrophilic character, excellent selectivity, toughness, ease to fabricate, and have resistance to degradation by chlorine ^{5,6}. However, CA membranes suffer from low flux, prone to compaction (loss of permeability at high pressure), and hydrolysis in alkaline and acidic medium ⁷.

Nanomaterials and nanoparticles consider are suitable additives to enhance membrane performance such as selectivity and permeability, fouling resistance, hydrophilicity, and inhibit macrovoid formation ⁸⁻¹⁰. Several studies have investigated the effect of nanoparticles in the polymeric membrane such as zeolite ^{11,12}, carbon nanotubes ¹³, graphene oxide ¹⁴, alumina (Al_2O_3) ¹⁵, clay ¹⁶, and titania ¹⁷. Moreover, the addition of the inorganic nanoparticles to the membrane can serve to induce an increase in the mean distance (free volume) between polymer chains and restrict the molecular motions of the polymer chains which can lead to simultaneous improvement in both selectivity and permeability ¹⁸. The major drawback of the addition of the nanoparticles is their strong tendency to agglomerate followed by insufficient dispersal in the membrane ¹⁹. Recent solutions for the agglomeration of nanoparticles in polymeric membranes include surface modification and optimization of the fabrication processes ²⁰.

The addition of SNPs to CA membranes has been studied before to investigate their effect on CA membranes using polyethylene glycol-600 as a pore-forming agent. The membrane preparation was done using a 2-stage phase inversion procedure by Ahmad, A., et al ²¹. The flux enhanced from 0.35 to 2.46 L/h.m² with an 11.41% relative increase in the salt rejection. Also, they have prepared membranes from CA, polyethylene glycol 300 conjugated with SNPs by thermally-induced phase separation method for removing MgSO_4 ¹⁰. A basic challenge within the preparation of nanocomposites membrane is the homogeneity within the mixing between the nanoparticles and the organic component, which is resolved by using a silane coupling agent as a surface modifier for the SNPs ²².

In this work, we investigated the fabrication of a CA composite membrane by the dry-wet phase inversion technique and studying the effect of SNPs addition prepared by sol-gel method on the

characteristic and performance of RO CA membranes will be carried out. The role of 3-aminopropyl triethoxysilane (APTES) on the modified SNPs as an additive for CA membrane with different ratios will be compared with pristine SNPs. The performance of the nanocomposite CA membranes represented in salt rejection and permeate water flux will be evaluated using brackish water of 10,000 ppm sodium chloride.

2. Materials and methods

Cellulose acetate was obtained from Across Organics Company with 39.8% acetyl content and its average number molecular weight was 100,000 Da. Acetone was purchased from Fisher Scientific Company. Dioxane was purchased from Cambrian Chemical Company. Acetic acid and methanol were purchased from Carlo Erba reagents SAS Inc. Ammonium hydroxide (25%) was purchased from Gateway Co. Ethanol was purchased from Carlo Erba reagent SPA Inc. (3-Aminopropyl) triethoxysilane (APTES) was obtained from Across Organic Company. Trimethyl orthosilicate (TMOS) was bought from Across Organics Company. Sodium chloride was supplied from MP Biomedicals, LLC, France.

2.1 Preparation of SNPs

A solution mixture of ethanol (50 mL), water (1 mL), and aqueous ammonia (2.7 mL) were added to a flask. An amount of TMOS (1.5 mL) was rapidly added to the mixture solution and magnetically stirred (200 rpm) for 3 hrs. at 40°C under reflux. Then TMOS (1 mL) was dropwise added into the above solution and kept stir for another 3 hrs. The SNPs were harvested by centrifugation at 9000 rpm for 10 minutes and washed twice with copious ethanol, and dried in an oven at 70°C for 24 h.

2.2 Preparation of MSNPs

An amount of the prepared SNPs (0.1g) were dispersed in ethanol (20 mL), and the solution was heated to 80°C under reflux. Then APTES (1 mL) was added to the solution. The mixture was boiled under reflux for 6 hrs, and followed by centrifugation at 9000 rpm for 10 minutes, washed with ethanol several times, and dried in an oven at 70° C for 24 hr.

2.3 Preparation of CA-RO nanocomposite membranes

CA-RO control membrane was prepared as reported by Ali et al ²³. SNPs and MSNPs with different ratios (0, 10, 30, 50, and 70 mg) were added to the solvent mixture and sonicated for 2 hrs to ensure complete dispersion before adding the CA powder. The nanocomposite membranes were denoted by the names S1, S3, S5, and S7 according to the concentration of SNPs of 10., 30, 50, and 70 mg respectively. The MSNPs nanocomposite membranes were denoted the names MS1, MS3, MS5, and MS7 according to the same concentration of MSNPs.

