Asian Journal of Chemistry; Vol. 25, No. 10 (2013), 5793-5797

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.OH94

Experimental Study on Removal of Nitrate from Wastewater Using Microbial Desalination Cells†

JIAN-PING CHENG[1,3], SHAOHUA CHEN[2], CHEN CHEN[3] and JIAQUAN WANG[3,*]

[1]School of Mechanical and Automotive Engineering, Hefei University of Technology, Hefei 230009, P.R. China
[2]College of Material and Chemical Engineering, Anhui University of Architecture, Hefei 230022, P.R. China
[3]School of Resource and Environment Engineering, Hefei University of Technology, Hefei 230009, P.R. China

*Corresponding author: E-mail: jiaquan.wang@163.com; erapple@163.com

AJC-13337

This study integrated desalination with the biodegradation of nitrate in the wastewater and electricity generated in a three-chambers microbial desalination cell by utilizing the mutual benefits among the above functions. The microbial desalination cell produced the maximum voltage output of 635.8 mV, achieved NO_3^--N removal efficiency exceeded 64.48 % and no NO_2^--N accumulation. Three microbial desalination cells were all proved to be the power source to successfully desalinate salt water at low concentration of 5 or 20 mg/L. The salt removal reached 88.1 %. The results showed that the microbial desalination cell could readily generated the electricity, desalinized in the middle chamber and removed the nitrate in the cathode chamber, these will enable us to optimize the performance of the microbial desalination cell and develop a more efficient process for both desalination in the middle chamber and wastewater treatment in the anode and cathode chambers.

Key Words: Microbial desalination cell, Electricity production, Nitrate removal.

INTRODUCTION

Microbial desalination cell is an emerging technology that is derived from microbial fuel cell and consists of anode chamber, middle chamber and cathode chamber. In an microbial desalination cell process, organic matter as energy source of bacteria in wastewater is oxidized by electrochemically active bacteria on the anode; the released electrons flow from the anode to the cathode, where oxygen is typically reduced. Cations and anions in salt water held in the middle chamber migrate into the cathode and anode, respectively, because of the potential gradient created between the anode and cathode. This phenomenon leads to water desalination and simultaneously generating electricity without electrical energy input or high water pressure. Extended works based on the proof-of-concept microbial desalination cell with ferricyanide cathode have been successively reported[1]. Other studies included air cathode microbial desalination cell[2], continuously operated up flow microbial desalination cell[3], stacked microbial desalination cell for increasing desalination rate[4], series assembly of microbial desalination cell for partial or complete seawater desalination[5] and simultaneous water desalination and hydrogen production using microbial desalination cell[6].

Nitrate contamination of groundwater has become a major concern and a worldwide problem in the recent years[7]. Because elevated nitrate concentrations in drinking water can cause methemoglobinemia in infants and stomach cancer in adults. The removal of nitrate is essential for water contaminated with nitrate. Physical and chemical processes such as reverse osmosis, ion exchange, electrodialysis and chemical denitrification have been developed for nitrate removal from water[8]. Although these techniques are effective in removing nitrate from contaminated water, they are very expensive for pilot scale operation with a limited potential application[9]. Owing to these limitations in the removal of nitrate from water and/or wastewater, microbial fuel cell has been used in removal of nitrate[10]. Glucose is carbon source of solution in anode chamber and released electrons; nitrate solution in the cathode chamber accepted electrons and had been reduced cathode chamber. The process can simultaneously generating electricity and remove the nitrate in the solution.

Therefore, the objective of this study is to test the hypothesis that the complementary functions of energy production, desalination of low-concentration salt water and removal of nitrate during an microbial desalination cell process. In this paper, the process of microbial desalination cell by modifying a small scale laboratory reactor that was originally developed to function as an microbial desalination cell was demonstrate that glucose was used as carbon source of solution in the anode

†Presented to the 6th China-Korea International Conference on Multi-functional Materials and Application, 22-24 November 2012, Daejeon, Korea

chamber, nitrate solution was used as electron acceptor in the cathode chamber, salt water was placed in the middle chamber.

