



Desalination of brackish water containing oil compound by capacitive deionization process

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ABSTRACT

The feasibility of using capacitive deionization (CDI) was investigated for the desalination of brackish water containing oil compound. The reproducibility, salt removal efficiencies, and current efficiencies were examined at various cell potentials and cell configurations. For the CDI cell constructed with only porous carbon electrodes, the results showed stable and reproducible adsorption and desorption characteristics. But the current efficiency was low at 49.3% at the cell potential of 1.4 V. The low current efficiency was attributed to the dissolved salt present in the pore volume of the carbon electrode. To increase the current efficiency, desalination experiments were performed using a membrane capacitive deionization (MCDI) unit cell, which employed ion-exchange membranes as ion selective layers in a CDI cell. The current efficiency increased to 90.2% under the same experimental conditions. MCDI tests were conducted using an influent containing octane to elucidate the effect of oil compounds on desalination efficiency. The experimental results showed that the MCDI system could be successfully applied to the desalination of brackish water containing oil compounds.

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1. Introduction

Water treatment is an essential part of the surface facilities for the steam assisted gravity drainage (SAGD) technique in heavy oil recovery areas. It plays a role in supplying clean water to steam generators for high-quality steam injection to subsurface oil sand formation [1]. One of the demands for the steam generators used in SAGD processes is to maintain a low content of hardness in the produced water. Otherwise, hardness in the boiler feed water builds significant amounts of scale in steam generators, causing serious problems in the overall operation. A traditional method to remove the hardness from water features a lime-softening operation followed by a filtration system and ion exchange [2]. However, such a conventional system is labor intensive and requires additional caustic chemicals and solid transportation. To overcome these disadvantages, alternative treatment methods have been suggested including evaporation and reverse osmosis [3–5]. Recently, operational costs have become the prime consideration for selecting a proper treatment technique because of rising energy costs.

Capacitive deionization (CDI) technology has attracted interest as a desalination technology since the 1960s, when the concept of CDI was first introduced by Murphy et al. [6]. Later, Johnson et al. [7] developed a porous-electrode model for ionic adsorption on porous carbon. CDI is an

electrostatic process that operates at a relatively low voltage (about 1–1.5 V) so that no electrolysis reactions occur at the electrodes [8–15]. When the water containing dissolved solids is pumped through a high-surface area electrode cell, the positive ions are attracted to the negatively charged plate (cathode), and the negative ions are attracted to the positively charged plate (anode). This concentrates the ions at the electrodes, thereby reducing their concentrations in the water. When the electrode capacity is exhausted, the electrodes must be regenerated by discharging the ions from the electrode surfaces. This is achieved by shorting the electrodes or reversing the polarity of the applied cell potential [16–18].

CDI is attractive for desalination technology because it requires low operating voltages, which require less energy than other technologies such as reverse osmosis (RO), electrodialysis (ED), and distillation. In addition, unlike membrane-based technologies, such as reverse osmosis and nanofiltration, CDI does not require high-pressure pumps and membranes. Also, as CDI removes ions through charge separation, its use avoids scaling problems commonly associated with membrane and distillation processes [19–21].

Conventional CDI is known to be energy inefficient because of the dissolved salt present in the pore volume of the carbon electrode [22]. When an electric potential is applied, counterions in the pore adsorb onto the electrode and co-ions are expelled from the electrodes. This means that ion adsorption and desorption occur simultaneously in the pore volume in the electrode, seriously reducing desalination efficiency. To solve this problem, Andelman [22] suggested a charge barrier placed adjacent to an electrode of a flow-through capacitor.

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Recently, Biesheuvel et al. presented a theoretical process model for CDI and MCDI cell, which describes the time-dependent electrical current and effluent ion concentration [23,24].

