

Impact of operating conditions on performance of capacitive deionisation for reverse osmosis brine recovery

Jing Yu, Jianjun Qin, Kiran A. Kekre, Balakrishnan Viswanath, Guihe Tao and Harry Seah

ABSTRACT

The study aimed at further developing an integrated capacitive deionisation (CDI)-based process to treat reverse osmosis (RO) brine from a water reclamation facility to increase the overall water recovery to more than 90% and to achieve a sustainable operation of the process with optimised conditions. The normalised treatment capacity of CDI membranes and voltage was optimised at 24.8 L/m²/h and 1.1–1.5 V, respectively. The operation time of CDI cell with membrane area of 0.8 m² was able to be extended to more than 1,000 h from the initial 72 h. Cleaning with both HCl at low pH and salt solution was good in removing foulants but cleaning with citric acid was not effective, as expected. The initiative cleaning strategy was found to be more effective in CDI fouling control and is recommended for long-term CDI operation. CDI cell efficiency for removal of ions reduced with operation time due to cleaning with surfactants at pH 10.5 which should be avoided in a future study.

Key words | capacitive deionisation, cleaning-in-place, RO brine, water recovery

Jing Yu
Jianjun Qin (corresponding author)
Kiran A. Kekre
Balakrishnan Viswanath
Guihe Tao
Harry Seah
Technology Department,
PUB,
Singapore's National Water Agency,
82 Toh Guan Road East, #C4-03,
Singapore 608575
E-mail: QIN_Jianjun@pub.gov.sg

Jing Yu
College of Environmental Science & Engineering,
Yangzhou University,
196 West Huayang Road,
225127 Yangzhou,
China

INTRODUCTION

Capacitive deionisation (CDI) is a technology for desalination and water treatment in which salts and minerals are removed from water by applying an electric field between two porous electrodes (Oren 2008). Recently, ion-exchange membranes have been introduced in CDI to improve desalting efficiency. Specifically, a cation-exchange membrane is placed in front of the cathode while an anion-exchange membrane is placed in front of the anode (Biesheuvel & van der Wal 2010). Capacitive deionisation with ion-exchange membrane integrates the advantages of CDI and ion-exchange membrane technology, which have shown great potential in energy efficiency as compared to other desalination technologies, such as reverse osmosis and distillation. The introduced ion-exchange membranes can directly restrict co-ions from accessing the electrodes and counter-ions can be easily absorbed by the electrodes, resulting in increased salt removal efficiency. The electrical field of CDI caused by a potential difference of about 1.1–1.5 V (direct current) between the two electrodes removes the

dissolved ions from the water as they pass the electric field. The anions and cations, which penetrate the ion-exchange membrane, are adsorbed in the electrode with opposite charge and a product stream with reduced salt concentration is obtained.

Reverse osmosis (RO) has been used for years in various industries to separate dissolved solids from water by forcing the water through a semi-permeable membrane. The process produces two streams: the permeate which is the product water from the process, and the concentrate (RO brine), which is the waste stream. RO brine is commonly disposed by discharge to surface water, deep well injection, evaporation pond disposal and evaporation to dryness and crystallisation, which usually cause adverse impacts on the environment or incur high costs (Brady *et al.* 2005). The management and utilisation of RO brine has become a global challenge (Adham *et al.* 2006). Capacitive deionisation as one of the electrosorption technologies has been viewed as a potential technology for brackish water

desalination and water reclamation (Welgemoed & Schutte 2005; Oh 2006; Yoram 2008; Avraham 2010; Biesheuvel & van der Wal 2010; Kim & Choi 2010; Seo *et al.* 2010; Li 2011) because CDI operates at low voltage and also possesses the feasibility of energy recovery (Oren 2008).

Recently, Tao *et al.* (2011) developed a CDI-based process with integrated pre-treatment to treat and recover RO brine from the water reclamation facility (NEWater factory) to achieve overall RO water recovery from the existing 75% to more than 90%. Their results showed that ion concentrations in CDI effluent were quite low except SiO₂ compared with RO feed water. RO product (CDI effluent as feed) was of good quality including low SiO₂ compared with NEWater. However, fouling and cleaning of the CDI cell were found to be issues for its sustainable operation. The objective of the study is to further develop the integrated CDI-based process to achieve a sustainable operation of the process with optimised conditions.

MATERIAL AND METHODS

The RO brine used in this study was from the second stage RO process of a water reclamation plant which reclaims treated secondary effluent from a municipal wastewater treatment plant (WWTP). The WWTP has a conventional activated sludge process, which consists of primary clarifier, aeration tank and secondary clarifier. The ultrafiltration (UF) and RO membrane process is employed to reclaim the treated secondary effluent, of which 25% is disposed of as RO brine.

