Water Science & Technology—WST | 62.7 | 2010

Effect of chloride concentration on nitrogen removal from landfill leachate in sequencing batch reactor after MAP pretreatment

M. Chen, S. He, Q. Yi and M. Yang

ABSTRACT

Leachate generated from landfill is becoming a great environmental challenge to China as it contains high concentration of COD, ammonium and some other substances. Nitrogen removal through the conventional nitrification-denitrification process is hampered by the low C/N ratio especially for the old age landfill sites and the high energy consumption for aeration. In this study, the combination of magnesium ammonium phosphate (MAP) precipitation and Sequencing batch reactor (SBR) was suggested as a new process for the treatment of high strength ammonium, and the effect of high concentration of Cl^- after MAP precipitation because of the use of $MgCl_2$ was investigated on SBR performance. The practical upper limit of Cl^- for nitrification was found to be 12,000 mg/L, above which resulted in significant accumulation of ammonium in SBR system. It is suggested that an ammonium removal of 70% was suitable for the MAP treatment to achieve a balance between increasing the C/N ratio and avoiding detrimental effect from high concentration of Cl^- in the succeeding SBR system. DGGE analysis indicated that high diversity of Ammonium oxidizing bacteria (AOB) could be maintained at a Cl^- concentration of 12,000 mg/L.

Key words | chloride effect, landfill leachate, MAP, nitrogen removal, SBR

M. Chen
S. He
Q. Yi
M. Yang (corresponding author)
State Key Laboratory of Environmental Aquatic Chemistry,
Research Center for Eco-Environmental Sciences,
Chinese Academy of Sciences,
P.O. Box 2871,
Beijing 100085,
China
E-mail: *mxchen@rcees.ac.cn*;
hslongrcees@163.com;
shfhf7e_0@163.com;
Yangmin@rcees.ac.cn

INTRODUCTION

Sanitary landfill has been widely used for municipal solid waste disposal in China due to its low cost and effectiveness. In Beijing, there has been constructed seventeen landfill sites in the suburbs, and these sites produce a large amount of leachate (about 8.0×10^5 to $9.0 \times 10^5\,m^3$ every year) (He *et al.* 2007). The removal of ammonium of high concentration (1,000–4,000 mg/L) from landfill leachate has therefore becoming a challenging problem in China. Sequencing batch reactor (SBR) method is a promising technology for leachate treatment (Ding *et al.* 2001; Yalmaz & Ozturk 2001; Neczaj *et al.* 2005; Laitinen *et al.* 2006), because proper control of the aerobic and anoxic cycles of a system is possible with a real-time control process using oxidation-reduction potential (ORP) and/or pH as parameters (Lo *et al.* 1994; Fuerhacker *et al.* 2000; Kim *et al.* 2004). However, insufficient electron donors hampered high efficient nitrogen removal from landfill leachate due to the low C/N ratios, especially for those landfill sites with an old age (Im *et al.* 2001). At the same time, high energy input and inhibition by free ammonia are the two other important factors for biological treatment of landfill leachate containing high concentrations of ammonium (Chung *et al.* 2003).

In recent years, magnesium ammonium phosphate (MAP) precipitation has been considered to be an effective method for landfill leachate treatment (Li & Zhao 2003; He *et al.* 2007). MAP, which is also called struvite, has a low solubility. When the combined concentration of Mg^{2+}, NH_4^+ and PO_4^{3-} exceed the solubility limit of MAP, precipitation of MAP quickly occurs, which can be easily

doi: 10.2166/wst.2010.443

separated from water phase. Two types of magnesium, $Mg(OH)_2$ and $MgCl_2$, are generally used for MAP precipitation treatment. Compared to $Mg(OH)_2$, $MgCl_2$ is more widely used because it dissociates faster than $Mg(OH)_2$ and results in shorter reaction time (Li & Zhao 2003). If a part of ammonium could be removed from landfill leachate through MAP precipitation, all of the problems associated with the biological treatment of high concentration ammonium could be solved.

