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Enhanced conductivity of monovalent cation exchange membrane with Chitosan/PANI composites modification

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The application of electrodialysis (ED) for desalination requires the use of natural seawater or river water, in which the presence of multivalent ions is inevitable. This currently limits the process performance. Membranes with selectivity for monovalent ions may overcome this limitation. This study used the method of electro-deposition with chitosan/aniline polymer as a modification material to coat a commercial anion exchange membrane in view of obtaining selectivity for monovalent ions. Chitosan was grafted with polyaniline through copolymerization using ammonium persulphate as an initiator. FTIR spectra of the composites revealed that there was a strong interaction between substituted polyanilines and chitosan. The method was used to prepare a series of membranes by varying the aniline ratio and polymerization time. The chemical composition and surface properties of the membranes were characterized by Fourier transform infrared (FTIR) spectroscopy and Scanning electron microscopy (SEM), respectively. Current–voltage curves and resistance were measured to characterize the transport properties of membranes and the membrane conductivity. The results show that the membrane conductivity increases with the aniline ratio; the selectivity initially increases with the aniline ratio, and then decreases again. The optimum modification condition was electrodeposition time 4 h with an aniline ratio of 0.4. Using the modified membrane in concentrated sea water, it was demonstrated that the modified membrane has an excellent selectivity towards monovalent cations.

Water impact

Electrodialysis is a promising technology for water desalination, however, the presence of multivalent ions may limit the process performance. In electrodialysis, the monovalent anion selectivity is a very important property of cation exchange membranes to remove multivalent ions from feed solutions and it can also protect the system against the precipitation of scalants. This study used the method of electro-deposition with chitosan/aniline polymer as a modification material to coat a commercial anion exchange membrane in view of obtaining selectivity for monovalent ions to overcome the limitation. At the same time, the resistance of membranes is under control. The results show that the membrane conductivity increases with the aniline ratio; the selectivity initially increases with the aniline ratio, and then decreases again. This study encourages and lays a foundation for preparation and application of monovalent cation exchange membrane.

1. Introduction

Electromembrane technology has been widely used in water desalination and concentration. As the core of any application of electrodialysis, ion exchange membranes play a key role in the progress of this technology.¹ Selective ion exchange membranes for the removal of specific valuable ions from waste solutions may allow for new applications for metals recovery, production of acids and bases, and the separation of ions with the same charge from mixed electrolyte solutions.² The presence of heavy metals in

wastewaters causes many problems due to their persistence in the environment, which also entails a high risk of heavy metal accumulation in the body tissues of living organisms due to their high solubility in the aquatic environments.³ Heavy metal removal can be achieved by conventional processes such as chemical precipitation, solvent extraction, ion exchange, adsorption and metal oxides.⁴ Despite being efficient and cheap, there are still some disadvantages in these methods such as incomplete removal of heavy metals, high energy consumption, slow removal rates and generation of toxic sludge.⁵ In the search for less expensive and more efficient methods, membrane separation processes have been paid much attention to. In electrodialysis, the monovalent anion selectivity is a very important property of cation exchange membranes to remove multivalent ions from feed solutions and it can also protect the system against the precipitation of scalants.

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Polyaniline (PANI) is an intrinsically conducting polymer with specific interest for ion exchange membranes.⁶ Because of excellent stability, redox reversibility, electrical conductivity and unique electrochemical property, PANI has been studied and applied in secondary batteries, biosensors, anti-static packaging materials, gas sensors, actuators, field effect transistors, memory devices and corrosion protection.⁷ PANI can be polymerized in the membrane matrix by chemical oxidation. Integration of PANI in the structure of an ion exchange membrane may allow for separation based on the size of the molecules or ions, their charge and charge density.⁸ It can also modify the hydrophobic and hydrophilic nature of ion-exchange membranes. Nagarale et al. prepared composite membranes by chemical polymerization of a thin layer of polyaniline (PANI) in the presence of a high oxidant concentration on a sulfonated cation-exchange membrane (CEM) and quaternary aminated anion-exchange membrane (AEM). The results showed that it is possible to separate different electrolytes using PANI composite ion-exchange membranes.⁹ Kumar et al. used polyaniline modified organic-inorganic hybrid cation-exchange membranes for the separation of monovalent and multivalent ions, and observed that the PANI modified membranes were more selective for Na^+ in comparison to Zn^{2+} and Al^{3+} .¹⁰ Sivaraman et al. used electrochemical modification with polyaniline to improve the permselectivity of cation exchange membranes.¹¹