2.4 Characterization techniques

The functional groups of the SNPs, MSNPs, and the prepared membranes were analyzed using Fourier Transform Infrared Spectroscopy (FTIR Spectrum BX 11 spectrometer FTIR LX 18-5255 Perkin Elmer). The surface morphology and cross-sectional images of the obtained membranes were studied using scanning electron microscopy (Joel JSM 5300, Japan EM). Samples were prepared as follows. The dried membranes were cut under liquid nitrogen and mounted on a brass plate. The membranes were then sputter-coated with a thin film of gold. Morphology and particle size were investigated using transmission electron microscopy (TEM) (JEOL, JEM-100CX). A small portion of SNPs and MSNPs powder was dispersed in ethanol. The solution undergoes ultrasonication for 10 minutes then we added one drop of this solution to the Cu grid to be analyzed. The hydrophilicity measurements of the surface of the membrane were measured using Rame-Hart, Instrument Company, France. A drop of distilled water of about 2 μL was placed on the membrane surface (3 cm $\times$ 2 cm) using a microsyringe (Hamilton Company, Reno, NV). The contact angle was measured within 20 sec after the water drop was placed. To improve the statistics of the contact angle measurement, each reported data point is the average of five measurements at different positions at the same condition. X-ray diffraction analysis were obtained using (X-ray 7000 Shimadzu-Japan) at room temperature. The Bragg angle has 2θ in the range from 10 to 80 degrees to determine the degree of crystallinity of the prepared SNPs and MSNPs. The X-ray source is Cu target generated at 30 kV and 30 mA with scan speed 4 deg /min.

2.5 Lab-scale RO performance test

Performance measurements represented in the salt rejection and water flux were carried out by a cross-flow RO unit which consists of a commercially available crossflow stainless-steel CF042 cell with a membrane area of 42 cm^2 , a hydraulic pump of maximum pressure 60 bar, with a pressure control valve and a gauge through rejection line. A flow meter F-550 (USA) was connected to obtain a constant flow of 1 liter/min. The membranes were flushed in the RO unit system with deionized water for 30 min until a steady permeate flux was achieved, then the saline water with an initial feed concentration of 10,000 ppm NaCl was introduced. The pH and the temperature of the feed solution were kept constant at 7 and 25°C, respectively. The salt concentrations were determined using a TDS meter (430 portable, Jenway, England). The permeate water flux was calculated using the following equation ²³:

$$\text{Permeate water flux} = \frac{Q}{A.t} \quad (1)$$

where Q is the quantity of permeate (L), A is the effective membrane area (m^2) and t is the time (hr).

The percentage of the salt rejection (SR) is calculated using the following equation ²³:

$$\text{Salt rejection} = \frac{C_f - C_p}{C_f} 100\% \quad (2)$$

where C_f is the salt concentration of the feed solution and C_p is the salt concentration of the permeate water.

3. Results and discussion

3.1 SNPs and MSNPs structure and crystallinity

The chemical structures of the SNPs and the MSNPs are analyzed using FTIR as displayed in Figure 1(a). The band around 3414 cm^{-1} is assigned to the --OH stretching vibrations of the silanol Si-OH groups or the adsorbed water molecules on the silica surface. A sharp peak at 1633 cm^{-1} is found as the scissor bending vibrations of the trapped water molecules in the silica. The strong band at 1105 cm^{-1} coincides with the asymmetric vibrations of the Si-O-Si bond. The weak band at 941 cm^{-1} signifies the Si-O asymmetric stretching vibrations of the silanol groups (Si-OH). An absorption moderate peak at 790 cm^{-1} is appointed to the stretching vibrations of the Si-O-Si bond. The band noticed at 455 cm^{-1} is owing to the bending vibrations of the Si-O-Si bond²⁴⁻²⁸. The characteristic bands of the MSNPs have the same as in the spectrum of SNPs. There is a peak at 3373 cm^{-1} caused by the existence of NH vibrations stretching results from ATEs. Furthermore, a peak has emerged at 2914.5 cm^{-1} is attributed to CH_2 vibrations (stretching). Additionally, at 1404 cm^{-1} there is a peak recognized to CH_3 bending vibrations²⁹. The characteristics bands of silica become weak after modification, which confirms that the silane molecules have been effectively grafted onto the SNPs surface³⁰.

