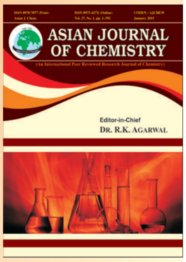
Asian Journal of Chemistry; Vol. 27, No. 6 (2015), 2082-2086

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17748



Electrosorption of Hardness Ions from Water with Activated Carbon Cloth Electrodes

BINGJIE DONG*, ZHAOHUI ZHANG, LIANG WANG, HONGWEI ZHANG and CHENG CHANG

College of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, P.R China

*Corresponding author: Tel/Fax: +86 22 83955163; E-mail: jjd263@163.com

Received: 2 April 2014; *Accepted*: 17 June 2014; *Published online*: 17 March 2015; AJC-16966

In this study, removal of hardness from water using a capacitive deionization system with activated carbon cloth electrodes was investigated. The dynamic study indicated that the hardness removal process followed the pseudo-first-order kinetics model and more than 90 % of the hardness ions could be removed during the first 0.5 h of the electrosorption process. Two types of regeneration methods were compared and the results showed that compared reversing electrodes' polarities, the regenerating method of short circuit of electrodes was more effective for activated carbon cloth electrodes regeneration. The hardness removal performance of activated carbon cloth electrodes could remain stable after five consecutive cycles of electrosorption/regeneration.

Keywords: Capacitive deionization, Electrosorption, Hardness removal, Activated carbon cloth electrode.

INTRODUCTION

Hard water is undesirable in either domestic water supply or industrial applications. High concentrations of hardness ions in water significantly reduce the product quality in some industrial fields, such as rinse and dyeing of textile[1]. In industrial circulating cooling water system and boiler make-up water system, hardness ions present in water would cause scaling of heat exchangers and boilers and even result in the explosion in severe cases[2,3]. When hard water is used as domestic water supply, its high mineral content decreases the household cleaning efficiency due to the reaction of hardness cations with soap anions[4,5].

In the past several years, the capacitive deionization process has attracted more and more interests as an emerging desalination and softening technology. Compared with other conventional desalination and softening processes, *e.g.*, chemical precipitation, multi-stage flash process, reverse osmosis, ion exchange and electrodialysis, capacitive deionization has many advantages such as low energy consumption, no membrane fouling, no chemicals addition and low requirement for influent pretreatment[6-8]. Furthermore, capacitive deionization is conducted at a relatively low electrical voltage (typically 0.8-2.0V)[9] and requires no chemicals for regeneration. Therefore, capacitive deionization is believed as an attractive environmental-friendly technology for hardness ions removal.

Nowadays, many researches on capacitive deionization have been concentrated on desalination performance and electrode materials, but few studies have been conducted on hardness removal using capacitive deionization. Lee *et al.*[10] investigated the desalination performance of a novel membrane capacitive deionization (MCDI) system which combined ion-exchange membranes with a capacitive deionization (CDI). The removal of typical cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) and anions (Cl^-, SO_4^{2-} and NO_3^-) from a power plant wastewater were studied, but no further discussion were carried out. Welgemoed and Schutte[11] developed an industrial type model of capacitive deionization using carbon aerogel as electrodes. In their application specific testing, the removals of typical cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, Zn^{2+} and B^+) and anions (Cl^-, SO_4^{2}, HCO_3^- and Br^-) from diluted artificial seawater were summarized. However, in these literatures, calcium and magnesium ions were proposed only as one of typical cations of feed water and no further studies about these hardness ions were proceeded besides their removal efficiency. Compared with the above reports, a systematic research about the removal of hardness ions by capacitive deionization were investigated by Seo *et al.*[12]. They analyzed the hardness removal efficiencies of activated carbon cloth electrodes and activated carbon composites electrodes and concluded that the suitable electrode materials for water softening should have abundant mesopores and branched micropores. Besides, the selective removal of divalent ions (Ca^{2+} and Mg^{2+}) and monovalent ions (K^+ and Na^+) were also compared. However, more researches are still needed to further investigate the capacitive deionization technology for water softening applications, such as the electrosorption kinetics of hardness ions, the influence of the coexisting anions, a more effective regeneration method, *etc*.

In this study, the removal kinetics of hardness ions by electrosorption with activated carbon cloth electrodes was investigated and the influences of hardness ions composition and coexisting anions on water softening process were extensively discussed. In addition, two types of regeneration methods were compared and the operation stability of the capacitive deionization system in multi-cycles was evaluated.