EXPERIMENTAL

Construction of microbial desalination cell: Based on a cubic-shaped microbial fuel cell, the microbial desalination cell was made of three cubic-shaped three chambers: anode chamber, cathode chamber and middle chamber, separated using AEM and CEM membranes (Fig. 1). An AEM (AMI-7001, Membrane International, Inc.) was inserted between the anode and middle chamber and a CEM (CMI-7000, Membrane International, Inc.) was placed between the middle and cathode chamber. Both AEM and CEM were first immersed in 2 M NaCl solution for 24 h, rinsed with deionized water and finally used in the reactor. Plastic rods were inserted into the structure of the anode and cathode chamber to prevent membrane deformation due to water pressure and reinforce the membranes. During desalination, the chloride ions moved into the anode chamber *via* the anion-exchange membrane and sodium ions migrated to the cathode side through the cation-exchange membrane. The inside volumes of the anode, middle and cathode chamber are 430 mL, 120 mL and 430 mL, respectively. The anode and cathode chambers were filled with cubic pieces of carbon felt with a size of approximately 48 cm^2 for bacterial growth. The two electrodes were linked to out resistors respectively through a copper wire and a data logger(ADC16; Pico Technologies limited, UK) was used to acqurie the microbial desalination cell's voltage.

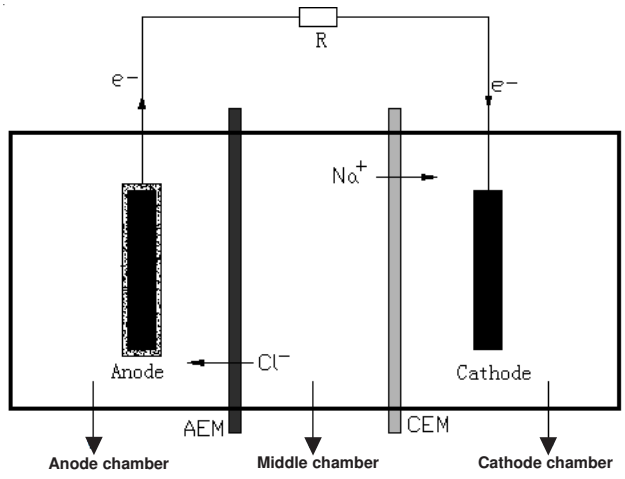

Fig. 1. Schematic diagram of three-chambers microbial desalination cell used in the study

Medium: The anode chamber of the microbial desalination cell was fed a solution of glucose (1000 mg/L) as an energy source in a nutrient solution (pH = 7) containing (per liter of deionized water): K_2HPO_4 6.571 g/L, KH_2PO_4 2.883 g/L, KCl 0.13 g/L, NH_4Cl 0.31 g/L, 12.5 mL of growth medium solution and 5 g of vitamin solution. The cathode chamber was fed a solution containing (per liter of deionized water): K_2HPO_4 6.571 g/L, KH_2PO_4 2.883 g/L and KNO_3 0.7218 g. The middle chamber was filled with 5 or 20 g/L NaCl solution.

Three Paralleled tests were designed in this study as Table-1 was shown.

TABLE-1
CONCENTRATIONS OF THE SOLUTION IN THE THREE-CHAMBERS OF THREE MICROBIAL DESALINATION CELLs USED

Reactor	Glucose (mg/L)	NaCl (g/L)	KNO_3 (mg/L)
MDC1	1000	5	30
MDC2	1000	20	30
MDC3	1000	20	50

Microbial desalination cell operation and experimental procedures: The anode and cathode chambers of microbial desalination cells were inoculated with microbial consortium previously enriched in a biocathode microbial fuel cell for a long time, the anode and cathode of which were originally inoculated with anaerobic sludge and aerobic sludge respectively sampled from a local municipal wastewater treatment plant. Nitrogen was been input after 15 min in order to remove the dissolved oxygen of the anode chamber, then the glucose was dissolved in the inorganic salt and was placed into the anode chamber and maintain anaerobic state. Used anolyte and catholyte were replaced with new media to start a new batch cycle when the reactor voltage dropped below 20 mV. Three microbial desalination cells were operated in parallel conditions at an external resistance of 1000 Ω.

