Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2022.28521

264 (2022) 54–61
July

Evaluation of total dissolved solids removal characteristics by recycling concentrated water in membrane capacitive deionization process

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Received 7 January 2022; Accepted 19 April 2022

ABSTRACT

The present study evaluated the removal characteristics of total dissolved solids (TDS) using recycled concentrated water generated through desorption in a membrane capacitive deionization (MCDI) process. As a result of 40-cycle experiments of the conventional MCDI process, stable adsorption and desorption were performed. In MCDI circulation process, TDS concentration in concentrated water increased; however, this did not affect the adsorption capacity, and treated water was obtained stably. The energy consumption as a function of the number of cycles in conventional MCDI process kept constant, but it gradually increased in the MCDI circulation process. The reason for this increase is that the amount of current changes with the concentration of feed water. Finally, as a result of comparing the yield of treated water per feed water, we observed that the conventional MCDI process requires an influent for both adsorption and desorption; however, the production of treated water is constant because it is produced only through the adsorption process. By contrast, the MCDI circulation process does not require a separate influent because it uses the concentrated water stored in the concentrated water tank during the desorption process. Thus, we observed that the yield gradually increased with the number of cycles.

Keywords: Membrane capacitive deionization (MCDI); Total dissolved solids (TDS); Constant voltage (CV); Circulation process

1. Introduction

As the usable water resources in the planet gradually decrease, efforts to use mineral water as drinking water or brackish water, which has a lower concentration of ionic substances than seawater, through desalination have continued [1]. One of the most important water treatment process for desalination and reuse of water is to remove ionic substances [2,3]. This is known as deionization or desalination. Desalination is a technology that removes salt from water. It is widely used in many sectors such as seawater desalination, circulation water for boilers, production of ultrapure water, cooling water in power plants, pollutants removal in groundwater, etc. [4]. Water treatment technology is becoming more important. The most widely used techniques for desalination are evaporation, ion exchange, reverse osmosis, electrolysis, etc. [5]. However, these techniques are mainly used for seawater desalination, and have problems such as high energy consumption during operation, generation of high level of salt wastewater during

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regeneration of ion exchange resin, periodic replacement due to membrane contamination, and deterioration in treatment capacity. In addition, when applied to desalination of brackish water having a low concentration of ionic substances, there is a disadvantage in that treatment costs are high. An emerging desalination technique that can solve these problems is the so-called capacitive deionization (CDI), which employs an electrochemical method actively studied since the mid-1990s [6–8]. CDI technology is based on ion removal in a solution through adsorption using electrostatic attraction of an electric double-layer (EDL). This EDL is generated on the electrode surface when an electric potential is applied through a carbon electrode with a large surface area and excellent electrical conductivity [9–13]. During adsorption, cations are adsorbed to the cathode and anions are adsorbed to the anode, and the electrode is regenerated by short-circuiting the voltage or applying a reverse potential to resorb the ions. Accordingly, all charged ions can be removed from solution [14].

However, CDI has a problem: low salt removal efficiency given that the ions are not completely removed during discharge [15]. The membrane capacitive deionization (MCDI) process, which combines an ion exchange membrane (IEM) with an electrode, has been actively studied since the mid-2000s to address this problem and improve performance [16–20]. The MCDI process combines anion and cation exchange membranes to selectively pass ions through adsorption and desorption in the electrode, exhibiting easy regeneration and maintenance [21]. Moreover, this technology constitutes a next-generation water treatment technology because it can reduce the salt removal rate and prevent direct contact between the electrolyte and the electrode, thereby reducing the electrode contamination [22–26].

The power supply method in the MCDI process is a critical factor that determines the desalination characteristics [27–29]. There exist constant current (CC) and constant voltage (CV) power supply methods [30]. The CC method presents higher efficiency in terms of energy consumption than the CV method, but its adsorption capacity is lower for the same period of time [31]. On the other hand, the CV method is faster and more efficient than the CC method in the desalination process, but the adsorption rate is not constant. Thus, the CC and CV methods are selectively used according to the purpose of the MCDI process [32–34].

