Desalination of simulated seawater by purge-air pervaporation using an innovative fabricated membrane

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ABSTRACT

An innovative polymeric membrane has been invented, which presents a breakthrough in the field of desalination membranes. It can desalinate simulated seawater of exceptionally high concentration to produce a high flux of potable water with over 99.7% salt rejection (%SR) in a once-through purge-air pervaporation (PV) process. A set-up was constructed for conducting the desalination experiments and the effect of initial salt solution concentration (C_i) and pervaporation temperature (T_pv) on the water flux (J), %SR, separation factor, and pervaporation separation index were determined. The membrane was prepared by the phase-inversion technique, of a specially formulated casting solution consisting of five ingredients, after which the membrane was subjected to a post-treatment by which certain properties were conferred. The results confirmed that the salinity of the pervaporate was independent of C_i (all %SR above 99.7). The best result was at T_pv = 70 °C, where J varied from 5.97 to 3.45 l/m² h for C_i = 40–140 g NaCl/l, respectively. The membrane morphology was confirmed to be asymmetric. The contact angle was immeasurable, indicating the membrane to be super-hydrophilic.

Activation energies computed using Arrhenius law were, under all conditions investigated, less than 20 kJ/mol K.

Key words | activation energy, cellulose acetate, desalination, membranes, pervaporation

INTRODUCTION

Water is a vital resource of life. As access to fresh water becomes increasingly limited in many areas of the world, the ability to desalinate seawater is expected to take on greater significance. Recently pervaporation (PV) has been exploited as a promising membrane separation technology, which separates mixtures by preferential removal of one component from others present in the mixture due to its higher affinity with, and/or faster diffusion rate through, a non-porous membrane. In the PV process mass transfer takes place by vapour pressure difference, and the liquid mixture is maintained at atmospheric pressure on the upstream, while the permeate is removed on the other side as a vapour, due to the low pressure achieved by using either a vacuum pump or a carrier purge gas on the downstream (Kulkarni et al. 2004). PV has been extensively used for separation or concentration of mixtures of aqueous–organic liquids, e.g. dehydration of alcohols (Hu et al. 2012; Kuila & Ray 2013; Pandey & Shahi 2013). It has also been widely used in the separation of azeotropic mixtures (Luyben 2009), separation of water from organic solvent (Lu & Chen 2011), removal of trace organics from water (Knight et al. 1999), and separation of organic mixtures (Smitha et al. 2004). However, there are only limited studies on the application of this technology in water desalination (Kuznetsov et al. 2007; Hamouda et al. 2011; Cho et al. 2011; Swenson et al. 2012). PV of an aqueous salt solution can be regarded as separation of a pseudo-liquid mixture containing free water molecules and bulkier hydrated ions formed by dissociation of the salt in water (Kuznetsov et al. 2007). Membranes used in previous studies on PV desalination include sulphonated polyethylene (Korin et al. 1996), quaternized polyethylene (Korgold et al. 1996), polyetherimide and polyether ester (Quiñones-Bolaños et al. 2005) in which fluxes were very low, although the PV temperature was in the region of 40–82 °C. The feed temperature was a crucial parameter due to the increase in diffusivity and reduction in viscosity that occurs on heating. However, the inherent permeability of the membrane polymer is also extremely important (Xie et al. 2011).
Gong et al. (2014) successfully prepared super hydrophilic nano-hybrid membrane by in situ ultraviolet irradiation of titanium dioxide (TiO$_2$) nano-particles embedded in poly-electrolyte complexes, in which the TiO$_2$ precursor solution was dynamically filtered through a layer-by-layer-assembled poly(ethylene-imine)/poly(acrylic acid) multi-layer under a specific pressure. The permeate flux was, however, only 865 g/m$^2$ h. The preparation of hybrid polymer super hydrophilic films has not proven to be feasible, as the uniform dispersion of TiO$_2$ nano-particles in the polymer is very difficult (Gong et al. 2014). Also, novel inorganic–polymer hybrid membranes were prepared by Zhu et al. (2012) by incorporation of nano-TiO$_2$ into regenerated cellulose by phase inversion and were tested in the separation of caprolactam–water mixtures by PV.