However, significant increase of Cl^- concentration is expected when $MgCl_2$ is used as the magnesium source for MAP precipitation. Since high concentration of Cl^- might inhibit nitritation process (Mosquera-Corral *et al.* 2005), it is necessary to evaluate the effects of increased Cl^- on SBR performance. In this study the combination of MAP precipitation with an SBR treatment was used for nitrogen removal. The aim of the research was to find the critical Cl^- concentration over which microbiological activities will be inhibited. The effect of Cl^- concentration on real time control parameters was also examined for optimizing SBR control.

METHODS

Wastewater and seed sludge

Landfill leachate used in this study was obtained from Liulitun Sanitary Landfill Site located in the northern suburb of Beijing after Up-flow Anaerobic Sludge Bed (UASB) treatment. The landfill site has been operated for 10 years. Wastewater was stored at 4°C before use. The characteristics of wastewater are summarized in Table 1. NaCl was added to wastewater for the investigation of the effect Cl^- concentration on nitrogen removal in SBR. The sludge was taken from aeration tank in the same landfill site. The average MLSS concentration of sludge was kept approximately at 7,000 mg/L. The average SRT was 32 d.

MAP pretreatment process

Mg^{2+} and PO_4^{3-} were added at a weight ratio of Mg^{2+}:PO_4^{3-}:NH_4^+ = 1.1:1.1:1.0 under the conditions of mixing time of 2 h and pH of 9.0. The pH of the supernatant was adjusted to pH 7.5 after the solid was removed for further treatment.

Sequencing batch reactor and operational strategies

The SBR was a cylindrical tank with an effective volume of 10 L. The system was operated with a fixed-time control as: influent feeding (10 min), anoxic/anaerobic phase (2 h), aerobic phase (3 h), sludge settling (30 min), and effluent discharge (10 min). The ORP, pH and DO probes were inserted into the reactor. ORP, pH and DO profiles were recorded during anoxic/anaerobic and aerobic phases using HACH Digital Differential pH/ORP Sensors and LDO™ Dissolved Oxygen Sensor, respectively.

Analysis methods

Parameters routinely assayed included COD, TOC, BOD_5, NH_4^+-N, NO_3^--N, NO_2^--N, PO_4^{3-}-P, mixed liquor suspended solids (MLSS), mixed liquor volatile suspended solids (MLVSS), total suspended solids (TSS). Samples were withdrawn from the reactor at the end of each cycle for analysis. Track analysis that covered an entire operation cycle was performed for NH_4^+-N, NO_3-N and NO_2^--N at different Cl^- concentrations. Mixed-liquor samples were taken during track analysis. NO_3^--N, NO_2^--N, PO_4^{3-}-P were analyzed with an ion chromatography (Metrohm 861, Metrohm, Switzerland). TOC was analyzed with a total organic carbon analyzer (Phoenix 8000, Terkmar Dohrmann, USA). Other analyses were performed in according with *Standard Methods* (NEPA 2002).

DNA extraction and PCR-DGGE analysis

DNA was extracted by TIANamp Bacteria DNA kit (G5606, Tian Gen Biotech (Beijing) Co. LTD.) from

Table 1 | The average composition of landfill leachate after anaerobic treatment

Alk. $CaCO_3$ (mg l^{-1})	COD_{Cr} (mg l^{-1})	BOD_5 (mg l^{-1})	NH_4^+-N (mg l^{-1})	Cl^- (mg l^{-1})	TP (mg l^{-1})	SS (mg l^{-1})	pH
11,120	12,000	4,250	2,800	2,000	13.8	3,200	7.5–8.1

500 mg of activated sludge in the reactor during experiment period every week. PCR-DGGE was carried out using the method of Wang *et al.* (2007) for total bacterial population analysis and using the method of Liu *et al.*(2007) for analysis of ammonia-oxidizing bacteria (AOB).