In addition to the use of PANI, natural polymeric materials are gaining great interest in the modification of membrane to the preparation of monovalent membranes. Chitosan is a natural polymer, a polysaccharide containing the functional groups -OH and - NH_2 , with promising properties such as its good film-forming ability, chemical inertness, high mechanical strength, hydrophilicity, biodegradability, bio-compatibility, nontoxicity and antibacterial properties. Therefore, chitosan has been widely used as a matrix for drug delivery systems, for the removal of heavy metals and transition metals and dyes. However, its application in monovalent membrane is rare. Wang et al. endowed a conventional cation exchange membrane with monovalent selectivity by photo-induced covalent immobilization and self-crosslinking of chitosan. The experimental results have shown that the modified method was promising due to its facility, low cost and efficiency.¹²

Recently chitosan/PANI has been synthesized and widely used in electrode materials,¹³ industrial wastewater treatment,¹⁴ gas sensing,¹⁵ thermal and electrode stability enhancement,¹⁶ and hydrogels.¹⁷ Remarkably, it has not been used for modification of ion exchange membranes. In this paper, a procedure to synthesize a monovalent cation exchange membrane based on these suggestions is reported. Substituted polyaniline/chitosan composites were chemically synthesized by using ammonium peroxydisulfate as oxidant and characterized by FTIR. The modified membrane was characterized with FITR and SEM, and the membranes were applied in electrodialysis to assess their performance.

2. Experiment

2.1 Materials

Table 1 Characteristics of the cation exchange membranes used in this study

Membrane type	Thickness (μm)	IEC (mmol g^{-1})	Area resistance (Ωcm^2)	Water uptake (%)	Transport number (%)
JAM-II-5	160-230	2.0-2.9	1-3	35-43	95-99

Cation exchange membranes (JAM-II-5) used for modification were supplied by Beijing Tingrun Membrane Technology Development Company. Table 1 lists selected properties of the membranes tested in this study. Chitosan was purchased from Aladdin (Shanghai, China). Aniline is provided by Shanghai Linfeng Chemical Company (Shanghai, China). The simulated seawater was provided by China National Sait Industry Corporation (China). Other chemicals, including $(\text{NH}_4)_2\text{S}_2\text{O}_8$, glutaric dialdehyde, NaCl, HCl, H_2SO_4 , NaOH, Br_2 , ZnSO_4 , ethylene diamine tetraacetic acid (EDTA), K_2SO_4 , toluene, sodium hypochlorite, thionyl chloride and methyl alcohol, were analytical grade and used directly without any purification. Indicators, phenolphthalein, Eriochrome black T (EBT) and methyl red, were all newly prepared and stored at low temperature.

2.2 Synthesis of PANI/chitosan composites

In a typical procedure, an aqueous solution of chitosan was prepared by dissolving 1 g of chitosan in 200 ml of aqueous acetic acid (2 wt%) for 24 h and then adding substituted aniline monomer in 200 ml 1 M HCl to form a homogeneous solution. An ammonium peroxydisulfate solution in 1 M HCl (APS, 20 g/L) was dropped into the above solution with vigorous stirring under N_2 atmosphere. The molar ratio of oxidant/monomer was 1.2. The polymerization was carried out for 10 h at room temperature. After that, the solution was centrifuged for 10 min at 10000 rpm. The precipitate was then redispersed in 2 wt% acetic acid and washed with deionized water, and centrifuged again. The washing procedure was repeated 3 times. The final composite was dried at 50°C for 24 h. The PANI/chitosan composite was synthesized using a range of ratio's. The reaction process is shown in Fig. 1.

