

PAPER



CrossMark
click for updates

Cite this: *Environ. Sci.: Water Res. Technol.*, 2015, 1, 516

Relation between operating parameters and desalination performance of capacitive deionization with activated carbon electrodes

Danyang Liu,^a Kuan Huang,^a Leijie Xie^a and Hao L. Tang^{*ab}

Electrosorptive batch experiments were conducted for the development of a statistical model to describe the relation between operating parameters and desalination performance of capacitive deionization (CDI) with activated carbon electrodes. Results showed that the statistical model reproduced the data well, with both regression and verification R^2 values above 0.85. The exponents in the statistical model, shown as 2.79, -0.45, and 1.05 for the applied voltage, spacer thickness, and retention time, respectively, revealed the importance of each factor in the correspondingly examined range. In addition, the effects of interactions between the factors were judged as significant, which could be explained by the electrical double-layer theory. The influence of initial salt concentration could be best characterized by the Langmuir isotherm. This work demonstrates that direct modeling of desalination performance with operating parameters is feasible and the results can be used to guide practical engineering applications.

Received 18th April 2015,
Accepted 3rd June 2015

DOI: 10.1039/c5ew00102a

rscl.li/es-water

Water impact

To guide practical implementations of capacitive deionization (CDI) systems for water desalination, quantitative methods to predict the CDI behavior based on operating parameters are essential but not available so far. This work presents a novel attempt at using a statistical modeling approach as a predictive tool to elucidate the relation between operating parameters and desalination performance of CDI. Although CDI is a complex process depending on various factors, our work demonstrates that direct modeling of electrosorption with operating parameters is feasible and the results can be used to guide practical engineering applications.

Introduction

As the availability of affordable clean water is becoming a critical issue worldwide, research on desalination technologies for seawater, brackish water, produced water, treated wastewater, *etc.* is of keen interest to scientists nowadays. Handling, treatment, disposal, and beneficial reuse of these waters have also been great challenges for industry and regulators.¹

To date, ion exchange, reverse osmosis, electrodialysis, and evaporation have been the most commonly used desalination technologies. However, their disadvantages including by-product formation, complex pretreatment and operation, and high energy consumption hindered many applications. Capacitive deionization (CDI), or electrosorption as referred in some literature, has emerged as a low-polluting, energy-

efficient, and cost-effective alternative to conventional desalination technologies.² It uses pairs of oppositely charged electrodes to attract ions from the saline water flowing between them, that is, cations move towards the cathode while anions move towards the anode. After the electrodes are saturated with ions, regeneration is performed by removing the electric field and the adsorbed ions are released into the regeneration stream. Carbon materials are known to be ideal candidate electrode materials due to their excellent electrical conductivity and large specific surface area.³ Since electrosorption of ions is an interfacial process, the use of a high surface area porous carbon for maximum contact area between the electrode and the water is beneficial for improving the desalination performance.⁴ Although many carbon materials (carbon aerogel, ordered mesoporous carbon, carbon nanotubes, graphene, *etc.*) have been studied,^{5,6} activated carbon stands out as a commercially available and cost efficient material.^{4,7} The good electrosorption performance of activated carbon electrodes is attributed to the optimum pore size for the passage of salt ions, and the mesostructure of activated carbon also facilitates the easy movement for

^a Department of Water Engineering and Science, College of Civil Engineering, Hunan University, Changsha, Hunan 410082, China

^b Minn Water LLC, Minneapolis, Minnesota 55441, USA

E-mail: HLT@HNU.EDU.CN, tang@minnwater.com; Fax: +1 (612) 584 1518; Tel: +1 (612) 584 1588

adsorption and desorption of ions.⁸ As a novel electrochemical process, CDI exhibits many advantages over conventional desalination technologies. Unlike ion exchange, it does not need salt for regeneration, and is therefore more environmentally-friendly than resin-based processes.⁹ In addition, it is a low-pressure non-membrane process operated at ambient conditions and low voltages with simple pretreatment like cartridge filtration, and therefore, minimization of processing costs and waste can be achieved.¹⁰

As an emerging technology, CDI is still in the developing stage and research remains to be done before it can be widely applied as a commercial technology. For instance, to design a CDI system, it is important to understand the relation between operating parameters and its desalination performance. Applied voltage, spacer thickness, and retention time are such parameters and must be adjusted to achieve both high salt electrosorption capacity and fast kinetics at the same time during CDI operation. To date, isotherm-based Langmuir and Freundlich equations have been typically applied to describe the adsorption performance of CDI,^{11,12} and they are expressed below:

Langmuir:

$$q_e = q_m K_L C_e / (1 + K_L C_e) \quad (1)$$

Freundlich:

$$q_e = K_F C_e^{1/n} \quad (2)$$

where q_e is the amount of adsorbed salt at equilibrium (in milligram per gram of activated carbon electrode, mg g^{-1}), q_m is the maximum amount of adsorbed salt (in mg g^{-1}), C_e is the equilibrium concentration of salt in solution (mg L^{-1}), while K_L , K_F and $1/n$ are constants of the corresponding system.