Although a significant amount of oil is typically removed from the produced water in heavy oil fields via some oil–water separation processes prior to the water treatment, a small amount of light oil is likely to be contained in the boiler feed water and its presence may impact the efficiency of CDI. In this study, we investigated the feasibility of the CDI process for the desalination of brackish water containing a model oil compound (octane). Capacitive deionization experiments were carried out at various operating conditions using a unit cell equipped with porous carbon electrodes. The salt removal efficiencies according to cell configuration were investigated along with the effect of oil compounds on capacitive deionization.

2. Experimental

2.1. Fabrication of the porous carbon electrode

A porous carbon electrode was fabricated for the capacitive deionization experiment. The electrode was prepared by mixing activated carbon powder (P-60; Daedong AC Corp., specific surface area = 1260 m²/g) and poly(vinylidene fluoride) (PVdF, MW = 530,000; Aldrich) as a polymer binder at a mass ratio of 88:12. Using di-methylacetamide (DMAc, Aldrich) as a solvent, these compounds were blended for 6 h to ensure homogeneity. The solution was then cast directly on a graphite sheet (F02511, Dongbang Carbon Corp., Korea) with a thickness of 200 μm using a doctor blade. The cast film was then dried at 50°C for 24 h to remove the solvent completely.

2.2. Construction of the capacitive deionization cell and desalination experiments

Capacitive deionization experiments were carried out in a flow-through system, depicted in Fig. 1. The system consisted of a reservoir, a peristaltic pump, a CDI unit cell, and a conductivity meter. The CDI unit cell consisted of two parallel porous carbon electrode sheets separated by a non-electrically conductive spacer (nylon cloth,

100 μm thick). This prevented an electrical short and allowed liquid to flow. The size of the carbon electrode was 100 × 100 mm. The graphite sheets were used as inert current collectors on the back side of the carbon electrodes. A plexiglass plate was used to assemble the upper and lower parts of the unit cell. To examine the effect of the ion-exchange membrane on the desalination efficiency, another unit cell was constructed with ion-exchange membranes. In this cell (MCDI), the cation exchange membrane (Neosepta CMX, Astom Corp., Japan) was placed in front of the cathode carbon electrode, and the anion exchange membrane (Neosepta AMX, Astom Corp., Japan) was placed in front of the anode carbon electrode.

Capacitive deionization experiments were carried out for each unit cell (CDI and MCDI). The feed solution was 17.1 mM NaCl (1000 mg/L). It was supplied continuously at a flow rate of 10 ml/min. A small concentration of octane (5 or 10 mg/L) was added to the influent solution to investigate the effect of oil compounds on desalination efficiency. A flow channel was created by punching a 1-cm-diameter hole in the center of the electrode so that the solution could be in contact with all sides of the electrode and could run through a spacer to the central hole. A conductivity meter was placed at the outlet of the cell to monitor changes in conductivity of the effluent during the adsorption and desorption periods. The potential of the cell was controlled with a potentiostat (WPG100, WonA Tech Corp.) connected to a personal computer for monitoring electrode potential and electrode currents over time. The applied cell potential ranged from 1.2 to 1.6 V. The CDI operation consisted of two cycles: adsorption and desorption. During the adsorption phase, a constant cell potential (1.2, 1.4, or 1.6 V) was applied to the electrodes for 150 s. The desorption phase began immediately after the adsorption phase at a cell potential of 0 V for 120 s.

3. Results and discussion

3.1. Changes in effluent concentration for the CDI and MCDI cell operations

Fig. 2(a) shows the changes in effluent NaCl concentration over time for the capacitive deionization experiment, using the CDI cell at the cell potentials of 1.2, 1.4, and 1.6 V. The NaCl concentration was