EXPERIMENTAL

Preparation of activated carbon cloth electrodes: The activated carbon cloth was provided by Jialiqi Carbon Fiber Co. Ltd. (China) and its main characteristics are shown in Table-1. Before preparing electrodes the activated carbon cloth was cut into pieces (100 mm × 100 mm) and boiled in deionized water for 2 h to remove the water-soluble and volatile impurities. The activated carbon cloth pieces were then dried at 105 °C in a vacuum oven for 3 h for further removal of the remaining volatile organic matters in micropores of the activated carbon cloth. The activated carbon cloth electrodes were prepared as follows: The graphite sheets were used as current collectors and treated activated carbon cloth was sticked to the graphite sheets with electrically conductive adhesive. The size of activated carbon cloth electrode was 100 mm × 100 mm.

TABLE-1
MAIN CHARACTERISTICS OF ACTIVATED CARBON CLOTH USED FOR THE ELECTRODE PREPARATION

Thickness (mm)	0.6
Specific surface area (m^2/g)	1417
Average pore size (nm)	1.697
Pore volume (cm^3/g)	0.6012

The configuration of a capacitive deionization unit cell is shown in Fig. 1. The capacitive deionization unit cell consisted of two parallel activated carbon cloth electrodes separated by a non-conductive sponge of 5 mm-thickness, which prevented the electrical short circuit and allowed the liquid to flow freely. A flow channel was created by punching a 5 mm-diameter hole in the corner of the electrode so that the solution contacted with all sides of the electrode.

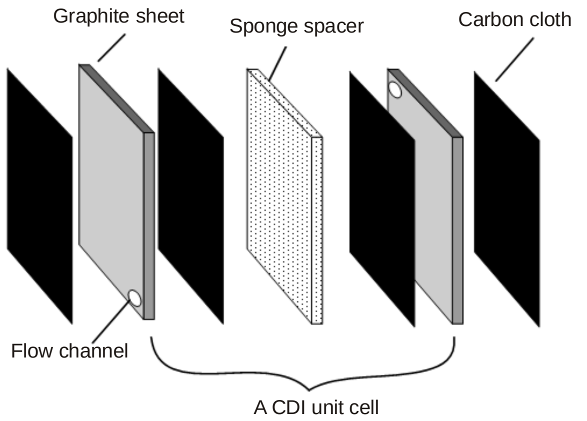


Fig.1. Configuration of a capacitive deionization unit cell

Experimental system: The capacitive deionization experimental system is depicted in Fig. 2. The influent was continuously pumped into a capacitive deionization stack by a peristaltic pump and the flow rate was fixed at 20 mL/min. A given potential was applied to the capacitive deionization stack using a potentiostat (TD1734A, Zhonghuan). The capacitive deionization stack is divided into five unit cells by three pairs of electrodes. All the anodes are connected together and all the cathodes are connected together with metal wires. The other ends of the metal wires are connected to the positive pole and negative pole of the potentiostat, respectively. Ca^{2+} was selected as the representative hardness ions to simulate the influent hardness by dissolving $CaCl_2$ in deionized water. The unit of hardness concentration is expressed as mg $CaCO_3$/L.

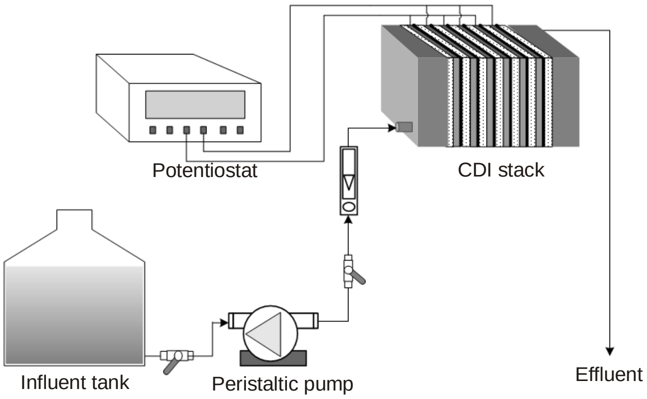


Fig. 2. Schematic diagram of capacitive deionization system

Batch experiments were conducted to investigate the electrosorption kinetics and the effect of ions composition on removal performance of hardness. The effluent of the capacitive deionization stack was recirculated to the influent tank. The hardness and conductivity in the influent tank and effluent were analyzed every 5 min by the ion chromatography (DX600, Dionex) and conductivity meter (sensION156, HACH). Each experiment continued until the effluent hardness did not change any more. To investigate the desirable method for the regeneration of activated carbon cloth electrodes, a series of continuous flow experiments was conducted. During the experiments the feed solution was passed through the capacitive deionization stack only once and the effluent was discarded. The effluent hardness and conductivity were analysed every 5 or 10 min.