It can be seen from the two expressions that they are both a function of salt concentration and reveal no direct relationship between the operating parameters and the desalination performance. Although some other CDI models^{13–16} are recently proposed, they may not be easily used. Instead of controllable operating parameters, these recent models were developed based on intrinsic system configurations (*e.g.* pore size distribution, surface area, capacitance, series resistance, surface group, *etc.*) that are difficult to adjust during operation. It is important to have a model that is practical in assisting system designs and operations.

Until now, direct modeling of the correlation between CDI performance and these operating parameters is not available. Statistical modeling has been widely used to elucidate the influence of various factors on many system behaviors. Tang *et al.*¹⁷ used statistical approaches to develop an empirical model to evaluate the effects of operating parameters on clean-bed head loss of crumb rubber filtration, and a high correlation between predicted head loss data and actual data was obtained, which outperformed the widely used Kozeny

and Ergun equations. It was hypothesized that an empirical model based on a statistical approach for describing salt adsorption as a function of applied voltage, spacer thickness and retention time could be a suitable tool to quantify the influence of these operating parameters on CDI performance for practical engineering use.

In this work, we conducted a series of electrosorptive batch tests under various levels of three operating parameters (applied voltage, spacer thickness, and retention time). The objective of this study was to develop a statistical model for elucidation of the relation between the operating parameters and the desalination performance of CDI. The study will aid in the practical engineering design and operation of CDI systems.

Materials and methods

CDI configuration and reactor setup

Fig. 1 presents the schematic diagram of the CDI configuration and reactor setup. The CDI assembly consisted of stainless steel mesh as current collectors, commercially available activated carbon as electrodes, and nylon mesh spacers to separate the electrodes. The activated carbon cloth (ACC, FM10) with a specific surface area of $1000 \text{ m}^2 \text{ g}^{-1}$ and a thickness of 0.5 mm was obtained from Chemviron UK. The ACC was pre-rinsed with DI water until conductivity in the rinsed water became stable and no more ions were further released. All materials were cut into $3.5 \times 3.5 \text{ cm}^2$ dimensions and assembled in sequence as shown in Fig. 1, and then the entire stack of all layers was firmly pressed together with a cable tie and placed in the reactor. The reactor included a CDI cell, a conductivity meter, a potentiostat as external power supply, and a magnetic stirring plate with a stirrer for mixing.

Electrosorptive batch experiments

The electrosorptive batch experiments were carried out at room temperature using 0.3 g of ACC as electrodes and 75 mL of NaCl solution (984 mg L^{-1}) with an initial conductivity of $2000 \mu\text{S cm}^{-1}$ – a typical value for some fresh water with high salinity and treated wastewater that requires further desalination to be reused. Prior to each experiment, the CDI unit was equilibrated with the tested feed water to eliminate

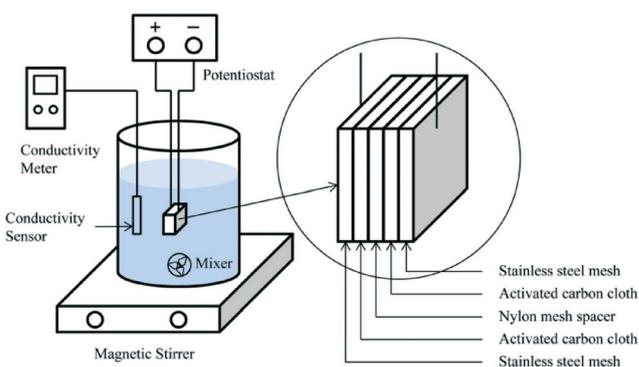


Fig. 1 Schematic diagram of CDI configuration and reactor setup.

the influence of physical adsorption. The supply voltage was adjusted by a DC potentiostat (RXN-305D, Shenzhen Zhaoxin Power Co. Ltd., China). The spacer thickness was adjusted by increasing or decreasing the layers of nylon mesh between the ACC electrodes. The conductivity of the NaCl solution was monitored by a conductivity meter (DDS-307, Shanghai Yueping Scientific Instruments Co. Ltd., China). The relationship between conductivity and NaCl concentration was obtained by preparing a calibration curve prior to the experiments. The electrosorption at retention time t (q_t , mg g^{-1}) was calculated using the following equation:

$$q_t = (C_0 - C_t)V/W \quad (3)$$

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the NaCl concentrations at time zero and time t , respectively, V (mL) is the volume of the NaCl solution, and W (g) is the mass of ACC in the CDI assembly.