Analyses and calculations: The cell voltage across the resistor was automatically recorded every 400s using a data acquisition system (PCI-1713,China). COD of each water sample was determined by rapid determination method of potassium dichromate[11]. A sample of each water sample was filtered (0.4 μm) and analyzed for NO_3^--N, NO_2^--N and NH_4^+-N which was determined by using ultraviolet spectrophotometry, *N*-(1-naphthyl)-ethylenediamine spectrophotometric method and Nessler's reagent colourimetric method. Electrical conductivity was determined by six parameters instrument (ULTRAMETER II™ 6P, USA). The migration rate of Cl^- was determined by silver nitrate titration method[12].

RESULTS AND DISCUSSION

Electricity generation: The comparison of the voltage generated in the three microbial desalination cells as was shown in Figs. 2-4. Data showed the three microbial desalination cells all could stably and continuously generate electricity and the curves of the voltage output are similar. During these processes, an instantaneous recovery of the voltage generation changed periodically and single peak appeared after anolyte was replaced each time. As shown in Fig. 2, three cycles of replacing anolyte lasted a total period of 550 h in MDC1 and obtained the maximum voltage of 237.1 mV in the first cycle. However, three cycles of replacing anolyte lasted a total period of 480 h in MDC2. 635.8 mV of the maximum voltage was observed in the first cycle as shown in Fig. 3. Equally four cycles of replacing the anode solution lasted a total period of 890 h in MDC3, the maximum voltage obtained was 683.6 mV in the first cycle.

During the process of traditional microbial fuel cell, voltage output should be stable before the source energy was used up, however voltage output immediately and continually

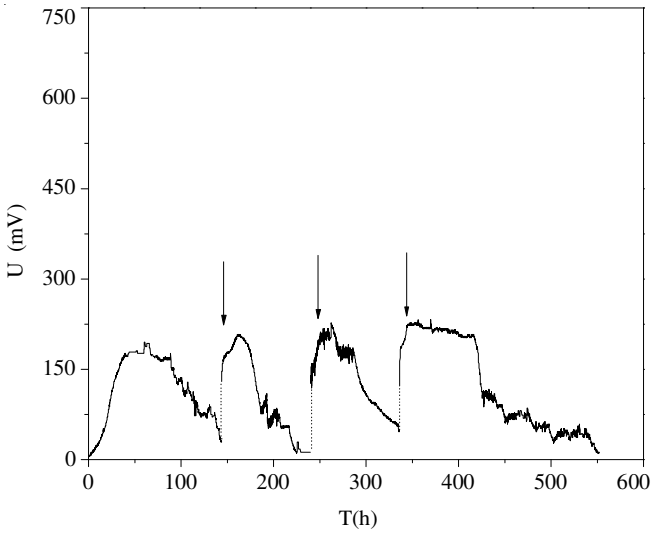

Fig. 2. Voltages generation in the MDC1 (arrows show anolyte replacement)