Electrochemical characterization of activated carbon cloth electrodes: The electrochemical properties of the activated carbon cloth electrodes were analyzed in a three-compartment cell by an electrochemical workstation (Versa. STAT3, Ametek). The activated carbon cloth electrode, platinum plate and saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively. Cyclic voltammetry measurement was carried out at the room temperature in 0.5 M NaCl electrolyte solution. The potential scan rate was set as 5 mV/s with the potential range of 0 to 0.4 V and the voltammograms of the electrodes were recorded after stabilization.

RESULTS AND DISCUSSION

Electrosorption kinetics: To investigate the electrosorption behaviour of activated carbon cloth electrodes, the hardness removals at different potentials are shown in Fig. 3. 266 mg/L $CaCl_2$ solution was used as influent and the potentials of 1, 1.2, 1.5, 1.7 and 2 V were applied to the capacitive deionization

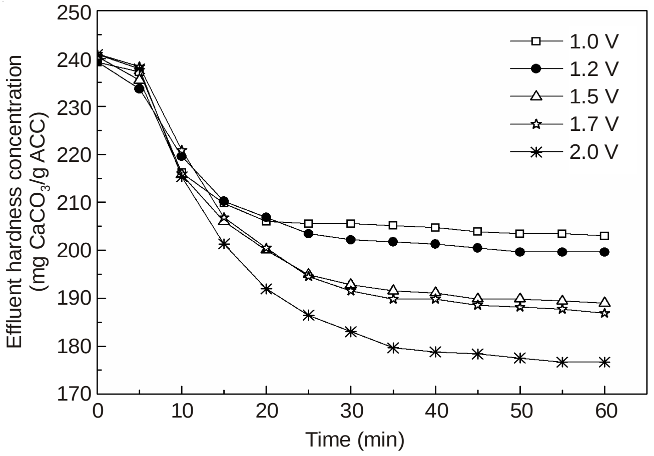


Fig. 3. Removal rate of the hardness at different potentials

stack, respectively. The results showed that in each experiment the effluent hardness concentration decreased rapidly during the initial 0.5 h and above 90 % of the total removal content was finished during this period. After continuous running for 55 min the effluent hardness concentration did not change any more, which meant the activated carbon cloth electrodes were saturated for hardness ions adsorption and needed regenerating before reuse. Therefore, the electrosorption process was continued for 60 min in each experiment. The maximum removal efficiency of hardness ions was calculated at the end of each experiment and the values indicated that the hardness removal ability by capacitive deionization increased with increasing the applied potential.

In order to further analyze the electrosorption process of hardness ions, the kinetics of hardness removal was analyzed at different potentials (Fig. 4). Both pseudo-first-order eqn. 1 and pseudo-second-order eqn. 2 adsorption kinetics model[13, 14] are employed to fit the experimental data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

where q_e and q_t are the amounts of hardness ions adsorbed at equilibrium and time t, respectively (mg $CaCO_3$ g^{-1} activated carbon cloth); k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}); k_2 is the rate constant of pseudo-second-order adsorption (g mg^{-1} min^{-1}). The fitting results are shown in Fig. 4 and more detailed parameters are listed in Table-2. It was found that the pseudo-first-order kinetics model fitted the experimental data better than the pseudo-second-order model based on the higher values of the correlation coefficient (R^2). The equilibrium absorption amounts of hardness ions, despite of theoretical values or experimental data, increased by around 20-30 % when the applied voltage increased by 0.2-0.3 V in the range of 1-1.7 V. However, the equilibrium absorption amounts of hardness only increased by 8-12 % when the potential increased from 1.7 to 2 V. Due to the increase of the electrostatic force, the adsorption rate of hardness ions onto activated carbon cloth electrodes increased. However, the efficiency of energy utilization decreased as the applied votage was high enough to induce the water electrolysis.

