Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.981761

57 (2016) 3254–3260
February

Taylor & Francis
Taylor & Francis Group

A statistical experimental investigation on arsenic removal using capacitive deionization

Wei Zhang[a,c,*], Mohamed Mossad[b], Javad Sadoghi Yazdi[d], Linda Zou[a]

[a]*Centre for Water Management and Reuse, University of South Australia, SA 5095, Mawson Lakes, Australia, Tel. +61 8 83023736; email: zhangwei811017@hotmail.com (W. Zhang), Tel. +61 8 83025489; email: linda.zou@mymail.unisa.edu.au (L. Zou)*
[b]*Faculty of Engineering, Public Works Department, Mansoura University, Mansoura, Egypt, email: mohamed_a_hakiem@hotmail.com*
[c]*Jiangnan Graphene Research Institute, Jiangsu 213149, Changzhou, P.R. China*
[d]*School of Natural and Built Environment, University of South Australia, SA 5095, Mawson Lakes, Australia, Tel. +61 8 83026908; email: javad.sadoghiyazdi@mymail.unisa.edu.au*

Received 26 June 2014; Accepted 23 October 2014

ABSTRACT

In this study, arsenic removal from water by a solar-powered capacitive deionization (CDI) unit was investigated. The Box–Behnken statistical experiment design (BBD) as an example of response surface methodology was used to investigate the effects of major process parameters. Initial arsenic concentration, pH, and background sodium chloride concentration were selected as independent variables in BBD, while arsenic removal was considered as the response function. The predicted values of arsenic removal obtained using the response functions were in good agreement with the experimental data. The current CDI technology was found to be an effective and reliable alternative for arsenic removal from water with higher than 80% removal achieved in all designated experiments. In general, CDI removal of arsenate ions favors higher pH and lower salinity conditions. This study showed that BBD methodology was an efficient and feasible approach in predicting the effects of different experimental conditions during an arsenate removal process by CDI.

Keywords: Capacitive deionization; Arsenic removal; Statistical design; Solar power

1. Introduction

Inorganic arsenic is naturally present at high levels in the groundwater of a number of countries and considered to be one of the greatest threats to public health. Due to its bio-accumulative nature, arsenic exposure through potable water can cause various degree of health issues from skin diseases such as pigmentation (i.e. dark and light stains on the skin) and keratosis (i.e. skin hardening in feet and hands) to lung, kidney, and bladder cancer [1]. World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA) have classified arsenic as a carcinogen and established a maximum guide value of 10 μg/L [2–4]. Groundwater with arsenic problems can be found in reducing environment (e.g. West Bengal, Bangladesh, Taiwan, Northern China, and Vietnam), oxidizing arid environments (e.g. Argentina, Chile, México, Peru, and Bolivia), and mixed oxidizing and reducing environments (e.g. South-western USA) [5]. In Western Australia, groundwater of the Gwelup area, Perth has been found to contain high level of arsenic (sometimes

---

*Corresponding author.

up to 7,000 μg/L) probably due to the exposure of pyritic sediments caused by reduced rainfall, increased groundwater abstraction for irrigation and water supply, and prolonged dewatering carried out during urban construction activities [6].

There are a number of available technologies in the literature for arsenic removal from water; however, many of them are usually associated with technical or economical limitations. For example, removal performance of ion exchange resins or adsorbents such as iron hydroxides and active alumina is strongly pH dependent and suffers from many interfering ions (e.g. sulfate, silicate, phosphate, fluoride, and organic compound) [7,8]; coagulation using alum or ferric salts has interfering ions (e.g. phosphate and silicate) and can also cause high level of undesirable residual ions (e.g. sulfate) in the treated water [9,10]; RO or nano-filtration has tendency of scaling and fouling and is pH sensitive [11]. Capacitive deionization (CDI), sometimes referred to as electro-sorption, is a water desalination technology using a small applied potential (1–1.5 V) to drive charged species (e.g. ions) in saline water to the porous surface of the electrodes. The ions removed from aqueous solution are temporally stored in the internal surface areas inside the porous electrodes and can be released by removing or reversing the applied voltage. CDI technology has demonstrated abilities in effective removal of ionic species from water with advantages such as low energy cost, low scaling tendency, less prone to interference ions, and no secondary regeneration wastes [12,13]. In most pH conditions, aqueous arsenic species usually carry a certain degree of charge, which makes CDI technology a viable candidate for its removal from water.