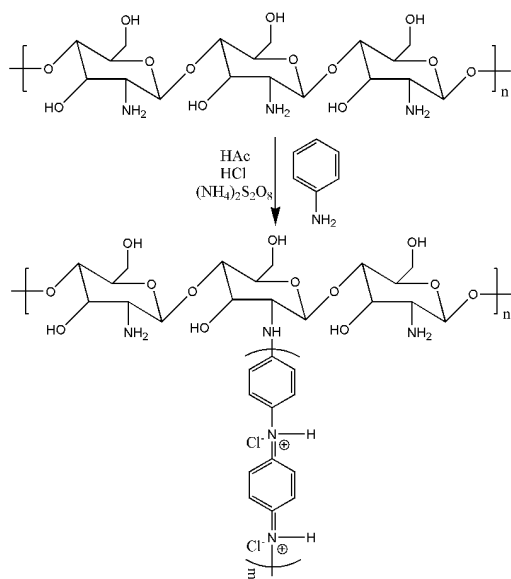


Fig.1 The polymerization reaction of chitosan and aniline

2.3 Preparation of the monovalent cation exchange membrane

Before the experiment, the cationic exchange membrane was rinsed with deionized water in an ultrasonic bath for 15 min to remove excess sodium chloride. The modification of the cationic exchange membrane was carried out in a two compartments cell separated by placing a CEM between the cathode and the anode. Compartment 1 was filled with PANI/chitosan solution in 1 M HCl, while compartment 2 was filled with 1 M HCl. A stainless steel electrode was applied as anode and a titanium electrode coated by ruthenium as cathode. The duration and current density for electrodeposition was set to 50 mA/cm². To avoid concentration polarization, mechanical stirrers were placed in each compartment. After electrodeposition, the modified membrane was dried at environmental conditions. Because the modified layer was attached to the surface of the membrane by physical adsorption, a crosslinking progress was induced to increase the stability. The dried membrane was immersed in a 500 mL glutaraldehyde solution at 35°C for 24 h. The obtained membrane was stored in 0.1 M NaCl for further use.

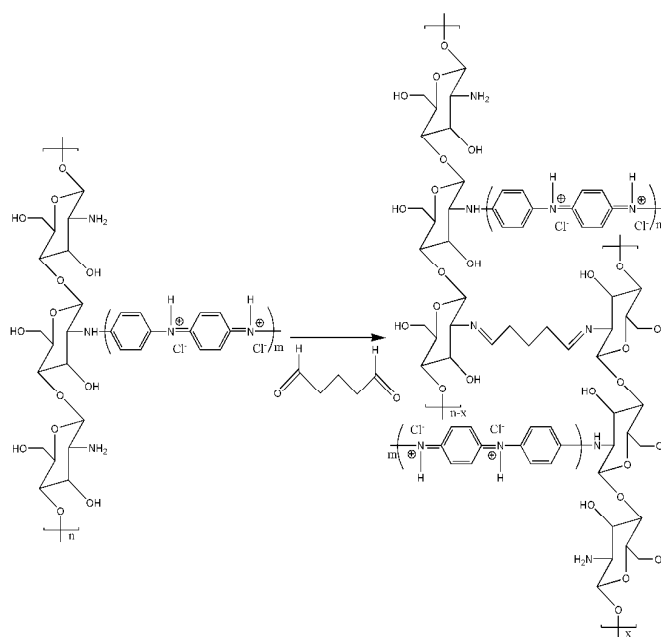


Fig. 2 The chemical reaction of crosslinking by glutaraldehyde

2.4 Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR)

