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Hardness removal in membrane capacitive deionization with a selective cation exchange membrane

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ABSTRACT

In this research, selective removal of hardness (Ca^{2+}, Mg^{2+}) from mixed ionic solutions was achieved with a membrane capacitive deionization (MCDI) cell. For the experimental process, the cation selectivity of an ion exchange membrane was verified through sorption equilibrium experiments. The membrane was then tested in a MCDI cell using feed waters with various compositions. The results showed that membrane selectivity favored divalent cations in the order $Ca^{2+} > Mg^{2+} \gg Na^+$. The MCDI results showed that the fraction of adsorbed Ca^{2+} ions was 0.48–0.82 for the mixed solutions of Na^+ and Ca^{2+} ions (the Ca^{2+} fraction was 0.17–0.30). Similar results were also obtained for the mixed solutions of Na^+ and Mg^{2+}, with a higher affinity observed for Mg^{2+} adsorption. However, the fraction of hardness ions that were removed decreased with increasing current density. Results indicate the importance of the membrane's ion selectivity for selective removal from a mixed ionic solution in MCDI operation.

Keywords: Membrane capacitive deionization; Ion exchange membrane; Selective removal; Hardness material; Adsorption equilibrium

1. Introduction

Desalination has been of constant interest as an important and practical means to solve water shortages. As a result, capacitive deionization (CDI) based on electrosorption has been actively researched since the mid 1960's. CDI has been considered a viable method because of its low energy consumption, high recovery and environmentally friendly characteristics [1–10].

The charged carbon electrodes in the CDI remove ions through adsorption induced by electrostatic attraction. As a result, the adsorption capacity of a carbon electrode is a key factor in CDI desalination. To improve the capacitance, various strategies, such as the utilization of different carbon materials, modification of the pore structures, and surface modification to the electrodes, have been proposed [11–16].

Although modifying the surface morphology of carbon electrodes can increase the capacitance, there is clearly a limit to increasing the adsorption capacity of carbon electrodes. In research related to CDI, the maximum capacity of the electrodes has been reported to be 15 mg/g [8]. Because of the limited adsorption capacity of the carbon electrodes, CDI is commonly conducted under low salt concentrations (< 3000 mg/L) [4,8].

Field operations involve the desalination of feed waters with various compositions; however, not all operations aim for the separation of all of the ions in the feed water. For example, in water softening, the removal of divalent cations (Ca^{2+}, Mg^{2+}) is the only process of interest. Additional ion removal in this process may lead to unnecessary resource usage. Ideally, desalination would only remove the ions of interest. Selectively adsorbing specific ions to the carbon electrode may lead to a higher treatment capacity.

In recent research, development in CDI technology has been focused on selective ion removal [17–20]. Kim et al. coated a nitrate selective polymer on the surface of a carbon electrode for enhanced separation. Their results showed a high removal of nitrate ions resulting from the selectivity of the polymer complex [17]. Additionally, Seo et al. confirmed

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a higher removal of divalent cations with CDI cells in mixed ionic solutions [19].

Because of the porosity of the carbon electrodes, CDI cells have low current efficiency [8,21]. To solve this problem, ion exchange membranes were coupled with carbon electrodes to construct membrane CDI (MCDI) cells [22–25]. If the membranes show high selectivity toward certain ions, MCDI cells can be used to remove specific ions from the mixed ionic feed water.

In the current research, cation selectivity in MCDI cells was tested with various ionic mixtures. Ion selectivity was verified through sorption equilibrium tests of the cation-exchange membrane. MCDI cell experiments were also conducted to test the hardness removal of various mixed solutions. Additionally, the relationship between current density and hardness removal was tested with the MCDI cell.

2. Experiment

2.1. Adsorption equilibrium of the cation exchange membrane

Sorption equilibrium experiments were conducted to evaluate the cation selectivity of the cation exchange membrane (Neosepta CMX, Astom Co., Japan) that was used in the MCDI cell. The CMX membrane was submerged in a 1.0 M NaCl solution for 24 h until the functional groups were fully bonded with a Na^+ ion. Deionized water was used to wash off the excess NaCl before the equilibrium experiments.