In this study, a CDI prototype unit coupled with solar power was used for first time as an alternative technology to remove the excessive arsenic from synthetic water sources. Response surface methodology (RSM) is an effective statistic technique for studying different complex chemical or physical processes [14]. Effects of CDI process parameters in this study such as arsenic concentration, background sodium chloride concentration, and pH value were studied using RSM, in order to understand the experimental conditions for arsenic removal using the current CDI unit. The results obtained will be helpful for the practical utilization of CDI technology in arsenic removal from different water sources.

2. Experimental

2.1. Description of solar-powered CDI prototype unit

The prototype of solar-powered CDI unit used in this work is shown in Fig. 1(a) and (b), where power of CDI unit is supplied by 4 × 1,000 kW solar panels mounted on the top and side of the unit. The solar power generated through the panel is stored in 8 lead acid batteries, which can provide CDI for its full power need. The excess power generated can also be accessed through power points installed in the trailer for auxiliary lighting and water pumping. Fig. 1(c) is a schematic diagram of the working process of the CDI unit. The influent flows into four assembled carbon electrode cells within the unit, arranged in two groups of double cells connected side by side in series. The electrodes within the cell are charged by an applied DC potential of 1.5 VDC. A complete CDI operation cycle takes 2.5 min and consists of a regeneration step and a purification step. The cycle begins with the regeneration step, which lasts 60 s. First, the effluent solenoid valve (SV2) and the influent solenoid valve (SV1) are closed and the power supply is turned off for 30 s. Then, the effluent waste solenoid valve and SV1 are opened and the power is turned on with the opposite polarity of 1.5 VDC for 30 s. Immediately following this, the purification step begins with the opening of the SV1 and SV2 and continue for 90 s.

The CDI cell primarily consists of graphite current collectors and porous activated carbon electrodes derived from coconut shell with a specific area of 800 m^2/g. Each activated carbon electrode pair was separated by a non-conductive polymeric membrane to prevent short circuiting. The electrodes were connected to the two sides of the DC power supply using connecting leads. Each cell assembly contained 200 sheets of activated carbon (100 cathodes and 100 anodes) measuring $158 \times 174 \times 0.3\ mm^3$, which was similar to those used in our previous study [15,16]. The total mass of activated carbon within a cell was estimated to be 1,354 g.

2.2. Experimental procedure and analytical methods

All the chemicals in this work were of reagent grade or better and were used without further purification. For the CDI experiments, all solutions were prepared with deionized (Millipore®) water and all glassware was previously acid-washed. Synthetic contaminated water samples with arsenic were prepared by adding sodium arsenate ($Na_2HAsO_4 \cdot 7H_2O$) as As (V) source and sodium chloride (NaCl) as background ions. Hydrochloric acid (HCl, 37%) and sodium hydroxide (NaOH) were used to adjust pH of water samples. Total dissolved solids (TDS) were measured by a conductivity monitoring meter (Hach HQ 40d). Before the sample extraction for analysis, the CDI unit will be run for at least one hour or 24 working cycles to ensure that the content (i.e. arsenic and TDS level)