Biological activated carbon (BAC) was used for organic removal and microfiltration (MF) was used for microorganism removal to protect subsequent the CDI cell. During the study, the system with a CDI membrane area of 0.8 m² was continuously operated on site at the desired water recovery of 75–80% with the feed of RO brine from the Kranji NEWater Factory, Singapore. Different pre-treatment methods prior to CDI were compared to extend the CDI cell lifespan. Various operating conditions of the CDI unit were investigated to optimise the effluent quality and process efficiency.

The desalting process of CDI consisted of three phases: purification, regeneration and purge. A product stream with lower salt concentration was generated during the

purification phase. By reversing the potential, regeneration took place and ions were released and expelled back into aqueous solution. During the purge phase, the aqueous solution with higher salt concentration in the cell was purged out from the cell into a concentrate stream. Each cycle consisted of a 1.6-min purification phase (product generation), a 1.7-min regeneration phase and a 0.5-min purge phase (concentrate generation). Different cleaning methods were tried and analysis of water samples was systematically conducted. CDI removal efficiency for ions as a function of time was monitored. The details in the experiments have been given in a previous study (Tao *et al.* 2011).

The pH and conductivity were measured using a portable meter (Model: 6 Psi Ultrameter II Myron L, USA). Online conductivity was measured by online conductivity meter (Model 8225 conductivity transmitter, Burkert fluid control systems, Germany), which was installed at the outlet of the CDI cell. Total dissolved solids (TDS) was determined in accordance with *Standard Methods* (APHA-AWWA-WEF 1998). Total organic carbon (TOC) was measured by 1010 TOC Analyzer (O.I. Analytical, USA). The anion and cation concentration were quantified using ion chromatography (LC20 chromatography, Dionex, USA).

RESULTS AND DISCUSSION

TOC of the RO brine was 22.3 ± 2.4 mg/L within the range 18.1–27.7 mg/L in this study. The RO brine was the concentrate of secondary effluent from the biological treatment process. Organic constituents in the secondary effluent, designated as effluent organic matter, are highly heterogeneous, containing a variety of compounds measured as dissolved organic carbon (DOC), ranging from low to high molecular weight; for example, polysaccharides, proteins, amino sugars, nucleic acids, humic and fulvic acids, organic acids and cell components. These complex and heterogeneous compounds can be classified into natural organic matter (NOM), synthetic organic compounds (SOC) and soluble microbial products (SMP) according to their origins, most of which are refractory (Shon *et al.* 2006). BAC as the pre-treatment in this study was able to achieve 10–25% TOC removal of RO brine (Figure 1), which is expected to reduce organic fouling of the CDI cell.

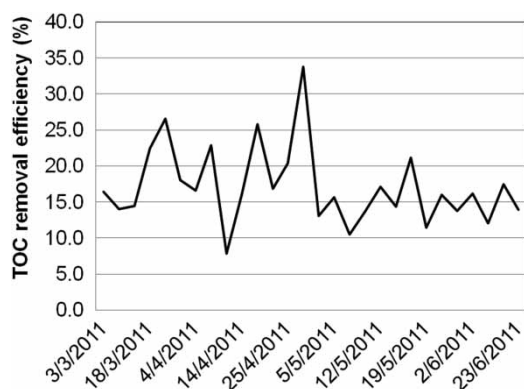


Figure 1 | TOC removal by BAC vs. time.

Figure 2 shows the effect of normalised treatment capacity of CDI on effluent quality, where the normalised treatment capacity is the flow rate per m^2 of CDI membrane area. It can be seen that effluent TDS increased quickly with the increase of treatment capacity until treatment capacity reached $24.8 \text{ L/m}^2/\text{h}$. After that, effluent TDS increased slightly against treatment capacity. However, internal circulation was observed to take place once treatment capacity exceeded $24.8 \text{ L/m}^2/\text{h}$, indicating a reduction in the energy efficiency of the CDI. Therefore, optimal treatment capacity was determined at $24.8 \text{ L/m}^2/\text{h}$ based on effluent quality and process efficiency.