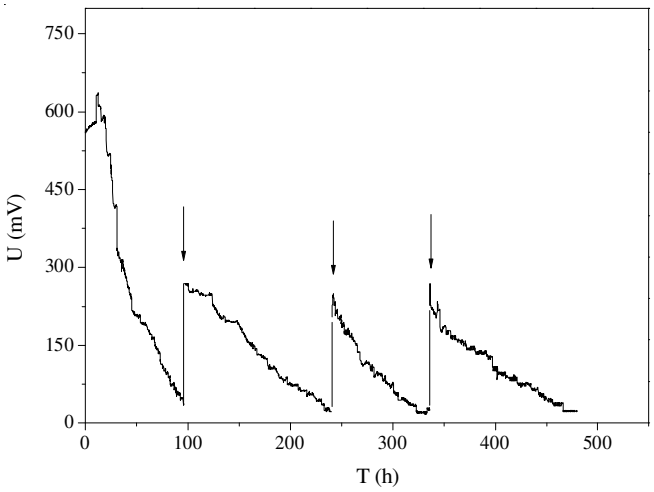

Fig. 3. Voltage generation in the MDC2 (arrows show anolyte replacement)

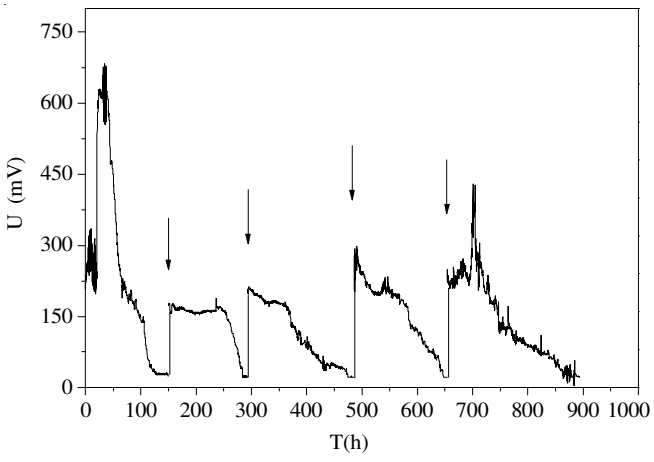

Fig. 4. Voltage generation in the MDC3 (arrows show anolyte replacement)

decreased after the maximal voltage output was achieved during the process of microbial desalination cells. The reason could be explained that ionic strength of NaCl solution in the middle chamber constantly reduced with the operation of microbial desalination cells, electric conductivity of the solution also continually decreased, namely the internal resistance of microbial desalination cell continually largened. MDC1 compared with MDC2, the alteration of voltage output was not obvious with the NaCl concentration increasing, the results were not in accord with the references[13]. MDC2 compared with MDC3, the alteration of voltage output was not conspicuous with the NO_3^--N concentration rising, maybe the NO_3^--N concentration itself was too low[14].

COD removal in the anode chamber: Glucose is an easily degradable representative of organics in the anode chamber of microbial fuel cell to support the growth of microorganisms. In order to indirectly investigate the effect of glucose on nitrate removal and electricity generated, the glucose COD removal in anode chambers were observed as shown in Fig. 5. Data showed the alteration trends of COD in anode chamber of the three microbial desalination cells are similar to voltage outputs'. An instantaneous recovery of COD changed periodically after anolyte was replaced each time. In the experiments, COD decreased from 1088 mg/L to 212 mg/L in MDC1, from 1008 mg/L to 188 mg/L in MDC2 and from 1084 mg/L to 251 mg/L in MDC3, namely COD removal efficiency all exceeded 80 %. These further made clear that glucose was nearly completely degraded, released electrons to nitrate in cathode chamber with external circuit and made them reduce.