In the conventional MCDI process, the feed water should be continuously supplied because the same feed water is used for adsorption and desorption, and consequently, the amount of yield, that is, treated water per feed water, is low. There were many tries to increase the yield by operating the process through reduction of the flow rate during desorption. However, the recovery rate does not significantly increase because desorption is performed using the same feed water. Therefore, in this study we evaluated total dissolved solids (TDS) removal characteristics by recycling the concentrated water generated during desorption in the MCDI process in order to apply it to a process in which water source exceed the water quality standard rather than high concentration TDS removal. To this end, we conducted a comparative analysis in terms of TDS concentration change, consumed energy, and yield between conventional MCDI process and MCDI circulation process.

2. Materials and method

2.1. MCDI configuration and devices

The porous carbon electrode used in this study was purchased from S company in Korea. MCDI module comprised a total of 225 bipolar electrodes with thickness of 150 μm and diameter of 20 cm, as shown in Fig. 1. Anion and cation exchange membranes were attached one by one on the upper and lower parts of each carbon electrode. A 90-μm spacer (nylon net) was inserted between the ion exchange membranes so that the fluid could pass through and could escape from the slope of the electrode to the center through a circular hole with a diameter of 2.5 cm.

The experimental devices of the conventional MCDI process were configured as shown in Fig. 2. Feed water was supplied to the MCDI module with a constant flow rate using a peristaltic pump (MK-07528-30, Masterflex, Germany). Likewise, constant voltage and current were simultaneously applied to the MCDI Module using a Potentiostat (Keysight E36313A, USA). The power was supplied with a constant voltage of 1.2 V in all experiments; a maximum of 10.0 A was allowed, and the current applied to the actual MCDI cell was continuously changing according to the concentration of feed water. The TDS concentration of the treated water passing through the MCDI module was measured every second using a TDS Meter (Multi 3620 IDS, WTW, Germany), and data were collected through a computer directly.

The experimental devices of the MCDI circulation process were configured as shown in Fig. 3. Although this process was similar to the conventional MCDI process, the concentrated water generated during the desorption process was separated and stored in a concentrated water tank and used only for the desorption process. Concentrated water in the tank was supplied to the MCDI module using another peristaltic pump. The remaining procedures related to the applied voltage and data collection were the same as in the conventional MCDI process.

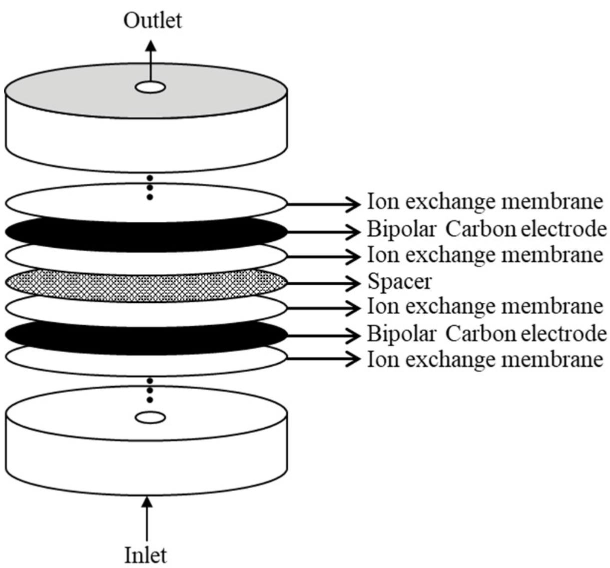

Fig. 1. Configuration schematic of the MCDI module.

2.2. Operation conditions

To evaluate the TDS removal characteristics using concentrated water during desorption in the MCDI process, an experiment was performed and compared with the conventional MCDI process; this is described in Table 1. The purpose of this study is not to remove high concentration of TDS such as seawater desalination as raw water, but to apply the MCDI process in which specific ions exceed water quality standards (e.g., groundwater, industrial cleaning water, district heating water, etc.). Therefore, the tap water with a TDS concentration of 120 mg/L was used as feed water to conduct the experiment; a voltage of 1.2 V and a flow rate of 0.2 m^3/h were applied to perform 5-min adsorption and desorption cycles. In step (1), water was produced by absorbing ions through the application of a constant voltage; in step (2), the MCDI module was cleaned by applying a reverse voltage. The same feed water was used in both steps (1) and (2). A total of 40 cycles were performed to evaluate the TDS removal characteristics.