Figure 3 illustrates the online effluent conductivity as a function of time within one purifying cycle under different voltages applied. The effluent quality was improved with increasing voltage. However, the voltage between 1.1 and 1.5 V was selected for the long-term operation in the study

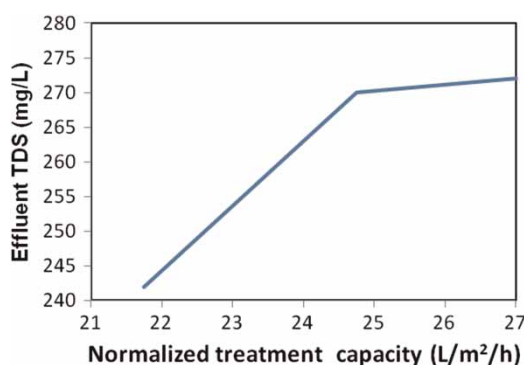


Figure 2 | Effect of normalised treatment capacity of CDI on effluent quality.

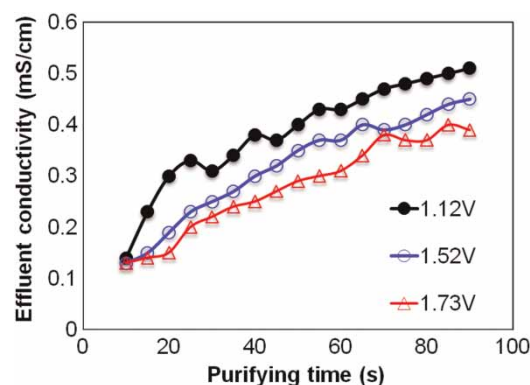


Figure 3 | Effect of voltage on effluent quality.

because the quality met the requirements and power consumption could be significantly saved.

It was found that the CDI cell lifespan (operating pressure limit at 20 psi) could be extended from the initial 72 h with the pre-treatment of BAC-MF to $>1,000 \text{ h}$ with the pre-treatment of BAC-MF- O_3 - NaHSO_3 (Figure 4). The starting value of cell pressure was observed to be different since a new CDI cell was used for Figure 5 even though their configuration was the same. A passive cleaning strategy was employed in Figure 4, while an initiative cleaning strategy was used in Figure 5. As for Figure 4, cleaning-in-place (CIP) was conducted when pressure increased significantly. In contrast, CIP was carried out initiatively before substantial pressure increase occurred. Therefore, a different pattern in pressure change was observed which was possibly due to the different cleaning strategies applied. Pressure variation in Figure 4 was higher than that of Figure 5. Especially, pressure increased by 50% from 14.4 to 21.5 psi in less than 150 hr up to the end of operation

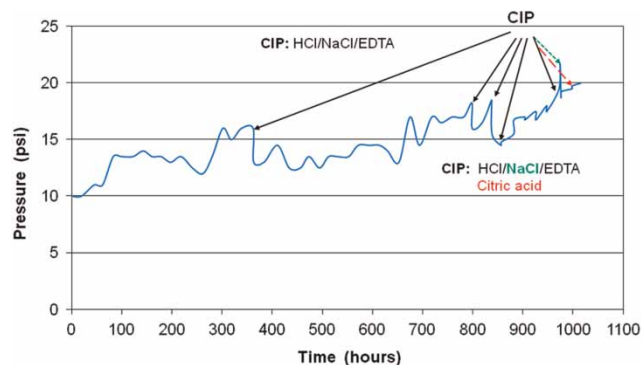


Figure 4 | CDI operating pressure vs. time (O_3 to disinfect the CDI feed).

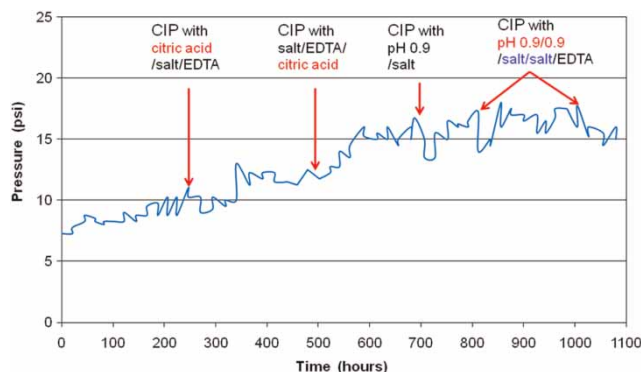


Figure 5 | CDI operating pressure vs. time (NaOCl to disinfect the CDI feed).

time, while pressure variation was observed to be even and stable at the end period in Figure 5. Even though different CIP solutions were applied in Figures 4 and 5, our results demonstrate that an initiative cleaning strategy is more efficient in CDI fouling control for a long-term operation.

