Effect of Desorption Methods on Electrode Regeneration Performance of Capacitive Deionization

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Abstract: Long regeneration time and substantial water usage in desorption cycles impose potential barriers for practical applications of capacitive deionization (CDI). In this research, a single-pass continuous-flow CDI cell was used to explore the effect of desorption methods on electrode regeneration performance. The results demonstrated effective nature of polarity reversal during electrode regeneration compared to the conventional short-circuit method. A reversed polarity with optimized duration and magnitude of cell voltage while purging with a proper flow scheme exhibited substantial reductions on regeneration time and flush-water usage during the desorption processes of CDI. The beneficial aspects of preferred desorption methods were attributable to minimization of a readsorption effect by limiting the rate of ion transport to the oppositely charged electrode. The results of this research are beneficial for improving the operational efficiency and cost-effectiveness of CDI systems for engineering applications. DOI: 10.1061/(ASCE)EE.1943-7870.0001245. © 2017 American Society of Civil Engineers.

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Introduction

Freshwater, an essential component for human consumption, is facing scarcity with the growth of population and industry. Conventional desalination technologies such as ion exchange, reverse osmosis, electrodialysis, and distillation are among options to produce clean water. However, their disadvantages, including by-product formation and high energy consumption, hinder many applications (Xu et al. 2008). In recent years, capacitive deionization (CDI) has come to be considered a low-polluting, energy-efficient, and cost-effective alternative to conventional water desalination technologies and currently attracts keen interest from worldwide researchers (Suss et al. 2015).

During the adsorption process of CDI ions are extracted from a water stream and stored within the structures of porous electrodes (Biesheuvel and Bazant 2010). The adsorption capacity depends on intrinsic properties of electrode materials (such as surface area, pore microstructure, pore-size distribution, surface group, etc.) (Gao et al. 2015) and operating conditions (such as cell voltage, electrode distance, retention time, solution conductivity, etc.) (Jande and Kim 2013, 2014; Huang et al. 2016). When the ion storage capacity is reached, a desorption (electrode regeneration) process is needed to release the ions, resulting in a stream concentrated in salt. An adsorption and a desorption step complete a cycle. As the ion transport rate in CDI is potentially limited by the macroscopic transport resistance in the pore microstructure (Suss et al. 2015), for optimum performance, a CDI system must be tuned to achieve faster kinetics of both adsorption and desorption.

Although CDI has been discussed for faster adsorption kinetics (Liu et al. 2015; Bian et al. 2016), few studies have focused on enhancing its subsequent desorption performance. Some researchers [Gabelich et al. 2002; T. D. Tran and D. J. Lenz, “Alternating-polarity operation for complete regeneration of electrochemical deionization system,” U.S. Patent 6346187 (2004); Leonard et al. 2009] used polarity reversal as a desorption method to rejuvenate a CDI system. The beneficial aspect of polarity reversal lies in the fact that a reversed voltage might momentarily expel the adsorbed ions from the electrode. A concern about polarity reversal was also raised by L.-R. Shiue et al. (“Deionizers with energy recovery,” U.S. Patent No. 6661643 (2013]) and Biesheuvel et al. (2011): the ions released from one electrode may be quickly adsorbed in the other one. Besides polarity reversal, a short circuit may also be used for desorption. However, it was related with a low efficiency, which was attributed to the slow release of remaining ions trapped in the electrodes’ porous structures (Cohen et al. 2013). Because slow desorption during the CDI operation is a potential barrier for its practical applications, enhancement in desorption performance is highly desirable because it reduces the time and volume of water used for regeneration.

Yao and Tang (2016) reported on the occurrence of readsorption during polarity reversal in desorption cycles of CDI. The work described in the present paper was devoted to expedite the desorption process based on the discharge method, reversed charging time, cell voltage, flush flow rate, and type of flush water in a single-pass CDI system. These parameters were examined for their effects on reductions of regeneration time and flush-water usage. As CDI moves into more commercial applications, the results from this study are helpful for water professionals in designing an efficient CDI system for production of desalinated clean water.