To verify the selectivity of hardness ions (Ca^{2+}, Mg^{2+}) from Na^+, equilibrium experiments were conducted with a mixed ionic solution containing Na^+ and Ca^{2+} (SC) and a solution containing Na^+ and Mg^{2+} (SM). Mixed solutions were composed of 5 meq/L Na^+ and five different concentrations (1, 2, 3, 4, and 5 meq/L) of Ca^{2+} and Mg^{2+} for the SC and SM solutions, respectively. The CMX membrane (4 × 4 cm^2) was submerged in each mixed solution for 24 h to reach sorption equilibrium.

Ion chromatography (IC) was used to measure the ionic concentration and composition of the mixed solutions after the sorption equilibrium to verify the ions that were sorbed to the membrane. Shodex C. columns (Y-50) were used for the IC and were operated at a channel velocity of 1.5 mL/min.

2.2. Carbon electrode preparation

Carbon electrodes were composed of powdered activated carbon (CEP-21K, PCT Co., Korea). The electrode slurry was manufactured by adding the activated carbon to an SBR emersion (EQ-Lib-SBR, MTI Co., USA) as a binder. The mixed solution was agitated in a centrifugal mixer (AR-100, THINKY Co., Japan) for 30 min to produce a uniform electrode slurry. The slurry was cast on graphite foil (F02511, Dongbang Carbon Co.) and then dried in an oven at 50°C for 3 h. The carbon electrode thickness was 160 μm with an SBR weight ratio of 10 wt%.

2.3. Configuration of MCDI unit cell

An MCDI unit cell was constructed with Plexiglas that was bolted together for the desalination experiments. Carbon electrodes measuring 10 × 10 cm^2 were inserted as anodes and cathodes. The cation exchange membrane (Neosepta CMX, Astom Co., Japan) was placed on the cathode, and an anion exchange membrane (Neosepta AMX, Astom Co., Japan) was placed on the anode. A 120 μm spacer (EX31–071/80 PW, NBC Meshtec Inc., Japan) was placed between the membranes for feed water injection. A 1 cm diameter hole was drilled into the center of the carbon electrode in order for the treated water to exit the cell. The structure of the MCDI cell has been described in previous researches [25,26].

2.4. MCDI experiments for multi-cation mixed solutions

The performance of the MCDI cell was tested with mixed solutions of various ionic concentrations. The composition and concentrations of the various solutions are summarized in Table 1. Three different Ca^{2+} concentrations were tested in a mixture of Na^+ and Ca^{2+} (SC mixture) to assess the selectivity. Na^+ was set to 5.0 meq/L, with three solutions each containing different concentrations of Ca^{2+} (1.0, 2.0, 3.0 meq/L). Three mixed ionic solutions with different Mg^{2+} concentrations (SM mixture) were also tested. A mixed solution of Na^+, Ca^{2+} and Mg^{2+} ions (SCM solution) with concentrations of 5.0, 2.0, 2.0 meq/L, respectively, was tested to verify the effect of current density on ion separation.

The MCDI experiments for SC and SM mixtures were conducted under a 5.0 A/m^2 current density until the potential reached 1.0 V. Once the potential was reached, the cell potential was changed to 0.0 V for 10 min for desorption. The SCM mixed solutions were tested under current densities of 5.0–15.0 A/m^2 to verify the relationship between the current density and the adsorption properties.

The mixed solutions entered the cell at a constant flow rate (50 mL/min), and the treated water was returned to the feed tank for circulation. The conductivity was constantly measured during each adsorption-desorption experiment. A data collector (eDAQ Pty Ltd., ED410) was connected to the conductivity probe (Vernier Co., CON-BTA) to record the conductivities at 3 s intervals. The adsorption-desorption process was conducted three times in order for the electrode adsorption to reach dynamic equilibrium.