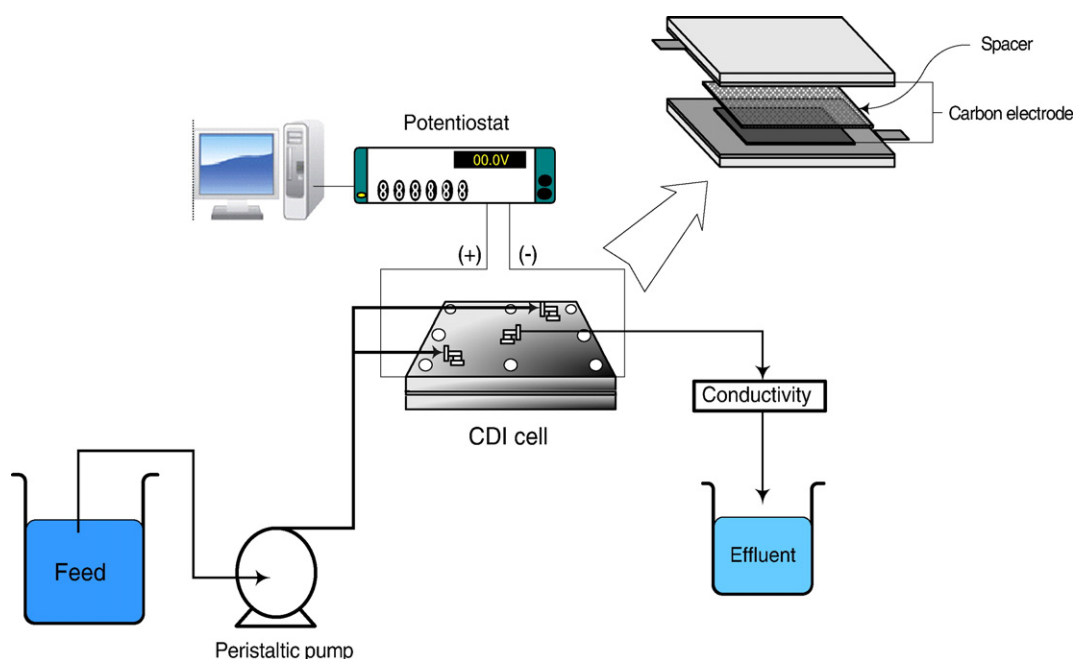


Fig. 1. Schematic diagram of capacitive deionization (CDI) experiments.

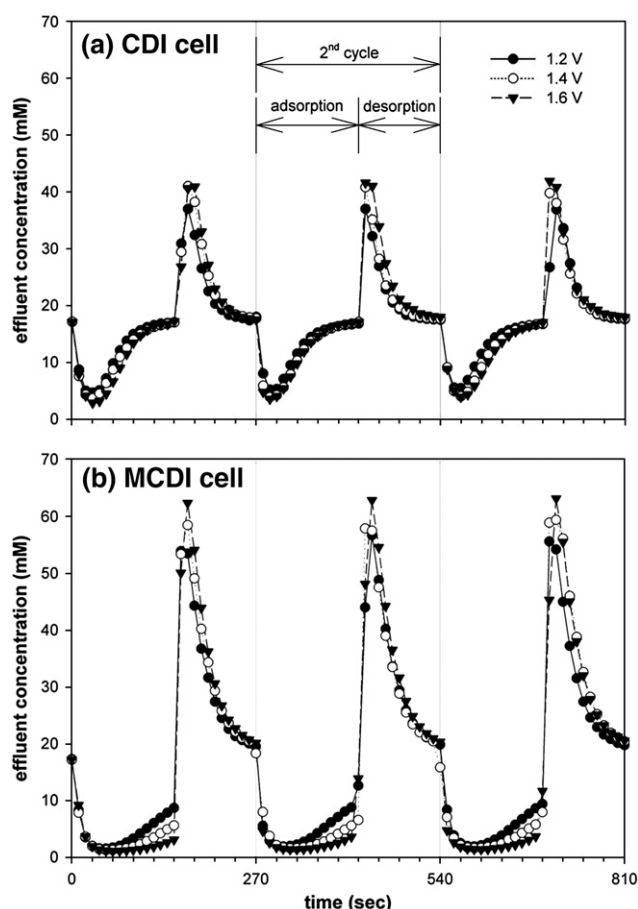


Fig. 2. Changes in effluent NaCl concentration at various cell potentials: (a) for the CDI cell, (b) for the MCDI cell.

determined from the linear relationship between NaCl concentration and conductivity. The operation of the CDI cell was stable and reproducible for each test. The results also showed that the removal rate increased with increases in cell potential. For a potential of 1.2, 1.4, and 1.6 V, the concentration of the effluent decreased significantly, reaching minimum values of 4.7, 3.7, and 2.8 mM, respectively, at about 30 s. Due to the limited ion adsorption capacity of the electrode the number of ions that is adsorbed to the electrode surface gradually decreases. Accordingly, the concentration increased after the minimum point, reaching an asymptotic level at about 120 s.