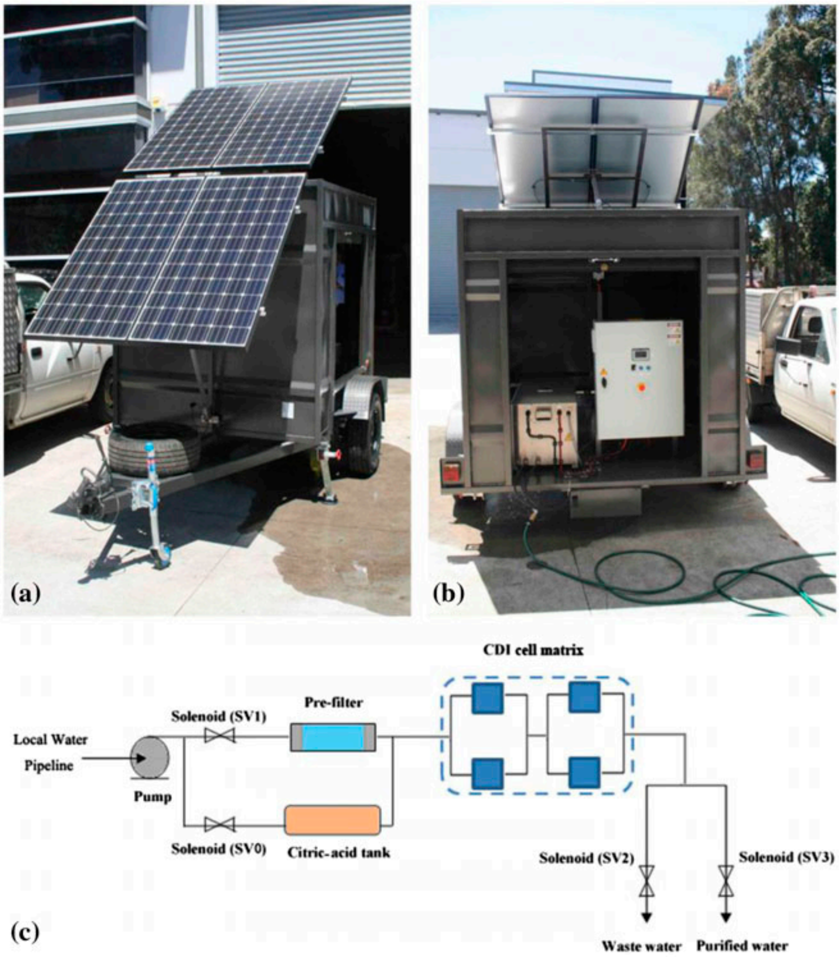

Fig. 1. Photographs (a) and (b) of solar-powered CDI prototype unit; (c) schematic diagram of the CDI unit.

in the treated water stream is stabilized. The concentration of total arsenic was measured by the inductively coupled plasma-optical emission spectrometry using EPA method 200.8.

2.3. Experimental design and statistical analysis

The Box–Behnken statistical experiment design (BBD) as an example of RSM was used to determine the effects of major CDI process parameters on arsenic removal efficiency [17,18]. For the CDI process in this work, process parameters of sodium chloride concentration (X_1), pH (X_2), and initial arsenic concentration (X_3) were chosen as independent variables. Sodium chloride concentration was varied between 0.2 and 1 g/L, while pH was ranged from 3 to 7, and initial arsenic concentration was ranged from 0.02 to 0.1 mg/L. The variables were coded according to the following equation:

$$x = (X_i - X_0)/\Delta X \qquad (1)$$

where x is the coded value, X_i is the corresponding actual value, X_0 is the actual value in the center of the domain, and ΔX is the increment of X_i corresponding to a variation of 1 unit of x. Therefore, the low, middle, and high levels of each parameter were designated as –1, 0, and +1. The range and center point values of the three independent variables are presented in Table 1. The experimental design consists of 12 factorial experiments and three replicates of the central point for estimation of errors. Arsenic removal efficiency (%) was selected as the responses for the combination of the independent variables given. Each designated experimental run was randomized to minimize the effects of unexpected variability in the observed responses. The mathematical model corresponding to the Box–Behnken design is:

Table 1
The BBD with coded and actual levels of three independent variables and the observed arsenic removal efficiency

	Coded and actual levels			
Test set	Sodium chloride concentration (X_1)	pH (X_2)	Initial arsenic concentration (X_3)	Arsenic removal efficiency (%)
1	−1 (0.2)	−1 (3)	0 (0.06)	94.2
2	−1 (0.2)	1 (11)	0 (0.06)	95.08
3	−1 (0.2)	0 (7)	−1 (0.02)	94.45
4	−1 (0.2)	0 (7)	1 (0.1)	98.65
5	0 (0.6)	−1 (3)	−1 (0.02)	88.3
6	0 (0.6)	1 (11)	−1 (0.02)	91.6
7	0 (0.6)	−1 (3)	1 (0.1)	93.66
8	0 (0.6)	1 (11)	1 (0.1)	97.34
9	1 (1)	0 (7)	1 (0.1)	97.14
10	1 (1)	−1 (3)	0 (0.06)	86.8
11	1 (1)	0 (7)	−1(0.02)	84.95
12	1 (1)	1 (11)	0 (0.06)	91.58
13	0 (0.6)	0 (7)	0 (0.06)	86.5
14	0 (0.6)	0 (7)	0 (0.06)	86
15	0 (0.6)	0 (7)	0 (0.06)	86.3

$$Y = a_0 + \sum_{i=1}^{3} a_i X_i + \sum_{i=1}^{3} a_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{m=i+1}^{3} b_{im} X_i X_m \qquad (2)$$

where Y is the dependent variable (removal efficiency), a_0 is the model constant, a_{i}, a_{ii}, and a_{im} are the model coefficients. They represent the linear, quadratic, and interaction effects of the variables. Analysis of the experimental design data, calculation of the predicted responses and coefficients, and graph plotting were carried out using MATLAB (Version 7, MathWorks®, Inc). The validity of the model and reliability of the statistical experimental strategies were determined by comparing the experimental and predicted values.

