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Desalination of a thermal power plant wastewater by membrane capacitive deionization

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Abstract

A membrane capacitive deionization (MCDI) system, the one that ion-exchange membranes were added onto a capacitive deionization (CDI) system, has been developed to test desalination performance for power plant wastewater. Several experiments were conducted to compare the MCDI with the CDI in desalination capacity and to determine optimal operation conditions using 1,000 ppm NaCl solution. Salt removal rate of the MCDI system was 19% higher than that of the CDI system. The flow rate and the direct current voltage at which the salt removal rate was the highest were 40 ml/min and 1.2 V, respectively. Desalination performance for the power plant wastewater was investigated at the given operation conditions. The maximum salt removal rate and electric energy consumption were about 92% and 1.96 Wh/L, respectively. It was concluded from this study that the MCDI system could successfully be applied for the reuse of power plant wastewater.

Keywords: Capacitive deionization; Desalination

1. Introduction

Water is an essential and fundamental resource in thermal power plants with various purposes: a make-up for boiler feed water, cooling bearings and equipment, and various plant services. Raw water used for these purposes at most power plants in Korea is drawn from a river basin. However, several power plants located in the capital area depend on a public enterprise for the supply of water. Accordingly, water bills for the plants are increasing year after year. So, the plants consider treatment and reuse of wastewater from various processes: water treatment, demineralizer system, etc. Since the treated wastewater contains only inorganic ions, it can be reused as raw water for various purposes after the ions are removed with cost-effective and environmentally friendly deionization technology.

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In order to remove ions from salty water, some kinds of processes such as ion exchange, reverse osmosis, and electrodialysis are used at present. Recently, capacitive deionization (CDI) using capacitive adsorption has been suggested to lower water treatment cost and prevent environmental pollution without the disadvantages that other processes have [1,2]. CDI is energy-efficient because it is operated at low voltages (0.8–1.4V) without high-pressure pumps, thermal heaters or high direct current voltage. In addition, this process is environmentally friendly because it requires no chemicals. In CDI, fouling associated with reverse osmosis or electrodialysis is also minimized because no sustained concentrates are formed.

CDI is an electrosorption process that removes inorganic ions by charge separation and acts as a "flow through" capacitor [3]. In CDI, an aqueous solution containing dissolved inorganic salts passes between matching pairs of activated carbon cloth electrodes on which electric potential is applied. Inorganic ions are held at the charged electrode surfaces and removed from aqueous solution. When the electrodes are saturated with ions, they can be regenerated by applying the reverse potential to allow the adsorbed ions to be released into the purge stream. This process might be important for future applications for water purification [4]. Although several studies for CDI have been conducted recently, they have been mainly carried out to develop new carbon materials to use as CDI electrodes [5,6].

In this study, in order to reuse a thermal power plant wastewater a membrane capacitive deionization (MCDI) system that shows higher desalination performance compared to CDI was developed and its salt removal rate and electric energy consumption were investigated. In addition, its optimal operation conditions such as the flow rate and the direct current voltage were determined. And the feasibility of applying the MCDI system to the reuse of a power plant wastewater was determined.

2. Experimental

2.1. Electrode material

The activated carbon cloth (ACC) made from phenolic resin (Kuraray Chemical, Japan) was used for MCDI and CDI electrodes. The specific surface area was obtained by the BET method [7]. Table 1 shows the main characteristics of the ACC.

Table 1
Main characteristics of ACC used for the electrode

Commercial name	CH900-10
Thickness, mm	0.6
Specific surface area, m^2/g	1117
Raw material	Phenolic resin

2.2. Ion-exchange membranes

The ion-exchange membranes (Tokuyama, Japan) were used to adsorb the ions selectively on the electrodes. The cation-exchange membrane is selectively permeable to cations and the anion-exchange membrane is selectively permeable to anions. Their low electric resistance affects the consumption of electricity for the MCDI. Their main characteristics are shown in Table 2.