Desorption of the CDI unit was conducted immediately after the sorption phase by applying a cell voltage of 0 V. The concentration of the effluent reached about 2.5-fold value of the influent. Most of the adsorbed ions were easily released from the electrode within about 1 min. This suggests that regeneration of the electrode can be conducted very efficiently in the CDI process.

Meanwhile, Fig. 2(b) shows the changes in effluent NaCl concentration over time for the MCDI cell at the cell potentials of 1.2, 1.4, and 1.6 V. Compared to the results obtained with the CDI cell, the ion removal rate improved considerably. The concentration of the effluent decreased with increases in cell potential from the initial 17.1 mM to 1.5, 1.3, and 1.1 mM at the cell potentials of 1.2, 1.4, and 1.6 V, respectively. One of the major differences in the results obtained from the CDI cell was that the concentrations increased slowly during the adsorption period. This indicates that ions are adsorbed continuously during the adsorption period. On the other hand, the concentration of the effluent reached about 60 mM at the desorption period, which is about 3.5 times that of the influent. These results demonstrate that the MCDI cell can be used effectively for the desalination of brackish water.

3.2. Changes in current for the CDI and MCDI cell operations

During the desalination experiments, the current that passed through the cell was recorded automatically at 1-sec intervals. Fig. 3 displays the current changes for the CDI and MCDI cell at the cell potential of 1.4 V. The current supplied was limited to a maximum ± 1 A because of the specifications of the potentiostat. For the CDI cell, the currents decreased significantly from 1.0 to 0.1 A within 60 s and then continued to decrease gradually. On the other hand, current changes for the MCDI cell were not significant during the adsorption period compared to the CDI cell. The results indicate that ion-exchange membranes functioned well in the MCDI cell configuration. The ions from bulk solution were transported through the membranes and adsorbed at the electrode surface.

The supplied current through the cell indicates the amount of ions adsorbed or desorbed at the electrode. The current efficiency (η_c) is defined as the amount of ions actually adsorbed divided by the total charges passed, as described by the following equation [25]:

$$\eta_c(\%) = \frac{c_f V_f F}{\int i dt} \times 100 \quad (1)$$

where, c_f is the average NaCl concentration of effluent (mol/L), V_f is the total volume of effluent (L), F is the Faraday constant (96,500 C/mol), and i is the current that passed through the cell (A).

The total charges supplied through the CDI and MCDI cell at the cell potential of 1.4 V were measured as 28.4 and 37.3 C, respectively. The amounts of NaCl adsorbed during the 150 s adsorption period were 0.15 and 0.35 mmol for the CDI and MCDI cell. From Eq. (1), the current efficiencies were calculated to be 49.3 and 90.2% at the cell potential of 1.4 V. The higher current efficiency for the MCDI cell over the CDI cell was attributed to the selective adsorption and desorption in the MCDI cell configuration. In the MCDI cell, counterions can freely move into and out of the electrode, while co-ion transport is blocked [24]. In the CDI cell configuration, however, counterions present in the pore volume of the electrode adsorb onto the electrode, whereas co-ions are expelled from the electrode [22]. Eventually, ions in the pore volume rather than ions from the bulk solution are adsorbed as the cell potential is applied. This is attributed to the decline in current efficiencies in the CDI cell configuration.