The study used a mixed-level factorial design to analyze the influence of the operating parameters. Three levels of applied voltage (0.6, 0.9, and 1.2 V) and spacer thickness (2, 4, and 6 mm) and 21 retention times from 0 to 60 min (0, 3, 6, 9, 12, 15, 18, 21, 24, 27, 30, 33, 36, 39, 42, 45, 48, 51, 54, 57, and 60 min) were investigated. The experiments started with pristine ACC for each defined spacer thickness condition, and for each condition 63 cycles (3 voltages \times 21 retention times) were performed. The maximum applied voltage was selected based on a value lower than the voltage for water electrodialysis (the voltage for water electrodialysis is about 1.23 V), while the maximum spacer thickness and retention time were selected based on practical engineering considerations such as the control of the CDI device in a small footprint while not sacrificing its desalination efficiency. To elucidate the effect of salt concentration during the electrosorption process, NaCl solutions with initial conductivity from 100 to 2000 $\mu\text{S cm}^{-1}$ were also tested under operating conditions of 1.2 V applied voltage, 2 mm spacer thickness, and 0–60 min retention time.

Statistical modeling

The statistical modeling process used a total of 189 electrosorption data sets (3 applied voltages \times 3 spacer thicknesses \times 21 retention times) obtained from the CDI treatment of NaCl solutions with an initial conductivity of 2000 $\mu\text{S cm}^{-1}$. Based on statistical requirements, 132 data sets (about 70% of the data sets) were randomly chosen to initiate the regression and the remaining 57 data sets (about 30%) were used to validate the corresponding regression results. Sigma Plot 10 (Systat Software Inc, Chicago, Illinois, USA) was used to conduct statistical multiple nonlinear regression. A multiplicative power-law relationship was used to model the electrosorption as a function of applied voltage, spacer thickness, and retention time. The statistical significance of each parameter was evaluated based on a p -value of 0.05 (the smallest choice of α that would allow the null hypothesis to be

rejected). The coefficient of determination (R^2) was used to evaluate the modeling results. An R^2 of 1.0 indicates that the model addresses all the variability of dependent variables, and it generally indicates a strong relation if R^2 is large. However, it does not guarantee a statistically valid model since a high R^2 can occur with insignificant parameters if only a few data observations are available.¹⁷ In this study, the model was validated by (1) examining the p -value of each parameter, and (2) comparing the regression R^2 and verification R^2 .

Results and discussion

CDI behavior

The electroadsorption/electrodesorption behavior of a typical CDI cell is illustrated in Fig. 2, which shows the adsorption and regeneration capability of the cell during the batch operation. A NaCl solution was used, because sodium and chloride occupy a large proportion of the electroadsorption capacity of the CDI electrodes due to their high concentration in target solutions in spite of their relatively low affinity compared to other ions.¹⁸ After the ACC electrodes were saturated with electroadsorbed ions and the electric field was removed, it took approximately 10 minutes to completely restore to the original state of initial conductivity, and greater than 90% of the electrodesorption was completed in the first 3 minutes. This batch operation test confirmed that complete regeneration could be achieved and the ACC had been pretreated to eliminate the interference of physical adsorption and the obtained adsorption data used in the following modeling process were all attributable to electrosorption.

Statistical modeling

A multiplicative power-law relationship, as a widely used approach in statistical regressions, is expected to be able to give better results compared to linear and power function approaches.¹⁹ In this study, it was used to model the electrosorption as a function of applied voltage, spacer thickness,

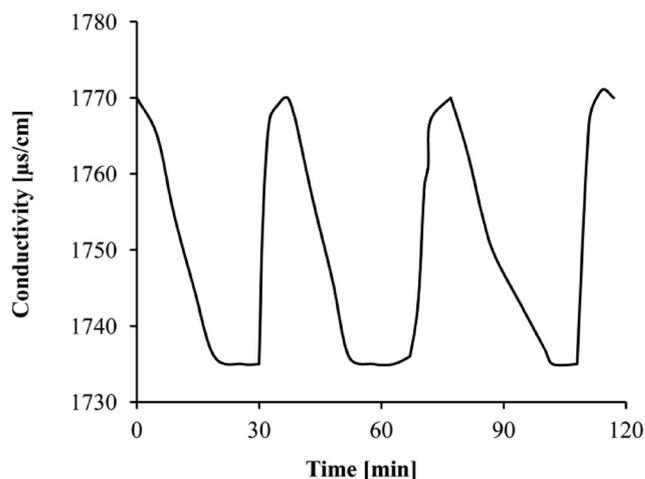


Fig. 2 Electroadsorption/electrodesorption behavior of a typical CDI cell in batch experiments.