The aim of the present work is to fabricate, by purge-air pervaporation, a novel hydrophilic cellulose-based membrane that is suitable for desalinating saline water of exceptionally high initial concentration and provides the highest possible flux and salt rejection (SR). The effect of solution concentration (C$_l$) and pervaporation temperature (T$_{pv}$) on the values of water flux (J) and %SR are to be evaluated. In addition, separation factor (a) and pervaporation separation index (PSI) are also to be computed. The morphology of the membrane is to be determined via examination by scanning electron microscopy (SEM), and Fourier transform infrared (FT-IR) spectra and the contact angle of fabricated membrane will then be determined. Finally, the activation energy ($E_a$) for permeation through the membrane is to be determined through application of the Arrhenius law.

**MATERIALS AND METHODS**

Cellulose acetate powder (CA) (product of Panreac, Egypt), acetone (A), dimethyl phthalate (DMP), and dimethyl formamide (DMF) (products of Adwic, Egypt), glycerol (G) and sodium chloride (products of El-Nasr Chemicals, Egypt) and sodium hydroxide (product of Chemajet, Egypt) were all used as received.

**Membrane preparation**

CA powder was added to a wide-mouthed glass-stoppered bottle, then dissolved in a mixture of solvents/additives. The mixture was initially mixed manually using a glass rod. The bottle was then stoppered tightly and shaken gently until complete dissolution had taken place, after which the mixture was left for 2 days for removal of air bubbles. The membrane was composed of CA, A, DMF, DMP, and G in definite proportions. The solution was cast into a membrane, on a smooth uniform glass plate of a casting assembly, using a doctor’s blade. The as-cast membrane was allowed to evaporate for exactly 0.5 minute, after which the glass sheet was immersed in ice-cold distilled water in a tray, for 1 hour for coagulation to take place. The membrane was subjected to complete deacetylation by steeping for 24 hours in an aqueous alkaline bath consisting of 1% sodium hydroxide and 20% sodium chloride. The membrane was then washed by repetitive rinsing in distilled water, and then stored in distilled water.

**Membrane characterization**

The cross-section morphology of the membrane was examined using SEM (JOELJSM 6360 LA, Japan). FT-IR spectra of the membrane was obtained by a VERTEX 70 spectrometer (Bruker Co., Germany). Water contact angle was measured to evaluate the hydrophilicity of the membrane surface. The static contact angles of water on the membrane surface were measured by a contact angle goniometer (JC-2000C Contact Angle Meter, Powereach Co., Shanghai, China). The average value of static contact angle on the membrane was calculated for at least five different locations on the membrane.

**Pervaporation testing**

A simple PV test cell was used in all the PV experiments. The cell consisted of two identical plexi-glass rectangular parts, 2.5 cm thick, 15 cm long, and 10 cm wide. Each part contained a compartment consisting of hexagonal grooves, 5 mm deep, with numerous lateral corrugations to induce partial turbulence of the flowing liquid on the feed side of the membrane. Before operation, the two cell halves were firmly held together such that the membrane completely separated the two halves. Rubber gaskets functioned as liquid seals. A schematic of the assembled unit is shown in Figure 1. It consisted of the PV test cell, a round-bottomed flask, an air blower, two small centrifugal pumps, an electric heater, a glass Liebig condenser, a thermometer, and a receiver flask. The membrane was placed in the test cell and the unit was connected. Two litres of heated NaCl solution were made to recycle through the top compartment of the cell. The pumps and the blower were operated and the permeate was collected in the receiver through the condenser through which ice-cold water was made to recycle. Recycling of the hot saline solution ensured constancy of its temperature adjacent to the membrane. The permeate was collected at different time intervals and then the concentration of
sodium chloride in the permeate was traced through conductivity measurements.