Table 1
Ionic compositions of feed solutions for MCDI experiments

Feed solutions		Concentration of ions (meq/L)			Equivalent fraction of hardness ions
		Na^+	Ca^{2+}	Mg^{2+}	
Na^+ and Ca^{2+} mixtures (SC mixture)	Na5 + Ca1	5.0	1.0	–	0.17
	Na5 + Ca2	5.0	2.0	–	0.29
	Na5 + Ca3	5.0	3.0	–	0.38
Na^+ and Mg^{2+} mixtures (SM mixture)	Na5 + Mg1	5.0	–	1.0	0.17
	Na5 + Mg2	5.0	–	2.0	0.29
	Na5 + Mg3	5.0	–	3.0	0.38
Na^+, Ca^{2+} and Mg^{2+} mixtures (SCM mixture)		5.0	2.0	2.0	0.44

3. Results and discussion

3.1. CMX membrane selectivity toward hardness ions

The performance of MCDI cells is assumed to depend on the ion selectivity of the membrane. Hence, CMX membranes, used in the MCDI cells, were tested for their ion selectivity. Fig. 1 shows the sorption equilibrium of Ca^{2+} and Mg^{2+} in the Na^+ and Ca^{2+} solution (SC) as well as the Na^+ and Mg^{2+} mixed ionic solutions (SM).

With the SC mixed solution, the fraction of Ca^{2+} in the membrane phase increased with higher fractions of Ca^{2+} in the solution. When the fractions of Ca^{2+} were in the range of 0.11–0.45 in the solution, the equivalent fraction increased to 0.76–0.91 in the CMX membranes, showing the high selectivity of the Ca^{2+} ions even at low concentrations. It has been known that ion exchangers show a much higher selectivity for divalent ions over monovalent ions because of higher charge [27], which results in the higher selectivity toward Ca^{2+} ion in the CMX membrane.

Results from the SM solution also showed high selectivity toward Mg^{2+} ions. Equivalent fractions of Mg^{2+} ion in the CMX membrane were 0.70–0.87 for the mixed solutions in which the equivalent fractions of Mg^{2+} were in the range of 0.12–0.46. Comparing the results, Ca^{2+} had a higher affinity toward the membranes than was observed for the Mg^{2+} ions.

For the ions to adsorb on the carbon electrode in the MCDI cell, they initially have to pass through the ion exchange membranes. Eventually, it can be deduced that the adsorbed ions on the electrode are proportional to the sorbed ions on the ion exchange membrane. Sorption equilibrium results show the selectivity of the ions in the following order: $Ca^{2+} > Mg^{2+} >> Na^+$. This indicates that the hardness removal will be favorable in the MCDI cell.

3.2. Selective removal of Ca^{2+} ions from Na^+ and Ca^{2+} mixtures

To evaluate the adsorption capacity of Ca^{2+} from the SC mixture, three different Ca^{2+} concentrations were tested (Na5 + Ca1, Na5 + Ca2, Na5 + Ca3). The current density in the MCDI cell was set to 5.0 A/m², and the cell was operated until the potential reached 1.0 V.

The ion concentration was measured in constant intervals during the adsorption process. Fig. 2 shows the change in ion concentration for the mixed solution of Na5 + Ca2. The results showed a constant decrease in the Na^+ and Ca^{2+} concentrations, indicating a steady adsorption rate. It also showed that Ca^{2+} has a higher adsorption rate compared to Na^+ ions.

The amount of adsorption of the individual ions is shown in Fig. 3. The results showed a linear increase in the adsorption of both ions, showing adsorption rates of 0.84 and 2.22 meq/min·m² for Na^+ and Ca^{2+} ions, respectively. The adsorption rate of a Ca^{2+} ion is 2.6 times faster than that of Na^{2+} ions.

Fig. 4 shows the equivalent fraction of ions adsorbed to the carbon electrode. The results show a large increase of Ca^{2+}

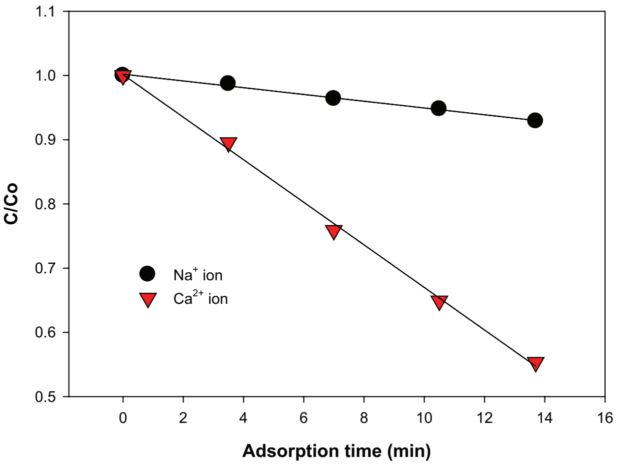

Fig. 2. Changes in ionic concentration during the adsorption process. The feed solution was a mixture of 5.0 meq/L Na^+ and 2.0 meq/L Ca^{2+}.