The operation conditions of the MCDI circulation process are presented in Table 2. As in the conventional MCDI process experiment, tap water with a TDS concentration of 120 mg/L was used as feed water, and the same flow rate and voltage were applied. In step (1), water was produced by absorbing ions through the application of a constant voltage; in step (2), the MCDI module was cleaned by circulating the concentrated water generated during the desorption process to the concentrated water tank. A total of 40 cycles were also performed to compare TDS removal characteristics with those of the conventional MCDI process.

3. Results and discussion

3.1. Change in TDS concentration during the conventional MCDI process

The change in TDS concentration during the conventional MCDI process was identified prior to evaluating the TDS removal characteristics of the MCDI circulation process. Tap water with TDS concentration of 120 mg/L was used as feed water, and a continuous experiment over 40 cycles was conducted by applying 5-min adsorption and desorption intervals. Fig. 4a and b show the TDS concentration change after 10 and 40 cycles, respectively. The experimental results of this study showed the average of the 3 experimental data, and the repeatability and reproducibility were almost similar.

Concerning the state of the experiment after 10 cycles, shown in Fig. 4a, the overall adsorption efficiency was stable, exceeding 95% during the adsorption process. Regarding the desorption process, the TDS concentration of the treated water decreased as much as the concentration of the feed water, indicating a stable desorption efficiency. The results after 40 cycles, shown in Fig. 4b, confirmed that both adsorption and desorption were stably performed even when the experiment continued for 40 cycles. This result means that treated water can be stably produced when the conventional MCDI process is conducted under these conditions.

3.2. Change in TDS concentration during MCDI circulation process

To compare with the experiment above described, we conducted an experiment to assess the change in TDS concentration during the MCDI circulation process. Only desorption was modified; the remaining parameters were set to the same values as in the conventional MCDI process. Fig. 5a and b show the change in TDS concentration after 10 and 40 cycles, respectively. As in previous experiment, the average of 3 experimental data was shown.

Fig. 5a shows that the adsorption process, which is a production process, presented a stable adsorption efficiency, as in the conventional MCDI process. However, regarding desorption, which is a cleaning process, it was observed that the TDS concentration increased as the experiment progressed. The results of the 40-cycle continuous experiment

Table 1
Experimental method of MCDI process

Experimental process	Water flow	Feed water	From	To	Applied voltage (V)	Flow rate (m^3/h)	Adsorption time (min)	Desorption time (min)
Produce	①→②→③	Tap water	Feed water tank	Treated water tank	1.2	0.2	5	–
Wash	①→②→④	Tap water	Feed water tank	Wastewater tank	1.2	0.2	–	5

Table 2
Experimental method of the MCDI circulation process

Experimental process	Water flow	Feed water	From	To	Applied voltage (V)	Flow rate (m^3/h)	Adsorption time (min)	Desorption time (min)
Produce	①→②→③	Tap water	Feed water tank	Treated water tank	1.2	0.2	5	–
Wash	⑤→①→②→④→⑤	Tap water	Concentrated water tank	Concentrated water tank	1.2	0.2	–	5