RESULTS AND DISCUSSION

Suitable C/N ratio for biological nitrogen removal in SBR

Nitrogen removals with and without C/N adjustment are compared in Figure 1. As shown in Figure 1a, nitrogen removal was incomplete without C/N adjustment. However, over 98% nitrogen removal was obtained when the C/N was adjusted approximately to 7.0 by adding methanol (Figure 1b). As shown in Figure 1b, some important points corresponding to the beginning or end of some specific reactions could be clearly identified. Point A was the feeding point, and the anoxic phase began after 10 min. Point B is known as the nitrate knee in ORP curve, which occurs when complete removal of nitrate was achieved. Point C signifies the beginning of the oxic phase. The initial rise on the pH curve (corresponding to the period between point C to Point D) was caused by carbon dioxide stripping from the system and the rapid consumption of VFA that produced during anoxic phase (Kim *et al.* 2004). Under oxic condition, NH_4-N decreased with time. Nitrate concentration increased with time as ammonia was being converted through nitrification. The decrease of pH was caused by the removal of ammonia from the system. Point D represented the end of nitrification and it is known as the ammonia valley. The complete removal of ammonia indicates the end of alkalinity consumption.

MAP pretreatment

Figure 2 shows the changes of C/N ratio and Cl^- concentration with $MgCl_2$ dose (the PO_4^{3-} dose was added at a fixed ratio to $MgCl_2$) in MAP pretreatment. Under an $MgCl_2$ dose of 13,000 mg/L, the NH_4^+-N removal, C/N ratio and Cl^- concentration were 70%, 6.5 and 12,000 mg/L, respectively. When the $MgCl_2$ dose was increased to 18,500 mg/L, the NH_4^+-N removal, C/N ratio and Cl^- concentration increased to 98%, 12 and 16,000 mg/L, respectively. As shown in Figure 1b, a C/N ratio of about 7 was sufficient for biological nitrogen removal. So an $MgCl_2$ dose of 13,000 mg/L might be suitable for satisfying the C/N ratio requirement and preventing the inhibition by high concentration of Cl^-.

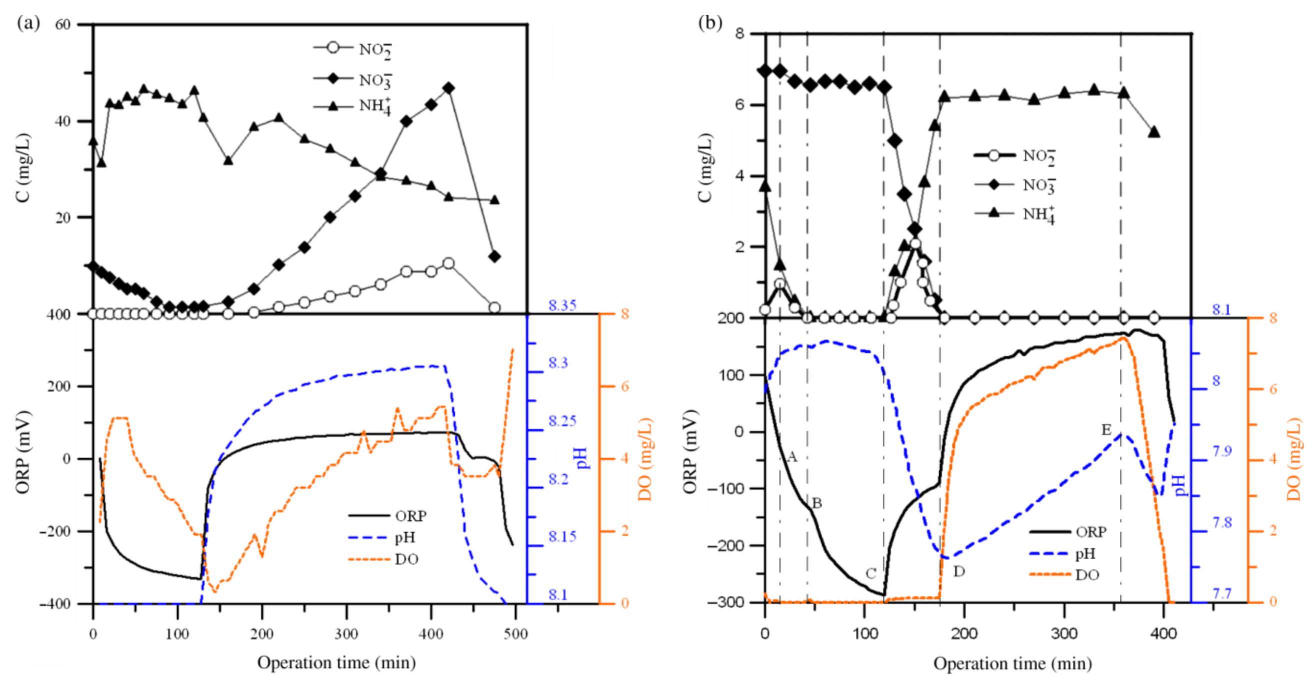

Figure 1 | ORP, pH and DO profiles in an SBR cycle without C/N adjustment (a) and with C/N adjustment using methanol (b).