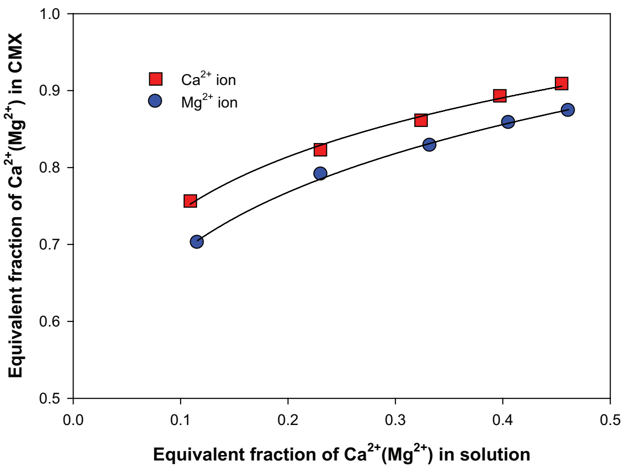

Fig. 1. The ion exchange isotherm of the CMX membrane in the mixed solution of $Na^+ + Ca^{2+}$ and $Na^+ + Mg^{2+}$. The concentration of Na^+ ion in the mixed solution was 5 meq/L.

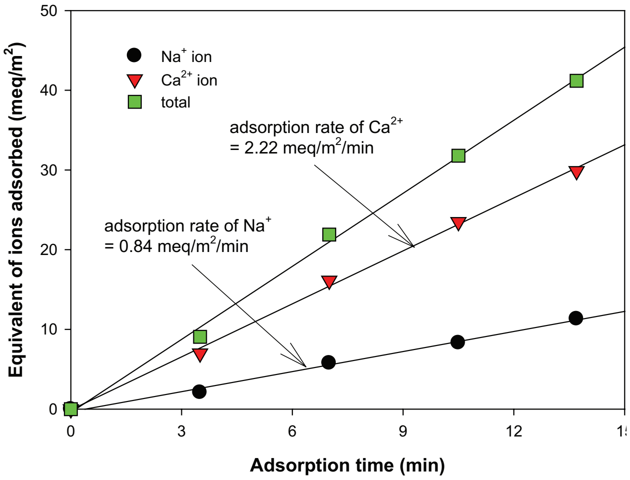

Fig. 3. The number of ions adsorbed as a function of adsorption time. The feed solution was a mixture of 5.0 meq/L Na^+ and 2.0 meq/L Ca^{2+}.

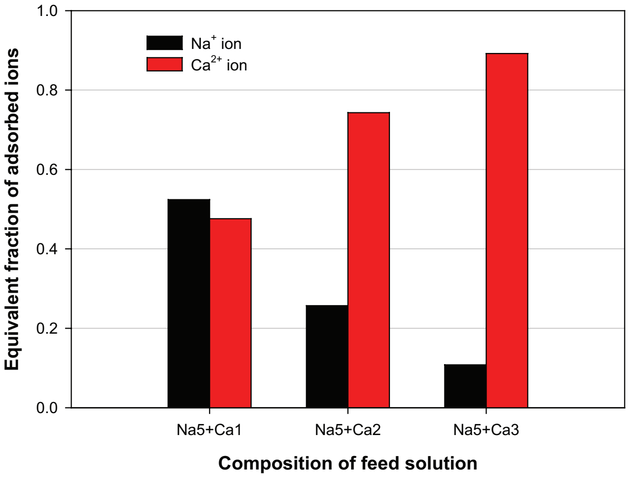

Fig. 4. Equivalent fractions of adsorbed ions with various feed solutions.