3. Results and discussion

The removal of arsenic from synthetic water source was investigated using solar-powered CDI unit with a fixed feed flow rate (3 L/min). The coded and actual levels of the three CDI process parameters in Table 1 were selected to investigate the importance of their effects on the arsenic removal efficiency of CDI unit. Table 1 also shows the observed arsenic removal efficiency of 15 designated experiments using BBD statistical approach with coded levels, where it can be seen that more than 80% removal was achieved in all cases. By applying multiple regression analysis on the experimental data, the relationship between response variable (i.e. arsenic removal) and three CDI process variables are fitted by the following second-order polynomial equation:

$$\begin{aligned} Y = {} & 1.137 - 0.438X_1 - 0.02X_2 - 3.059X_3 + 0.006X_1X_2 \\ & + 1.248X_1X_3 + 0.006X_2X_3 + 0.21X_1^2 + 0.0015X_2^2 \\ & + 26.065X_3^2 \end{aligned} \qquad (3)$$

The predicted values of arsenic removal efficiency were determined by the response function of the quadratic model with the obtained coefficients. The experimental results and the predicted values of arsenic removal efficiency using CDI are plotted in Fig. 2. The high value of regression coefficient ($R^2 = 0.9726$) indicates that the model predictions fit satisfactorily with the experimental observations with high dependence and correlation. The value of adjusted R^2 (0.9651) suggested that the total variation of about 96% for arsenic removal was attributed to the independent variables and only less than 4% of the total variation cannot be explained by the quadratic model. Fig. 3 shows the residuals of the quadratic model plotted against the predicted values of arsenic removal efficiency, where the residual points on the plot appear to be randomly scattered around zero. Therefore, it is reasonable to assume that the error terms have a mean of zero and the fitted quadratic model is valid.

The statistical significance of the response function was checked by F-test, and some of the analysis of variance (ANOVA) results for the response surface quadratic model and model terms are summarized in Table 2. The p values are usually used to estimate

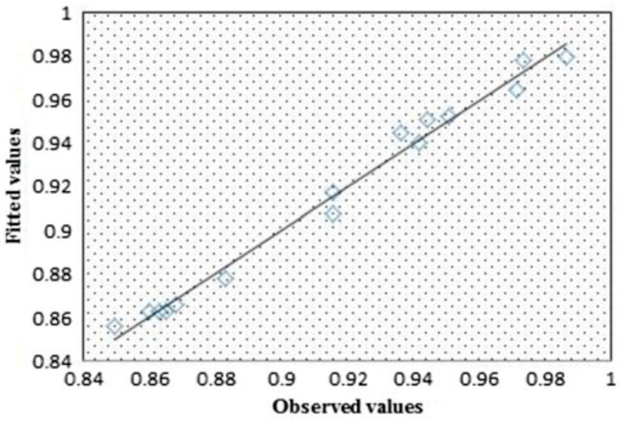

Fig. 2. Observed values of arsenic removal efficiency vs. predicted values of the fitted quadratic model.

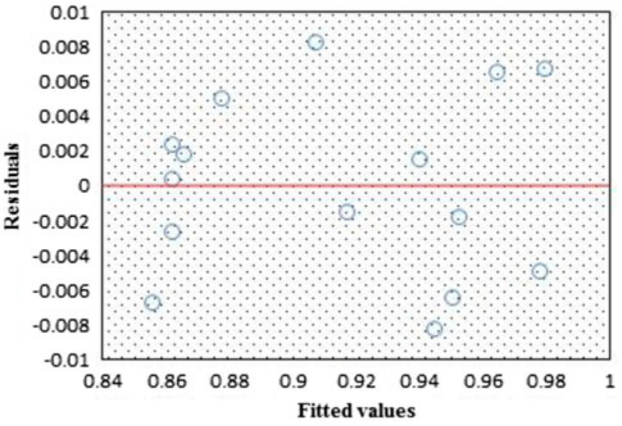

Fig. 3. Fitted quadratic model residuals vs. the predicted values of arsenic removal efficiency.

