Influence of surface charge and solution pH on the performance characteristics of a nanofiltration membrane

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Abstract

Acetyl cellulose nanofiltration membrane (NF) was manufactured by a dry/wet phase inversion process and studied on its performance characteristics for the electrolyte solutions NaCl, MgCl 2, Na 2SO 4 with a concentration range of 10^{-3}–10^{-2} N at various pH values. It was shown that the multivalent cation Mg^{2+} or sulfate anion SO_{4}^{2-} present in non-symmetrical electrolytes makes the membrane more positively or negatively charged as a result of their adsorption on the amphoteric pore surface, which greatly increases the membrane selectivity up to 85–95% for these electrolyte solutions. Meanwhile, with respect to 1:1 electrolyte solution NaCl the rejection capacity is low (R≤30–40%) because there is essentially no adsorption on the membrane surface. For a feed source made of the RO retentate the experimental data showed that the fabricated membrane possesses high rejection capacity for multivalent ions such as SO_{4}^{2-} (R=85.7%) and Mg^{2+} (R=93.5%) and low selectivity for monovalent salts such as NaCl (R=33.7%). The following salts rejection sequence with respect to symmetric and non-symmetric electrolyte solutions has been set up: R_{Na_2SO_4} > R_{NaCl} > R_{MgCl_2} and R_{MgCl_2} > R_{Na_2SO_4} > R_{NaCl} at pH≥7 and pH≤7, respectively. The fact that at pH values above 7 rejection of sodium chloride is higher than that of magnesium chloride, although its ion size is smaller than that of the latter, can be explained only by charge exclusion effect. From these results it can be concluded that Donnan exclusion effect is the predominant mechanism for salt removal by NF membranes.

1. Introduction

Development of integrally skinned asymmetric membranes by Loeb and Sourirajan in 1960s was a major breakthrough in membranes technology [1]. Among their numerous types nanofiltration membranes have become the most important advance in membranes technology due to their advantages such as low operation pressure, high flux, high retention of multivalent ions and organic molecules above 300 Da and relatively low operation and maintenance cost [2]. Furthermore, today the demands on membrane performance continue to increase as far as water quality requirements become more and more stringent. These requirements imply selective removal of certain dissolved species, such as hardness, iron, natural organic matter (NOM), pesticides, trihalomethane formation potential compounds (THMFP) and organic material which causes color, while leaving some level of salts in the water so that it does not become aggressive. This circumstance makes NF membrane the unique means that is capable to meet the above mentioned water quality demands.

At present nanofiltration is widely used in many fields of human activities such as pharmaceutical industry, drinking water treatment, environment protection and etc [3]. NF membranes are particularly suitable for the treatment of colored and acidic (sulfated) waters, which have long been a problem for the communities in southern regions of Vietnam.

The objective of this study is fabrication of cellulose acetate (CA) nanofiltration membranes by dry/wet phase inversion method and investigation of influence of surface charge and solution pH on their performance characteristics in the presence of multivalent Mg^{2+} and SO_{4}^{2-} ions in order...
to truly understand rejection mechanism and predict NF membrane performance for separation of different solubles.

2. Experimental

2.1. Materials, chemistry and membrane preparation

Cellulosic acetate (CA) purchased from Merck (Germany) was used as a membrane material. Acetone and formamide purchased also from Merck were used as a solvent and non-solvent, whereas pure water was used as a coagulation medium. Sodium chloride, sodium sulfate, magnesium chloride as well as hydrochloric acid and sodium hydroxide were supplied by Quangzhou CRF, China. Electrolytes solutions with different pH-values were prepared with ultrapure water produced by RO and EDI (electrodeionization) devices. Hydrochloric and sodium hydroxide solutions were used for pH adjusting.

The casting solution is a mixture of acetyl cellulose dissolved in acetone as a solvent and formamide as a non-solvent. The solution was kept at room temperature for 48 h to stabilize its homogeneous state and remove the bubbles.

The asymmetric NF membranes were fabricated by dry/wet casting method [4,5], whereby the polymer solution was poured onto a glass plate at ambient temperature, sheared by a special device and after certain evaporation time in air immersed into an aqueous bath, where it retained for at least one day. The thickness of manufactured membrane is about 100–200 μm.

2.2. Membrane performance measurement

The membrane performance tests were carried out in a permeation cell as shown schematically in Fig. 1. Rectangular membrane plates were mounted in a plastic membrane test chamber by a porous support and tightened by a silicon rubber frame. Effective permeation area of the membrane was 20×25 cm². Feed pressure was kept at about 4 bar, while permeate side was open to atmosphere. Experiments were carried out at ambient temperature (27 °C). The solute rejection and flux rate were measured using the electrolyte solutions NaCl, Na₂SO₄, and MgCl₂ at different pH values. Permeate was collected in a graduated cylinder for flux and other measurements. Conductivity (TDS) was measured using a conductivity meter, model HACH Sensions 156, while pH of the tested solutions was measured by a pH meter, model HACH DR/1500. Concentration of cations Na⁺ and Mg²⁺ were determined by AAS method, sulfate and chloride anions—by densitometry measurement using a multimeter, model Odyssey (HACH), and Morh’s volumetric method, respectively. Each set of data was determined as average of three replicates.