adsorption with increasing Ca^{2+} concentrations. The fraction of Ca^{2+} ion in the Na5 + Ca1 solution was 0.17, and the adsorbed fraction of Ca^{2+} was 0.48. Although Na^+ ion concentration was 5 times higher than that of Ca^{2+} ion in feed solution, the adsorbed Ca^{2+} ion was similar with Na^+ ion. The result can be explained by the high selectivity of the CMX membrane toward Ca^{2+} ion. As can be seen in Fig. 1, the fraction of Ca^{2+} ion in the CMX membrane is 0.80 when the Na5 + Ca1 mixed solution reaches an adsorption equilibrium with the CMX membrane. The higher adsorption of Ca^{2+} ion in MCDI test is attributed to the high selectivity of CMX membrane for Ca^{2+} ion. Meanwhile, it is noticeable that the adsorbed Ca^{2+} fraction (0.48) in MCDI test shows a difference with the adsorption equilibrium value (0.80). This means that adsorption equilibrium between the Na5 + Ca1 mixed solution and the CMX membrane was not reached. With the Na5 + Ca3 solution, however, the adsorbed fraction of Ca^{2+} ions increased to 0.89. In summary, feed water containing a Ca^{2+} fraction of 0.17–0.38 adsorbed 0.48–0.89 on the carbon electrodes.

Under the influence of the electric field, the fluxes of the ions are proportional to the ion's concentration and mobility [27,28]. The mobility of Na^+ and Ca^{2+} are 5.19×10^{-8} and 6.16×10^{-8} $m^2/s{\cdot}V$, respectively [28]. The adsorbed amount of ions at a carbon electrode should correlate with the ionic concentration and mobility. Thus, the equivalent fraction of adsorbed Ca^{2+} ions should be 0.19, 0.32, and 0.42 for the three SC solutions. However, the equivalent fractions were 0.48, 0.74, and 0.89, showing more than twice the estimated values. This is because of the high selectivity of Ca^{2+} ions with the CMX membrane.

3.3. Selective removal of Mg^{2+} ion from the mixture of Na^+ and Mg^{2+} ions

To verify the selectivity of Mg^{2+} ions, three mixed solutions containing different fractions of Mg^{2+} ions were tested in the MCDI cell. Fig. 5 shows the adsorption of each ion in the Na5 + Mg2 solution while the MCDI cell was operating at 5.0 A/m^2.

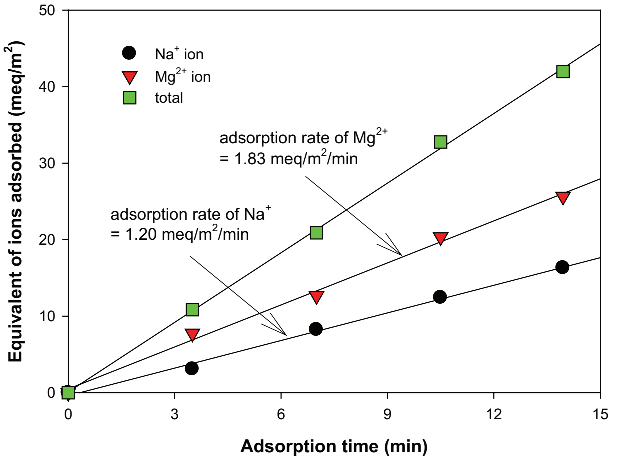

Fig. 5. The number of ions adsorbed as a function of adsorption time. The feed solution was a mixed solution of 5.0 meq/L Na^+ and 2.0 meq/L Mg^{2+}.

SM solutions had similar results to that of SC solutions, showing linear adsorption to the carbon electrodes, which indicated that the Na^+ and Mg^{2+} ions each adsorb at a constant rate. Adsorption rates of Na^+ and Mg^{2+} were 1.20 and 1.83 $meq/min{\cdot}m^2$, respectively, indicating a 50% faster adsorption of Mg^{2+} compared to Na^+.

Fig. 6 shows the results of the desalination with MCDI cells with three different SM solutions. As expected, the fraction of adsorbed Mg^{2+} increased with the increase of Mg^{2+} fraction in the feed solution. The fraction of adsorbed Mg^{2+} ions was 0.39–0.82 depending on the Mg^{2+} fraction in the feed solution (0.17–0.38).

Without the CMX membrane, the adsorption of Mg^{2+} in the three different solutions, because of the mobility, would be 0.18, 0.30, and 0.39 for Na5 + Mg1, Na5 + Mg2, Na5 + Mg3 solutions, respectively. However, with the MCDI cell, the adsorbed fractions were 0.39, 0.64, 0.82, respectively, which was more than twice the amount that was calculated without the membrane. The results show the high selectivity of the MCDI cells with Mg^{2+} ions.