In addition, Figure 4 shows that the first three CIP with HCl/NaCl/EDTA could bring the pressure down; however, the subsequent two CIP were not effective. CIP using 5% NaCl alone plus overnight soaking (Figure 4, dashed line arrow) performed well but CIP using 2% citric acid had no effect. Moreover, Figure 5 further indicates that citric acid was not effective for CIP no matter whether it was used at the beginning or the end of the CIP programme. CIP with HCl at pH 0.9 plus 5% NaCl could effectively reduce the pressure. CIP with repeated pH 0.9 and NaCl plus 0.2% EDTA also helped to keep the pressure from rising, which

can be explained by the tabulated analysis in Table 1. Both CIP at pH 0.9 showed similar effectiveness in removing the scalants. CIP with 5% NaCl mainly remove colour and some organics. The removal of certain scalants could be attributed to the presence of a high concentration of NaCl.

Figure 6 shows that CDI removal efficiency for cations was more than 93% at the beginning and gradually reduced after 3.5 months' operation. Insignificant differences were observed in the removal of monovalent and divalent ions by the CDI during the overall operation time. Some studies found that monovalent ions were more effectively removed than divalent ions (Gabelich *et al.* 2002), while the opposite results were reported by other studies (Xu *et al.* 2008; Seo *et al.* 2010). However, our data show that there was no significant preference in the removal of monovalent and divalent ions. Moreover, the removal efficiency reduction for monovalent ions (K^+ , Na^+) seems faster than that for divalent ions (Ca^{++} , Mg^{++}). However, Figure 7 illustrates that for anions the removal efficiency reduction for higher valent anions (PO_4^{3-} , SO_4^{2-}) was faster than that for low valent anions (Cl^- , NO_3^-). The results indicated that the CDI cell efficiency decreased with time; the most probable reason could be attributed to the exchange membranes (especially the cation exchange membrane) ageing due to CIP with SLS/EDTA (surfactants) at pH 10.5. As a result, CDI removal efficiency for TDS as shown in Figure 8 reduced from 88 to 74% after five CIP. In the next study, CIP with SLS/EDTA will be avoided.

Table 1 | Analysis of first and second cleaning solutions with the same fresh chemical

Parameter	Unit	CIP at pH 0.9		CIP with 5% NaCl	
		First	Second	First	Second
Calcium	mg/L	420	290	93.9	18.2
Colour	Hazen	10	10	150	100
Fluoride	mg/L	10.3	10.1	<0.5	<0.5
Iron	mg/L	2.05	2.39	0.011	0.0074
Magnesium	mg/L	45.3	14.3	9.71	3.52
Phosphate	mg/L	1,643	1,192	33.71	18.69
Silica SiO ₂	mg/L	18.5	7.04	2.5	1.44
Strontium	mg/L	0.86	0.56	0.18	0.056
Sulphate	mg/L	67	57	72	0.27
TOC	mg/L	–	–	21.1	11

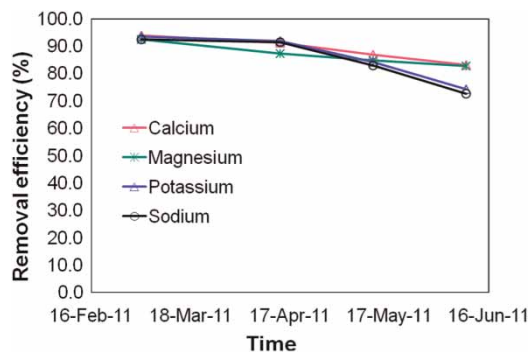


Figure 6 | Removal efficiency for cations vs. time.

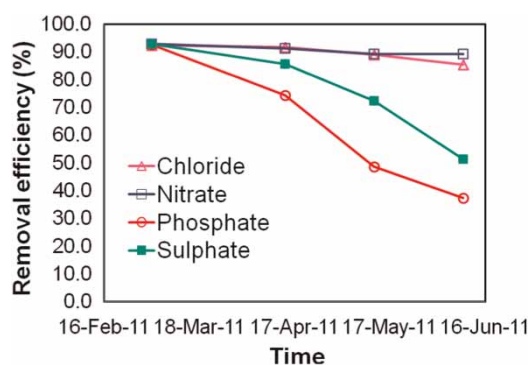


Figure 7 | Removal efficiency for anions vs. time.

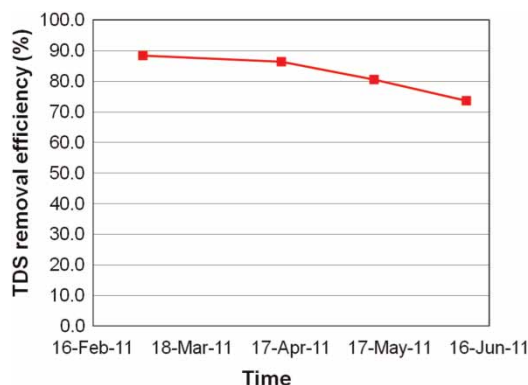


Figure 8 | Removal efficiency for TDS vs. time.