3.3. Effect of oil compounds on desalination efficiency

Capacitive deionization technology is the most energy efficient, and it can overcome the disadvantages of conventional desalination technologies, i.e., reverse osmosis, distillation, and ion-exchange

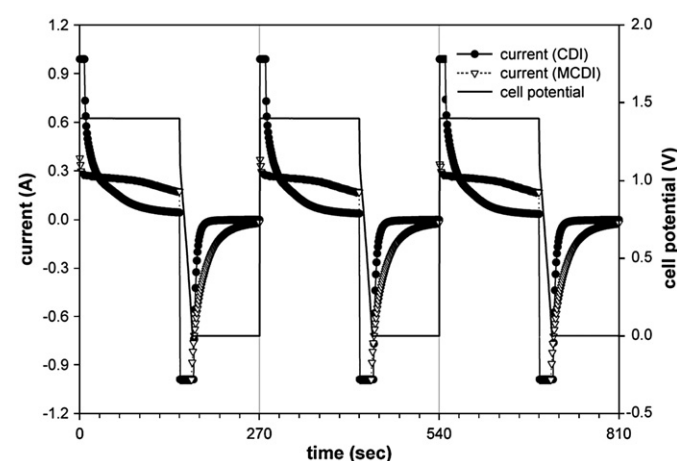


Fig. 3. Changes in current over time for the CDI and MCDI cell operation at the cell potential of 1.4 V.

processes. Nevertheless, CDI has not been verified as a powerful desalting technology because of the lack of long-term operating results and data on electrode pollution caused by organic (fouling) and inorganic (scaling) compounds [8].

We carried out CDI experiments to investigate the effect of oil compounds on the desalination efficiency of the CDI process using the MCDI cell. The influent containing 5 or 10 mg/L of octane in 17.1 mM NaCl was pumped into a cell. A cell potential of 1.4 V was applied for 150 s. After the adsorption process, 0 V cell potential was applied to regenerate the electrode. To observe the changes in desalination efficiency with continuous runs, 11 cycles of CDI tests were performed continuously under the same conditions.

Fig. 4 shows the concentrations of effluent measured at the 1st, 5th and 11th cycle. The changes in concentration during the adsorption and desorption periods were not significant based on the number of the cycle. However, the concentrations increased slightly during the adsorption period with higher octane content in the influent.

We gathered effluent solution during the adsorption periods at each cycle to evaluate the average salt removal efficiency (η_s). The average salt removal efficiencies were calculated with the following equation and are depicted in Fig. 5 for even cycle numbers:

$$\eta_s(\%) = \left(1 - \frac{c_f}{c_o}\right) \times 100 \quad (2)$$

where c_o and c_f are the NaCl concentration of influent and average concentration of effluent, respectively.

The salt removal efficiencies for the influent without octane were about 80% and were stable over all cycles. The efficiencies, however, decreased to 75 and 69% in the second cycle for the solution containing 5 and 10 mg/L of octane, respectively. Moreover, the salt removal efficiencies decreased with the number of cycles, from 75 to 69% and from 69 to 67% for 5 and 10 mg/L octane, respectively. The efficiencies did not decrease linearly, but approached constant values at the end of cycle. The reason for this tendency may be attributed to the adsorption equilibrium of octane on the ion-exchange membrane surface. In other words, octane is adsorbed onto the ion-exchange membranes and equilibrates after a period of time. Octane adsorbed on the membrane may interrupt the adsorption of ions on the electric double layer, resulting in a decrease in salt removal efficiency.

The adsorption of octane on the membrane was monitored by measuring the total organic carbon (TOC) concentration in the effluent. Fig. 6 displays the TOC concentration of the effluent solution during the sorption and desorption periods for the influent containing 5 mg/L octane. The TOC concentration increased slightly up to sixth cycle for the sorption period. This implies that octane in the influent