Figure 1 (b) shows XRD patterns of SNPs and MSNPs. The broadband appears at Bragg angle 2θ of 24° which is associated with amorphous silica. All forms of silica have a short range of order solids composed of silicon and oxygen atoms. SiO_2 is a silicon oxide made up of linear triatomic molecules in which a silicon atom is covalently bonded to two oxygens. The Si atom shows tetrahedral coordination with four O_2 atoms surrounding a central Si atom and consequently the SNPs forms three-dimensional networks in which each Si atom is covalently bonded in a tetrahedral manner to 4 oxygen atoms. The absence of any sharpened peaks confirms the amorphous structure of silica^{24,26,30,31}.

3.3 Morphological study of SNPs and MSNPs

The microstructure of the SNPs and the MSNPs are examined in Figure 1(c, d) by TEM. The SNPs have a uniform, homogeneous spherical structure with a controlled average particle size of 26-51 nm. On the other hand, the MSNPs are slightly irregular in shape and seem approximately spherical. The diameter of these nanoparticles is estimated to be about 26.7-29.1 nm. The agglomeration shown in the figure may be due to the inhomogeneous surface functionalization via the post-synthetic grafting method as has been explained by Gu et al³².

Figure (1) Characterization of SNPs and MSNPs. FTIR spectra (a), XRD patterns (b), TEM images (c, d).

3.4 Nanocomposite membranes properties and their desalination performance

3.4.1 Chemical structure of nanocomposite membranes

As shown in Figure 2 (a), for the control CA and nanocomposite membranes based on SNPs there is broadband at 3484 cm^{-1} and a peak at 1372 cm^{-1} which are designated for stretching and bending vibration of the OH, respectively. The peak at 2940 cm^{-1} is characteristic of the aliphatic C-H group and the stretching vibration of the C=O bond is observed around 1748 cm^{-1} . The peaks at 1636 cm^{-1} and 1512 cm^{-1} represent the free water molecule and the stretching mode of the C=C bond, respectively. The bending vibration of CH_2 is observed at 1434 cm^{-1} , the band at 1234 cm^{-1} is attributed to the stretching vibration of the C-O group, the absorption band at 1054 cm^{-1} is corresponded to the ether linkage C-O-C from the glycoside unit, and the peak at 908 cm^{-1} is assigned to the (pyranose ring) out-of-plane C-H bend³³⁻³⁷. It is noticed that the intensity of the carbonyl band of the CA control membrane has decreased with the addition of SNPs in the composite membrane, which confirmed the development of hydrogen bonding between the carbonyl and the hydroxyl groups. There is a slight shift from 1748 cm^{-1} for the CA control membrane to 1743.8 cm^{-1} for S7, which confirmed the carbonyl group interaction through hydrogen bonding with SNPs. These results indicate the interactions of SNPs in CA nanocomposite membranes³³.

Figure 2(b) illustrates the impact of various concentrations of MSNPs on the CA membrane. It is noticed that there are two overlapping bands that occurred with an increase in the intensity of the peaks and the peak at 3484 cm^{-1} is assigned to the OH group in the CA control and NH_2 group for the MSNPs. The other overlapping at 1636 cm^{-1} is assigned to the water of crystallization in the CA membrane and the NH_2 group in the modified MSNPs.^{33-36,38}. These results prove that the CA membrane has been successfully modified with the NH_2 group.

Figure 2: FT-IR spectra of CA nanocomposite membranes: Different concentrations of SNPs (a), Different concentrations of MSNPs (b).

3.4.3 Morphology of CA nanocomposite membranes

The addition of SNPs and MSNPs to the CA membrane has a great effect on the membrane morphology and structure. The SEM images in Figure 3 depict distinct changes in the morphology of the CA control membrane and the CA-SNPs nanocomposite membranes concerning the surface layer, cross-section, and the bottom of the membranes as a result of varying SNPs concentrations. All the surfaces of the membranes, including the CA control membrane, show a ridge and valley

structure. Notably, the cross-section structure of the CA control and the nanocomposite membranes reveals fingers within sponge structure, Nonetheless, the nanocomposite membranes fingers have a different form than the control membrane. Due to the hydrophilic nature of SNPs, the solvent-nonsolvent exchange in the phase inversion process is accelerated and formed a dense skin layer ¹⁸. In the case of the S3 membrane, more voids are formed with respect to CA control membrane and S1 membrane ³⁹. Further increase of the SNPs concentrations from S5 to S7, the polymer solution viscosity is slightly increased, causing delayed demixing and agglomeration of SNPs with lower voids in the cross-section structure. This agglomeration also forms pores in the bottom surfaces. The formed dense skin layer limits the exchange of the solvent and nonsolvent in the nanocomposite and thus, suppresses the pore formation in the membranes ^{18,40-42}. From the measurements of the membranes' dense layer thickness, it can be concluded that, as the concentration of SNPs increases, the dense layer thickness increases. The dense layers thickness of the CA-SNPs nanocomposite membranes is 1.18, 1.43, 1.62, 1.72, and 1.81 μm for CA control, S1, S3, S5, and S7 membrane, respectively.