and retention time. The expression of the model was presented as follows:

$$\text{Electrosorption} = K \times [\text{applied voltage}]^a \times [\text{spacer thickness}]^b \times [\text{retention time}]^c \quad (4)$$

where electrosorption, applied voltage, spacer thickness, and retention time were presented in the units of mg g^{-1} , V, mm, and min, respectively, while K was a unitless constant characteristic of the system.

Regression was performed with 70% of data sets and the results are summarized in Table 1. The p -value of the constant K was 0.0013, which was less than 0.05. The p -values of the operating parameters – applied voltage, spacer thickness, and retention time – were all less than 0.0001, showing that these factors were significant. Standard errors of these factors gave the ranges of the variability. In addition, the regression results passed the normality test. Therefore, all factors included in the model correlate with the desalination performance.

The statistical model was further validated by the 57 remaining data sets. The predicted electrosorption data with the actual observations during the experiments are illustrated in Fig. 3. The 45° lines in the figure depicted the hypothetical electrosorption estimates that were precisely equal to the actual values. Each R^2 value was calculated between the predicted data versus actual data and the 45° line. It was found that the regression R^2 and verification R^2 values were 0.8559 (Fig. 3a) and 0.8648 (Fig. 3b), respectively, which were both higher than 0.85. Therefore, the statistical model reproduced the electrosorption data well and was a suitable tool for interpretation of the relation between the operating parameters and the desalination performance of CDI.

The data points deviating from the 45° lines imply underestimation or overestimation of electrosorption. The discrepancy may be attributed to the intrinsic properties that were not addressed by the modeling process. In addition, recent publications^{20–23} detailed how the desalination performance of CDI relates to the potential distribution and the electrode stability during prolonged cycling. The research resembled the practical start-up of a CDI system with pristine activated carbon electrodes followed by continuous cycling and allowing no extra time for pre-charging prior to a new cycle. To improve the accuracy of the statistical data, the charging time and the number of cycles may be controlled.

Interpretation of the modeling results

Fig. 4 is a 3D figure showing the distribution of the statistical model predicted electrosorption data under various

Table 1 Parameters in the statistical model

Parameter	Value	Standard error	p -Value	Normality test
K	0.13	0.04	0.0013	Pass
a	2.79	0.19	<0.0001	
b	-0.45	0.06	<0.0001	
c	1.05	0.08	<0.0001	

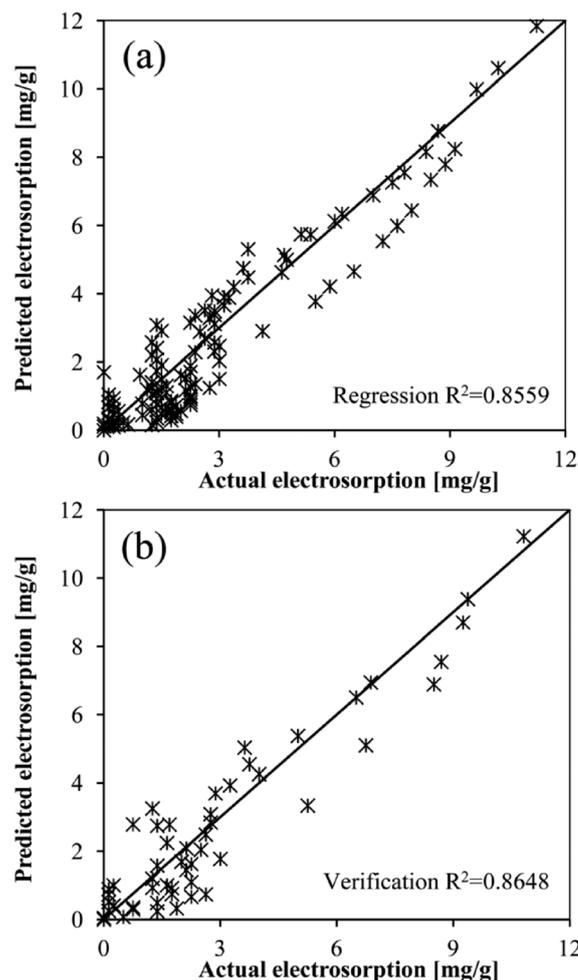


Fig. 3 Statistical model predicted data versus actual observations: (a) regression results with 70% data; (b) verification results with 30% data.