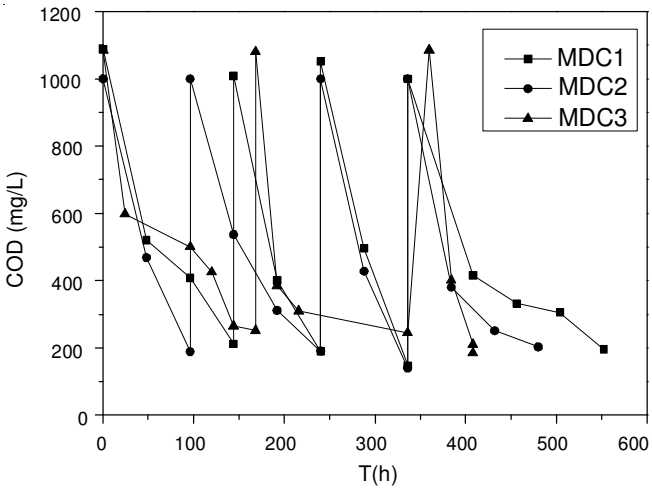

Fig. 5. COD removal in the anode chamber

Nitrate reduction in the cathode chamber: The NO_3^--N concentration changed with time as shown Fig. 6. It can be found that the NO_3^--N concentration decreased in the first cycle from 30.42 mg/L to 12.1 mg/L in MDC1, from 31.23 mg/L to 11.0 mg/L in MDC2 and from 50.97 mg/L to 23.70 mg/L in MDC3, NO_3^--N removal efficiency respectively exceeded 62.27, 64.48 and 53.50 %. Fig. 7 showed NO_2^--N, NH_4^+-N changed with time. From the Fig. 7, there are no NO_2^--N accumulated in the microbial desalination cells in every cycle, however, the NH_4^+-N concentration increased by 80.64, 11.67 and 21.50 mg/L respectively in the three microbial desalination cells after 504 h' operation. The results are different from the reference in the microbial fuel cell that the NH_4^+-N concentration increased firstly then decreased[10].

All the experimental results indicated that there is a denitrification of NO_3^--N in the cathode chamber. The NO_3^--N in cathode chamber obtained the electrons that glucose was