The changes in the modified and unmodified anion-exchange membrane surface morphology were observed by scanning electron microscopy (S-4700 Hitachi, Tokyo, Japan). SEM images of membranes were taken after being dried in a vacuum oven, and then coated with gold. FTIR spectra measurements were taken to provide information about the chemical structure of the unmodified and modified membranes. The chemical composition of the membrane surface was analyzed by FTIR (Nicolet 6700). Membrane samples used for FTIR analysis were dried at 25 °C under vacuum before characterization. The FTIR spectra analysis was done using a Nicolet 6700 spectrometer. Scans were taken with 4 cm⁻¹ resolution between 500 and 4000 cm⁻¹.

2.5 Diffusion dialysis measurement and current-voltage curves

Conductivity-time curves were used to determine the concentration of ions through diffusion. These curves reflect the ion concentration directly. Here, diffusion dialysis experiments with a 1 M NaCl diluted compartment cell and an initial concentrated compartment cell of deionized water were carried out. The concentration gradient drives ions across the membrane; the effective membrane area was 25 cm². A two-compartment cell was applied for the current-voltage curve measurements. Each compartment had a volume of 200 mL, and the two compartments were separated by the membrane. The current through the electrodes was supplied by direct current power supply and the electrical current was recorded by an ATEN APS3005Dm potentiostat/galvanostat. The potential difference between the two sides of the membrane was measured by a multimeter (Mode: LINI-T UT39A) equipped with two platinum filaments located at 1.0 mm

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approximately in front of each membrane surface. Mechanical stirrers were placed in each compartment.

2.6 Resistance measurements

The experiments were taken in a four-compartment cell, 0.5 mol/L Na_2SO_4 was chosen as electrode solution and 0.5 mol/L NaCl was used as test solution. A multimeter linked with Ag/AgCl electrodes was applied to detect the voltage between the membranes. When the current is 0.4 A, the voltage U can be measured by the multimeter. The voltage U_0 for a blank experiment when there is no membrane was measured as well. The membranes were immersed in 0.5 mol/L NaCl for 30 min before each experiment. The area of the membrane was 7.065 cm^2 . The resistance of the membrane can be calculated according to the following equation:

$$R = \frac{U - U_0}{I} \times S \quad (1)$$

where R is the resistance of the membrane, and I is the current applied in the experiments. The average value of at least three measurements were made as the resistance.

2.7 Electrodialysis experiments

The selectivity of the membranes can be evaluated by electrodialysis. A series of electrodialysis experiments was conducted to measure the selectivity of the membrane samples. The electrodialysis experiments were performed in a four-compartment cell (effective membrane area: $5 \text{ cm} \times 5 \text{ cm}$; solution volume: 200 mL), as described before.¹⁸ The dilute compartments were fed with 200 mL 0.5 M H_2SO_4 while the concentrated compartment salt solution was 15 g/L ZnSO_4 in 0.5 M H_2SO_4 . 0.5 M K_2SO_4 solution was selected as electrode solution in order to avoid dissolution of stainless steel. A stainless steel electrode was applied as anode and a titanium electrode coated by ruthenium as cathode. The duration and current density for electrodialysis was set to 100 min and 50 mA/cm^2 , respectively. The leakage of Zn^{2+} ion can be measured according to the following equation:

$$M_{\text{leakage}}^{n+} \% = \frac{M_{\text{con-cell}}^{n+}}{M_{\text{mass}}^{n+}} \quad (2)$$

where $M_{\text{con-cell}}^{n+}$ is the mass of M^{n+} in concentrated cell, and M_{mass}^{n+} is M^{n+} in the concentrated and diluted cell. The concentration of Zn^{2+} ion was determined by titration using EDTA. Ca^{2+} , Mg^{2+} , Al^{3+} were determined by Atomic Absorption Spectrophotometry (Tas-990, Beijing, China).

When the membranes were applied at sea water concentration, the concentrated and dilute compartment were both fed with 200 mL sea water; the duration and current density remained unchanged.