Table 2
Some of the ANOVA results of the second-order polynomial equation for arsenic removal efficiency using CDI

Source	Term coefficient	*F* value	*p*-Value
Intercept	1.137	41.9955	<0.0001
X_1	−0.438	10.1316	0.00016
X_2	−0.02	4.2865	0.00781
X_3	−3.059	7.0758	0.00087
X_1X_2	0.006	2.2239	0.07674
X_1X_3	1.248	4.5563	0.00607
X_2X_3	0.006	0.2167	0.83701
X_1^2	0.21	7.3643	0.00072
X_2^2	0.0015	5.0139	0.00405
X_3^2	26.065	9.1395	0.00026
Model	–	43.96	0.00031

whether *F* value is large enough to indicate statistical significance and used to check the significance of each coefficient. The p values of model and model terms lower than 0.05 indicate that they are statistically significant. In this work, the model is statistically significant due to *F* value and very low probability value (0.00031) and thus, model equation can adequately be used to describe the arsenic removal under a wide range of operating conditions. Similarly, coefficients of most model terms are significant except for two cross-product coefficients (X_1X_2 and X_2X_3).

The quadratic three-dimensional response plots are presented in Fig. 4 to study certain interactions between the pH, initial arsenic, and sodium chloride concentration as well as their individual effects on arsenic removal efficiency. During the CDI process, arsenate ions are removed through the mechanism of electro-sorption. When using a small applied potential (1–1.5 V), all charged species (e.g. ions) in saline water are driven to and adsorbed on the porous surface of the electrodes. As a result, background ions (i.e. chloride) would compete with target ions (i.e. arsenate) for effective electro-adsorption and thus reduce its removal rate, especially when the concentration of background anions is several orders higher than their counterparts. Fig. 4 shows that response gradient of arsenic removal efficiency tends to decrease toward the end of highest sodium chloride concentration tested in this study. On the other hand, it is noteworthy that the initial arsenic concentration seems to have much less significant effect on the arsenic removal efficiency within its boundary conditions (0.02–0.1 mg/L) in this study. Fig. 4 shows that responses of high arsenic removal efficiency are spread across the whole range of arsenic concentration.

The species of aqueous arsenate ions is critically dependent on solution conditions. A pH diagram can show the dominant arsenate species under different conditions and also gives a guide to adjustment of pH for the formation of desired ones. Depending on pH, Fig. 5 shows that arsenate will be present as H_3AsO_4 or its derived anionic species, such as AsO_4^{3-}, $HAsO_4^{2-}$, and $H_2AsO_4^-$. Based on our previous studies [16], the preferential electro-adsorption of a specific ion during a CDI process was controlled by the properties of the ion, such as charge and hydrate radius. Generally, ions with higher charge and smaller hydrate radius are preferably adsorbed onto porous electrodes. As the pH value of solution shift to more alkaline region, the formation of arsenate species with higher charge (such as $HAsO_4^{2-}$ and AsO_4^{3-}) increases and this would give rise to higher arsenic removal efficiency. This is confirmed in Fig. 4, where responses of higher arsenic removal efficiency mostly fall into the higher pH range. It is also interesting to note that the aforementioned effect of competing chloride ions