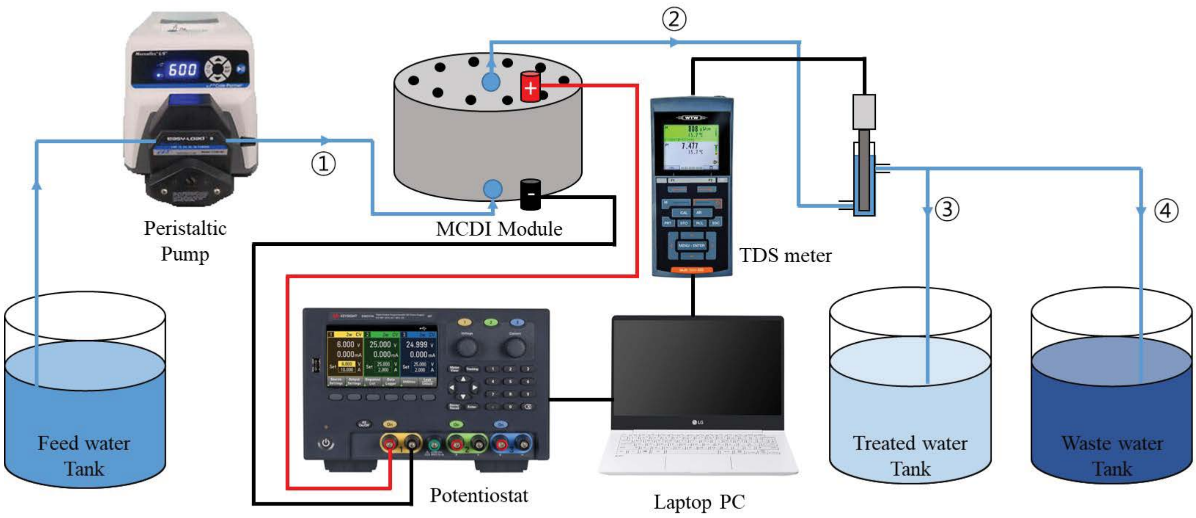

Fig. 2. Schematic diagram of the MCDI process.

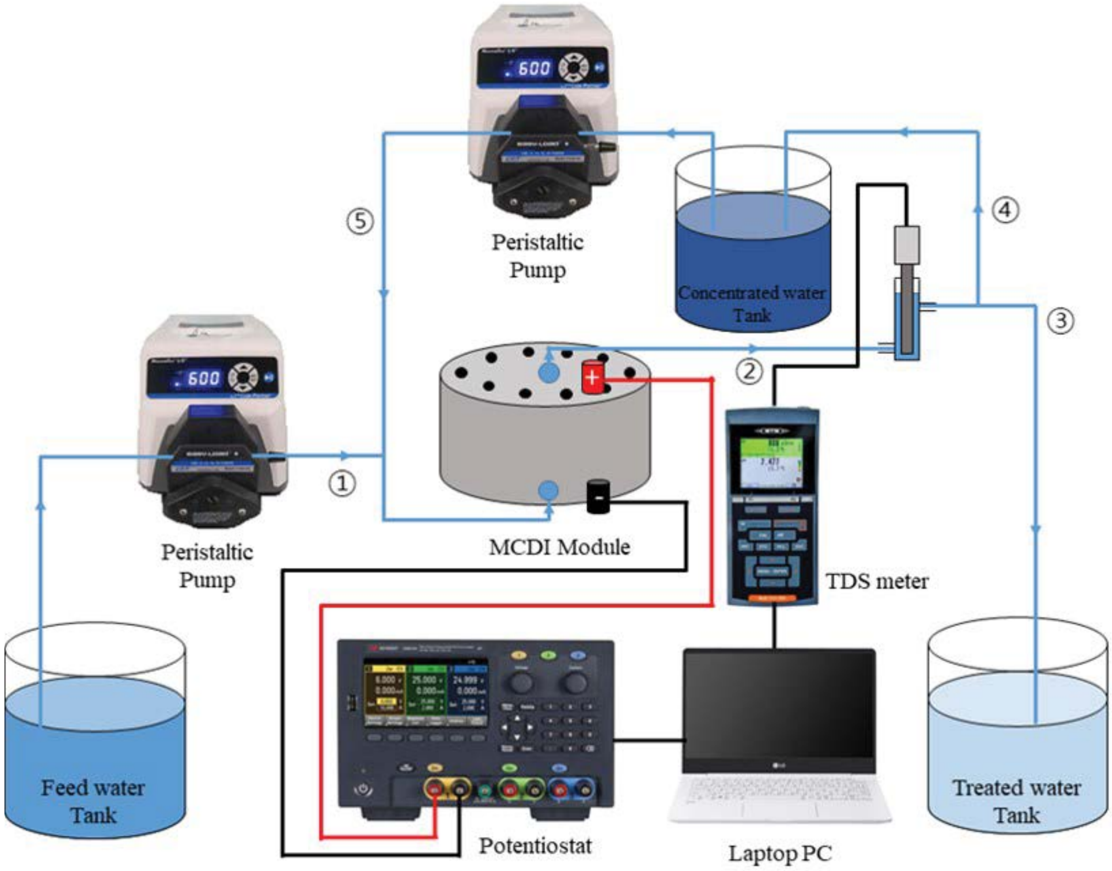

Fig. 3. Schematic diagram of the MCDI circulation process.