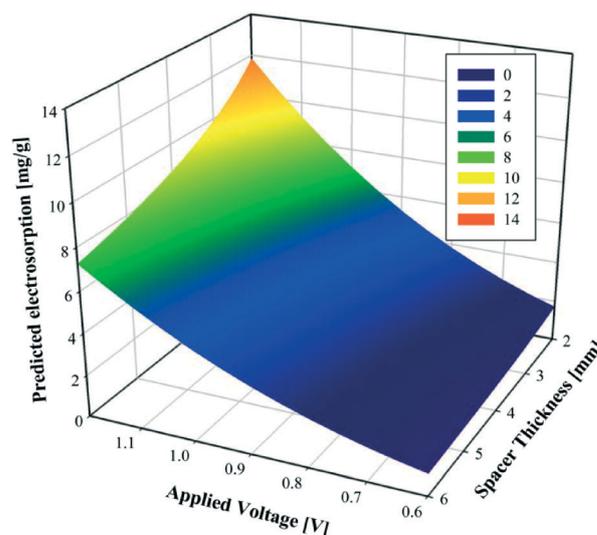


Fig. 4 Statistical model predicted electrosorption under various combinations of applied voltage and spacer thickness in 60 min CDI treatment of a NaCl solution with an initial conductivity of $2000 \mu\text{S cm}^{-1}$.

combinations of applied voltage and spacer thickness. Based on the results, it could be presumed that the operation of a CDI system with good desalination performance would benefit from a higher voltage, a smaller spacer thickness and a longer retention time. Since these factors included in the model correlate with electrosorption, the value of the constant (a , b and c) related to each factor shows the importance of that factor in the correspondingly examined range, as discussed in sections below.

Effect of applied voltage. The exponent of applied voltage, shown as 2.79 in this study, implied a substantial influence of this operating parameter on electrosorption. The observed positive correlation indicates that a higher voltage corresponds to higher electrosorption, which is attributed to a thicker electrical double layer (EDL) and stronger Coulombic interactions between the electrodes and charged ions.²⁴ Therefore, it can be deduced that a lower salt concentration in the effluent of a CDI system can be expected with increased applied potential. However, it should be noted that the faster increase in electrosorption with an increase of applied voltage could not be addressed by a linear relationship. The exponent of 2.79 in the statistical model was greater than 1, showing that as the applied voltage increased from 0.6 to 1.2 V, the electrosorption response became exponential. This was in agreement with the results of Porada *et al.*¹⁴ who reported a nonlinear relationship between cell voltage and salt adsorption. Porada *et al.*⁴ suggested an EDL voltage of above 0.5 V during a symmetrical CDI cell design. Tsouris *et al.*²⁵ found that 1.2 V was an optimum value for the applied voltage and increasing the voltage above this value did not result in a greater removal capacity for ions. This was attributed to the increased parasitic effects of water electrolysis.²⁶ Therefore, for best engineering practice, it is recommended that CDI be operated at a cell voltage of 1.2 V – a voltage slightly lower than the voltage for water electrodiolysis (1.23 V).

Effect of spacer thickness. The exponent of spacer thickness, shown as -0.45 in this study, implied that the factor inversely correlated with electrosorption. Smaller spacer thickness means shorter distance for the ions to travel to the electrodes under an applied potential, which improves the desalination performance. In addition, because the adsorption capacity of electrodes is mainly affected by the EDL capacity due to the electrostatic attractive force between the ions and the electrodes,¹⁰ a smaller spacer thickness leads to the formation of a thicker EDL and lower electric resistance in the solution between the electrodes, both of which are beneficial for electrosorption. Although a smaller spacer thickness is theoretically preferred for higher electrosorption, for best engineering practice, there should be a thorough consideration of the increased potential of short circuit and clogging and decreased saline water treatment capacity if the spacer thickness is made too small.