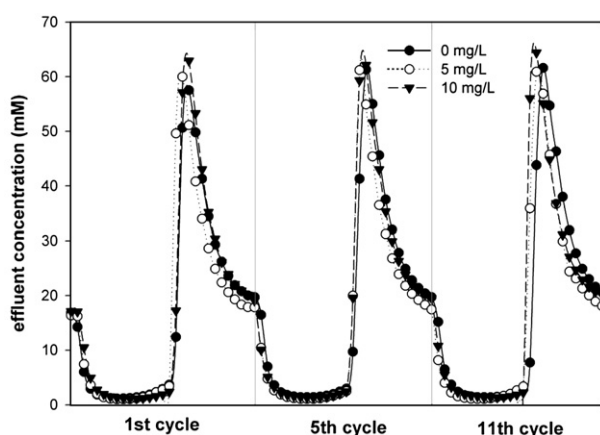


Fig. 4. Changes in effluent NaCl concentration for the 1st, 5th and 11th cycle of MCDI cell operation at the potential of 1.4 V using influent of 17.1 mM NaCl containing octane.

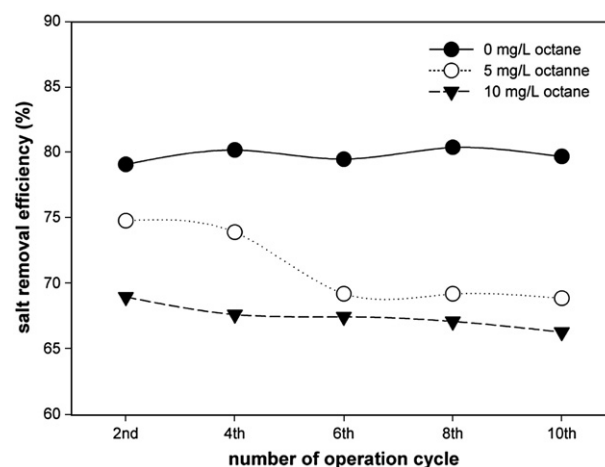


Fig. 5. Changes in salt removal efficiencies according to the number of operation cycle.

was adsorbed on the membrane and that it reached equilibrium. In addition, the observed TOC concentrations were higher for the desorption period than the sorption period. We suspect that the octane adsorbed on the membrane was desorbed partly along with the ions during the desorption process. From these results, we conclude that octane can diminish the salt removal efficiency and that the extent of the decrease depends on the octane concentration in the influent.

4. Conclusion

In this study, we analyzed the feasibility of CDI process for the desalination of brackish water containing a model oil compound (octane). Capacitive deionization experiments were carried out under various operating conditions using a CDI cell equipped with porous carbon electrodes. The operational results showed stable and reproducible adsorption and desorption characteristics. The MCDI cell displayed a higher salt removal efficiency and current efficiency compared to the CDI cell because of the selectivity of ion-exchange membranes. Desalination performance for brackish water containing octane was also investigated. Salt removal efficiencies decreased with increases in the concentration of octane in the influent. However, no appreciable decline in MCDI performance was observed after a certain number of cycles. The experimental results demonstrated that the MCDI system with ion-exchange membranes could be applied successfully for the desalination of brackish water containing oil compounds.

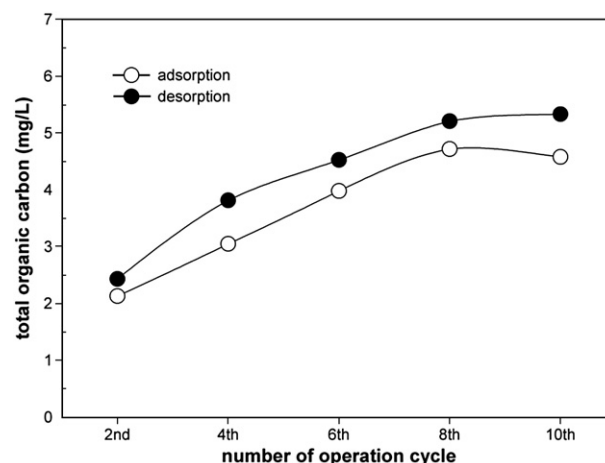


Fig. 6. Changes in TOC concentration in the effluent during adsorption and desorption periods according to the number of operation cycle.

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