Materials and Methods

System Setup and CDI Structure

The CDI system, including a CDI cell, a potentiostat as external power supply, a peristaltic pump with influent and effluent tubes, a magnetic stirring plate, and two containers for influent and effluent storage, respectively, was designed in a continuous single-pass
flow mode (Fig. 1). As the saline water was pumped through the CDI cell, the effluent was collected and analyzed via a conductivity meter. The CDI cell, measuring 28.2 cm long, 12.4 cm wide, and 1.6 cm tall, had an effective volume of 450 mL and contained a pair of flow-by electrodes, which were commercially available activated-carbon cloth (ACC) (FM10, Chemviron, U.K.) with a specific surface area of 1,000 m$^2$/g and thickness of 0.5 mm. The raw ACC was cut into two pieces with a dimension of 25.6 × 11.8 cm each, weighing 18.4 g total, and was prerinsed with deionized (DI) water until conductivity in the rinsed water became stable and no more ions were released. The channel between the ACC electrodes in the CDI cell was maintained at 8 mm wide via a rubber gasket while titanium wires attached to the ACC were used as current collectors. The channel width was chosen according to the engineering consideration of reducing the short-circuit risk as a result of protruding fibers from the electrodes during prolonged operations. Polyethylene plates were then firmly pressed to seal and immobilize the entire stack of all layers.

**CDI Operation**

Analytical-grade NaCl was used to make synthetic raw saline water (1,613 μS/cm, 793 mg/L NaCl solution) for the experiments. Prior to each run, the CDI cell was first equilibrated with the raw water until the effluent conductivity was equal to that of the influent. A cell voltage of 1.2 V was then applied while electroadsorption was conducted in a closed-loop operation. A concentration-time plot of a typical adsorption-desorption cycle during the closed-loop operation is shown in Fig. 2. To ensure that all desorption tests started at the same electrode saturation level, the peristaltic pump recirculated 450 mL of the feed water through the CDI cell until the conductivity reading decreased to 1,499 ± 2 μS/cm, indicating a salt concentration of 737 ± 1 mg/L, and the ACC electrodes reached a salt electroadsorption amount of 1.37 ± 0.03 mg/g. The system was then switched to a single-pass desorption mode, and the original saline water (1,613 μS/cm, 793 mg/L NaCl solution), unless noted otherwise, was used to flush the cell. The effluent was collected during the regeneration for conductivity measurement to determine the concentrations of NaCl in solution. The desorption process continued until all the previously electroadsorbed salt was released, which was determined by the change of cumulative NaCl concentration in the effluent container. The flush-water usage and time were also recorded corresponding with the conductivity data.

Table 1 indicates the operating conditions of five series of desorption experiments. Series 1 was designed to assess the impact of discharge methods on desorption efficiency. Electrode regeneration took place by power disconnection, short circuit, and polarity reversal with short circuit, respectively. Series 2 was designed to assess the impact of reversed charging time during polarity reversal on desorption efficiency. The examined duration of polarity reversal was from 0 to 14 min. Comparisons were also made between scenarios of flow and no-flow conditions during polarity reversal to explore the potential of the latter condition on reducing flush-water usage. Series 3 was designed to investigate the impact of flush flow rate on desorption efficiency. Flush flow rates of 22.5, 30, 45, and 90 mL/min, which were equivalent to flow velocities of 0.38 × 10$^{-3}$, 0.50 × 10$^{-3}$, 0.76 × 10$^{-3}$, and 1.5 × 10$^{-3}$ m/s for the specific system and led to a hydraulic retention time of 20, 15, 10, and 5 min, respectively, in the CDI cell, were explored. Series 4 was used to assess the impact of reversed cell voltage on desorption efficiency. The examined reversed cell voltages were from 0 to 1.2 V. Series 5 was used to evaluate the impact

![Fig. 1. Schematic diagram of CDI configuration and reactor setup in the desorption mode](image1)

![Fig. 2. Concentration-time plot of a typical adsorption-desorption cycle during the closed-loop operation of the CDI system](image2)
of flush-water type on desorption efficiency. Raw water, product water after CDI treatment, and DI water were investigated.