TABLE-2
ELECTROSORPTION PARAMETERS OF PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETICS FOR HARDNESS AT DIFFERENT POTENTIALS

U (V)	Pesudo-first-order			Pesudo-second-order		
	q_e	k_1	R^2	q_e	k_1	R^2
1.0	3.5592	0.0837	0.9707	4.3790	0.0199	0.9492
1.2	4.3792	0.0638	0.9708	5.6924	0.0103	0.9533
1.5	5.6982	0.0554	0.9627	7.6656	0.0062	0.9466
1.7	7.2511	0.0606	0.9744	9.5234	0.0057	0.9578
2.0	8.1411	0.0529	0.9600	11.0745	0.0040	0.9448

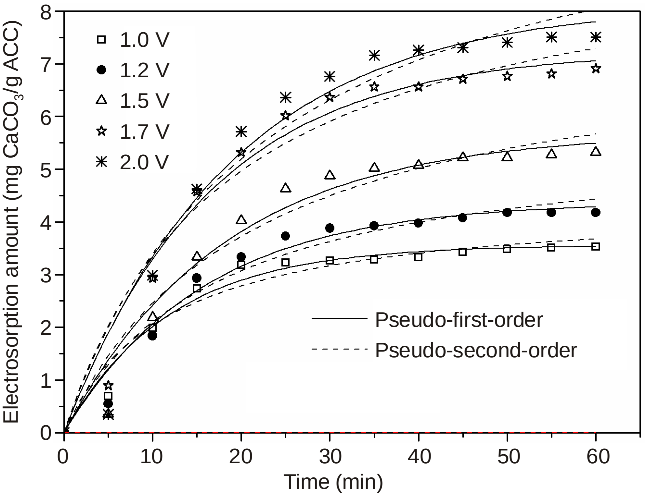


Fig. 4. Electrosorption kinetics of removal of hardness ions

Regeneration of activated carbon cloth electrodes: In capacitive deionization system a regeneration process was required as the electrodes were saturated and lost its electrosorption capability for ions. Two regenerating approaches were compared for the activated carbon cloth electrodes regeneration, namely polarity reversal of electrodes and short circuit of electrodes. For the polarity reversal of electrodes, the influent flow rate was constant and the power supply was turned off for 5 min to start the regeneration and then an opposite polarity of 1.7 VDC was applied to the activated carbon cloth electrodes for 50 min; for the short circuit of electrodes, the anodes and cathodes were directly connected together with metal wires to start the regeneration and the whole regeneration process lasted for 55 min. Fig. 5 shows a continuous operation of 210 min, consisting three consecutive phases of electrosorption (phase-I), regeneration (phase-II) and electrosorption (phase-III). It should be noted that during the whole operation process the feed flow rate was kept at 20 mL/min, the hardness concentration in the influent was maintained at about 204 mg $CaCO_3$/L by dissolving 1132 mg $CaCl_2$ in 5 liters distilled water and the regeneration process lasted for 55 min.

As shown in Fig. 5, the effluent hardness started to increase after continuous electrosorption of 90 min, which indicated that the electrodes of capacitive deionization should be regenerated. The electrodes were regenerated by polarity reversal of electrodes and short circuit of electrodes, respectively (phase-II in Fig. 5). It can be found from Fig. 5 that after the electrodes were shorted the effluent hardness increased rapidly from 204 to 274 mg $CaCO_3$/L in the initial 25 min of regeneration and the effluent hardness decreased gradually from 274 to 225 mg

$CaCO_3$/L by the end of regeneration. This means that the hardness ions electrosorped by the activated carbon cloth electrodes were desorbed into solution during the whole regeneration (phase-II). Therefore, an effective regeneration of the electrodes was obtained. However, for the polarity reversal of electrodes, only in the initial 5 min of regeneration the effluent hardness increased from 204 to 247 mg $CaCO_3$/L due to the electrostatic repulsion between the electrode and the adsorbed ions. A new electrosorption process formed again under the reversed voltage as the regeneration proceeded for 15 min, which impeded the full desorption of the hardness ions on the activated carbon cloth electrodes, especially those adsorbed into the porous network of activated carbon cloth. After 0.5 h of regeneration the effluent hardness increased gradually again. Therefore, a really effective regeneration of the electrodes only happened at the first 15min of the regeneration process.

During phase-III the hardness removal efficiency for the electrodes regenerated with the method of short circuit of electrodes was significant higher than that of the electrodes regenerated with the method of reversing electrodes' polarities. Compared the electrosorption processes before and after regeneration (phase-I and phase-III in Fig. 5), the maximum removal of hardness decreased by 11.7 % for the electrodes regenerated by polarity reversal. However, no significant deterioration was observed for the hardness removal performance after the electrodes were regenerated by short circuit. The results also confirmed that short circuit of electrodes was a more effective regeneration method for electrode regeneration.