The retention and permeate flux were investigated as a function of working parameters such as ionic force, permeate flux, pH and nature of multivalent ions present in the solutions. Each experiment consists of a permeation of about 500–600 ml of solution at a fixed pressure. The permeate obtained at steady state was then analyzed. Since the concentration polarization could be considered as negligible according experimental conditions, the retention rate was calculated as

$$R_{obs} = \left(1 - \frac{C_p}{C_f}\right) \times 100$$ (1)

where $C_p$ and $C_f$ are the solute concentration in the permeate and the feed solutions, respectively.

The transport of the solute through NF membrane can be described using Spiegler–Kedem equation [6,7]

$$R_{obs} = \sigma \left(\frac{1 - \exp\left(-\frac{1-\sigma}{P_s} J_v\right)}{1 - \exp\left(-\frac{1-\sigma}{P_s} J_v\right)}\right)$$ (2)

where $\sigma$ and $R_{obs}$ are the maximum and observed rejection coefficients, respectively, $P_s$, the solute permeability, $J_v$, the water (permeate) flux.

For pressure driven NF membrane process the solute flux through the membrane can be described as the sum of a convective and a diffusive flux. Solute transport by convection takes place because of an applied pressure across the membrane, while a concentration difference on both sides of the membrane causes diffusive transport.

From Eq. (2) it can be seen that the observed rejection rate increases with increasing water flux and reaches a limiting value $\sigma$. The values of $P_s$ and $\sigma$ can be obtained from experimental data and by using Push equation [8,9] derived from Kedem–Katchalsky model

$$\frac{1}{R} = \frac{1}{\sigma} + \left(\frac{L_D}{L_p} - \sigma^2\right) \left(\frac{L_p \Pi}{\sigma J_v}\right) = A_1 + A_2 \frac{1}{J_v}$$ (3)
where $L_D$ represent the osmotic permeability coefficient, $L_p$, the pure water permeability and $P$, through-membrane pressure.

Plotting the experimental values of $1/R$ vs. $1/J_v$ one can find the intercept and the slope which permit to define $\sigma$ and $L_D$.

3. Results and discussions

Cross-sections of the prepared membranes were studied with scanning electron microscope (SEM) using a Japanese model JSM 5410 LV-JEOL scanning with potential of 15 kV in order to achieve magnification to 10,000×. Fig. 2 demonstrates SEM images of some NF membranes manufactured with different time of solvent evaporation in air. SEM photo (a) and (b) represent cross-sections of CA membranes obtained with the proper time of evaporation and with a time less than that, respectively. It can be seen that the fabricated membranes have the morphology with clear asymmetric pores and the thickness of the skin layer (active layer) depends on the proper time of evaporation and with a time less than that, respectively. Fig. 2. SEM images of NF membranes manufactured under different time of solvent evaporation in air: (a) Cross-section of the NF membrane obtained with an appropriate evaporation time; (b) Cross-section of the NF membrane obtained with evaporation time less than the appropriate one; (c) Surface section of the NF membrane skin layer; (d) A small site of the membrane surface with a skin layer stripped off.

To verify whether the fabricated membranes belong to the nanofiltration category we used the retentate effluent from RO filtration of tap water for preparing feed source, the composition of which was illustrated in Table 1. The analytical results of filtration process were also presented in this table. The experimental data show that the fabricated membrane possesses a high rejection for multivalent ions $\text{SO}_4^{2-}$ ($R = 85.7\%$) and $\text{Mg}^{2+}$ ($R = 93.5\%$) and low selectivity for monovalent salt NaCl ($R = 33.7\%$). These finding confirm that the fabricated CA membranes belong to the NF category.

Influence of surface charge and solution pH on the membrane selectivity with respect to binary electrolytes 1:1, 1:2 and 2:1 such as NaCl, Na$_2$SO$_4$ and MgCl$_2$ has been investigated. In Fig. 3 the rejection of a fabricated membrane versus three salts was plotted against the permeate flux $J_v$. At pH $\geq$ 7 the membrane showed the higher the rejection capacity and the lower the permeate flux. Photo image (c) represents a surface section of NF membrane skin layer, which shows rather uniform distribution of the nanosize-order pores. Photo image (d) demonstrates a small site of the membrane surface whose skin layer was stripped off and dense hollow cavities were revealed underneath.

| Analyte         | $\text{NH}_4^+$ (mg/L) | Hardness (mg/L) | TDS (mg/L) | $\text{Cl}^-$ (mg/L) | $\text{SO}_4^{2-}$ (mg/L) | $\text{Na}^+$ (mg/L)* | $\text{Mg}^{2+}$ (mg/L) |
|-----------------|------------------------|-----------------|------------|----------------------|--------------------------|------------------------|-------------------------|
| Feed source     | 0.82                   | 310             | 388        | 56                   | 14                       | 68                     | 42.3                    |
| Permeate        | 0.70                   | 62              | 115        | 14                   | 2                        | 45.1                   | 2.76                    |
| Rejection (%)   | 13.6                   | 80.0            | 70.4       | –                    | 85.7                     | 33.7                   | 93.5                    |