3. Results and discussion

3.1. The modification of commercial CEMs

The electrodeposition method to modify CEMs by PANI/chitosan composites is based on the fact that PANI/chitosan composites with positive charges migrate directly towards the cathode when a direct current field is present. Due to the high molecular weight of the composite and the small pore size of the membrane, the PANI/chitosan composites are not transported across the membranes and finally deposit on surface of the membrane. The formation of the modified layer was controllable to some extent through the adjustment of parameters such as electrodeposition time and current density.¹⁹

The membrane surface morphology observed by SEM is displayed in Fig. 3. From these pictures, it can be seen that the membrane surface becomes smoother after modification compared to the unmodified membrane. Additionally, small pores previously appearing on the surface of unmodified membranes were not observed anymore on surface of modified membrane, which means that these pores might be covered by the modified layer. These experiments confirm the existence of a PANI/chitosan composite layer.

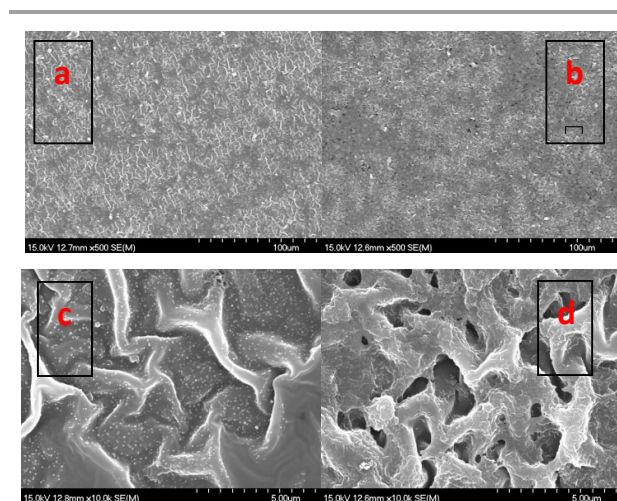


Fig. 3 SEM micrograph of pristine and modified membrane

(a) unmodified membrane magnified 500 times. (b) modified membrane magnified 500 times. (c) unmodified membrane magnified 10000 times. (d) modified membrane magnified 10000 times.

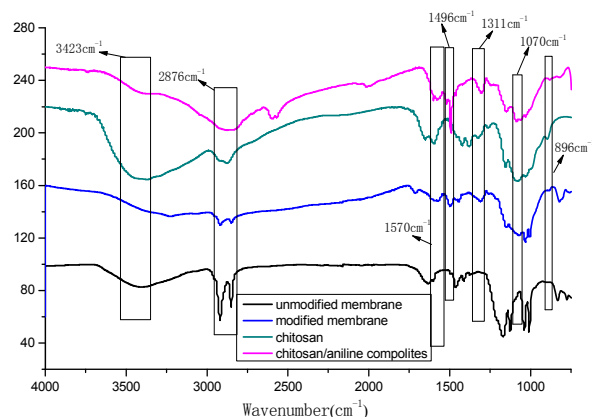


Fig. 4 FTIR of PANI/chitosane hybrid composites and membranes before and after modification

The FTIR spectra of the PANI/chitosan composites are shown in Fig. 4. The spectrum shows a broad band at 3423 cm^{-1} that can be assigned to the stretching vibration of OH and NH groups. The bands at 2876 cm^{-1} correspond to CH stretching of aliphatic groups.¹⁵ The main characteristic absorption peaks of chitosan/PANI composites at 1596 cm^{-1} , 1470 cm^{-1} , 1311 cm^{-1} , 1070 cm^{-1} and 896 cm^{-1} were attributed to C=C stretching of the quinoid ring (Q, representing quinoid ring), C=C stretching of the benzenoid ring (B, representing benzenoid ring),¹⁶ aromatic C-N stretching,²⁰ the mode of N=Q=N, in-plane, and out-plane vibrations of multi-substitution on the benzene ring and deformation of the benzene ring. The FTIR spectrum of chitosan/PANI composites shows all the significant characteristic bands of both chitosan and PANI with shifts in the position of the bands.

