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Removal of hardness by electrodialysis using homogeneous and heterogeneous ion exchange membranes

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ABSTRACT

The effect of membrane characteristics on removal of hardness ions from its dilute solutions using electrodialysis (ED) system by applying batch recirculation mode has been investigated. Two types of membrane pairs were used. Type I: Ionac MC3470 and MA3475 (Sybron Chem. Co.); Type II: Neosepta CMX and Neosepta AMX (Astom Corp.). These membranes have different ionic permselectivity, electrical resistance and thickness. In the first part of the study, the effects of the feed concentration, dilute flow rate and dilute pH on the hardness removal were investigated using Type I membranes. The optimum values for feed concentration, flow rate and pH were determined as 0.01 M, 2.6 mL/s and 6.8, respectively. In the second part, the experiments were conducted at different voltage values using Type II membranes under the optimum conditions of these variables obtained. The 95% removal of Mg^{2+} with the energy consumption of 2.07 kWh/mol and 93% removal of Ca^{2+} with the energy consumption of 2.12 kWh/mol were obtained in 200 min, applying 20 V potential using Type I membranes. On the other hand, the 100% removal of Mg^{2+} was achieved by the energy consumption of 1.69 kWh/mol in only 60 min. and the removal of Ca^{2+} was 98.3% with the energy consumption of 3.39 kWh/mol in 170 min. applying 20 V and using Type II membranes. The results obtained from this study showed that the membrane characteristics affect the efficiency of the ED significantly.

Keywords: Hardness removal; Electrodialysis; Ion-exchange membrane

1. Introduction

Membrane-based processes have been used in the areas of separation and purification. These processes are quite economical because of lower energy requirements than traditional separation processes such as distillation. It also has a modular design and so it is easy to scale-up the membrane processes. Advances in membrane technology, especially in new materials, have made it more compelling than traditional, energy intensive and environmentally undesirable processes. Membrane processes are classified according to driving forces [1]. Electrodialysis (ED) is one of the most common membrane separation techniques that uses the electrical potential difference as the driving force [2,3]. The performance of the ED process has greatly affected the characteristics of the used ion exchange membranes. An ideal ion-exchange membrane has high permselectivity, high electrical

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conductivity, high mechanical strength, high chemical and thermal stability, low production cost and moderate degree of swelling. Most of the commercially produced synthetic membranes meet these properties. However, there are some significant differences between the properties of ion exchange membranes. For example, while homogeneous ion exchange membranes possess excellent electrochemical properties, heterogeneous membranes have relatively high electrical resistance due to the longer pathway of the mobile ion in the heterogeneous structure and a lower permselectivity because of a leakage of co-ions through water-filled gaps in the membrane matrix [4]. On the other hand, mechanical strength of homogeneous membranes is weak, whereas heterogeneous membranes are excellent in their mechanical strength [5].

ED has been applied for the potable water production from brackish water and seawater [6,7], production of organic acids [8], purification of ionic liquid systems [9], softening of water [10,11] and removal or recovery of metal ions [12–14] due to its advantages such as being environmentally friendly, high separation performance, ease of operation and low energy consumption [2].

Water requirements for manufacturing processes are supplied river, lake and deep wells. Most of them contain hardness ions. These ions induced scaling problems in installations such as steam boiler can also lead to serious failures. Therefore, removal of these ions from waters has been an area of substantial technological interest in all over the world [15].

The aim of this work is to investigate the performance of homogeneous and heterogeneous ion exchange membranes in ED system for removal of hardness ions from dilute solutions. The effect of applied potential, flow rate, pH and concentration was also determined in view of removal efficiency and energy consumption.

2. Material and method

2.1. Experimental set-up and membranes

The experimental set-up consisted of specially designed ED cell which was made of acyrilic, power supplier, three peristaltic pumps and independent liquid lines as shown in Fig. 1.