2.3. MCDI and CDI performance

Adsorption capacity of ions on electrodes was measured using bench-scale MCDI or CDI apparatus shown in Fig. 1. Aqueous solution with applied flow rates of 40–100 ml/min was pumped into the stack by a peristaltic pump (PP-600DW, Poong lim Co., Korea) at the bottom and exited at the top. The direct current voltage of 0.8–2.0 V was applied by a rectifier (Agilent E3633A, USA). Conductivity was monitored by a conductivity meter (Swan Unicon 4, Swiss). Ion concentration was determined by ion chromatography (Dionex-DX500) and inductively coupled plasma spectrometry (Shimadzu, ICPS-1000).

Table 2
Main characteristics of cation-exchange and anion-exchange membranes

	Cation-exchange membrane	Anion-exchange membrane
Commercial name	CM-1	AM-1
Type	Acidic cation permeable	Basic anion permeable
Ion form	Na-form	Cl-form
Electric resistance, Ω-cm^2	0.8–2.0	1.3–2.0
Thickness, mm	0.15	0.15

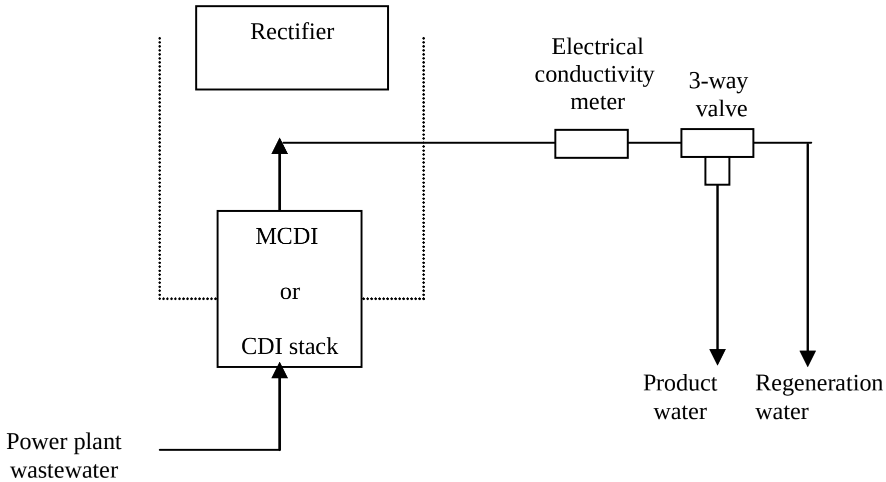

Fig. 1. Schematic flow diagram of a bench scale MCDI or CDI system.

An MCDI stack consists of one or more cells attached in series. Each cell consists of two parallel electrode plates that have a dimension of 300 mm wide × 1,000 mm long × 0.6 mm thick. Electrodes were contacted with the cation-exchange membrane or the anion-exchange membrane that has a dimension of 500 mm wide × 1,020 mm long × 0.15 mm thick on the inside and contacted with current collectors on the outside as shown in Fig. 2. Also, the ion-exchange membranes were placed to face each other on the opposite sides of a flow spacer.

Elements of a CDI stack are the same as those of the MCDI stack less ion-exchange membranes as shown in Fig. 3.

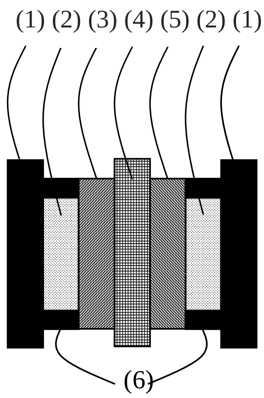

Fig. 2. Schematic diagram of the MCDI cell: (1) current collector, (2) electrode, (3) cation-exchange membrane, (4) flow spacer, (5) anion-exchange membrane, (6) gasket.

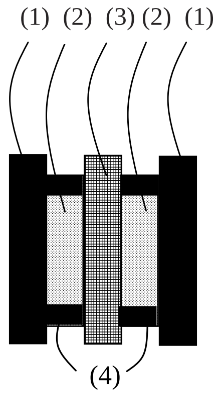

Fig. 3. Schematic diagram of the CDI cell: (1) current collector, (2) electrode, (3) flow spacer, (4) gasket.