Effect of retention time. Jande and Kim¹⁶ included the flow rate as a factor in the modeling of single-pass CDI operation, and suggested a different effect compared with that of

batch-mode CDI. Retention time is a term that illustrates the length of period that saline water stays in contact with the CDI electrodes. The term is applicable in both batch-mode and single-pass CDI operations, and was therefore modeled in this study instead of the flow rate. The exponent of retention time, shown as 1.05 in the statistical model, implied a positive correlation between this operating parameter and electrosorption. This is because an increased retention time allows the solution to complete the required ion transfer for purification. Li and Zou²⁶ observed a steep adsorption at the beginning of the CDI process, indicating a high adsorption rate constant followed by a decreasing trend with lowered conductivity in the solution as the retention time increased further. The exponent of 1.05 found in this study demonstrated a close-to-linear relationship which resembled the first phase at the beginning of the CDI process, indicating that the electrodes were not saturated yet in the modeling process of the batch experiments. Therefore, increasing the retention time before the saturation of electrodes is beneficial for electrosorption. For best engineering practice, it is recommended that the optimum retention time be determined based on the inflection point of the electrosorption curve. Before the inflection point, there is an approximately linear relationship as revealed in the statistical model and the improved electrosorption can be obtained by increasing the retention time through decreasing the flow rate or increasing the number of CDI cells connected in parallel, which allows more time for ion transfer from the saline water to the CDI electrodes. After the inflection point, the improvement of electrosorption by increasing the retention time slows down as revealed by Li and Zou,²⁶ and there would be practical considerations to balance the footprint and cost of CDI systems for engineering applications.

Interactions between the factors. A mixed-level factorial calculation with the assistance of MINITAB 15 (Minitab Inc., State College, Pennsylvania, USA) was conducted to analyze the standardized effects of each factor and their interactions, and the results are shown in Fig. 5. The threshold value, as

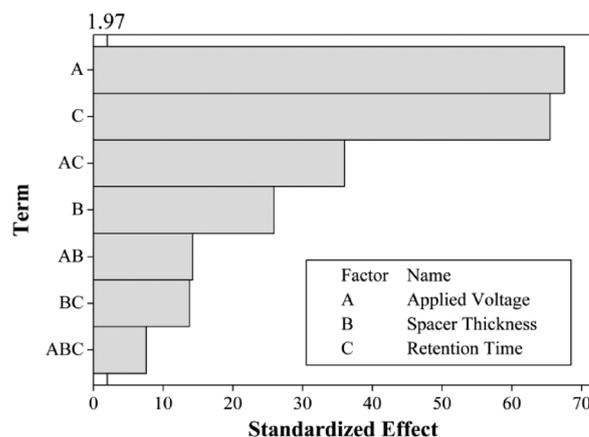


Fig. 5 Pareto chart of the standardized effects showing the results of factorial calculation. (Response is based on observed electrosorption in mg g^{-1} . Significance level = 0.05).

denoted by the vertical line in the Pareto chart of the standardized effects, was determined to be 1.97 with a significance level of 0.05. It is not surprising to find that the individual factors were significant and their standardized effects were in agreement with the absolute values of their exponents ($|\text{applied voltage}| > |\text{retention time}| > |\text{spacer thickness}|$). It is worth mentioning that all interactions between the factors were judged as significant, since their p -values were less than 0.05. This is because the applied voltage, spacer thickness and retention time all affect the electro-sorption by the same mechanism, which is the EDL theory describing the Coulombic interactions and facilitation of ion transfer to the electrodes as discussed in the previous sections. Being more specific, AC indicates the combined effect of applied voltage and retention time, as a higher voltage relates to less required time to complete ion transfer. AB presents the combined effect of applied voltage and spacer thickness, as a higher voltage and a smaller spacer thickness both contribute to a thicker EDL. BC describes the combined effect of spacer thickness and retention time, as a smaller spacer thickness also results in less required time to complete ion transfer. ABC is an indication of the combined effect of all three factors. Among the effects of these interactions, the interaction between applied voltage and retention time showed a much higher effect than others, suggesting a wise move to firstly adjust these two operating parameters to obtain the desired desalination performance for engineering practice.

Isotherm-based models

Initial salt concentration was not considered as an operating parameter for the statistical model in this study. However, its influence has been well characterized by isotherm-based models, *i.e.* Langmuir and Freundlich equations. To further investigate the CDI behavior under the influence of initial salt concentration, five electro-sorptive batch experiments with NaCl solutions were carried out under an applied voltage of 1.2 V and a spacer thickness of 2 mm. The initial conductivity of NaCl solutions was 100, 200, 500, 1000, and 2000 $\mu\text{S cm}^{-1}$, respectively. The obtained electro-sorption data were fitted by Langmuir, Freundlich, and the least-squares fitting logarithmic equation, which is expressed as follows:

$$q_e = a \times \ln(C_e) + b \quad (5)$$

where q_e is the amount of adsorbed salt at equilibrium (mg g^{-1}), C_e is the equilibrium concentration of salt in solution (mg L^{-1}), while a and b are constants characteristic of the system.