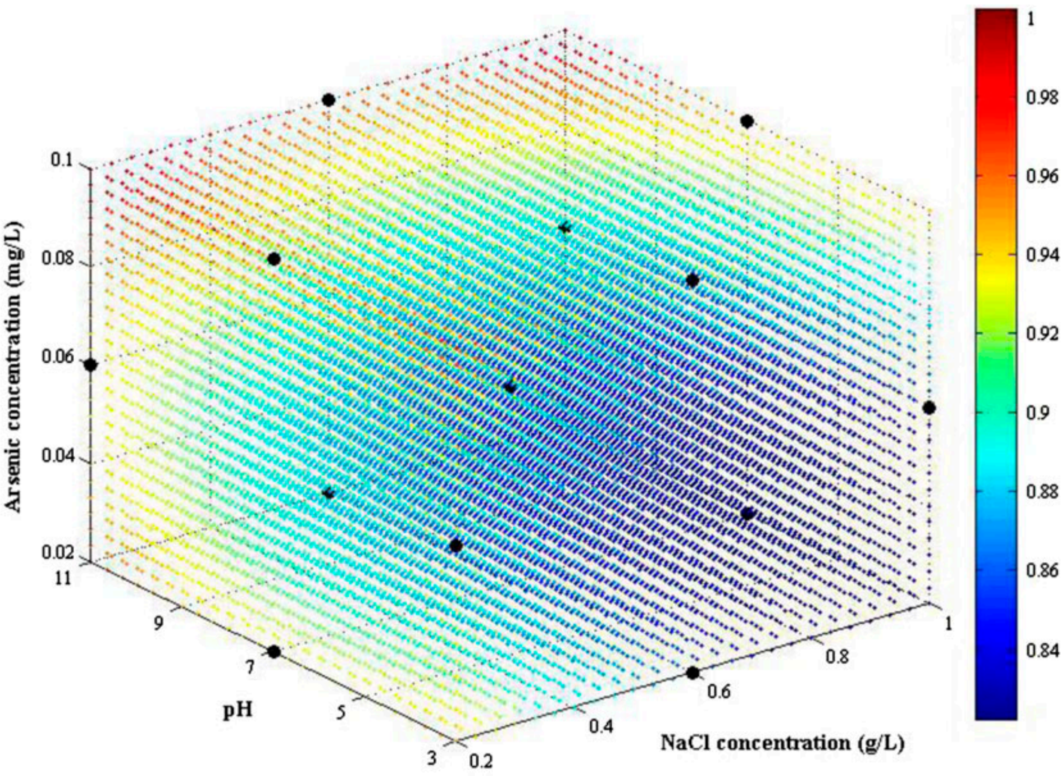

Fig. 4. Quadratic response surface plots showing effects of pH, arsenic, and NaCl concentration and their combination on the arsenic removal efficiency, which is represented in the color bar. Black dots represent the designated experimental conditions and their predicted responses within the design space.

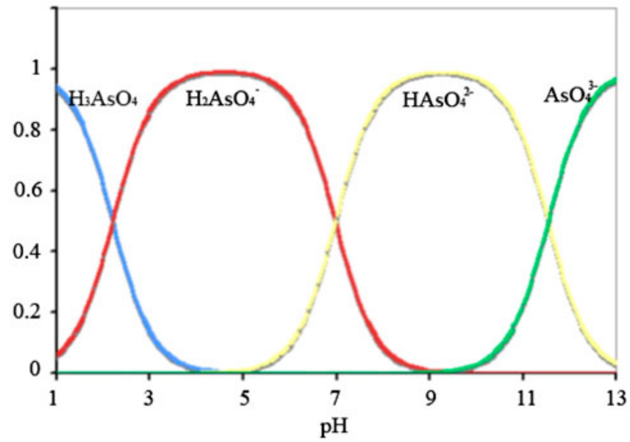

Fig. 5. A pH diagram of aqueous arsenate species abundance.

was more pronounced in lower pH range. This was most likely because arsenate species carries less charge in the acidic environment and thus are less preferable for electro-sorption against monovalent chloride ions of significantly higher concentration. In comparison with more popular arsenic removal method, such as coagulation, it appears that CDI removal of arsenate does not have a typical optimal pH range.

With the boundary conditions of experimental design in this work, the maximum arsenic removal efficiency was calculated to be 100% by solving the regression equation under the experimental conditions of $X_1 = 0.9$, $X_2 = 11$, and $X_3 = 0.1$. The minimum arsenic removal efficiency was calculated to be 84.22% under the experimental conditions of $X_1 = 0.86$, $X_2 = 5$, and $X_3 = 0.04$. In order to determine the accuracy of the predicted model, two experiments different from BBD points were also carried out. The two aforementioned conditions, where the highest and the lowest arsenic removal efficiency were calculated based on Eq. (3), were used. The experimental and predicted values were compared in Table 3. Validation experiments confirmed the suitability and the accuracy of the model. The predicted values were in close agreement with the experimental values. Therefore, BBD was a reliable and effective method in predicting the effects of different experimental conditions during an arsenate removal process by CDI. The analysis showed that the form of the model chosen to explain the relationship between the process parameters and the response is correct and can be used to navigate the design space.