Table 1
Performance characteristics of a cellulose acetate membrane manufactured by dry/wet phase inversion method. Through-membrane pressure, 60 psi; permeate flux, 2.30 L/m$^2$ h bar; cross-flow rate, 24L/h; $T$, 27 °C.
following salt rejection sequence: $R_{\text{Na}_2\text{SO}_4} > R_{\text{NaCl}} > R_{\text{MgCl}_2}$, the same as found in other works [10–12]. In Fig. 4 the inverse rejections of these salts were plotted as a function of $1/J_V$. The obtained linear relationship between the inverse rejection and inverse permeate flux confirmed the validity of the Kedem–Katchalsky model for the fabricated membrane and intercept permits to calculate maximum rejection $\sigma$ (Eq. 3), the values of which were found as follows: $\sigma_{\text{Na}_2\text{SO}_4} = 0.955; \sigma_{\text{NaCl}} = 0.598$ and $\sigma_{\text{MgCl}_2} = 0.514$. The experimental data presented in Figs. 3 and 4 proved that the observed decrease in rejection selectivity from asymmetric 1:2 to symmetric 1:1 and then to asymmetric 2:1 electrolytes could be explained evidently only by the surface charge exclusion effect. In NaCl solution, commonly used to characterize the RO membrane, $R$-values did not exceed 0.6, indicating low selectivity of the CA membrane for NaCl separation. In sodium sulfate solution retention coefficients easily attained highest values with increasing permeate flux. This is because of strong adsorption of two-charged $\text{SO}_4^{2−}$ on the membrane pores surface resulting in increase of Donnan exclusion. Thus the electrochemical mechanism of rejection is responsible for the improvement of membrane selectivity up to more than 95% [11,12]. In the case of 2:1 electrolyte solutions MgCl$_2$, there is an inverse effect, when a significant reduction of selectivity takes place. It is known that at low concentration $C_I \leq 10^{-2}$ N, CA membrane is negatively charged, so that positively charged $\text{Mg}^{2+}$ ion freely passes through the membrane, hence the membrane selectivity is lowest. Obviously, at higher concentration the rejection starts to increase because $\text{Mg}^{2+}$ ions start to be adsorbed on the pores surface resulting in higher positive charge, hence in stronger rejection.

Fig. 5 illustrates the membrane selectivity with respect to NaCl, $\text{Na}_2\text{SO}_4$ and MgCl$_2$ versus solution pH. By virtue of the fact that CA membrane possesses amphoteric properties, at decreased pH the dissociation of the functional carboxyl groups is suppressed and simultaneously protonation of the amine groups takes place resulting in change of charge signs and growth of positive charge on the membrane pores surface, enhancing retention of $\text{Mg}^{2+}$ ions and diminishing that of $\text{SO}_4^{2−}$ anions. Contrastingly, the increase of pH values favors dissociation of the functional carboxyl groups and deprotonation of the amine groups resulting in the growth of membrane negative charge, thus enhancing and reducing rejection of sulfate and magnesium ions, respectively. In the case of symmetric 1:1 NaCl solutions, there is only insignificant change in rejection of the electrolyte and the charge effects do not play a role because there is essentially no adsorption on the membrane pores surface. Evidently at higher pH the pores surface becomes more negative (due to dissociation of the functional carboxyl groups), therefore $\text{Na}^{+}$ ions more freely pass through the membrane and so reduce its selectivity with respect to NaCl. On the other hand, at low pH values protonating reaction of the amine groups takes place and increases the positive charge of the membrane and so hinders $\text{Na}^{+}$ ions to pass through, thus enhances rejection capacity to the solute.

**4. Conclusion**

Cellulose acetate membranes have been manufactured by a dry/wet phase inversion process and studied on their performance characteristics for the electrolyte solutions NaCl, $\text{Na}_2\text{SO}_4$ and MgCl$_2$ at various pH values. It was shown that multivalent ions $\text{Mg}^{2+}$ and $\text{SO}_4^{2−}$ present in non-symmetric electrolytes make the membrane more positively or negatively charged as a result of their adsorption on the amphoteric pores surface, greatly enhancing the membrane selectivity for these electrolyte solutions. The following salts...
rejection sequence has been set up: $R_{\text{Na}_2\text{SO}_4} > R_{\text{NaCl}} > R_{\text{MgCl}_2}$ at pH $\geq 7$ and $R_{\text{MgCl}_2} > R_{\text{Na}_2\text{SO}_4} > R_{\text{NaCl}}$ at pH $\leq 7$. The fact that rejection of sodium chloride at pH above 7 is higher than that of magnesium chloride, although its ion size is smaller than that of the latter, can be explained only by charge exclusion effect. From the results it can be concluded that Donnan exclusion effect is the predominant mechanism for salt removal by NF membranes.

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