MCDI results show a higher selectivity of Ca^{2+} ions compared to Mg^{2+} ions. MCDI experiments were carried out with various compositions of SC and SM solutions. The

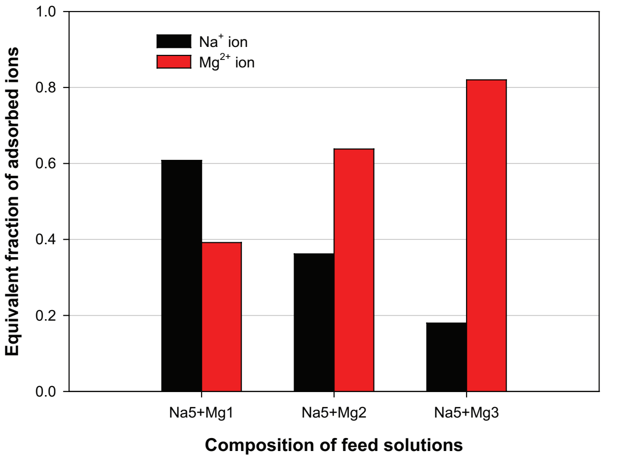

Fig. 6. Equivalent fractions of adsorbed ions with various feed solutions.

fractions of Ca^{2+} (or Mg^{2+}) in the feed solution were 0.17–0.38. However, the fraction of adsorbed hardness ions were 0.48–0.89 for the SC mixtures and 0.39–0.82 for the SM mixtures, showing higher selectivity of Ca^{2+} ions compared to Mg^{2+} ions. This is because of the higher selectivity of Ca^{2+} ions in the CMX membranes.

Results from the MCDI cell indicate that the adsorption of ions rely on the selectivity of the membranes. It should be noted that with lower ion fractions in the mixed solution, the adsorption to the carbon electrodes are different with the sorption equilibrium of the CMX membranes (Fig. 1). With the SM solution containing a 0.38 Mg^{2+} fraction, the fraction of adsorbed Mg^{2+} was 0.82, which is similar to the equilibrium value of 0.85 in the CMX membrane that is shown in Fig. 1. However, when the Mg^{2+} fraction was 0.17 in the mixed solution, the adsorbed Mg^{2+} fraction on the carbon electrode was 0.39, which was much lower compared to the sorption equilibrium value of the CMX membrane (0.70). This indicates that the Mg^{2+} fraction in the CMX membrane deviates from the sorption equilibrium value with decreasing the Mg^{2+} fraction in the feed solution.

3.4 Effect of current density on the selective removal of hardness ions

A desalination experiment was conducted for the SCM mixture under current densities from 5.0 A/m^2 to 15.0 A/m^2. Fig. 7 shows the adsorption per time when operated at 7.5 A/m^2. The results showed linear adsorption with the SCM mixed solution, showing a constant adsorption rate of each ion.

The adsorption rates of Na$^+$, Ca^{2+}, and Mg^{2+} were 0.75, 1.96, 1.73 meq/min·m^2, respectively. The SCM solution showed adsorption rates in the order of Ca^{2+} > Mg^{2+} >> Na$^+$, matching the sorption equilibrium results of the CMX membrane. This indicates that with MCDI operations, the selectivity of the membrane toward each ion influences the adsorption to the carbon electrode. It has been known that the ion exchanger tends to prefer the counter ion with the higher mobility [27]. The mobility of Ca^{2+} ion is higher than that of Mg^{2+} ion, which leads to the higher adsorption of Ca^{2+} than Mg^{2+} ion.