The FTIR spectra of the membranes after modification are similar to those of PANI/chitosan composites. The intensity of the absorption band at 2876 cm^{-1} and 1173 cm^{-1} decreases after the modification with PANI/chitosan composites. The main characteristic absorption peaks of PANI/chitosan composites at 1596 cm^{-1} , 1470 cm^{-1} , 1311 cm^{-1} , 1070 cm^{-1} and 896 cm^{-1} can also be observed from the FTIR of the modified membrane. This confirms the occurrence of electrostatic interactions between the positively charged thin layer and the negatively charged groups in the membrane matrix.²¹

3.2 Diffusion dialysis and current-voltage curves experiments

It was found that the conductivity of the concentrated cell increases with time because of the diffusion of NaCl from one compartment to the other compartment (Figure 5). It is noticeable that while the modified membrane was used, the conductivity of the concentrated cell increased more slowly. This is attributed to the formation of the modified layer which hinders the transport of NaCl across the membrane.

Some problems, such as the increase in membrane resistance and the decrease in limiting current density, were frequently

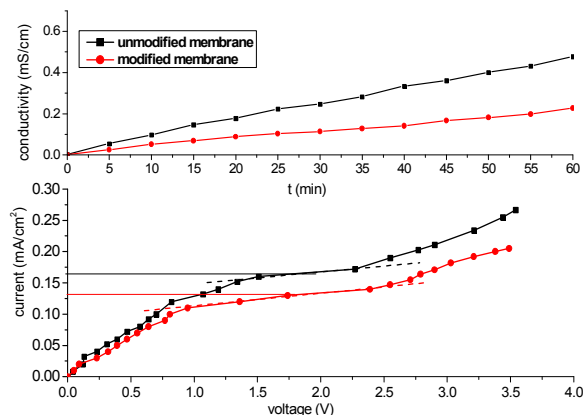


Fig. 5 Conductivity-time curves and current-voltage curves of unmodified, modified membrane in 0.25 M HCl

encountered during the membrane modification for endowing monovalent selectivity. Accordingly, the current-voltage curve was investigated to study the interfacial phenomena of the modified membrane. A linear part in the current-voltage curves was observed at low current densities. This is usually denoted as the "ohmic region" referring to the electrical resistance to ion transport across the solution-membrane interface and inside the IEM.¹ The region following the linear region is the limiting current region. In this region the current density varies slightly with the increase of the potential. The limiting current resistance (R_{lim}) is estimated by taking the current values at the inflection point of the curve in the limiting current region. The region where electroconvection occurs is the electro-convective region. When the slope of the current-potential curve increases drastically again, the electro-convective region is reached. The currents in this region are larger than the limiting current.

The increase of the Ohmic resistance and electro-convective resistances is ascribed to the fact that the modified layer hinders the transport of ions through the membrane. It can also be seen that the limiting current measured for an unmodified membrane is higher than for a modified membrane. This is due to the fact that the formation of the modified layer enhances concentration polarization. Furthermore, the region of limiting current is expanded. A longer plateau length may arise from the following reasons. Firstly, the multivalent ion cannot permeate the modified membrane. This results in an expansion of the area of the retention layer. Only when a higher current is applied, the retention layer can be damaged. Secondly, as can be concluded from the SEM micrographs, the modified membrane becomes smoother. Rubinstein et al. estimated that a 10% increase in the surface roughness results in a 30% decrease of the plateau length. Since the surface roughness decreases, the plateau length should indeed increase here as well.²²