Table 3
Comparison of the experimental and predicted values for different Box–Behnken experimental design points

Arsenate concentration (mg/L)	Sodium chloride concentration (g/L)	pH	Arsenic removal efficiency (%)	
			Observed	Predicted
0.04	0.86	5	82.6	84.2
0.1	0.9	11	98.15	100

4. Conclusion

Arsenic removal from water by a solar-powered CDI unit was investigated. The BBD as an example of RSM was used to investigate the effects of major process parameters. Initial arsenic concentration, pH, and background sodium chloride concentration were selected as independent variables in BBD, while arsenic removal was considered as the response function. The current CDI technology was found to be an effective and reliable alternative for arsenic removal from water. WHO arsenic guidance value compliance (<0.01 mg/L) was achieved with higher than 80% removal in all designated experiments. The predicted values of arsenic removal obtained using the response functions of the quadratic model were in good agreement with the experimental data. By increasing the solution pH, formation of more desired arsenic species could be obtained and so is the higher arsenic removal efficiency. In general, CDI removal of arsenate ions favors higher pH and lower salinity conditions. This was observed consistently between the experimental boundary conditions of current experimental design space. This study showed that BBD methodology was an efficient and feasible approach in predicting the effects of different experimental conditions during an arsenate removal process by CDI.

Acknowledgments

The authors acknowledge the financial support of the National Centre of Excellence in Desalination (NCED), which is funded by the Australian Government through the Water for the Future initiative, and LT Green Technology, Australia, for supplying the CDI prototype.

References

[1] C. Jain, I. Ali, Arsenic: Occurrence, toxicity and speciation techniques, Water Res. 34 (2000) 4304–4312.
[2] National Research Council, Arsenic in Drinking Water, National Academy of Sciences, Washington, DC, 2001.
[3] WHO, Guidelines for Drinking-water Quality, addendum to vol. 1, recommendations Geneva, 1998.
[4] US Environmental Protection Agency, Panel 14: National Primary Drinking Water Regulations: Arsenic and Clarifications to Compliance and New Source Contaminants Monitoring, vol. 66, p. 194, 2001, Washington, DC.
[5] P.L. Smedley, D.G. Kinniburgh, A review of the source, behaviour and distribution of arsenic in natural waters, Appl. Geochem. 17 (2002) 517–568.
[6] S. Applyard, J. Angeloni, R. Watkins, Arsenic-rich groundwater in an urban area experiencing drought and increasing population density, Perth, Australia, Appl. Geochem. 21 (2006) 83–97.
[7] D. Giles, M. Mohapatra, T. Issa, S. Anand, P. Singh, Iron and aluminium based adsorption strategies for removing arsenic from water, J. Environ. Manage. 92 (2011) 3011–3022.
[8] D. Mohan, C. Pittman Jr., Arsenic removal from water/wastewater using adsorbents—A critical review, J. Hazard. Mater. 142 (2007) 1–53.
[9] A. Oehmen, R. Valerio, J. Llanos, J. Fradinho, S. Serra, M. Reis, J. Crespo, S. Velizarov, Arsenic removal from drinking water through a hybrid ion exchange membrane—Coagulation process, Sep. Purif. Technol. 83 (2011) 137–143.
[10] C. Hu, H. Liu, G. Chen, J. Qu, Effect of aluminum speciation on arsenic removal during coagulation process, Sep. Purif. Technol. 86 (2012) 35–40.
[11] H. Saitua, R. Gil, A. Padilla, Experimental investigation on arsenic removal with a nanofiltration pilot plant from naturally contaminated groundwater, Desalination 274 (2011) 1–6.
[12] L. Zou, G. Morris, D. Qi, Using activated carbon electrode in electrosorptive deionisation of brackish water, Desalination 225 (2008) 329–340.
[13] M. Mossad, L. Zou, A study of the capacitive deionisation performance under various operational conditions, J. Hazard. Mater. 213–214 (2012) 491–497.
[14] M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escaleira, Response surface methodology (RSM) as a tool for optimization in analytical chemistry, Talanta 76 (2008) 965–977.
[15] W. Zhang, M. Mossad, L. Zou, A study of the long-term operation of capacitive deionisation in inland brackish water desalination, Desalination 320 (2013) 80–85.
[16] M. Mossad, W. Zhang, L. Zou, Using capacitive deionisation for inland brackish groundwater desalination in a remote location, Desalination 308 (2013) 154–160.
[17] D. Montgomery, Design and Analysis of Experiments, third ed. Wiley, New York, NY, 1991.
[18] M. Sullivan, Statistics Informed Decisions Using Data, Pearson Education, Upper Saddle River, NJ, 2004.