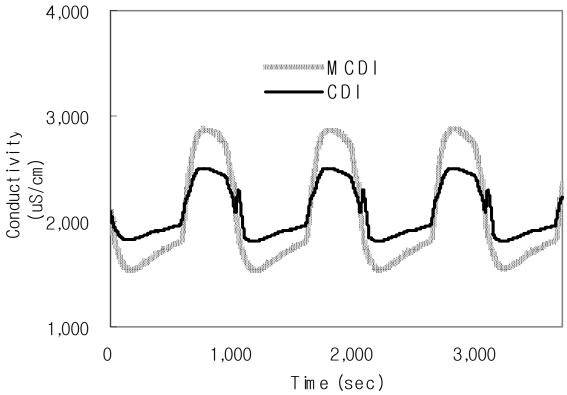

Fig. 4. Operation and regeneration profiles of CDI and MCDI at electric field of DC 1.2 V and flow rate of 40 ml/min.

4. Results and discussion

4.1. The desalination performance of MCDI compared to CDI

While an electric potential is applied to activated carbon cloth electrodes, ions move from solution to ACC electrodes and are adsorbed on them. When the electrodes become saturated with ions, ions are no longer adsorbed on them. And then, the electrodes have to be regenerated to remove the ions that are adsorbed on them. Electrode regeneration is conducted by applying the reversed electric potential to the electrodes. Anode and cathode in the operation phase changed to cathode and anode respectively in the regeneration phase by the reversed electric potential. In the regeneration phase, the electrodes are supposed only to release the ions that are adsorbed on them. But the operation and regeneration curves in CDI are asymmetrical due to different kinetics associated with ion uptake onto, and removal from, the carbon surface [6]. In other words, Ion adsorption and ion desorption occur simultaneously on the electrodes in CDI. However only ion desorption occurs in MCDI in the regeneration phase because ion-exchange membranes prevent ion adsorption on the electrodes. Therefore, salt removal capability of MCDI is higher than that of CDI and the regeneration time is shorter in MCDI than in CDI as shown in Fig. 4.

Ions are continuously moved from solution to the electrode surface and adsorbed on it until the electrode is saturated with ions. Due to the limited ion adsorption capacity of the electrode, however, the number of ions that are moved and adsorbed to the electrode surface gradually deceases during the operation cycle. Accordingly, the conductivity of the flow gradually increases as the electrode is saturated with ions in the MCDI and CDI cells during the operation cycle. In other words, ion adsorption capacity of the cells falls gradually as the cells are saturated with ions and the conductivity of the outlet water increases gradually until it reaches the conductivity of the inlet water during the operation cycle.

During the operation cycle, much more ions are adsorbed in the MCDI cell than the CDI cell as shown in Fig. 4. During the regeneration cycle, much more ions that were adsorbed during the cycle are desorbed and released from the MCDI cell than from the CDI cell. So, the conductivity of the flow in the MCDI cell is higher than that of the flow in the CDI cell in the regeneration cycle.

Although the regeneration time of the CDI cell in one cycle is longer than in the MCDI cell, the regeneration time needed for the release of adsorbed ions only during the operation cycle is the same in both cells. The reason that the regeneration time in one cycle of the CDI cell is longer than that of the MCDI cell is that adsorption and desorption of ions proceed simultaneously at the beginning of the operation cycle. Due to this reason, the shoulder peak appears in the CDI as shown in Fig. 4. But, in the MCDI cell, only desorption of ions proceeds because the ions cannot pass through the ion-exchange membrane.

After the DC voltage of 1.2 V was applied to MCDI or CDI for 10 min, the reversed DC voltage was applied to them for 5 min.

For the comparison of the performance under different conditions, the product concentration was expressed as salt removal rate that is defined as follows:

$$\text{Salt removal rate (\%)} = \frac{C_f - C_p}{C_f} \times 100$$

where C_f is feed concentration and C_p is the lowest product concentration.

Salt removal rates for MCDI and CDI are presented in Table 3. The salt removal rate of sodium ions in MCDI is 19% higher than in CDI. And the salt removal rate of chloride ion in MCDI is 19% higher than in CDI.

4.2. Optimum flow rate and electric field

In order to determine optimum operation conditions for MCDI, the effects of flow rate and electric field for desalination performance were investigated. Fig. 5 shows the effect of the flow rate on the desalination efficiency for 1,000 ppm NaCl solution at 40, 60, 80, and 100 ml/min. Although all graphs show the same pattern, the desalination efficiency decreases as the flow rate increases. At a flow rate of 40 ml/min, the highest salt removal capability is achieved. These results show that the salt removal rate depends on the residence time of the solution on the electrodes. To increase the salt removal rate, more time for mass transfer is needed.