3.3 Resistance measurements of the modified membranes

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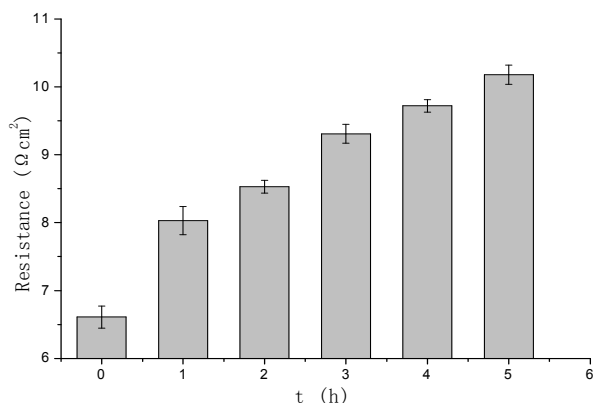


Fig. 6 Electrical resistance of the modified membrane as a function of deposition time while aniline content is 0.4

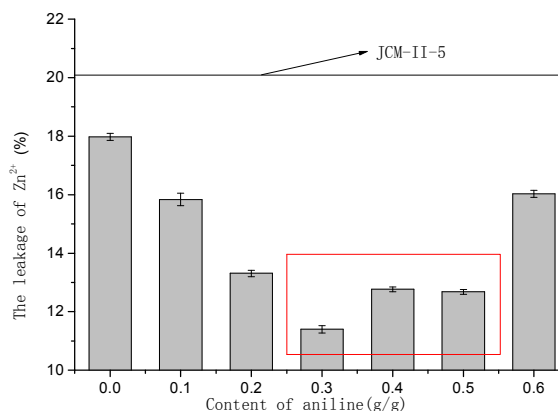


Fig. 7 Effects of the content of aniline on leakage of Zn²⁺

Fig. 6 shows that the immobilization of the chitosan/PANI composite results in an increase of the membrane resistance. Generally speaking, this should be attributed to the presence of the cationic layer which hinders the transport of cations across the modified membrane.²⁵ Moreover, it can be observed that the membrane resistance was increased remarkably after deposition for different periods of time. The longer the deposition time, the higher the resistance the membrane. This is due to the fact that with time the modified membrane becomes thicker, enhancing the permselectivity and the electrostatic repulsion phenomenon, which may also result in a high resistance. From the slope of the curve, it is obvious that the modified membrane resistance increased slowly with time.

3.4 Electrodialysis experiments

3.4.1 Determination of the content of aniline

In Fig. 7, the effect of the content of aniline on leakage of Zn²⁺ is discussed. The black line represents the unmodified membrane, with an ion leakage of 20.2%; the zero value of aniline content represents the chitosan modified membrane. The leakage of Zn²⁺ is lower when the content of aniline is zero, due to the size exclusion effect. With the increase of the aniline content, the leakage of Zn²⁺ decreases substantially because of the formation of side polyaniline chains on the chitosan. When the content of aniline is in the range of 0.3–0.5, the leakage of Zn²⁺ remains at a stable level of about 12%. In this range, a higher content of aniline may make the electrostatic repulsion effect more expressed, but the pore size becomes larger due to the decrease in the content of chitosan. The size effect and the electrostatic repulsion effect are mutual constraints, so that the leakage is stable. When the content of aniline is higher than 0.5, the detachment of the modified layer becomes problematic. In these conditions, the chitosan/PANI composite is brittle and the amount of chitosan is not sufficient to support the modified layer.

Table 2 The leakage of Ca²⁺ and Mg²⁺ when sea water was used in electrodialysis

	The concentration of Ca ²⁺ in the diluted cell (mg • kg ⁻¹)	Leakage of Ca ²⁺ (%)	The concentration of Mg ²⁺ in the diluted cell (mg • kg ⁻¹)	Leakage of Mg ²⁺ (%)
Unmodified membrane	811.5	57.8	116.94	85.4
Modified membrane	1263.41	34.3	598.34	25.3