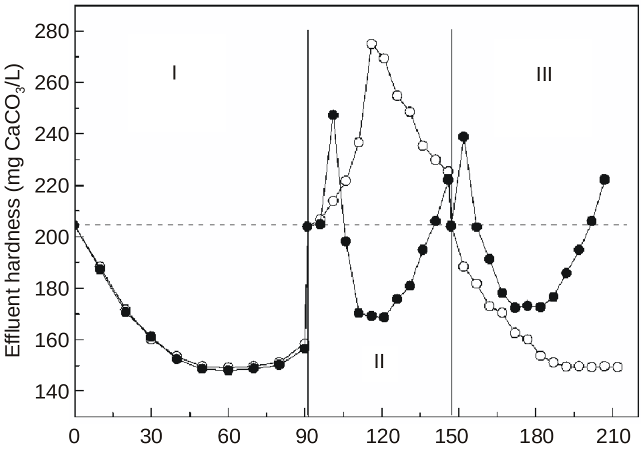


Fig. 5. Comparison of short circuit of electrodes (○) and polarity reversal of electrodes (●) for electrode regeneration. The applied voltage was 1.7 V and the influent hardness was maintained at 204 mg $CaCO_3$/L

In order to achieve a higher treatment capacity of hardness removal, a capacitive deionization stack with six pairs of electrodes were applied and the effective area of each cell still was 100 cm^2. The consecutive cycle of electrosorption/regeneration were performed for the evaluation of capacitive deionization performance for hardness removal. Continuous treatment was conducted with a flow rate of 20 mL/min and 80 min of electrosorption and 50 min of regeneration were selected based on the previous results. The short circuit of electrodes was used as the regeneration method.

The effluent hardness during five consecutive electrosorption/regeneration cycles is presented in Fig. 6. The hardness concentration in treated water decreased gradually until a minimum value of 120 mg $CaCO_3$/L after 60 min of each electrosorption phase. The hardness concentration in waste stream decreased gradually from about 420 mg $CaCO_3$/L to 200 $CaCO_3$/L by the end of each regeneration phase. The maximum removal efficiency of hardness was around 41% and the significant decrease of performance during the long-term process was not observed. The results indicated that the capacitive deionization stack performance for hardness removal was quite stable.

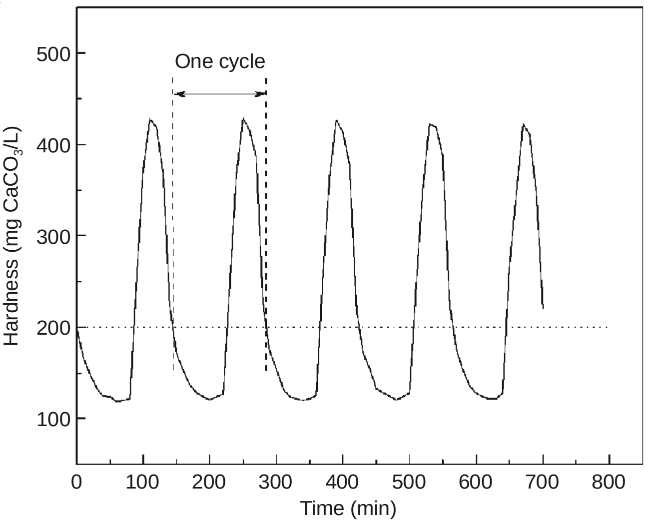


Fig. 6. Operational performance during five consecutive electrosorption/desorption cycles at a flow rate of 20 mL/min, a potential of 1.7 V and $CaCl_2$ concentration of 222 mg/L

Cyclic voltammetry is an important method to evaluate the capacitive characteristics of electrodes for electrosorption. The cyclic voltammograms of the activated carbon cloth electrodes for each cycle of the five consecutive electrosorption/regeneration cycles were measured in 0.5 M NaCl electrolyte solution (Fig. 7). All the cyclic voltammograms were symmetrical in the potential range from 0 to 0.4 V with small deformation from rectangular curves. The current steadily increases or decreases with changing the voltage and no evident oxidation/reduction peak in cyclic voltammetry curves were found. Therefore, it can be inferred that no electrolysis reaction existed during this process except for electrosorption/desorption. The electrosorption/desorption was a reliable and highly reversible process.