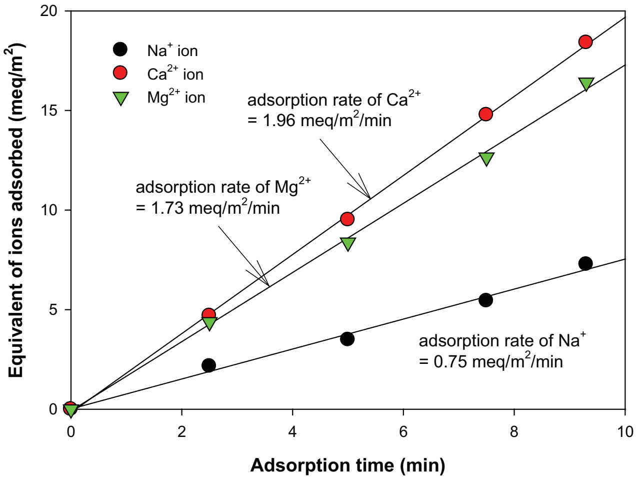

Fig. 7. The number of ions adsorbed as a function of adsorption time at the current density of 7.5 A/m^2. The feed solution was a mixed solution of 5.0 meq/L Na$^+$, 2.0 meq/L Ca^{2+} and 2.0 meq/L Mg^{2+}.

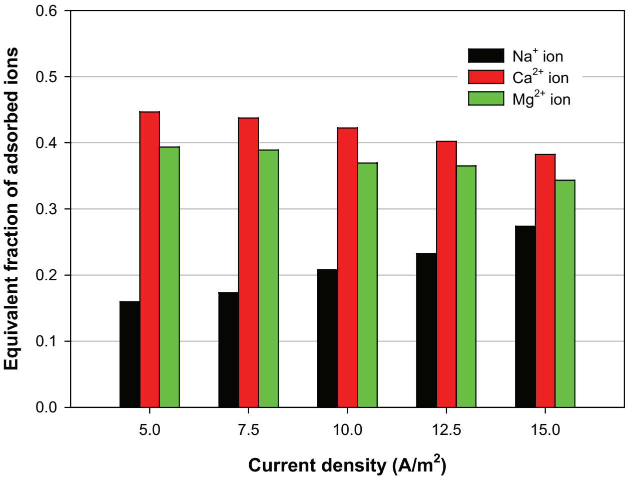

Fig. 8. Equivalent fractions of adsorbed ions with various current densities.

Fig. 8 shows the fraction of each ion adsorbed to the carbon electrode with various current densities. Although the fractions of Na$^+$, Ca^{2+}, and Mg^{2+} in the feed solution were 0.56, 0.22, and 0.22, respectively, the adsorption of the ions were in the order of Ca^{2+} > Mg^{2+} >> Na$^+$. It can be seen in Fig. 8 that the fraction of the ions changes with the current density. With increasing current density, the fraction of Ca^{2+} decreases from 0.45 to 0.38. Mg^{2+} also decreased from 0.39 to 0.34 while Na$^+$ increased from 0.16 to 0.27.

When an electric current charges the MCDI cell, the ions that are sorbed to the CMX membrane move toward the carbon electrode. During this process, the ions in the feed water move toward and attach to the ion exchange groups in the membrane. If this process occurs slowly, adsorption equilibrium will be maintained between the CMX membrane and feed solution. However, as the adsorption rate becomes faster by applying higher current density, the ionic fraction in the CMX membrane will deviate from the equilibrium condition [20]. In this case, a high concentration of Na$^+$ ions has a higher possibility to attach to the ion exchange groups in the CMX membrane. This leads to a decrease in Ca^{2+} and Mg^{2+} adsorption and an increase in the adsorption of Na$^+$ ion with increasing current density. Although the hardness removal is reduced with increased current density, the CMX membranes can still perform as a useful means for hardness removal. For the SCM mixture, the fraction of hardness ions was 0.73–0.84 depending on the current density. The research above shows that MCDI cells can be successful in selectively removing hardness from the mixed solution.

4. Conclusion

MCDI cells were studied for their selective removal of hardness ions; CMX membranes were tested for their ion selectivity. Various mixed ionic solutions were tested for the relationship between the CMX membrane selectivity and the fraction of ions that were adsorbed in the MCDI operation.

Sorption equilibrium results showed high selectivity toward Ca^{2+} and Mg^{2+} ions compared to the Na^+ ions. The adsorption to the electrode was proven to be relevant to the selectivity of the membranes. Additionally, it was discovered that the selectivity of the membranes decreased with increasing current density.

The current research indicates the importance of the selectivity of the membranes in MCDI systems. Additionally, it is essential to maintain the sorption equilibrium of the ion exchange membrane at a higher current density. If maintaining similar values in water content, ion-exchange membranes with high ion exchange capacity will be a possible solution for achieving high selective removal at a high current density.

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