**PV membrane performance**

Performance of the PV membrane is determined by the values of $J$, %SR, $\alpha$, and PSI and $E_a$ as follows, in which:

$$J = \frac{Q}{A \cdot t}$$  \hspace{1cm} (1)

$$\%SR = \frac{C_i - C_f}{C_i} \times 100$$  \hspace{1cm} (2)

$$\alpha = \frac{Y_w}{Y_s} \times \frac{X_w}{X_s} \times 100$$  \hspace{1cm} (3)

$$\text{PSI} = J \times \alpha$$  \hspace{1cm} (4)

where $Q$ is the mass of the permeate collected in time $t$, $A$ is the effective membrane area, $C_i$ and $C_f$ are the initial and final solution concentration, $Y$ and $X$ are the weight of water in the pervaprate and feed, respectively; the suffix $w$ refers to water and $s$ refers to solute.

The dependence of flux on $T_{pv}$ could be expressed by Arrhenius law as follows and from which $E_a$ could be computed:

$$J = A_p \exp \left( - \frac{E_a}{RT} \right)$$  \hspace{1cm} (5)

where $A_p$, $R$, and $T$ are the pre-exponential factor, universal gas constant and feed temperature in absolute units, respectively. $E_a$ is determined from the plot of $\ln(J)$ versus $1/T$. A linear relationship is produced from which $E_a$ is computed from the slope of the straight line.

**RESULTS AND DISCUSSION**

In this work, the innovative membrane prepared by our group was initially examined for the morphology of its cross-section by SEM, FT-IR, and contact angle, and then $J$, %SR, $\alpha$, and PSI were determined. The variables $C_i$ and $T_{pv}$ were evaluated as to their effect on the membrane performance. $E_a$ was computed during PV, at different $C_i$ values.

**Characterization of fabricated membranes**

Figure 2 presents the cross-section micrograph of a perfect asymmetric membrane showing the skin layer (thickness 20–25 μm) with mini-pores which are responsible for rejecting the salt. The mini-pores gradually enlarge from the top surface to the underside of the membrane in which very large voids are apparent. This unique morphology allowed perfect rejection of salt by the skin layer, while offering high fluxes due to the porous structure of the remaining matrix.

The FT-IR spectra of the fabricated membrane are illustrated in Figure 3, from which it is clear that the membrane has OH functional group (3000–3750 m$^{-1}$). Besides the typical hydroxyl group which makes the membrane superhydrophilic due to the presence of three OH groups per anhydro-glucose unit, the additional peak at 1640–1650 m$^{-1}$
clarifies the adsorption of water, which not only assists in the make and break of hydrogen bonding of water but also causes easy permeation of water across the membrane. In addition, the peak at 1125 – 1170 m⁻¹ is attributed to C–O–C asymmetric stretching vibration (arabinose side chain), while the peak at 1040 – 1050 m⁻¹ is assigned to C–O stretching in C–O–C glycosidic bonds, both of which confirmed the existence of the ether linkages between the anhydro-glucose units and the asymmetric stretch of the arabinose side chain. It has also been verified that none of the solvents/additives were retained in the membrane matrix and that they were leached out during coagulation and post-washing.

It is generally accepted that contact angles indicate whether the surface is hydrophilic or otherwise, so that if the liquid molecules are strongly attracted to the solid molecules, then the liquid drop will completely spread out on the solid surface, corresponding to a contact angle of 0°. In this case, the surface is super-hydrophilic, which was the case of our membrane, which gave 0° contact angle. Accordingly, the result emphasizes the super-hydrophilic nature of our membrane.