**Calculation and Data Analysis**

Conductivity of the saline water was monitored by a conductivity meter (DDS-307, Shanghai Yueping Scientific Instruments Co. Ltd., Shanghai, China). The relationship between conductivity and NaCl concentration was obtained by preparing a calibration curve prior to the experiments. The desorption percentage at time \( t \) was calculated using Eq. (1)

\[
D_t = \frac{m_{dt}}{m_a} \times 100\%
\]

where \( D_t \) = desorption percentage (%) at time \( t \); and \( m_a \) (mg) and \( m_{dt} \) (mg) = mass of adsorbed salt in electroadsorption cycle and mass of cumulative desorbed salt in desorption cycle at time \( t \), respectively. In the present study, \( m_a \) was determined based on the difference between cumulative effluent concentration (mg/L) of recirculated water used in the closed-loop operation prior to the desorption tests, while \( m_{dt} \) was determined based on the volume (L) of the water in the single-pass desorption.

Regeneration time \( t_R \) was determined based on the time (min) required to achieve complete desorption. Flush volume \( (FV) \) is a parameter describing the usage of flush water for complete regeneration. It was obtained by normalizing the flush-water volume for regeneration \( (V_R, \text{ liter}) \) based on the effective volume of the CDI cell \( (V_C, \text{ liter}) \) [Eq. (2)]

\[
FV = \frac{V_R}{V_C}
\]

Lower \( t_R \) and \( FV \) values were indicators of preferred desorption methods as a result of faster desorption kinetics and higher water production.

### Results and Discussion

#### Effect of Discharge Methods

Fig. 3 presents results of Series 1 experiments showing the effect of three discharge methods on electrode regeneration. The raw water was used to flush the cell during the desorption process and the flush-water flow rate was maintained at 30 mL/min, leading to a 15-min retention time in the CDI. By disconnecting the power supply, the longest regeneration time \( t_R = 66 \text{ min} \) was observed among the three methods. In the meanwhile, the \( FV \) of 4.4 indicated the largest amount of water was consumed to flush the cell. Short circuit resulted in a \( t_R \) of 40 min and a \( FV \) of 2.7, which significantly improved the desorption performance. This was attributable to a faster dissipation of accumulated energy by shorting the capacitor and a quicker reduction of electrostatic forces attracting the electroadsorbed ions. Polarity reversal appeared to be able to further improve the desorption performance, with observed \( t_R \) and \( FV \) reduced to 20 min and 1.3, respectively. The results indicate that the momentary expulsion by the reversed voltage would be beneficial for expedition of desorption and reduction of flush-water usage. Disadvantages regarding the application of reversed polarity mainly lie in a possible readsorption effect; that is, the ions would leave one electrode and then be adsorbed by the other one (Biesheuvel et al. 2011; Yao and Tang 2016). The results of the present study imply that it is possible to regenerate the electrodes at a faster rate while minimizing the effect of readsorption by polarity reversal. Because of the beneficial aspects of polarity reversal on electrode regeneration, the method is further examined for optimization strategies in the following sections.