The electric energy consumption and the salt removal rate at various flow rates are illustrated in Fig. 6. The salt removal rate decreases as the flow rate increases. Especially, the salt removal rate decreases highly when the flow rate changes from 40 ml/min to 60 ml/min. The electric energy consumption also decreases as the flow rate increases.

Considering the salt removal rate, it can be seen that the optimum flow rate is 40 ml/min.

Fig. 7 shows the effect for DC voltage on the desalination efficiency at 0.8, 1.2, 1.6, and 2.0 V. All conductivity graphs show the same pattern as those in Fig. 6. The desalination efficiency increases as the DC voltage increases. However, the electric energy consumption also increases as the DC voltage increases as shown in Fig. 8. The salt removal rate for DC voltages of 1.6 V is similar to that of 2.0 V. These results show that energy is wasted at the DC voltage of above 1.6 V. Also, pH is changing irregularly at the DC voltage of above 1.6 V due to water electrolysis as shown in

Table 3
Salt removal rates for MCDI and CDI

	Feed	Product		Salt removal rate, %	
		MCDI	CDI	MCDI	CDI
Electric conductivity, μS/cm	2,000	1,495	1,850		
Sodium, mg/L	1,020	698	885	32	13
Chloride, mg/L	976	681	872	30	11

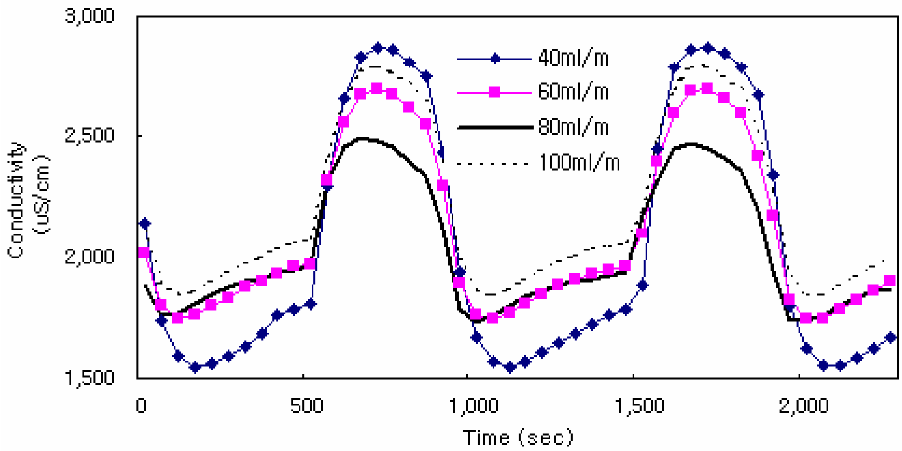

Fig.5. The effect of the flow rate on the desalination efficiency at DC 1.2 V.

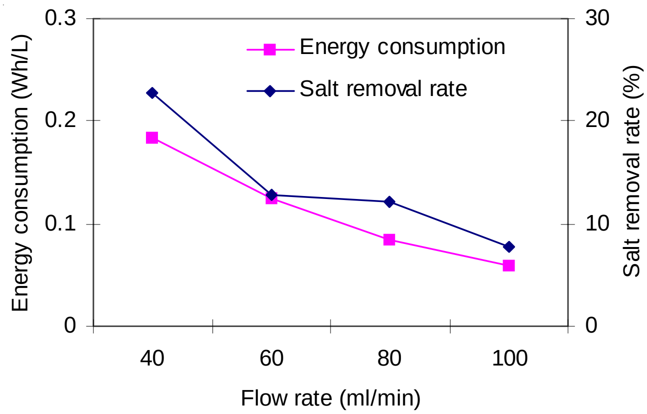

Fig. 6. The energy consumption for various flow rates at DC 1.2 V.