Effect of Cᵢ on PV membrane performance

Effect of Cᵢ is presented in Figures 4–7. Figure 4 clarifies the effect of Cᵢ on J at various Tᵢ, from which it is clear that the highest flux (5.97 l/m² h) was obtained at Cᵢ = 40 g/l at Tᵢ = 70 °C. Moreover, the flux declined by about 1 l/m² h on increasing Cᵢ from the range of 34–60 g/l to about 140 g/l, at all Tᵢ tested, which indicates that the membrane, due to its super hydrophilicity, is only slightly affected by the salt concentration, which is an advantage. It is also observed that the minimum flux is almost 2 l/m² h at 50 °C, which is much higher than for other membranes cited in the literature for the dehydration of alcohols (Chapman et al. 2008; Hu et al. 2012; Kuila & Ray 2015; Pandey & Shahi 2013). It is also observed that the flux increases directly with Tᵢ as indicated in the figure.
However, it is noteworthy that our membrane was fabricated by a simple, single step, and cheap phase inversion technique by which the super-hydrophilic cellulose-based asymmetric membrane was generated. In contrast other membranes especially prepared for desalination by pervaporation were based on very sophisticated and complicated multi-stage fabrication methods involving electrospraying of PVA and electrospinning polyacrylonitrile superimposed on a polyethylene terephthalate layer to complete the composite membrane (Liang et al. 2014), and sulphochlorination and amination followed by quaternization of already made polyethylene hollow fibres (Korngold et al. 1996). Liang et al. (2014) illustrated that the fluxes of their membrane were 8.53, 7.24, and 5.57 l/m² h when the initial NaCl solution concentrations were 5, 35, and 50 g/l, respectively.

To this end, water fluxes of 2.5 and 0.39 kg/m² h were reported for feed concentrations of 100 and 5500 mg/l Na⁺ respectively by Swenson et al. (2012) when using several deposits of dense natural clinoptilolite, which exhibited both high zeolite content and essentially no macroporosity or inter-crystalline voids. These values are much lower than those obtained in our present work. Moreover, in a study by Xie et al. (2014) a hybrid organic–inorganic membrane was synthesized via a sol–gel route, in which the effects of heat treatment on the separation of aqueous salt solution in terms of J and %SR were determined. The authors used an aqueous salt solution containing only 2 g/l as the feed solution, yet the fluxes achieved were all less than 6 kg/m² h despite very dilute feed solution concentration being used. However, %SR approached 99.5. In addition, Ben Hamouda et al. (2011) prepared polyether block amide (PEBAX) membranes from commercial hydrophobic PEBAX 2533 granules, by dissolving the copolymer in dimethyl-acetamide at 100 °C. The obtained 20 wt% solution was cast on a heated glass plate at 60 °C, followed by evaporating the solvent at 60 °C in an oven, then drying under vacuum at 80 °C. It was demonstrated in their work that the water flux varied inversely with NaCl concentration, reaching 1.8 kg/m² h at 0.3 mol/dm³ which decreased to 1.22 kg/m² h at 3.5 mol/dm³. The method is energy-intensive, while in comparison, our membrane does not need any heating in its preparation. In addition the flux is much lower than in our case. Furthermore, Cho et al. (2011) claimed a high water flux of 1.9 kg/m² h at 69 °C by the application of pervapourative seawater desalination, using
a NaA zeolite membrane, which exhibited 99.9% SR. They attributed the high flux to the electrostatic interaction between the surface charge and the polar water in which the surface charge was positive in the seawater whereas in the pure water it was negative making the water flux in the seawater much higher than that in the pure water at $T_{pv}$, lower than 100 °C. The high rejections were attributed to a joint size exclusion/charge exclusion/surface evaporation mechanism. The higher water flux and low $E_a$ (37.39 kJ/mol) were explained by the reduced electrostatic interaction between the positive surface charge and the polar water. However, Cho et al. (2011) obtained a maximum flux of 6.111 kg/m²·h at a feed of only 0.135 M NaCl at pH = 5.79, which is a much lower $C_i$ than in our case. In this regard, in our present work, $J = 5.97$ l/m²·h was reached when $C_i$ was much higher (40 g/l), which indicates the high performance of our membrane, in desalinating highly concentrated seawater.