#### Effect of Duration of Polarity Reversal

Fig. 4 illustrates desorption performance achieved at various duration of polarity reversal. To further reduce the flush-water usage, a no-flow condition during polarity reversal was also examined. The no-flow case described a scenario wherein there was no flushing...
flow during the temporary phase of polarity reversal. Because a complete desorption procedure here included a temporary polarity reversal followed by a consistent short circuit, the flush volume was generated during the latter short-circuit phase. The raw water was used to flush the cell and the flow rate was maintained at 30 mL/min, leading to a 15-min retention time in the CDI. A V-shape was observed for both $t_R$ and $FV$ as the duration of reversed polarity increased from 0 to 14 min. For the specific system, the optimum duration appeared to be 8 min, as judged by the lowest $t_R$ (18 min) and $FV$ (0.7) under a no-flow condition. This indicated that with a reversed charging time of 8 min, the influence of readesorption was minimum. A longer reversed charging time would lead to a negative impact by moving the ions from one electrode to another, resulting in a drastic decrease in desorption performance.

Furthermore, the no-flow condition reduced the $t_R$ and $FV$ from 20 min and 1.3 to 18 min and 0.7, respectively, showing a potential of further improving the desorption efficiency. The results suggested practical operations with stagnant water during polarity reversal prior to purging. In addition, the duration of polarity reversal needs to be adjusted by pilot testing to find an optimum reversed charging time for mostly trapped ions exiting the pores without being trapped again in the pores of the oppositely charged electrode.

**Effect of Flush Flow Rate**

Fig. 5 presents results of the Series 3 experiments exploring the effect of flush flow rate on desorption performance of CDI. It was found that a higher flow rate was associated with faster desorption. As the flush flow rate increased from 22.5 to 90 mL/min, a reduction of $t_R$ from 30 to 16 min was observed. The $FV$, however, did not show the same decreasing trend in the range of flow rate between 22.5 and 45 mL/min, and the values appeared to stabilize at 1.1 ± 0.1. A significant increase in $FV$ was observed only at the highest tested flow rate of 90 mL/min. Hence, from the practical engineering point of view, a relatively high flush flow rate is preferred to achieve fast desorption kinetics. A higher flow rate leads to a lower residence time of the solution inside the cell (Zhao et al. 2010; Mossad and Zou 2012; Porada et al. 2014), which leaves less time for the ion transport from the bulk solution into the opposite electrode, thus minimizing the readesorption effect and resulting in a decreased $t_R$. Xu et al. (2008) also reported a shortened regeneration time at a high flush flow rate. Meanwhile, they also reported a rather high volume of brine production. Therefore, it is important to take both $t_R$ and $FV$ into consideration because the system will only be effectively optimized when the $t_R$ and $FV$ are both optimum.

**Effect of Reversed Cell Voltage**

The Series 4 experiments examined reversed cell voltages from 0.3 to 1.2 V for potential impact on desorption performance. It is known that salt adsorption to activated carbon occurs via some kind of affinity between the ions and adsorbing surface, and even without the application of an electric field, the adsorbed ions can still remain on the surface for a period of time (Leonard et al. 2009; Biesheuvel et al. 2014). It is important to apply a reversed cell voltage that is high enough to overcome the affinity of the ions held on the electrodes. By applying a reversed cell voltage ≤ 0.6 V with stagnant water during polarity reversal, the resultant $t_R$ (44 min) and $FV$ (2.4) were both unsatisfactory (Fig. 6). Significant improvement was observed when the reversed cell voltage increased higher than 0.6 V, with a corresponding $t_R$ and $FV$ decreased to 32 min and 1.6 at 0.9 V, respectively. The initial desorption percentage at the start of purging also increased from 10 to 23%. The results indicated that a reversed cell voltage greater than 0.6 V could be high enough to overcome the affinity between
the ions and adsorbing surface. It was also found that a further increase of the reversed cell voltage from 0.9 to 1.2 V resulted in an observed $t_R$ and $FV$ reduced to 24 min and 1.1, respectively, indicating that a high reversed cell voltage is preferred. However, a reversed cell voltage of higher than 1.2 V is not recommended because of parasitic concerns of increased water electrolysis and expedited ageing of carbon materials (Ratajczak et al. 2014).