Compared the cyclic voltammograms of the five electrosorption/regeneration cycles, high consistency between the five cyclic voltammetric curves can be found. This indicated that significant decline in the specific capacitances of the activated carbon cloth electrodes did not happend after five consecutive electrosorption/regeneration cycles. The performance of activated carbon cloth electrodes was very stable during the long-term process and short circuit of electrodes was a very effective regeneration method.

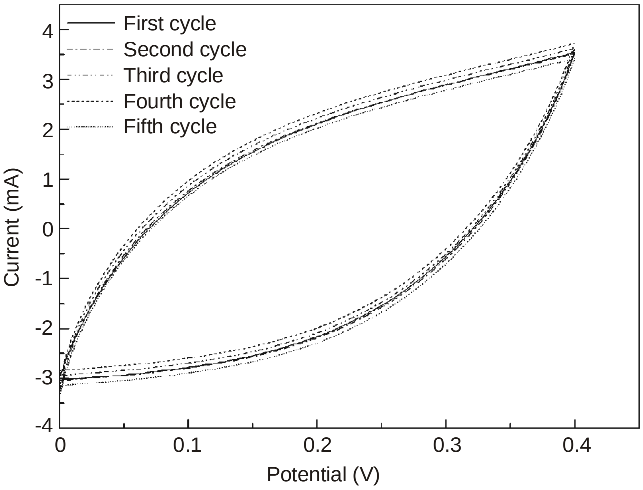


Fig. 7. Cyclic voltammograms of activated carbon cloth electrode in a solution of 0.5 M NaCl at a sweep rate of 5 mV/s

Conclusion

This research has systematically investigated the electrosorption performance of hardness ions by activated carbon cloth electrodes. The hardness removal efficiency in capacitive deionization system increased with increasing the applied potentials and batch experiments indicated that the electrosorption equilibrium was obtained after 60 min of running and above 90 % of total removal content was finished at the first 0.5 h of the electrosorption process. Kinetics analysis showed that the electrosorption of hardness ions followed the pseudo-first-order kinetics model and the equilibrium absorption amounts of hardness ions increased with the applied voltage. The short circuit of electrodes was a more effective method for activated carbon cloth electrodes regeneration. The maximum removal efficiency of hardness was 41% when six pairs of electrodes were used in a capacitive deionization stack. The capacitive deionization system removed the hardness ions stably during the consecutive five electrosorption/regeneration cycles and no obvious capacitance decline was observed according to the cyclic voltammograms.

ACKNOWLEDGEMENTS

This work was financially supported by the National Natural Science Fund of China (51108315, 51138008, 21206125 and 51308391).

REFERENCES

1. C.W. Kan, *Fibers Polymers*, **9**, 317 (2008).
2. M.A. Arugula, K.S. Brastad, S.D. Minteer and Z. He, *Enzyme Microb. Technol.*, **51**, 396 (2012).
3. V. Sivasankar and T. Ramachandramoorthy, *Chem. Eng. J.*, **171**, 24 (2011).
4. J. Park, J.H. Song, K.H. Yeon and S.H. Moon, *Desalination*, **202**, 1 (2007).
5. W.X. Fang, L. Shi and R. Wang, *J. Membr. Sci.*, **430**, 129 (2013).
6. Y.J. Kim and J.H. Choi, *Water Res.*, **44**, 990 (2010).
7. G. Wang, B.Q. Qian, Q. Dong, J.Y. Yang, Z.B. Zhao and J.S. Qiu, *Sep. Purif. Technol.*, **103**, 216 (2013).
8. C.J. Feng, C.H. Hou, S.H. Chen and C.P. Yu, *Chemosphere*, **91**, 623 (2013).
9. M. Mossad and L. Zou, *J. Hazard. Mater.*, **213-214**, 491 (2012).
10. J.B. Lee, K.K. Park, H.M. Eum and C.-W. Lee, *Desalination*, **196**, 125 (2006).
11. T.J. Welgemoed and C.F. Schutte, *Desalination*, **183**, 327 (2005).
12. S.-J. Seo, H. Jeon, J.K. Lee, G.-Y. Kim, D. Park, H. Nojima, J. Lee and S.-H. Moon, *Water Res.*, **44**, 2267 (2010).
13. M. Elkhaiary, *J. Hazard. Mater.*, **147**, 28 (2007).
14. Z.L. Chen, C.Y. Song, X.W. Sun, H.F. Guo and G.D. Zhu, *Desalination*, **267**, 239 (2011).