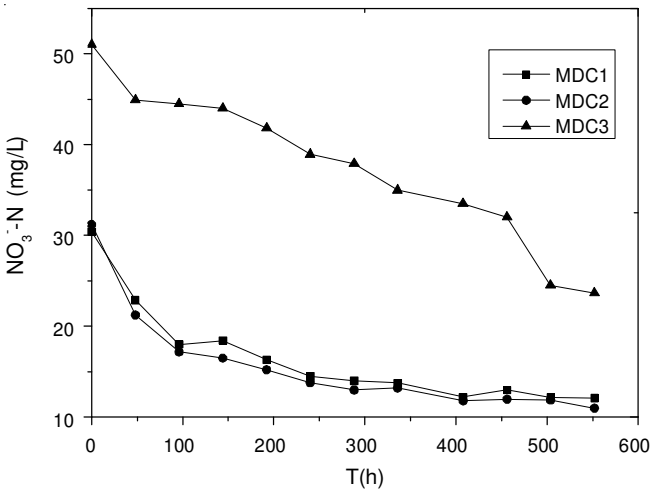

Fig. 6. Removal of NO_3^--N

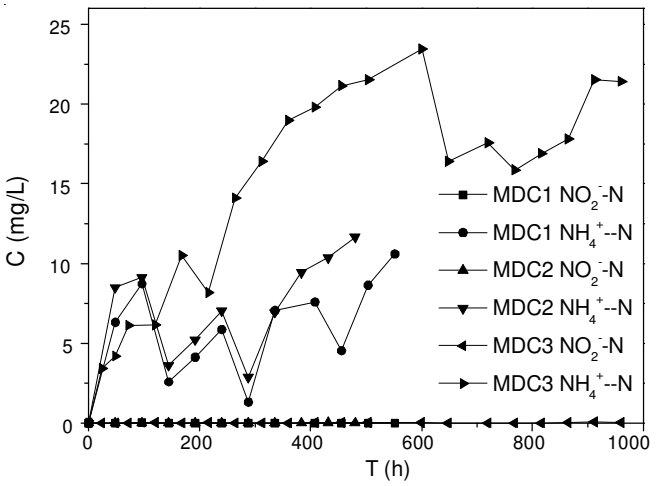

Fig. 7. Removal of NO_2^--N, NH_4^+-N

degraded in anode chamber by microorganisms to release electrons that were transmitted by external circuits to reduce. The degradation of NH_4^+-N generally achieved by interaction of nitrification-denitrification and ammonia evaporation[15]. In the tests, phosphate buffer solution was added to both anolyte and catholyte, pH of the solution has no obvious changes, the volume of NH_4^+-N decreased a little by ammonia evaporation. At the same time NH_4Cl solution added in the anode solution. As we all known, it is easy that NH_4^+ migrate from the anode chamber to cathode chamber even there is an anion exchange membrane (AEM). So it caused the NH_4^+-N accumulation. Surplus of NO_3^--N, generation of NO_2^--N and NH_4^+-N together are less than the original volume of NO_3^--N, maybe some volume of nitrate turn into nitrogen in the experiments, because bubble ascending was observed sometimes.

Desalination performance in the middle chamber: To validate the applicability of the microbial desalination cell in salt water, desalination tests with 5 and 20 g/L NaCl wastewater were further conducted. The conductivity and the Cl^- concentration in the middle chamber of MDC1, MDC2 and MDC3 are summarized in Figs. 8 and 9. The water in the middle chamber was efficiently desalinated at both initial concentrations. Conductivities of the middle chamber obviously decreased from 9.25 to 5.02 ms/cm in MDC1, from 30.25 to 4.89 ms/cm in MDC2, from 28.33 to 5.41 ms/cm in MDC3 respectively. Based on the change in solution conductivity, the salt removals at each microbial desalination cell were about 66.1, 88.1 and 80.1 % respectively. Desalination efficiency is lager in MDC1 than in MDC2 and MDC3 because of the higher NaCl concentration, it was explained that the Cl^- concentration reducing resulted in internal resistance of microbial desalination cell rising, it was not beneficial for long time and effective operation.