Fig. 6 shows the correspondence between the actual data and the three fitting lines. In general, all models reproduced the data well, and high correlations between actual salt adsorption and predicted salt adsorption were obtained. Table 2 shows that the Langmuir equation correlated better with the experimental data according to an R^2 of 0.9746

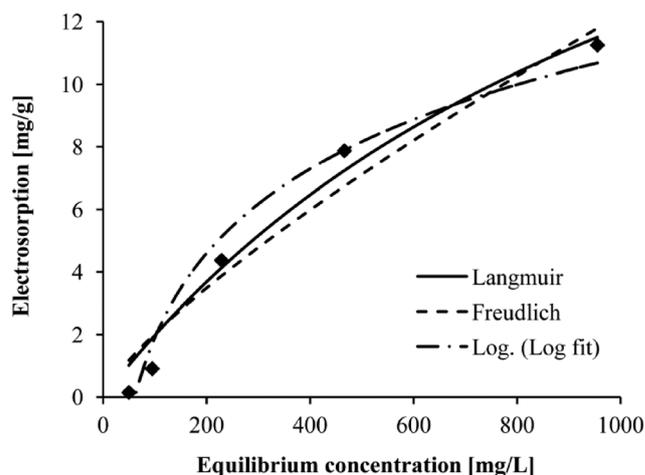


Fig. 6 Langmuir, Freundlich, and logarithmic model predicted electro-sorption versus actual observations in 60 min CDI treatment of NaCl solutions with different initial conductivities from 100 to 2000 $\mu\text{S cm}^{-1}$.

followed by the logarithmic equation ($R^2 = 0.9722$) and Freundlich equation ($R^2 = 0.9550$). This implied that the ion sorption could be described by the Langmuir isotherm, indicating monolayer adsorption.²⁷ It can be deduced that as the saline water flows between a series of electrode pairs, the electro-sorption of each pair decreases as the electrolyte solution concentration drops.¹⁸ This implies that during the operation of a CDI device with multiple pairs of electrodes in series, the electrodes in front may have saturated, while the electrodes in the end may not. For best engineering use, it is important to propose a design that can make the best use of the saturation capacity of all electrodes to avoid frequent regeneration and increase water production.

Other researchers conducted similar experiments to plot salt concentrations versus electro-sorption with different materials as electrodes,^{11,12,26,28} and their data were in agreement with Langmuir isotherms as well, indicating monolayer coverage of the electrode surface area.²⁹ This phenomenon suggests that the monolayer adsorption is primary during the electro-sorption process. Since the electro-sorption behavior of CDI would follow the Langmuir isotherm, the desalination performance at other feed salt concentrations could be predicted by the isotherm-based model for engineering use.

Table 2 Parameters in the Langmuir, Freundlich, and least-squares fitting logarithmic equations

Equation	Parameter	Value
Langmuir	q_m	26.1783
	$K_L (\times 10^{-4})$	8.2038
	R^2	0.9746
Freundlich	K_F	0.0565
	$1/n$	0.7783
	R^2	0.9550
Logarithmic	a	3.8873
	b	-15.993
	R^2	0.9722

Conclusions

CDI is a complex process and modeling is an important approach for gaining a thorough understanding of its desalination performance for practical engineering use. In this paper, a series of electrosorptive batch experiments were conducted for the development of a statistical model to describe the relation between operating parameters (applied voltage, spacer thickness, and retention time) and desalination performance of CDI with activated carbon electrodes. The statistical model was validated by statistical requirements. It reproduced the data well, with both regression and verification R^2 values above 0.85. It can be deduced that operation of a CDI system with good desalination performance would benefit from a higher voltage, a smaller spacer thickness and a longer retention time. The exponents in the statistical model, shown as 2.79, -0.45, and 1.05 for the applied voltage, spacer thickness, and retention time, respectively, revealed the importance of each factor in the correspondingly examined range. In addition, the effects of interactions between the parameters were judged as significant, which could be explained by the electrical double-layer theory. The influence of initial salt concentration could be best characterized by the Langmuir isotherm, which can be used to predict the desalination performance at other feed salt concentrations. This work demonstrates that direct modeling of desalination performance with operating parameters of CDI is feasible and the results can be used to guide practical engineering applications. A future study will explore how the modeling process described in this paper depends on other electrode materials and salt constituents.

Acknowledgements

This research was supported, in part, by Minn Water (Minneapolis, Minnesota, USA) under project no. 1390501914. The authors acknowledged Ningbo Chuanming Electrosorption Equipment Co. Ltd. (Ningbo, China) for assistance on acquiring materials for the bench work.