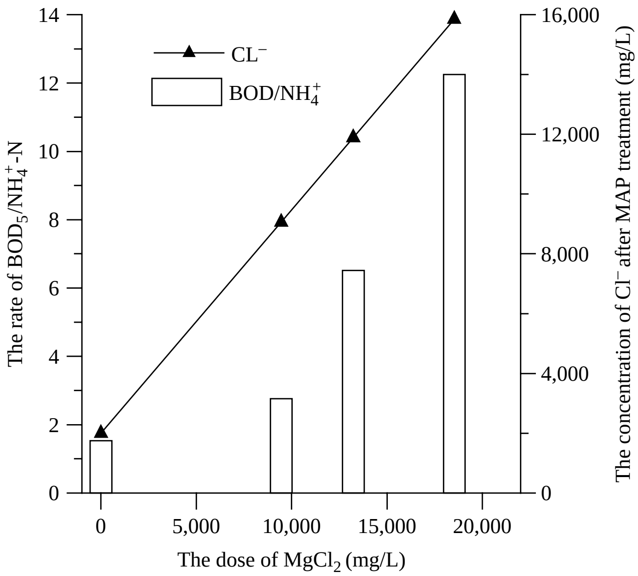

Figure 2 | Changes of C/N ratio and Cl⁻ concentration with $MgCl_2$ doses.

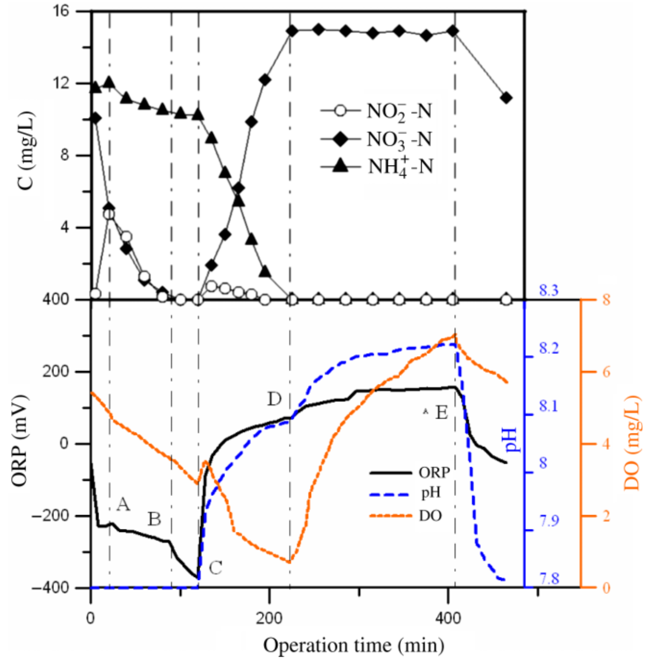

Figure 4 | ORP, pH and DO profiles in an SBR cycle after MAP pretreatment (Cl⁻, 12,000 mg/L).

To identify the effect of Cl⁻ concentration on NH_4^+-N removal in the SBR, the UASB effluent of leachate adjusted to a C/N ratio of 7.0 by adding methanol was used as raw wastewater, and NaCl was added to adjust the Cl⁻ concentration as shown Figure 3. When the Cl⁻ concentration was reached to 14,500 mg/L within 2 days, significant accumulation of NH_4^+-N was observed. It is clear that the biological system could not bear a Cl⁻ concentration as high as 14,500 mg/L.