Fig. 9. The pH is varied from acidic to alkaline corresponding to the operation and regeneration processes at DC 2.0 V and at DC 1.6 V it becomes alkaline only. At present, the authors do not understand this phenomenon. However, it can be assumed that electrolysis reactions at both anode and cathode proceed with the same degree to each other at a sufficiently high voltage such as DC 2.0 V and proceed with different degree to each other at DC 1.6 V.

Considering both the salt removal rate and the energy consumption, it can be seen that the optimum DC voltage is 1.2 V.

4.3. Desalination of power plant wastewater by MCDI

4.3.1. Overview of wastewater treatment and MCDI processes

Wastewater that is generated at a thermal power plant can be classified in two kinds of wastewater: daily wastewater and aperiodic wastewater. Daily wastewater includes wastewater from the water treatment system, demineralizer system, housing workshop, cooling system, equipment drain, etc. Aperiodic wastewater includes various kinds of equipment cleaning wastewater.

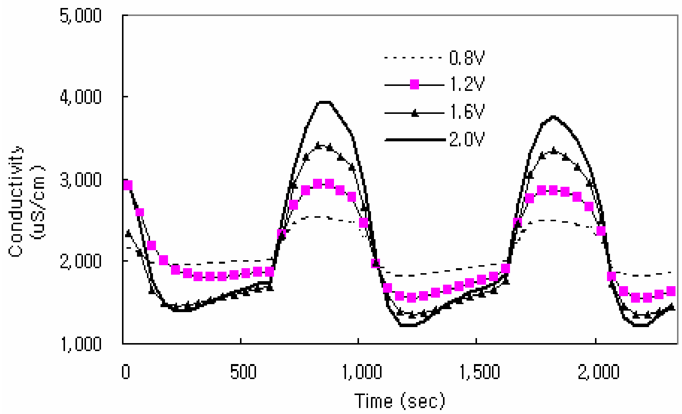

Fig. 7. The effect of the DC voltage at a flow rate of 40 ml/min.

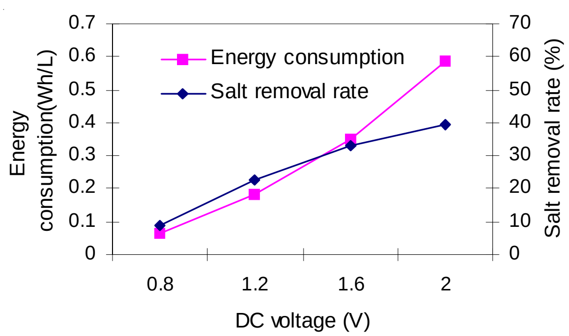

Fig. 8. The energy consumption for various DC voltages at a flow rate of 40 ml/min.

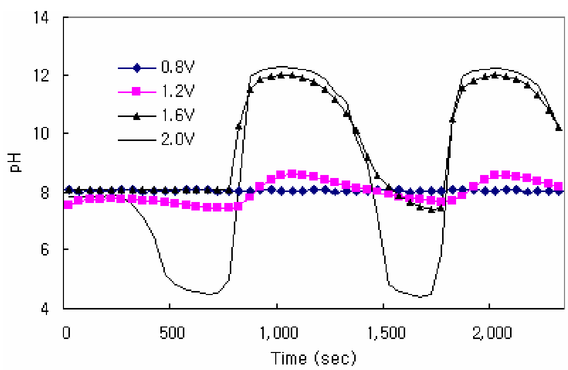

Fig. 9. pH change for various DC voltages at a flow rate of 40 ml/min.

This paper presents a study of the reuse of daily wastewater only. A diagram of generalized daily wastewater treatment for a typical thermal power plant and MCDI processes is illustrated in Fig. 10. The daily wastewater is treated by various processes such as those shown in Fig. 10 and is discharged to the sea. The treated wastewater flows into the MCDI system inlet just before being discharged to the sea.

In the MCDI system, the wastewater was only used for making product water and regeneration water. The product water is sent to a raw water tank to be reused as industrial water at a power plant and the regeneration water is discharged to the sea. The regeneration water contains only inorganic ion concentrates.