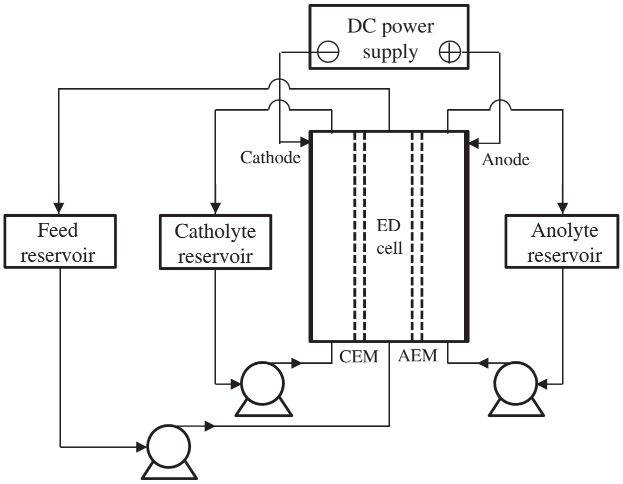

Fig. 1. Experimental set-up (CEM: cation exchange membrane, AEM: anion exchange membrane).

The cell was composed of three compartments separated by ion-exchange membranes. Electrode compartments were on both sides of central compartment. The thickness of all compartments was 1 cm. Distilled water acidified by HCl to pH 3 was circulated through the electrode compartments at a flow velocity of 0.5 mL/s. The reservoirs capacities of anode, cathode and feed (dilute) solution were 500 mL. In all compartments, solutions were circulated in a batch mode using peristaltic pumps and fed from the bottom of the cell. Experiments were carried out in potentiostatic mode using DC power supply. A pH meter was used to measure the pH variations of the streams.

Two types of membrane pairs were used. Type I: Ionac MC3470 and MA3475; Type II: Neosepta CMX and Neosepta AMX. The characteristic properties of ion exchange membranes used in the ED experiments are shown in Table 1. The carbon fiber anode and stainless steel cathode were used. The effective area of the membranes and electrodes inside the cell was 76 cm^2 [16].

2.2. Experimental procedure

In the first part of the study, the effects of the applied potential, feed concentration, feed flow rate and feed pH on the hardness removal were investigated using Type I membranes. Experiments were conducted at different feed concentration (0.005 and 0.01 M), dilute flow rate (2.6 and 5.2 mL/s), pH of dilute solution (3 and 6.8) and voltage (10, 20 and 30 V) values. Only one parameter was varied in each experiment. In the second part, the experiments were conducted under the optimum conditions of feed concentration, flow rate and pH, which were determined according to the experimental results from part I, at different voltage values (10, 20 and 30 V) by using Type II membranes. All experiments were performed in potentiostatic mode and at ambient temperature.

Table 1
Typical characteristics of membranes

	Type I		Type II	
Manufacturer	Sybron Chem. Co.		Astom Corp.	
Membranes	MC 3470	MA 3475	Neosepta CMX	Neosepta AMX
Type	Heterogeneous	Heterogeneous	Homogenous	Homogenous
Ionic form	Na^+	Cl^-	Na^+	Cl^-
Permselectivity (%)	96	99	≥ 98	≥ 98
Electrical resistance ($\Omega\,cm^2$)	14 (in O.1 N NaCl) 5 (in 1 N NaCl)	17 (in O.1 N NaCl) 8 (in 1 N NaCl)	2.5–3.5 (in O.5 N NaCl)	2.5–3.5 (in O.5 N NaCl)
Ion exc. capacity (meq/g dry membrane)	1.4	1	1.5–1.8	1.4–1.7
Thickness (mm)	0.50–0.52	0.50–0.52	0.17–0.19	0.16–0.18
Burst strength (kPa)	Min. 1.38	Min. 1.38	≥0.4	≥0.25

2.3. Chemicals and analysis

Ca^{2+} and Mg^{2+} solutions were prepared from their chloride salts with distilled water and fed into the central compartment. The molar ratio of Ca^{2+} to Mg^{2+} was 1:1 in feed solution. Dilute reservoir was sampled at regular time intervals during the run for analysis. The concentration of hardness ions were determined by titration method using 0.02 M EDTA solution. The pH was adjusted with HCl or NaOH. All chemicals are reagent grade.