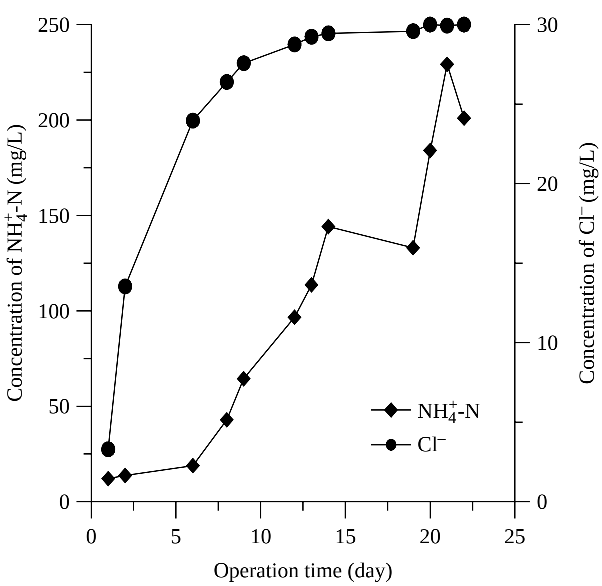

Figure 3 | The effects of increasing Cl⁻ on nitrification.

Figure 4 shows the track analysis in a cycle of SBR using MAP effluent as the influent with a C/N ratio of about 7.0 and Cl⁻ concentration of 12,000 mg/L. It is clear that complete nitrification- denitrification cycle was achieved successfully under the above conditions. Control points of pH and ORP corresponding respectively to different reaction status occurred clearly, and the ammonium removal rate was over 90%.

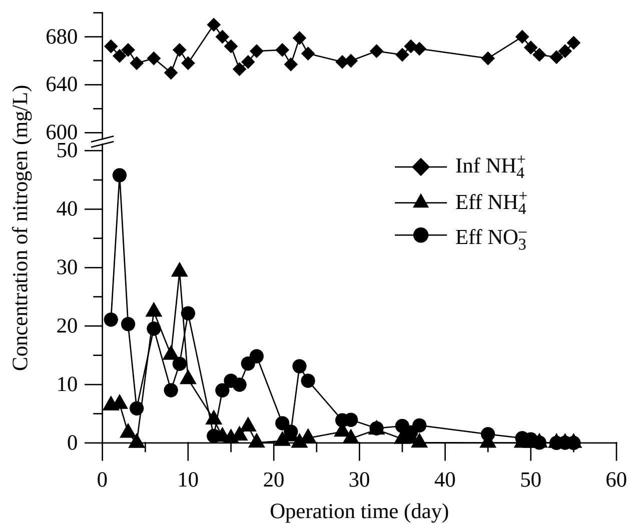

Figure 5 | SBR performance after MAP pretreatment during two months.

Table 2 | Average water quality of SBR effluent

TOC ($mg\,l^{-1}$)	COD_{Cr} ($mg\,l^{-1}$)	NH_4^+-N ($mg\,l^{-1}$)	NO_3^--N ($mg\,l^{-1}$)	TN ($mg\,l^{-1}$)	Cl^- ($mg\,l^{-1}$)
172 ± 21	580 ± 36	<0.01	12.9 ± 1.7	13.6 ± 2.2	12,000

SBR treatment after MAP pretreatment

Based on the balance between the requirement for a proper C/N ratio and the requirement for preventing the negative effects of Cl^- on microbiological activity, 70% ammonia removal rate through MAP precipitation was suitable. The SBR was operated for 2 months after MAP pretreatment, and the performance is shown in Figure 5 and Table 2. The ammonium concentration in effluent was below 5 mg/L from day 15, and the nitrate concentration was below 5 mg/L from day 28, respectively. During the stable operation period, above 98% of nitrogen removal rate can be kept.

PCR-DGGE analysis

Changes of microbial community structures during the 2-months operation are illustrated in Figure 6a for AOB and Figure 6b for total bacteria, respectively. During the operations of the SBR which was fed with the MAP pretreated leachate (Cl^- concentration was 12,000 mg/L),