depicted in Fig 5b show that the adsorption efficiency was stable but the TDS concentration during the desorption process continued to increase. It is concluded that an important factor related to desorption is to discharge ions that have escaped from the cell of the MCDI module used for cell regeneration to the outside of the module. This factor is more relevant than the concentration of the solution during the desorption process.

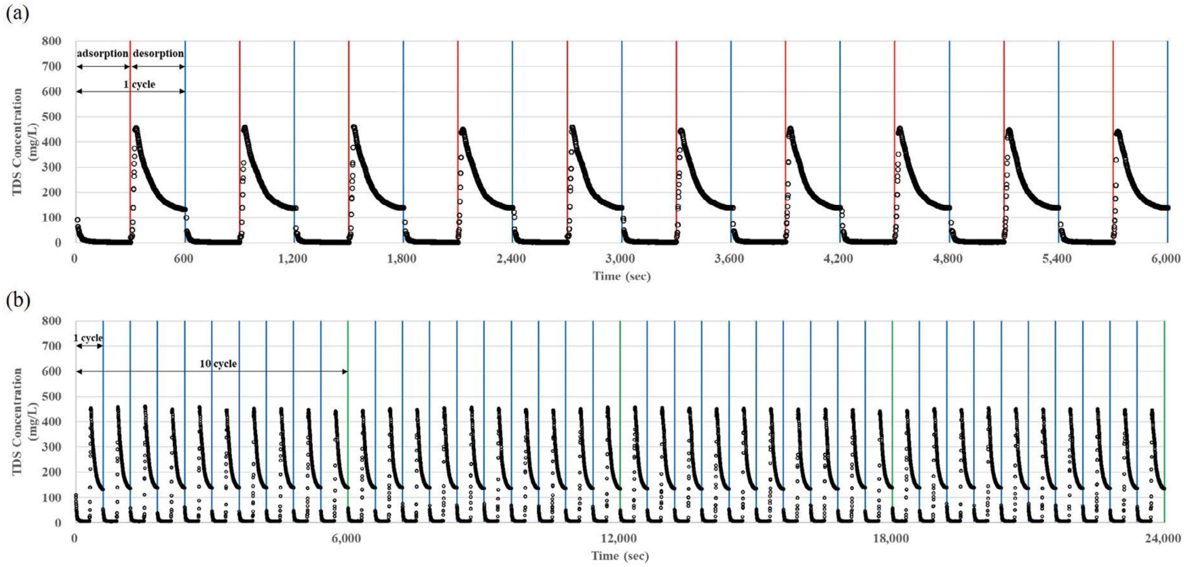

Fig. 4. TDS concentration of adsorption and desorption after (a) 10 cycles and (b) 40 cycles of the MCDI process.

3.3. Change in TDS concentration for each cycle

Based on the experimental results of the two processes previously described, we compared the changes in TDS concentration after 1, 10, 20, 30, and 40 cycles of each process. The results are presented in Fig. 6a and b. Fig. 6a shows the experimental results for the conventional MCDI process. Note that the difference in TDS concentration between the adsorption and desorption processes was not significant on a cycle basis. Regarding the MCDI circulation process, whose results are shown in Fig. 6b, it was found that the TDS concentration in the desorption process increased with the TDS concentration in the concentrated water tank as the cycle progressed. Given that there was any other difference in TDS concentration during the adsorption process, it is concluded that desorption with concentrated water does not affect the adsorption process.