3. Results and discussion

The variables that affect the performance of ED process can be evaluated in two groups as easily controllables such as applied electric potential, concentration, flow rate, temperature, membrane type and arrangement, and difficultly controllables including feed solution pH, ambient temperature, concentration polarization and precipitation on the membrane surfaces [14]. In this study, the effect of applied voltage, feed concentration and pH, dilute flow rate and membrane type was investigated. To interpret the results obtained, the energy consumptions per mole of removed hardness ions were calculated according to Eq. (1):

$$\text{Energy consumption (kWh/mol)} = \frac{E\int_0^t I\mathrm{d}t}{(C_0 - C)\,V_{\mathrm{dil}}} \tag{1}$$

where E is the applied potential (V), V_{dil} is the circulated volume of dilute solution (L), C_0 is the initial concentration of hardness ion (mol/L), C is the concentration of hardness ion in time t (mol/L), I is the current (A) and t is the time (h).

3.1. Effect of concentration

It can be seen from Figs. 2 and 3 that the hardness removal and energy consumption increase when the initial concentration of Ca^{2+} and Mg^{2+} increases from 0.005 to 0.01 mol/L. The electrical conductivity of the ion exchange membrane can be increased by increasing the ionic charge density [1]. Also, the electrical resistance of the solution decrease with increasing feed concentration. At a constant cell voltage, the transfer rate of ions from the dilute compartment to the concentrate compartment accelerates due to reduction of electrical resistances of the solution and membrane at higher concentrations [7].

3.2. Effect of dilute flow rate

The flow rate of dilute compartment was varied from 2.6 to 5.2 mL/s at a fixed flow rate of electrode

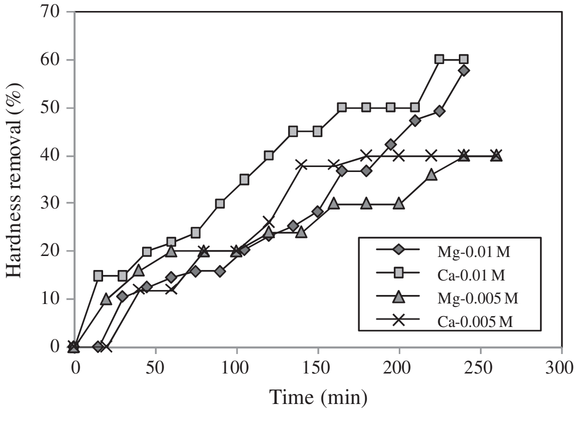

Fig. 2. Variation of hardness removal with time at different concentration (applied voltage: 10 V, pH 6.8, flowrate: 2.6 mL/s).

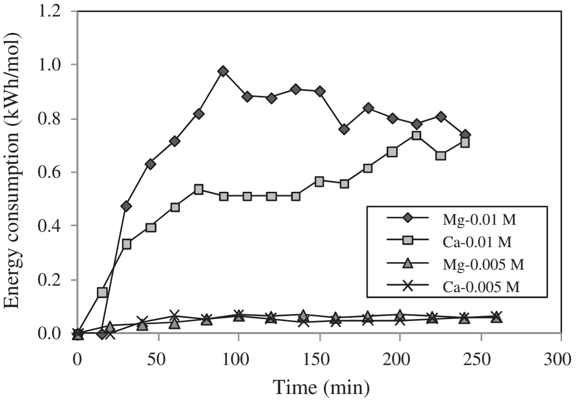

Fig. 3. Variation of energy consumption with time at different concentration (applied voltage: 10 V, pH 6.8, flow rate: 2.6 mL/s).

compartments of 0.5 mL/s. Removal efficiency at a high flow rate was greater than that in a low one as shown in Fig. 4. The transfer rate of ions in ED is controlled by the transfer in solution, in membrane and in the boundary layer. The highest possible flow rate is applied in order to reduce the boundary layer thickness [17]. Increasing the flow rate clearly moderates the effect of concentration polarization [7]. Also, the stack resistance significantly decreases with increasing flow rate [18].