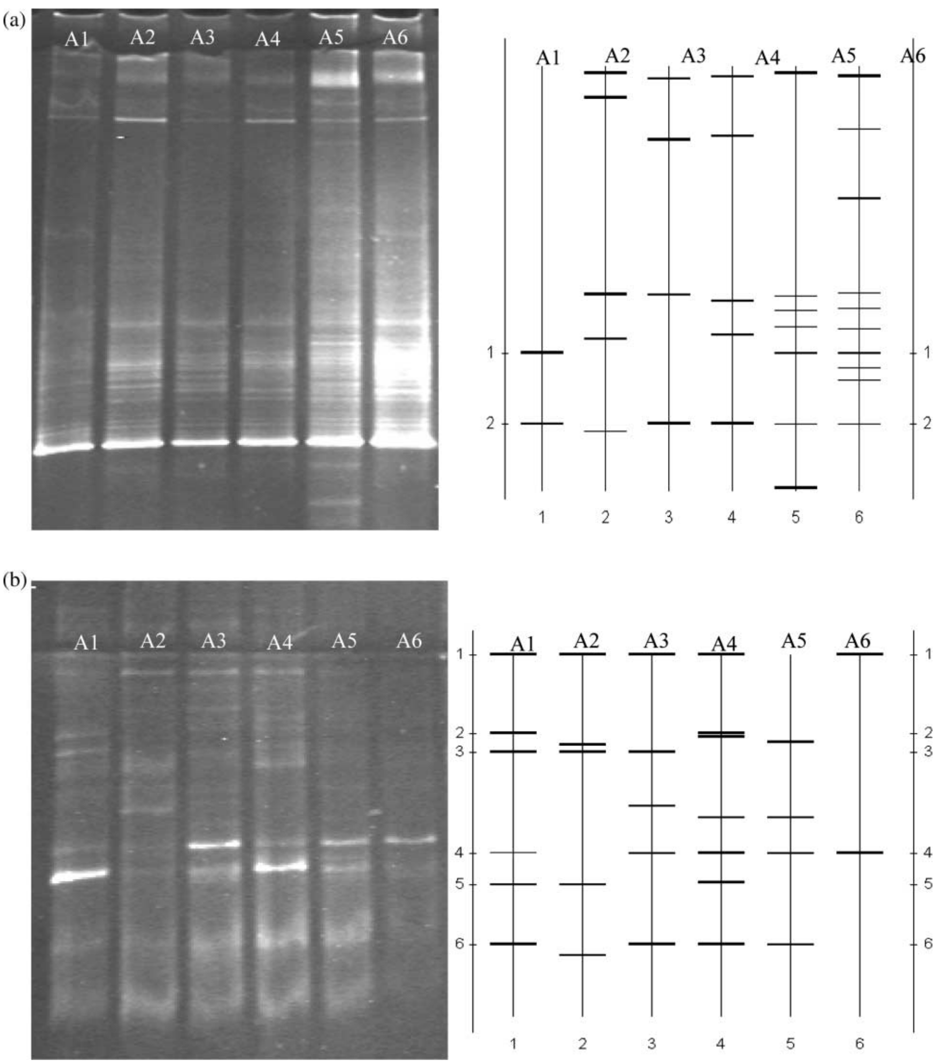

Figure 6 | DGGE profiles of PCR-amplified 16S rRNA gene segments from DNA extracted from sludge samples. (a) for AOB communities (b) for total bacteria communities. A1–A6 were sampled from SBR (Cl^- concentration was 12,000 mg/L), weekly. The left side shows the DGGE patterns, and the right side gives the analysis results of lane comparison from the DGGE patterns using Quantity One 4.3.0 software.

dominant groups of bacteria community have changed. Increase of band number was observed for AOB from the DGGE gel (Figure 6a), with the maximum bands observed in sample A6 (week 6), indicating that diversity of AOB has increased with the extending of operation. So it is possible that Cl^- concentration of 12,000 mg/L will not inhibit the growth of AOBs. As for total bacteria, the band number was relatively stable except for A6 (Figure 6b), indicating that the bacterial diversity did not change much during the operation period. Further efforts on identification of dominating AOBs and total bacteria are continued.

CONCLUSIONS

In this study, the combination of MAP precipitation with an SBR treatment was used for nitrogen removal for old age landfill leachate. MAP process increased the C/N ratio by decreasing ammonium concentration in raw wastewater. High concentration of Cl^- after MAP pretreatment would have a detrimental effect on the microbiological activity in the succeeding SBR system. The practical upper limit of Cl^- concentration for SBR was 12,000 mg/L in this case. Based on the balance between the requirement for a proper C/N ratio and the requirement for preventing the negative effects of Cl^- on microbiological activity, 70% ammonia removal rate through MAP pretreatment was suitable. During the long term operation of the SBR which was fed with the MAP pretreated leachate (Cl^- concentration was 12,000 mg/L), high diversity of AOB was achieved in the SBR together with a sound nitrogen removal performance.