3.4. Comparison of energy consumption and recovery rate

The energy consumption and recovery rate of the conventional MCDI process and MCDI circulation process are shown for comparison in Fig. 7a–c, respectively. Fig. 7a shows the energy consumption after 10–40 cycles for both the conventional MCDI process and the MCDI circulation process. Note that the energy consumption of the conventional MCDI process remained constant even when the number of cycles increased. In this experiment, the current changed as a function of the feed water concentration given that a constant voltage of 1.2 V was applied. Accordingly, in the conventional MCDI process, tap water with constant TDS concentration of 120 mg/L was used as the feed water during adsorption and desorption. Thus, the low energy was consumed even for an increasing number of cycles. By contrast, given that the MCDI circulation process reuses the concentrated water during desorption, the feed water supplied to the MCDI device during the desorption process was concentrated water. Thus, the TDS concentration gradually increased, resulting in an increase in energy consumption. Accordingly, the energy consumption compared to the amount of water produced for each cycle is compared and shown in Fig. 7b. The conventional MCDI process showed a constant energy consumption per treated water, but the MCDI circulation process showed similar results as the amount of treated water increased compared to the feed water as the cycle progressed.

To compare the yield of the conventional MCDI process and the MCDI circulation process, Fig. 7b shows treated water per feed water for each cycle. Note that the conventional MCDI process presented a constant yield even when the number of cycles increased. This seems to be because the feed water of the conventional MCDI process is used for both adsorption and desorption, but the treated water is produced only through the adsorption process. Nevertheless, given that the MCDI circulation process reuses the concentrated water stored in the concentrated water tank during the desorption, so separated feed water is not required during such process. Therefore, it is concluded that as the number of cycles increases, the yield gradually increases as well.

4. Conclusion

In this study, we investigated the TDS removal characteristics of the MCDI circulation process by reusing the concentrated water which generated during desorption process. As a result of TDS concentration change experiment during the conventional MCDI process, we observed that stable efficiency was achieved when 5-min cycles of adsorption and desorption at a flow rate of 0.2 m^3/h. Given that the MCDI circulation process uses concentrated water during desorption, the TDS concentration in the desorption process increased as the experiment proceeded, but the water could be stably produced because such concentration does not affect the adsorption process. We also found that an important factor is the discharge of the ions that escape from the electrode to the spacer outside the

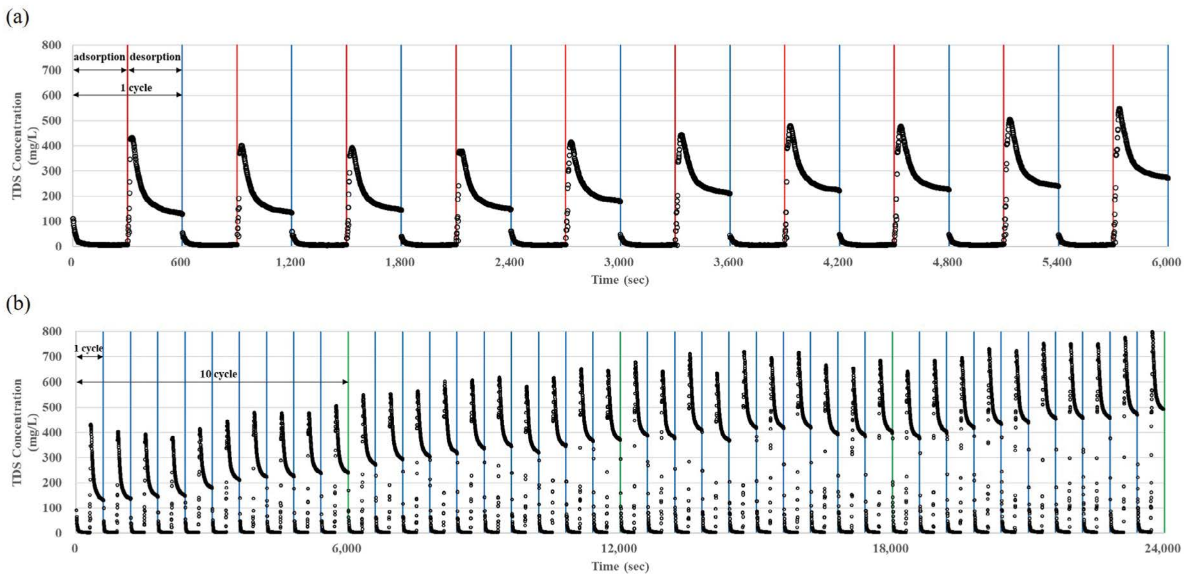

Fig. 5. TDS concentrations of adsorption and desorption after (a) 10 cycles and (b) 40 cycles of the MCDI circulation process.