Fig. 5 shows the variance of energy consumption with time at different feed flow rates. The energy consumptions per mole of removed Ca^{2+} and Mg^{2+} ions at flow rate of 2.6 mL/s were significantly higher than that at the flow rate of 5.2 mL/s.

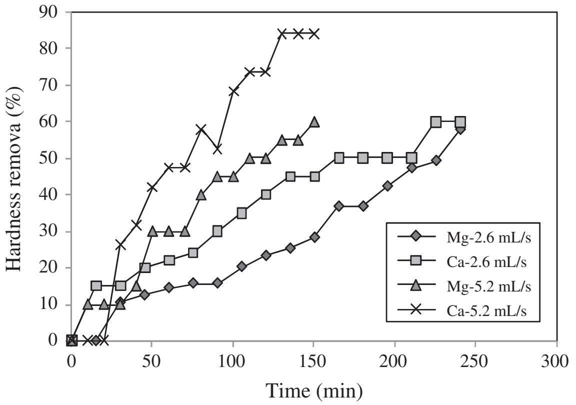

Fig. 4. Variation of hardness removal with time at different flow rates (feed conc.: 0.01 M, pH 6.8, voltage: 10 V).

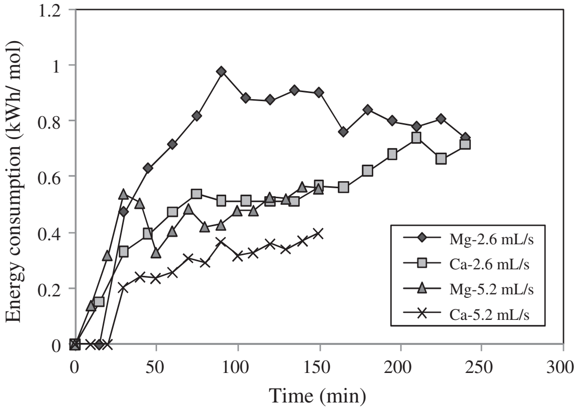

Fig. 5. Variation of energy consumption with time at different flow rates (feed conc.: 0.01 M, pH 6.8, voltage: 10 V).

3.3. Effect of pH

Figs. 6 and 7 show the plot of hardness removal and energy consumption as a function of time for pH 3 and 6.8. Operation at pH 3 resulted in low removal efficiency and high energy consumption. The experiments demonstrated that the operation at acidic or neutral pH has obvious effect on the removal of hardness ions. The differences between the removal rates of Ca^{2+} and Mg^{2+} ions might be attributed to the different ionic sizes and ion mobilities in ion exchange membranes [15]. Also, we measured the pH values of dilute and electrode compartments. In all experiments; the pH of dilute, anode and cathode compartment at the end of the experiments were about 10, 2 and 10.5, respectively. Eqs. (2) and (3) summarize the water reaction at the electrodes:

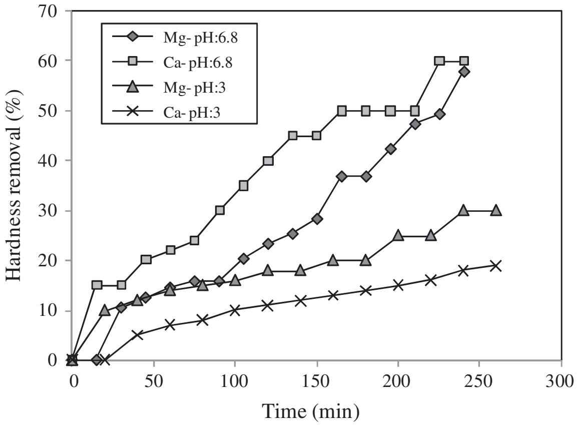

Fig. 6. Variation of hardness removal with time at different pH (feed conc.: 0.01 M, voltage: 10 V; flow rate: 2.6 mL/s).