FUTURE WORK

Usage of chemicals such as NaHSO_3 in the process after NaOCl disinfection will be reduced and the cost evaluation will be conducted in the follow-up testing programme.

CONCLUSIONS

The conclusions from the pilot study are summarised as follows:

- The optimal treatment capacity of CDI membranes and voltage were $24.8 \text{ L/m}^2/\text{h}$ and $1.1\text{--}1.5 \text{ V}$, respectively.
- The operation time of CDI cell with membrane area of 0.8 m^2 was able to be extended to more than 1,000 h from the initial 72 h.
- Cleaning using both HCl at low pH and salt solution was good to remove foulants but cleaning using citric acid was not effective.
- CDI cell efficiency for removal of ions reduced with operation time due to cleaning with surfactants at pH 10.5 that should be avoided in a future study.
- Initiative cleaning strategy is recommended for long-term CDI operation.

ACKNOWLEDGEMENTS

Contributions from L. X. Ho, G. Guek and Y. Gu in the study are appreciated.

REFERENCES

- Adham, S., Oppenheimer, J. & Kumar, M. 2006 Innovative approaches to RO concentrate management: Beneficial reuse and concentrate minimization. In: *Proceedings of the WEFTEC*, Dallas, TX, pp. 4334–4344.
- APHA-AWWA-WEF 1998 *Standard Methods for the Examination of Water and Wastewater*, 20th edn. APHA-AWWA-WEF, Washington, DC.
- Avraham, E. 2010 Limitations of charge efficiency in capacitive deionization processes III: The behavior of surface oxidized activated carbon electrodes. *Electrochim. Acta* **56**, 441–447.
- Biesheuvel, P. M. & van der Wal, P. M. 2010 Membrane capacitive deionization. *J. Membr. Sci.* **346**, 256–262.
- Brady, P. V., Kottenstette, R. J., Mayer, T. M. & Hightower, M. M. 2005 Challenges and research needs. *J. Contemp. Water Res. Educ.* **132**, 46–51.
- Gabelich, C. J., Tran, T. D. & Suffet, I. H. M. 2002 Electrosorption of inorganic salts from aqueous solution using carbon aerogels. *Environ. Sci. Technol.* **36**, 3010–3019.

- Kim, Y.-J. & Choi, J.-H. 2010 Improvement of desalination efficiency in capacitive deionization using a carbon electrode coated with an ion-exchange polymer. *Water Res.* **44**, 990–996.
- Li, L. Z. 2011 Ion-exchange membrane capacitive deionization: A new strategy for brackish water desalination. *Desalination* **275**, 62–66.
- Oh, H.-J. 2006 Nanoporous activated carbon cloth for capacitive deionization of aqueous solution. *Thin Solid Films* **515**, 220–225.
- Oren, Y. 2008 Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review). *Desalination* **228** (1–3), 10–29.
- Seo, S. J., Jeon, H., Lee, J. K., Kim, G. Y., Park, D., Nojima, H., Lee, J. & Moon, S. H. 2010 Investigation on removal of hardness ions by capacitive deionization (CDI) for water softening applications. *Water Res.* **44**, 2267–2275.
- Shon, H. K., Vigneswaran, S. & Snyder, S. A. 2006 Effluent organic matter (EfOM) in wastewater: Constituents, effects and treatment. *Environ. Sci. Technol.* **36**, 327–374.
- Tao, G., Viswanath, B., Kekre, K., Lee, L. Y., Ng, H. Y., Ong, S. L. & Seah, H. 2011 RO brine treatment and recovery by biological activated carbon and capacitive deionization process. *Water Sci. Technol.* **64** (1), 77–82.
- Welgemoed, T. J. & Schutte, C. F. 2005 Capacitive Deionization Technology™: An alternative desalination solution. *Desalination* **183**, 327–340.
- Xu, P., Drewes, J. E., Heil, D. & Wang, G. 2008 Treatment of brackish produced water using carbon aerogel-based capacitive deionization technology. *Water Res.* **42**, 2605–2617.
- Yoram, O. 2008 Capacitive deionization (CDI) for desalination and water treatment – past, present and future (a review). *Desalination* **228**, 10–29.

First received 8 February 2013; accepted in revised form 7 July 2013. Available online 16 December 2013