**Effect of Flush-Water Type**

T. D. Tran and D. J. Lenz [*“Alternating-polarity operation for complete regeneration of electrochemical deionization system,”* U.S. Patent 6346187 (2004)] suggested the use of DI water as one of options to completely rejuvenate a CDI system. However, purging with DI water may not be practical for large-scale engineering applications. The Series 5 experiments explored the effect of different flush-water types on desorption performance. The raw water, product water, and DI water used in the experiments showed conductivity values of 1,613, 287, and 16 μS/cm, respectively. In the “Effect of Flush Flow Rate” section, a flow rate of 45 mL/min was found optimal for the system because it was able to achieve both low regeneration time (18 min) and flush volume (1.0), as shown in Fig. 5. Therefore, it would be more meaningful to investigate the effect of flush-water type based on the available optimal condition at a flow rate of 45 mL/min. In order to reduce the potential interference from errors of controlling the exact time during polarity reversal, a short circuit was used as the only discharge method. As shown in Fig. 7, improvement in desorption performance was observed by purging with water of lower conductivity. Because an uncharged carbon pore possesses equal amount of counterions and coions (Suss et al. 2015), purging with product water or DI water changed the equilibrium state of the electrodes by producing a favorable ion concentration gradient and facilitated the release of ions during regeneration. Because ion concentration gradient and electric field were considered as two driving forces for transport of ions in CDI (Biesheuvel et al. 2009), the impact of electric field was removed by short-circuiting the electrodes. Therefore, the improvement in desorption performance was only attributable to the ion concentration gradient caused by purging with a lower conductivity solution. Furthermore, although a $t_R$ of 16 min and an $FV$ of 1.6 with DI water (Fig. 7) was the lowest in the short-circuit experiments, similar $t_R$ and $FV$ values (Fig. 5) were also observed with raw water by optimization of desorption methods. It is obvious that purging with raw water is considered more practical in engineering applications.

**Implications of Optimization of Desorption Methods for CDI**

Results of the study are important for the water industry. It was found that it is possible to minimize the potential readsoption effect during polarity reversal by a careful control of operating conditions. Results show that improved regeneration performance could be achieved by optimizing the duration and voltage of reversed polarity and the flow rate of flush water. The conclusions are in accordance with those of Leonard et al. (2009), who reported an increase of regeneration rate when a potential of appropriate sign and magnitude was applied to a CDI system. Considering that the interpretation of these effects was largely empirical, further development of models for the adsorption and desorption principles is needed for quantitative explanation. In recent years, CDI with ion-exchange membranes [a process named membrane-CDI (MCDI)] has been studied as a process to restrict coions from accessing the electrodes, which could also minimize the effect of readsoption during polarity reversal. Although researchers (Li and Zou 2011; Cohen et al. 2011; Kim et al. 2013; Liang et al. 2013) found that the regeneration of MCDI could be more efficient than CDI because the selective shielding of membranes, one should also take into account the disadvantages of using membranes such as the cost of membranes, increases in system volume, added resistance for solution flow and ion transport, membrane fouling and the associated replacement cost, etc. In the present study, optimization of desorption methods were suggested to improve the cost-effectiveness of CDI. Although polarity reversal also has energy consumptions (Dlugolecki and van der Wal 2012; Kim et al. 2015), a tradeoff could be maintained from economic perspectives for best engineering applications.

**Conclusions**

This research discussed the effect of desorption methods when regenerating electrodes in a CDI system. The results demonstrated effective nature of polarity reversal during electrode regeneration compared to the conventional short-circuit method. A polarity reversal with optimized duration and magnitude of reversed cell voltage while purging with a proper flow scheme exhibited substantial reductions on regeneration time and flush-water usage during the desorption processes of CDI. The beneficial aspects of preferred desorption methods were attributable to minimization of a readsoption effect by limiting the rate of ion transport to the oppositely charged electrode. The results obtained from this research can promote CDI further by enhancing its operational efficiency and cost-effectiveness for engineering applications.

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**References**