The SEM images in Figure 4 display distinct changes in the morphology between the CA control membrane and the CA-MSNPs nanocomposite membranes. All the nanocomposite membranes exhibit ridge and valley surfaces. Increasing the MSNPs concentration in the CA membranes causes some agglomeration of MSNPs which results in relatively delayed demixing in nanocomposite membranes with a high concentration of MSNPs (50 and 70 mg) in comparison with a lower concentration of MSNPs (10 and 30 mg) in the nanocomposite membranes. Thus, the formation of macrovoids in the membrane matrix is suppressed ⁴⁰⁻⁴². The membranes' surface tends to be smoother, and the surface roughness decreases as the concentration of MSNPs increases. The bottom of the CA control membrane is a smooth and flat structure while the modified membranes tend to be smoother, and fewer bends are observed. All CA-MSNPs nanocomposite membranes exhibited a fingers-like structure in the cross-section, separated by thick walls of sponge structure, except MS1 which showed a distinct tear structure shape. It is obvious that as the concentration of the MSNPs increases the dense thin layer of the membrane increases. The dense layer is 1.18, 1.3, 1.56, 1.66, and 1.88 for CA control, MS1, MS3, MS5, and MS7 membrane, respectively.

Figure 3: SEM images of control CA and CA-SNPs nanocomposite membranes with different ratios.

Figure 4: SEM images of control CA and CA- MSNPs nanocomposite membranes with different ratios.

3.4.4. Membranes' hydrophilicity

Figure 5 (a and b) manifests the relationship between SNPs and MSNPs concentrations in the CA nanocomposites and their water contact angle measurements. As the SNPs concentration in the CA nanocomposite membrane increases, the measured water contact angle is slightly increased. This is maybe due to their agglomeration on the membrane surface. The water contact angle of the control CA is 54.5 degrees, while the water contact angle measurements for the CA-SNPs nanocomposite membranes are ranged from 66.2 to 56.6 degrees. However, for the CA- MSNPs nanocomposite membranes, they maintain their hydrophilic nature compared with the CA control membrane. Generally, the values of water contact angle tend to slightly decrease from (MS1 to MS5) by increasing the MSNPs concentration in the CA nanocomposite membranes. MS5 has a water contact angle of 52.28 degrees. This is the least water contact angle obtained for the CA-MSNPs nanocomposite membrane. This is due to the hydrophilic amino groups attached to the silica surface ⁴³. Then, increasing the concentration of MSNPs to 70 mg causes an increase in the water contact angle (57.42 degrees). This increase in water contact angle measurement is attributed to the agglomeration of MSNPs.

Figure 5: Water contact angles of different SNPs (a), MSNPs (b) on CA membranes.

3.4.5 The membranes' performance

Figure 6 (a and b) presents the influence of SNPs concentrations on nanocomposite membranes salt rejection and permeate water flux for 10,000 ppm NaCl feed under different operating pressures from 8 to 50 bar. All the membranes salt rejection is decreasing with escalating pressure, and this is expected due to the concentration polarization phenomena. For all nanocomposite membranes, they show a sudden decrease in salt rejection compared to the CA control membrane which shows a gradual decrease in salt rejection. The sudden decrease is may be attributed to the generation of small nonselective voids existing between SNPs and the CA polymer chain ²⁵. The CA control

membrane has 96% salt rejection at 10 bar and declined to 85% during the operating pressure between 14 and 25 bar, then it is ruptured at 28 bar. For S1, S3, and S5 the salt rejections decreased with increasing the pressure and could not tolerate the pressure of more than 20 bar. However, S7 indicates a decrease in rejection between 10 and 18 bar to reach 64% of salt rejection. Then the salt rejection increases again from 20 bar to about 35 bar and it appears a plateau region of stable salt rejection behavior up to 48 bar then it is ruptured at 50 bar. This is due to the densification of the dense skin layer on S7 surface ⁴⁴. This trend can be explained based on that the addition of SNPs causes a formation of the thicker skin layer and raises the viscosity of the polymer and SNPs solution. This results in the suppression of microvoids, and the formation of a dense layer of the S7 membrane ¹⁸.