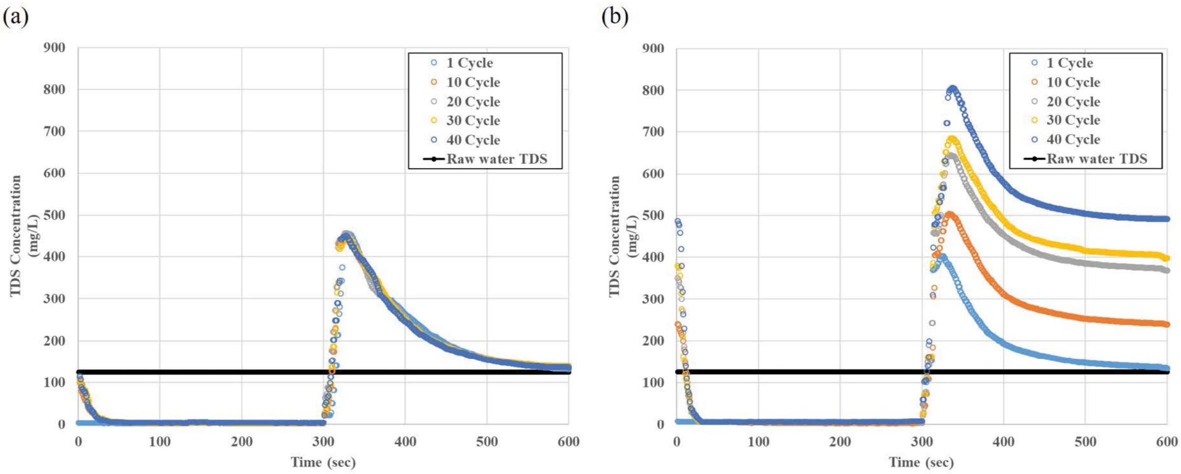

Fig. 6. Change in TDS concentration for each cycle of (a) MCDI and (b) MCDI circulation processes.

MCDI module due to the application of reverse voltage. This factor is more relevant than the TDS concentration of the feed water used for desorption. We also analyzed the change in TDS concentration as a function of the number of cycles. The conventional MCDI process showed a constant TDS concentration change even when the number of cycles increased. In the MCDI circulation process, the TDS concentration in the desorption process increased as the TDS concentration in the concentrated water tank generated during the desorption process increased with the number of cycles. However, the adsorption efficiency was found to be stable. We also compared the energy consumption per cycle. We found that the energy consumption of the conventional MCDI process was constant, but that of the MCDI circulation process gradually increased. In this case, it can be assumed that the current change depends on the concentration of the feed water because we applied a constant voltage of 1.2 V. Finally, we also compared the yield by calculating the amount of treated water vs. the feed water. The conventional MCDI process requires feed water for both the adsorption and desorption processes, but given that the treated water is used only for the adsorption process, the yield was found to be constant even when the experiment progressed. However, the yield gradually increased as the experiment progressed because the MCDI circulation process reuses the concentrated water generated in the desorption process.

The MCDI process has a disadvantage in that concentrated water is inevitably generated when producing treated water. This is very disadvantageous when raw water with a limited amount of feed water is used, such as groundwater. The MCDI circulation process proposed in this study requires more power consumption than MCDI process. However, there is an advantage of securing a large amount of treated water compared to the feed water. If the MCDI