4.3.2. Desalination of wastewater by MCDI

Operation conditions that have been obtained from NaCl solution were applied to desalination tests for power plant wastewater. The tests were conducted at a flow rate of 40 ml/min and the applied DC voltage of 1.2 V using MCDI. In this

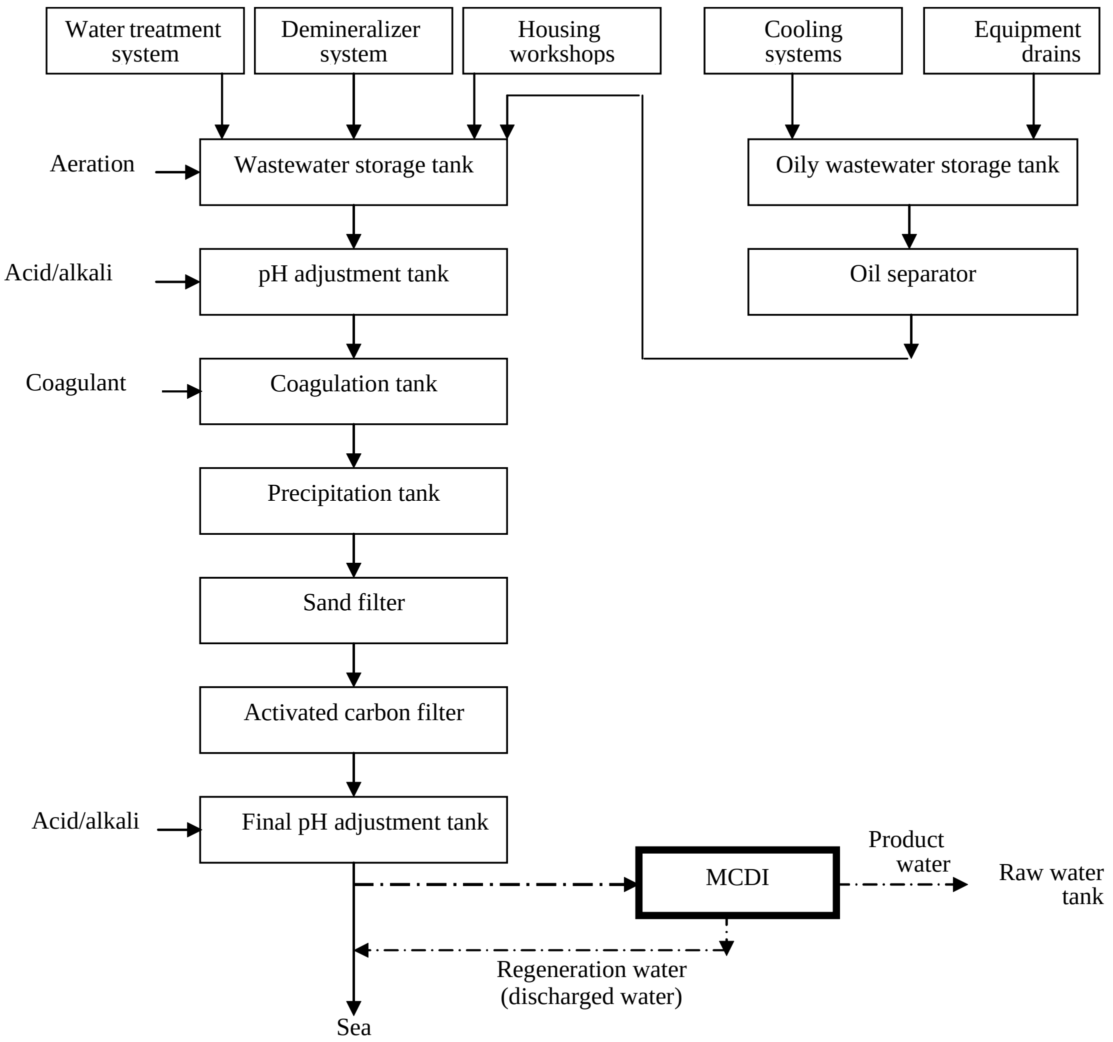

Fig. 10. Diagram of generalized daily wastewater treatment for a typical thermal power plant and MCDI processes.

test, ACC electrodes with areas of 2 m^2 in total were used in the MCDI system.