For all membranes, as indicated by Figure 6 (b), the permeate water flux has increased with the increasing of the operating pressure. This is due to the increasing trans-membrane pressure, which significantly enhances the pure permeate water flux during the period of operation. The highest permeate water flux obtained is 60 L/m².h at 50 bar for the S7 membrane. Although S7 has a rejection less than the CA control membrane it shows a better permeate water flux throughout the operation. At 10 bar, as a reference pressure for all the membranes, S1 has a permeate water flux of 2.6 L/m².h compared to the CA control membrane which has 1 L/m².h. However, S1 shows a decrease in rejection compared to the CA control by only 1%. On the other hand, during the operating process and increasing the SNPs in the nanocomposite membrane an enhancement of the permeate water flux until it reached the maximum in a membrane in S7 is observed. This is due to the formation of voids in the S7 membrane that facilitated the water transport.

Figure 7 (a) shows the performance of the CA- MSNPs nanocomposite membranes in terms of salt rejection out of 10,000 ppm NaCl feed under different operating pressures from 8 to 35 bar. The salt rejection of all membranes decreases with the pressure because of the concentration polarization phenomena. It is noticed that the rejection of MS7 increases with the operating pressure and reaches 91.6% at 34 bar. This may be due to the dense skin layer compaction which affected the rejection of the nanocomposite membrane ⁴⁴. Also, the viscosity may have played a role here, the MS7 membrane tends to be dense because of the presence of a high concentration of MSNPs (70 mg), which will lead to increasing the viscosity of the solution and consequently this membrane tends to have a sponge structure with the formed dense skin layer. Under continuous operation and increasing pressure, the skin layer may tend to be compacted and more impermeable to salt penetration ⁴⁴.

Figure 7 (b) depicts the variation of permeate water flux of CA- MSNPs nanocomposite membranes out of 10,000 ppm NaCl feed under different operating pressures from 8 to 35 bar. For all the nanocomposite and control membrane, as the operating pressure increases the permeate water flux increases. This is due to the increasing impact of the driving force of the penetration of water. It is noticed that for the operating pressure that ranges from 10 to 20 bar, the permeate water flux of both MS1 and the CA control membrane is almost constant. Then the permeate water flux of the CA control membrane increases until it reaches its highest value at 26.18 L/m².h at 28 bar. While the permeate water flux of the MS1 membrane increases also with the operating pressure to reach its highest value at 3.8 L/m².h at 26 bar. The MS3 membrane shows the highest permeate water flux among other nanocomposite membranes with a value of 35.7 L/m².h at 24 bar. Then the permeate water flux decreases to 32.13 L/m².hr at 26 bar and this behavior is attributed to the membrane compaction. MS5 and MS7 have permeated water flux less than that of MS3 due to the

agglomeration effect of the MSNPs in MS5 and MS7. The compaction of the membrane has a significant role where the polymer chains are forced to occupy a smaller total volume of space, under continuous and the increased pressure. In this case, the water penetration through the membrane is difficult and the salt permeability reduces as seen in MS7⁴⁴. For MS5 and MS7 membranes, the maximum permeate water flux values produced is 24.99 L/m².h at 22 bar and 5.33 L/m².h at 34 bar, respectively.

Figure 6: Salt rejection versus feed pressure of the membranes with different SNPs concentration (a). Permeate water flux versus feed pressure of membranes with different SNPs concentrations (b).

Figure 7: Salt rejection versus feed pressure of the membranes with different MSNPs concentration (a). Permeate water flux versus feed pressure of membranes with different MSNPs concentrations (b).

Conclusion

The properties of the nanoparticles and their preparation method have influenced the membrane properties and performance. SNPs prepared by the sol-gel method have influenced the CA membrane, the significant effect was the increase in permeate water flux of $1.6 \text{ L/m}^2\cdot\text{hr}$ more than the CA control membrane which had $11.6 \text{ L/m}^2\cdot\text{hr}$. The MSNPs addition enhanced the CA membrane desalination performance due to the hydrophilic amino group on its surface, but the inhomogeneous surface functionalization via post-synthetic grafting as it was seen in the TEM image has led to the agglomeration of the MSNPs and hence affected the performance in that way. The addition of MSNPs enhanced the permeate water flux but there was a tradeoff in salt rejection. But the interesting thing for the addition of both SNPs and MSNPs at their concentration of 0.07% at both membranes they endured a high pressure unlike the CA control membrane which ruptured at 28 bar, they ruptured at 50 bar, hence at this concentration of SNPs and MSNPs the mechanical properties were enhanced.

Declaration of interest statement

The authors declare that this work has not been done or published before and no competing financial interest.

Author contributions

Amira S. Mohammed Ali and Marwa Khalil contributed to ideas, experiment execution, and interpretation of the data and writing of the manuscript. Moataz Soliman, Sherif Kandil, and Shaker Ebrahim supervised the experiments and edited the manuscript.

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