Figure 5 illustrates the effect of $C_i$ on %SR. It is observed that in all cases %SR is higher than 99.7, indicating that SR is independent of $C_i$ and $T_{pv}$, which proves that the membrane is of exceptionally high performance as regards flux as well as %SR. However, it is worth noting that it was initially intended to investigate the membrane performance in the range $C_i = 34$–60 g/l, which is typical for seawaters, but a few experiments were conducted at exceptionally high $C_i$ to test the membrane performance under drastic conditions. The results proved, to our surprise, from Figures 4 and 5, that the highest %SR ($\geq$99.9) was obtained under these high $C_i$ conditions, at which $J$ varied between 2 and 4 l/m²·h, which is a promising result that enables the membrane to be applied in membrane crystallization for the production of salt crystals plus extra fresh water, thus sustaining zero liquid discharge methodology, from reverse osmosis (RO) brines, and assisting in protection of the environment (Ji et al. 2010).

Figure 6 clarifies the effect of $C_i$ on the $\alpha$ at various $T_{pv}$. It is noteworthy that $\alpha$ is inversely proportional to $T_{pv}$ at extremely high $C_i$, reaching 30,667, at $C_i = 140$ g/l at 50 °C. This result may be attributed to the fact that at lower temperatures, lower salt contents are liable to diffuse with the pervaporate. This result is dramatic and has never been reached in all papers cited in the literature for membranes used in the dehydration of alcohols except for Gong et al. (2014) with $\alpha = 189,981$. However, at much lower $C_i$ in the range 30–60 g/l, $\alpha$ varies between 377 and about 5,168 at all $T_{pv}$ used. This point is of great interest in that this particular membrane may be used in desalinating the brines resulting from RO desalination units before dumping into the sea, to minimize pollution of the environment, obtain extra fresh water and concomitantly obtain much more concentrated brines which can yield salt crystals in crystallization ponds more rapidly. Moreover, membrane crystallization can be effected by using the membrane distillation (MD) technique with hydrophobic membranes to obtain salt crystals with additional fresh water, as a second step (Edwie & Chung 2013). In this way the combined desalination using our innovative membrane by PV followed by MD coupled with membrane crystallization resulted in zero liquid discharge.

The effect of $C_i$ on PSI is observed by inspecting Figure 7. It is noticed that PSI increases directly with $C_i$ at all $T_{pv}$, reaching 55,932 l/m²·h at 80 °C. This is an extremely high value. However, the value of PSI seems to be much more affected by the value of $\alpha$ rather than $J$, especially in our present case since $\alpha$ is much larger than $J$.

**Effect of $T_{pv}$ on PV membrane performance**

Effect of $T_{pv}$ on flux at different $C_i$ is illustrated in Figure 8, which indicates that $J$ increases with increase in $T_{pv}$, as expected. The figure also indicates that $J$ varies inversely with $C_i$. Accordingly, high $T_{pv}$ is preferred. Figure 9 clarifies the effect of $T_{pv}$ on %SR, which shows that extremely high SRs (over 99.7%) are obtained at all $C_i$ in the range 40–140 g/l. Once again, this result emphasizes the exceptional SR ability of our fabricated membrane, due to its distinct morphology.

The effect of $T_{pv}$ on the value of $\alpha$ is depicted in Figure 10. It shows that $\alpha$ is very high at almost all values of $T_{pv}$, ranging from 50 to 80 °C. Although varying widely,
however, $\alpha$ tends to be around 1,700 at lower $T_{pv}$ due to lower energy provided. Moreover, the present membrane has proven to provide exceptionally high %SR especially at the highest $C_i$ studied in the present work, as shown in Figure 9.