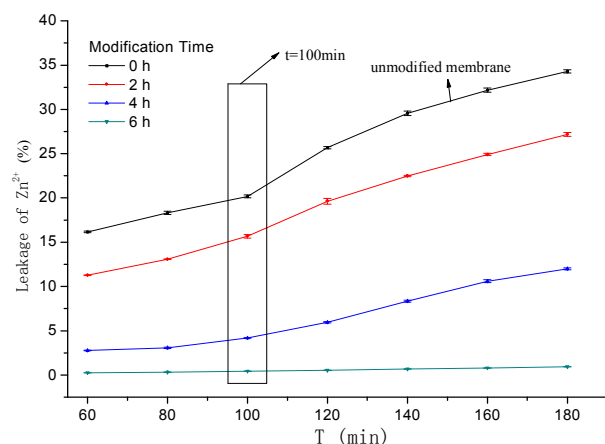


Fig. 8 The leakage of Zn^{2+} during the electro dialysis

3.4.2 Determination of electro-deposition time

In Fig. 8, the leakage of Zn^{2+} during electro dialysis is shown. The leakage of Zn^{2+} at different times was detected. It can be seen that the leakage of Zn^{2+} increases with time, and the membrane has a stable performance. When the time was fixed at 100 min, it can be concluded that with the increase of electro-deposition time, the leakage of Zn^{2+} during the electro dialysis becomes smaller. This is due to the fact that the modified layer has a significant effect on the transport of ions. When the modification time is 6 h, it can be seen from the Fig. 8 that Zn^{2+} (nearly) cannot permeate anymore through the membrane. In this step, the modified layer may be too thick, so that the membrane was turned into a bipolar membrane. Thus, the optimum electro-deposition time is 4 h.

3.4.3 Sea water concentration

Table 2 shows the leakage of ions when the simulated seawater (Ca^{2+} : 1823.5 $\text{mg}\cdot\text{kg}^{-1}$; Mg^{2+} : 806.1 $\text{mg}\cdot\text{kg}^{-1}$, conductivity: 59.4 mS/cm , pH 6.65) was applied. The time of electro dialysis was 100 min, current density was 50 mA/cm^2 .

As shown in Table 2, both the leakage of Ca^{2+} and the leakage of Mg^{2+} decreased. The leakage of Ca^{2+} decreased from 57.8% to 34.3% and the leakage of Mg^{2+} decreased from 85.4% to 25.3%. The leakage of Mg^{2+} diminished by about 60.1%, and that of Ca^{2+} decreased much less, by 23.5%. If only electrostatic exclusion is taken into consideration, the selective separation between Ca^{2+} and Mg^{2+} ions by modified CEMs should be the same. However, the measured results indicate that it is different. This may ascribed to the fact that the small pore size of the modified layer can affect the transport of ions. The hydrated Mg^{2+} ion has a radius of 0.429 nm, whereas the hydrated Ca^{2+} ion has a radius of 0.412 nm.²³⁻²⁴ The larger the ion, the more sterical hindrance it experiences when transported through the membrane. During the transport of the two ions through the CEM, the smaller Ca^{2+} encounters less sterical hindrance than Mg^{2+} while the electrostatic repulsion is equal. Therefore, the different selectivity of Ca^{2+} and Mg^{2+} ions may result from a combined effect of an electrostatic and steric barrier.

4. Conclusions

In this article, membranes modified by chitosan/PANI composites were developed and shown to be effective for ion exchange membranes. The results demonstrate that transport of divalent cations was affected by the presence of the modified layer. Current-voltage curves and diffusion dialysis experiments were used to assess ion transport through the membrane. The limiting current decreases and the current-limiting region expands due to the formation of the new layer. Resistance measurements of the modified membranes show that the growth rate of the membrane resistance is slow. When the modified membrane was used with seawater, it had a high selectivity measured as a low Ca^{2+} and Mg^{2+} leakage. This study demonstrates the potential of mono-valent selective membranes based on this material category for CEM modification, and also broadens the application field of chitosan/PANI composites.

Acknowledgments

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