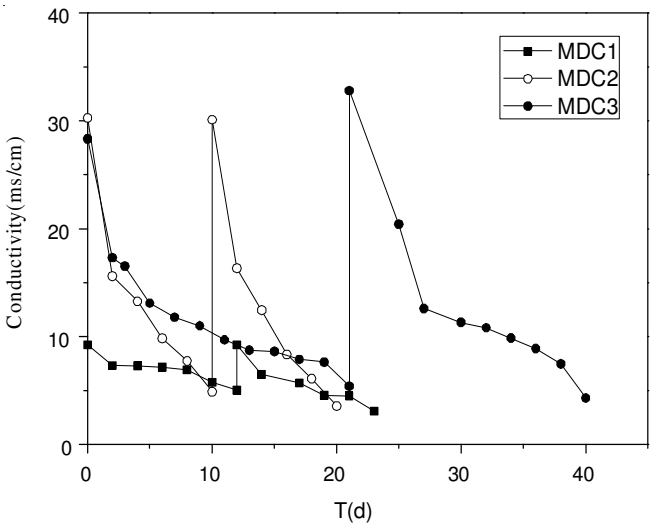

Fig. 8. Conductivity in the middle chamber

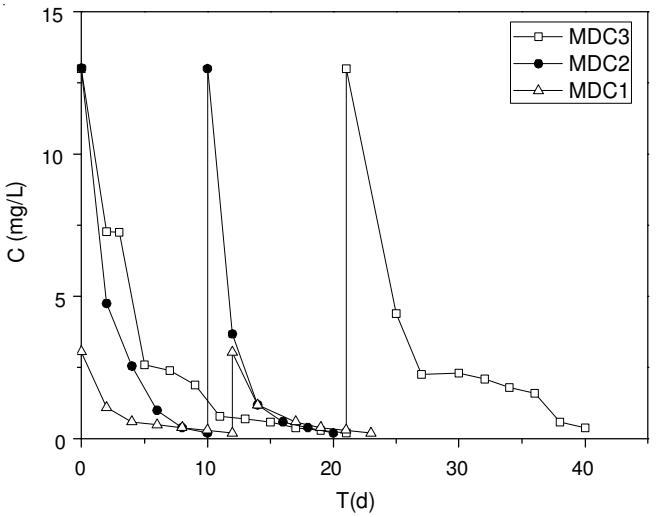

Fig. 9. Cl^- in the middle chamber

The Cl^- moved from middle chamber to anode chamber continually, the migration rate is 0.136 mg/L/d and reduced from 3.05 mg/L to 0.2 mg/L in MDC1, the migration rate is 0.610 mg/L/d and reduced from 13.02 mg/L to 0.2 mg/L in MDC2, the migration rate is 0610 mg/L/d and reduced from 13.00 mg/L to 0.2 mg/L in MDC3. During the experiments, when the Cl^- concentration fell to 0.2 mg/L, NaCl solution was replaced to the middle chamber to maintain the charge balance of microbial desalination cell due to the long operation. The rate of MDC1 was obviously low than of MDC2 and MDC3, because of the initial Cl^- concentration difference. MDC2 was close to MDC3, its results were very similar to the voltage output, maybe it was explained by low NO_3^--N concentration.

Conclusion

In this study, three paralleled microbial desalination cells were designed and investigated that all microbial desalination cells can simultaneously and successfully degraded the organics in the anode chamber, desalinized in the middle chamber, removed the nitrate in cathode chamber and generated the electricity. The microbial desalination cell produced the maximum voltage output of 635.8 mV and achieved NO_3^--N removal efficiency exceeded 64.48 %. Three microbial desalination cells were proved to be the power source to successfully desalinate salt water at low concentration of 5 or 20 mg/L. The desalination rate was 0.610 mg/L/d. The results and experiences obtained from this study will enable us to optimize the performance of the microbial desalination cell and develop a more efficient process for both desalination in the middle chamber and wastewater treatment in anode and cathode chambers.

ACKNOWLEDGEMENTS

This research was supported the Opening up Projects of Environmental Science and Engineering Laboratory of Jiangsu Province (No. 060710E2).

REFERENCES

1. Xiao-Xin CAO, Xia Huang, Peng Liang, *et al*., *Environ. Sci. Technol.*, **43**, 7148 (2009).
2. M. Mehanna, T. Saito, J. Yan, M. Hickner, X. Cao, X. Huang, B.E. Logan *et al*., *Energy Environ. Sci.,* **3**, 1114 (2010).
3. K.S. Jacobson, M.D. David and Z. He, *Environ. Sci. Technol*., **45**, 4652 (2011).
4. X. Chen, X. Xia, P. Liang *et al*., *Environ. Sci. Technol*., **45**, 2465 (2011).
5. Y. Kim and B.E. Logan, *Environ. Sci. Technol*., **45**, 5840 (2011).
6. H. Luo, P.E. Jenkins and Z. Ren, *Environ. Sci. Technol*., **45**, 340 (2011).
7. Lihui Zhang, Guomin Cao, Mei Sheng, *et al*., *Water Purif. Technol.*, **29**, 4 (2010).
8. J.J. Bi, C.S. Peng and H.Z. Xu, *Ground Water*, **32**, 97 (2010).
9. Zang-Fang Jin, Wenteng Liu, Zhi-yun Pan, *et al*., *Technol. Watertreatment*, **32**, 34 (2006).
10. Wang Jiaquan, Xia Xuelan, Chen Shaohua, *et al*., *Acta Scientiae Circumstantiae*, **31**, 254 (2011).
11. Haijuan Wei, Jiguo Huang, Guoyuan Jia, *et al*., *Environ .Sci. Technol.*, **29**, 45 (2006).
12. Shaozhi Kang, *Jilin Hydraulic*, **314**, 8 (2010).
13. Youwei Cui, Yongzhen Peng and Jing Li, *Environ. Sci.*, **2**, 488 (2009).
14. T. Yi and W.F. Harper, *Water Environ. Res.*, **81**, 2320 (2009).
15. J.R. Kim, Y. Zuo, J.M. Regan, *et al*., *Biotechnol. Bioeng.*, **99**, 1120 (2008).