The effect of $C_i$ on PSI is illustrated in Figure 11, from which it is verified that the value of PSI is greatly dependent on $\alpha$ rather than $J$. The reader is asked to compare the general shape of the curves in the present figure to those in Figure 10 relating $\alpha$ with $T_{pv}$. It is noteworthy that the highest value of PSI achieved in the present investigation is identical to that obtained from Figure 11, namely 55,932 l/m² h.

**Activation energy**

Figure 12 illustrates an Arrhenius plot from which $E_a$ was calculated from the plot relating the flux as $\ln(J)$ and the reciprocal of absolute temperature ($T_{pv}$), the pre-exponential factor ($A_p$), gas constant, and $E_a$, the latter computed from the slopes of the lines. The sharp variation of $E_a$ with $C_i$ is clarified in Figure 13. $E_a$ values were 21.71, 19.83, 15.94, and 20.21 kJ/mol K at 40, 48, 50, and 140 g NaCl/l, respectively, from which it is clear that the values obtained are low to a great extent, which is translated into the great ease of permeation of vapour/water through our innovative membrane. An average value of $E_a$ at $T_{pv}$ in the range $C_i = 40$–140 g/l equals 19.42 kJ/mol K. For the sake of comparison, $E_a$ was found to be 37.39 kJ/mol K by Cho et al. (2014) for water transport through NaA zeolite membranes, whereas Xie et al. (2011)
found $E_a$ varied from 23.8 to 20.1 kJ/mol K when the salt concentration in the feed was increased from 0.2 to 5.0 wt% for hybrid organic–inorganic membrane. However, the lowest $E_a$ was when $C_i = 50$ g/l, which may be due to production of a reasonable quantity of vapour which easily permeates the super-hydrophilic membrane; at the same time the salt amount is not very high, such that it will block the vapour at the boundary layer, in the vicinity of the membrane’s surface. This explains why at higher $C_i$ than the aforementioned situation $E_a$ becomes larger, since the opposite of the previous reasoning takes place. In other words, at lower $T_{pv}$ the vapour generated is less, whereas at higher $C_i$ the salt mass fraction is great causing some concentration polarization as well as reducing the mass fraction of water flowing adjacent to the membrane’s surface, resulting in greater resistance to diffusion and permeation, despite the membrane being super-hydrophilic.

CONCLUSIONS

From the present work the following conclusions were arrived at:

1. An innovative super-hydrophilic membrane was fabricated by a facile method using the phase inversion technique.
2. The membrane consisted of cellulose regenerated from a casting solution comprising CA dissolved in definite proportions of A, DMF, DMP, and G.
3. The membrane micrograph of SEM examination proved the membrane to be of a unique asymmetric morphology with a thin rejection layer of minute pores, and a matrix of intact pores that gradually increase in size to form very large voids near the underside of the membrane.
4. The contact angle was unreadable (could not be read), demonstrating the membrane’s super-hydrophilicity.
5. Exceptionally high flux reaching 5.97 l/m² h and remarkable SRs above 99.7% were obtained.
6. The membrane resulted in extremely high %SR approaching 100 at high $C_i = 140$ g NaCl per litre of solution, which has not been reported in the literature before.
7. The flux increased directly with $T_{pv}$, while %SR was not affected by $T_{pv}$ and was at all times greater than 99.7, for $C_i$ up to 140 g/l.
8. Separation factors increased strongly with $C_i$, reaching 30,667 at $C_i = 140$ g/l; also, extremely high values of PSI were obtained (55,932 l/m² h at 80 °C and $C_i = 140$ g/l), which, to the best of our knowledge, has never been reported in the literature. Thus, the membrane is extremely suitable for desalinating exceptionally high salt-water concentrations by PV.
9. Activation energies, obtained from the Arrhenius equation, were under all conditions investigated less than 21.71 kJ/mol K, which proves the great ease of vapour permeation through the membrane.

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