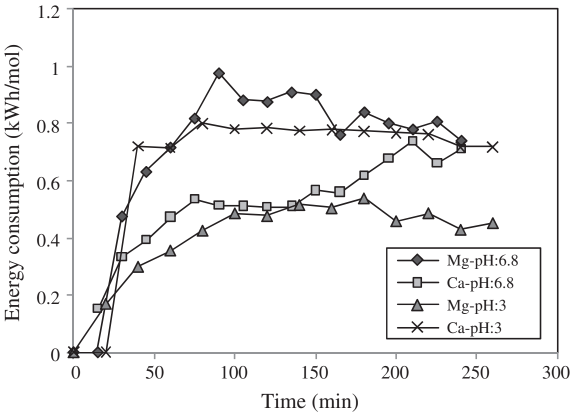

Fig. 7. Variation of energy consumption with time at different pH (feed conc.: 0.01 M, voltage: 10 V; flow rate: 2.6 mL/s).

$$\text{Cathode:} \quad 4H_2O + 4e^- \rightarrow 2H_2\uparrow + 4OH^- \tag{2}$$

$$\text{Anode:} \quad 2H_2O \rightarrow O_2\uparrow + 4H^+ + 4e^- \tag{3}$$

The electrical potential to initiate water dissociation to H^+ and OH^- is 1.23 V. The rate of water dissociation is proportional to the current [1]. This phenomenon leads to increasing of pH in the cathode compartment and decreasing of pH in the anode compartment. The rapid increase of the dilute compartment pH may be due to accelerated water dissociation caused by the precipitation of metal hydroxide on the surface of the cation exchange membrane. Park et al. reported that a thin layer of metallic hydroxide formation on the membrane-solution interface decreases the water dissociation potential [19]. When the ion exchange membranes were separated from the stack after 50 h operation, it was seemed that the white metal hydroxide spots were formed on the surface of the cation exchange membrane.

3.4. Effect of cell voltage and membrane type

Two kinds of membranes of different structures have been chosen. The variation of hardness removal in the dilute stream with operation time at different applied voltages for two types of membrane is illustrated in Fig. 8(a) and (b).

It was observed that the higher removal efficiency could be achieved at higher voltage levels. Also, as the applied voltage increases, the treatment process would be completed in a shorter time. The amount of ions transported throughout the membrane is directly proportional to the electric current or current density. The current density is determined by the applied voltage and the total resistance of the membrane stacks [1]. An increase in potential increases current density. Therefore, an increase in the electrical field enhances the mass transfer and migration of ions.

The removal of hardness ions increased regularly with time, depending on potential gradient over the bed, but higher voltages induced greater energy consumptions (Fig. 9(a) and (b)). When the applied voltage exceeds a certain value, current density would increase to limiting current density, therefore it will lead to concentration polarization and intensive water splitting in dilute compartments [15,20]. In potentiostatic operation mode, the current decreases with time because of the increasing stack resistance during ED. This phenomenon leads to prolonged treatment time

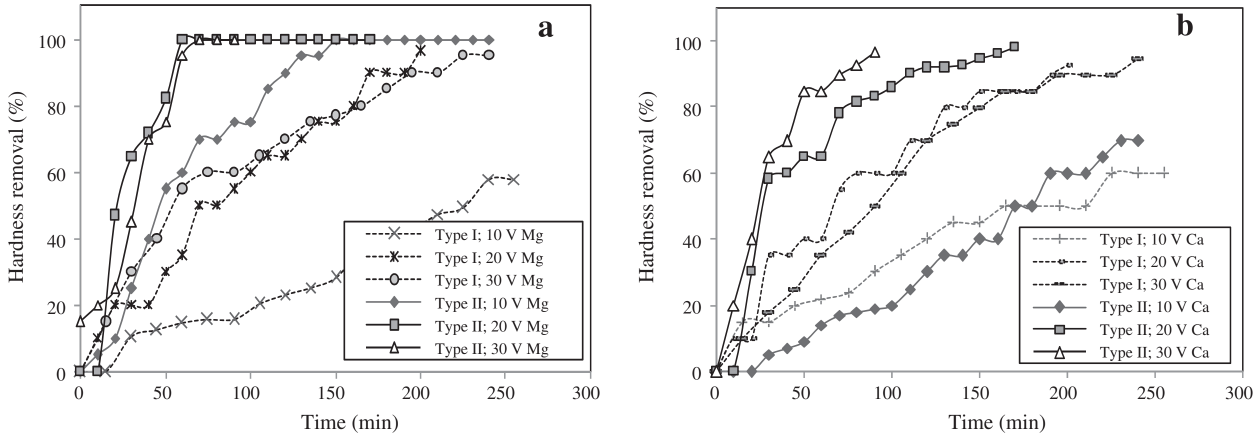

Fig. 8. The effect of applied potential on the removal efficiency (a) Mg^{2+} (b) Ca^{2+} (feed concentration: 0.01 M, pH 6.8, flow rate: 2.6 mL/s).