The detailed ionic analysis results for the MCDI feed and product streams of the power plant wastewater and salt removal rate are shown in Table 4. It can be seen from the feed water analysis that the main ionic species are sodium and chloride ions. These ions come from spent process water of thermal power utilities that is mainly generated in pure water treatment operations. The composition ratio of ionic species in the wastewater is similar to that in seawater. About 85% of the ions in the wastewater and about 90% of the ions in the seawater are sodium and chloride ions. Unlike ion exchange or reverse osmosis, MCDI shows better removal characteristic for smaller, monovalent ions than for larger, divalent ions [6]. Thus, the adsorption tendency of ions in the wastewater may be similar to that in seawater in the MCDI system although the concentration of NaCl in

Table 4
Water quality and salt removal rate of MCDI

Specification	Feed	Product streams	Salt removal rate, %
pH	7.1	6.9	—
Electric conductivity, μS/cm	5,400	250	—
Calcium, mg/L as $CaCO_3$	441	35	92
Magnesium, mg/L as $CaCO_3$	108	9	92
Sodium, mg/L as $CaCO_3$	2,299	105	95
Potassium, mg/L as $CaCO_3$	30	4	87
Chloride, mg/L as $CaCO_3$	2,797	145	95
Sulfate, mg/L as $CaCO_3$	150	7	95
Nitrate, mg/L as $CaCO_3$	144	10	85

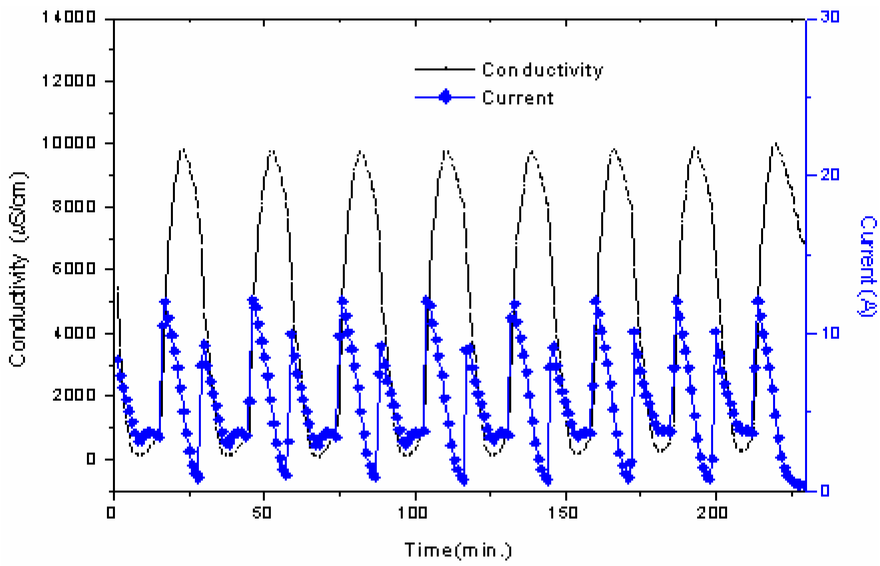

Fig. 11. Multiple adsorption/regeneration cycles at electric field of DC 1.2 V and flow rate of 40 ml/min.

seawater is much higher than that in wastewater. Table 4 also shows that all ions exhibit high salt removal rates. About 92% of feed water inorganic ions were removed and the electric conductivity of product streams was 250 μS/cm.

Fig. 11 shows the MCDI outlet conductivity and stack current graphs over 8 consecutive adsorption/regeneration cycles. The graphs show the same pattern in all cycles. No appreciable decline in the MCDI performance was observed until 500 cycles.

The electric energy consumption that was calculated from the applied potential, the stack current, and time measurements were about 1.96 Wh/L.

5. Conclusions

A membrane capacitive deionization unit that has a much higher efficiency than a capacitive deionization system was designed and tested for desalination of power plant wastewater. The highest salt removal rate is observed at an electric field of DC 1.2 V and a flow rate of 40 ml/min. The salt removal rate was about 92%. The electric energy consumption value was 1.96 Wh/L. No appreciable decline in the MCDI performance was observed after a certain number of cycles. After further studies of comparing the energy requirement of the MCDI system with that of the RO, electrodialysis and other suitable systems under the same conditions, the MCDI process may be applied to reusing power plant wastewater economically and environmentally friendly.

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