References

- 1 C. Forrestal, Z. Stoll, P. Xu and Z. Ren, *Environ. Sci.: Water Res. Technol.*, 2015, **1**, 47–55.
- 2 L. Zou, G. Morris and D. Qi, *Desalination*, 2008, **225**, 329–340.
- 3 Y.-J. Kim, J.-H. Kim and J.-H. Choi, *J. Membr. Sci.*, 2013, **429**, 52–57.
- 4 S. Porada, R. Zhao, A. van der Wal, V. Presser and P. M. Biesheuvel, *Prog. Mater. Sci.*, 2013, **58**, 1388–1442.
- 5 Y. Gao, L. Pan, H. Li, Y. Zhang, Z. Zhang, Y. Chen and Z. Sun, *Thin Solid Films*, 2009, **517**, 1616–1619.
- 6 Y. Wimalasiri and L. Zou, *Carbon*, 2013, **59**, 464–471.
- 7 M.-W. Ryoo and G. Seo, *Water Res.*, 2003, **37**, 1527–1534.
- 8 L. Zou, L. Li, H. Song and G. Morris, *Water Res.*, 2008, **42**, 2340–2348.
- 9 K. C. Leonard, J. R. Genthe, J. L. Sanfilippo, W. A. Zeltner and M. A. Anderson, *Electrochim. Acta*, 2009, **54**, 5286–5291.
- 10 P. Xu, J. E. Drewes, D. Heil and G. Wang, *Water Res.*, 2008, **42**, 2605–2617.
- 11 H. Li, L. Zou, L. Pan and Z. Sun, *Environ. Sci. Technol.*, 2010, **44**, 8692–8697.
- 12 Z. Chen, C. Song, X. Sun, H. Guo and G. Zhu, *Desalination*, 2011, **267**, 239–243.
- 13 R. Zhao, P. M. Biesheuvel, H. Miedema, H. Bruning and A. van der Wal, *J. Phys. Chem. Lett.*, 2010, **1**, 205–210.
- 14 S. Porada, L. Borchardt, M. Oschatz, M. Bryjak, J. S. Atchison, K. J. Keesman, S. Kaskel, P. M. Biesheuvel and V. Presser, *Energy Environ. Sci.*, 2013, **6**, 3700–3712.
- 15 Y. A. C. Jande and W. S. Kim, *Sep. Purif. Technol.*, 2013, **115**, 224–230.
- 16 Y. A. C. Jande and W. S. Kim, *J. Ind. Eng. Chem.*, 2014, **20**, 3356–3360.
- 17 H. L. Tang, J. M. Regan, S. E. Clark and Y. F. Xie, *J. Environ. Eng.*, 2011, **137**, 55–62.
- 18 M. Mossad and L. Zou, *J. Hazard. Mater.*, 2012, **213–214**, 491–497.
- 19 Z. Tang, M. A. Butkus and Y. F. Xie, *Environ. Eng. Sci.*, 2006, **23**, 561–569.
- 20 E. Avraham, M. Noked, Y. Bouhadana, A. Soffer and D. Aurbach, *Electrochim. Acta*, 2010, **56**, 441–447.
- 21 I. Cohen, E. Avraham, Y. Bouhadana, A. Soffer and D. Aurbach, *Electrochim. Acta*, 2013, **106**, 91–100.
- 22 X. Gao, A. Omosebi, J. Landon and K. Liu, *J. Electrochem. Soc.*, 2014, **161**, E159–E166.
- 23 X. Gao, A. Omosebi, J. Landon and K. Liu, *Energy Environ. Sci.*, 2015, **8**, 897–909.
- 24 H. Li, L. Zou, L. Pan and Z. Sun, *Sep. Purif. Technol.*, 2010, **75**, 8–14.
- 25 C. Tsouris, R. Mayes, J. Kiggans, K. Sharma, S. Yiacoumi, D. DePaoli and S. Dai, *Environ. Sci. Technol.*, 2011, **45**, 10243–10249.
- 26 H. Li and L. Zou, *Desalination*, 2011, **275**, 62–66.
- 27 C. J. Gabelich, T. D. Tran and I. H. Suffet, *Environ. Sci. Technol.*, 2002, **36**, 3010–3019.
- 28 X. Z. Wang, M. G. Li, Y. W. Chen, R. M. Cheng, S. M. Huang, L. K. Pan and Z. Sun, *ECS Solid State Lett.*, 2006, **9**, E23–E26.
- 29 Z.-H. Huang, M. Wang, L. Wang and F. Kang, *Langmuir*, 2012, **28**, 5079–5084.