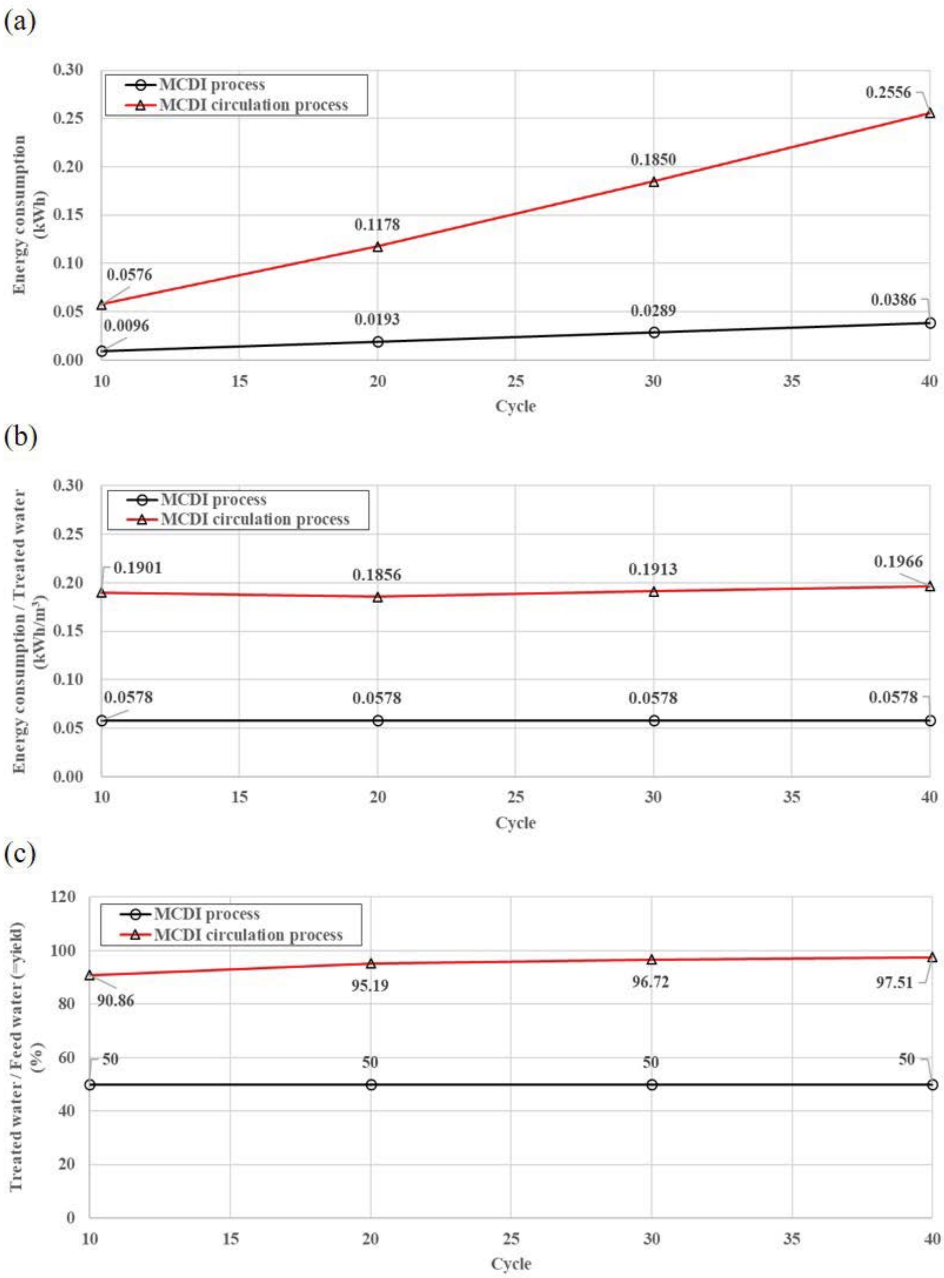

Fig. 7. Comparison of (a) energy consumption, (b) energy consumption per treated water and (c) yield as a function of the number of cycles of the MCDI and MCDI circulation process.

circulation process can be used with low power consumption based on this high yield, it is judged that it can be effectively applied to the water treatment process in the future.

Acknowledgement

This work was supported by Korea Environment Industry & Technology Institute (KEITI) through Project for developing innovative drinking water and wastewater technologies Program, funded by Korea Ministry of Environment (MOE) (2020002700003).

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