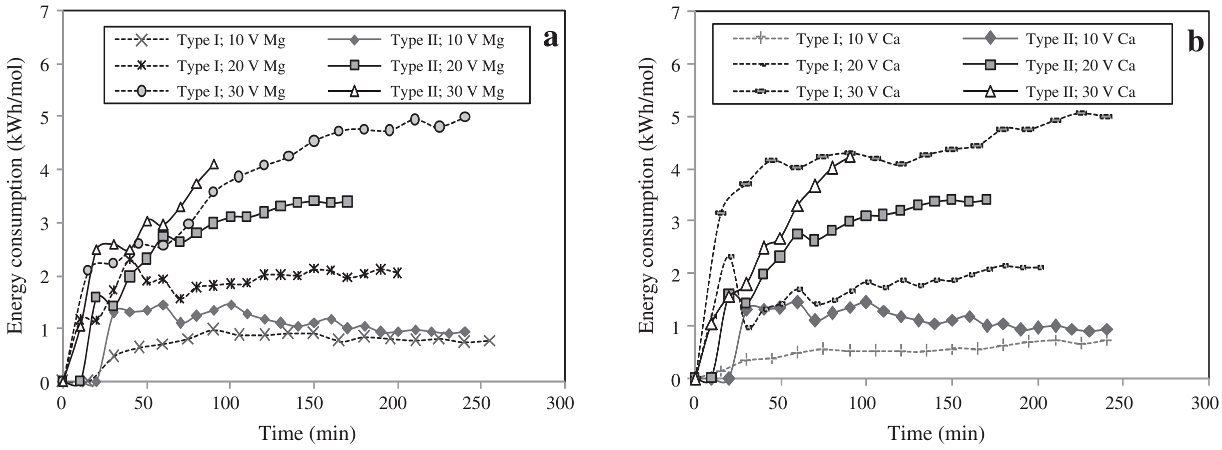

Fig. 9. The effect of applied potential on the energy consumption (a) Mg^{2+} and (b) Ca^{2+} (feed concentration: 0.01 M, pH 6.8, flow rate: 2.6 mL/s).

[5,21]. Also, Volodino et al. reported that the potential drop and the rate of water splitting are higher in the case of heterogeneous membrane under the same average current density [22]. Moreover, membrane resistivity for the Type II membranes due to homogenous structure were lower than those for the Type I membranes. For this reason, current density was higher for Type II membranes, and that significantly increases the ionic fluxes of Ca^{2+} and Mg^{2+} [23]. Thus, the time of process was reduced for Type II membranes. Similar results had been obtained by Lee et al. [18]. The homogeneous membrane pair showed better performance in view of hardness removal efficiency and process duration. The higher performance of Neosepta membranes is related to the characteristic properties shown in Table 1. In addition, Neosepta AMX and CMX membranes, based on polyvinyl chloride, are inexpensive membranes [24].

4. Conclusion

The operating parameters (flow rate, feed concentration, pH, applied voltage and membrane type) on hardness removal and energy consumption of laboratory-scale ED cell were investigated. It was found that increasing the voltage, flow rate and concentration increases the hardness removal. It can be observed that the energy consumption was increased with increasing voltages and time for two membranes. Although the energy consumption was higher in the experiments using Neosepta membranes, approximately 100% removal efficiency was obtained in a short time. The results obtained from this study showed that the membrane characteristics affect the efficiency of the ED significantly. It was indicated that the ED process with homogeneous membranes could be used for an efficient removal of hardness ions from water under optimized conditions.

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