ACKNOWLEDGEMENTS

The authors appreciate Dr. Li Dong, Mr. Yu Tao, Mr. Gu Xin and Mr. Qi Rong for providing DNA extract and PCR-DGGE analysis methods and advice. The authors appreciate the financial support of this work provided by the Chinese National 863 Project (2007AA06Z344) and the National Natural Science Foundation of China (20077085).

REFERENCES

Chung, J., Bae, W., Lee, Y. W., Ko, G. B., Lee, S. U. & Park, S. J. 2003 Investigation of the free ammonia concentration upon leachate treatment by shortcut biological nitrogen removal process. IWA International Specially Symposium on strong Nitrogenous and Agro-Wastewater, June 11–13, 2003, Seoul, Korea, pp. 93–104.

Ding, A., Zhang, Z., Fu, J. & Cheng, L. 2001 Biological control of leachate from municipal landfills. *Chemosphere* **44**, 1–8.

Fuerhacker, M., Bauer, H., Ellinger, R., Sree, U., Schmid, H., Zibuschka, F. & Puxbaum, H. 2000 Approach for a novel control strategy for simultaneous nitrification/denitrification in activated sludge reactors. *Water Res.* **34**(9), 2499–2506.

He, S., Zhang, Y., Yang, M., Su, W. & Harada, H. 2007 Repeated use of MAP decomposition residues for removal of high ammonium concentration from landfill leachate. *Chemosphere* **66**, 2233–2238.

Im, J., Woo, H., Choi, M., Han, K. & Kim, C. 2001 Simultaneous organic and nitrogen removal from municipal landfill leachate using an anaerobic-aerobic system. *Water Res.* **35**(10), 2403–2410.

Kim, J., Chen, M., Kishida, N. & Sudo, R. 2004 Integrated real-time control strategy of nitrogen removal for swine wastewater treatment using sequencing batch reactors. *Water Res.* **38** (14–15), 3340–3348.

Laitinen, N., Luonsi, A. & Vilen, J. 2006 Landfill leachate treatment with sequencing batch reactor and membrane bioreactor. *Desalination* **191**, 86–91.

Li, X. Z. & Zhao, Q. L. 2003 Recovery of ammonium-nitrogen from landfill leachate as a multi-nutrient fertilizer. *Ecol. Eng.* **20**, 171–181.

Liu, X. C., Yang, M., Zhang, Y., Yang, X. P. & Gan, Y. P. 2007 Microbial community comparison of different biological processes for treating the same sewage. *World J. Microbial. Biotechnol.* **23**, 135–143.

Lo, C. K., Yu, C. W., Tam, N. F. Y. & Trayor, S. 1994 Enhanced nutrient removal by oxidation-reduction potential (ORP) controlled aeration in a laboratory scale extended aeration treatment system. *Water Res.* **28**(10), 2087–2094.

Mosquera-Corral, A., Campos, F. & Mendez, R. 2005 Partial nitrification in a SHARON reactor in the presence of salt and organic carbon compounds. *Process Biochem.* **40**, 3109–3118.

Neczaj, E., Okoniewska, E. & Kacprzak, M. 2005 Treatment of landfill leachate by sequencing batch reactor. *Desalination* **185**, 357–362.

Wang, Z. Y., Li, J., Hesham, A., He, S. W., Zhang, Y., Wang, Z. J. & Yang, M. 2007 Co-variations of bacterial composition and catabolic genes related to PAH degradation in a produced water treatment system consisting of successive anoxic and aerobic units. *Sci. Total Environ.* **373**(1), 356–362.

Water and wastewater monitoring and analysis method 2002 NEPA 4th edition. Environmental Science Press.

Yalmaz, G. & Ozturk, I. 2001 Biological ammonia removal from anaerobically pre-treated landfill leachate in sequencing batch reactors (SBR). *Water Sci. Technol.* **43**(3), 307–314.