

Nitrogen removal via nitrite from municipal landfill leachate

WU Lina, PENG Chengyao, ZHANG Shujun, PENG Yongzhen*

Key Laboratory of Beijing for Water Quality Science and Water Environment Recovery Engineering, Beijing University of Technology, Beijing 100124, China. E-mail: cai@emails.bjut.edu.cn

Received 18 November 2008; revised 29 June 2009; accepted 14 July 2009

Abstract

A system consisting of a two-stage up-flow anaerobic sludge blanket (UASB), an anoxic/aerobic (A/O) reactor and a sequencing batch reactor (SBR), was used to treat landfill leachate. During operation, denitrification and methanogenesis took place simultaneously in the first stage UASB, and the effluent chemical oxygen demand (COD) was further removed in the second stage UASB. Then the denitrification of nitrite and nitrate in the returned sludge by using the residual COD was accomplished in the A/O reactor, and ammonia was removed via nitrite in it. Last but not least, the residual ammonia was removed in SBR as well as nitrite and nitrate which were produced by nitrification. The results over 120 d (60 d for phase I and 60 d for phase II) were as follows: when the total nitrogen (TN) concentration of influent leachate was about 2500 mg/L and the ammonia nitrogen concentration was about 2000 mg/L, the short-cut nitrification with 85%–90% nitrite accumulation was achieved stably in the A/O reactor. The TN and ammonia nitrogen removal efficiencies of the system were 98% and 97%, respectively. The residual ammonia, nitrite and nitrate produced during nitrification in the A/O reactor could be washed out almost completely in SBR. The TN and ammonia nitrogen concentrations of final effluent were about 39 mg/L and 12 mg/L, respectively.

Key words: short-cut nitrification; up-flow anaerobic sludge blanket; anoxic/aerobic reactor; sequencing batch reactor; landfill leachate

DOI: 10.1016/S1001-0742(08)62443-2

Introduction

Sanitary landfill method is commonly used to treat municipal refuse in China. Compared to other means, sanitary landfill is the cheapest. However, landfill leachate, a strongly polluted wastewater, has become the subject of recent interest (Palma *et al.*, 2002). Leachate is considered the aqueous effluent generated as a consequence of rainwater percolation through wastes, the inherent water content of wastes themselves and biochemical processes in cells of waste (Renou *et al.*, 2008). The pollutant composition of landfill leachate is very complicated, and its characteristics vary a lot depending on the environmental conditions. The concentrations of organic material and ammonia nitrogen are high in fresh leachate, while matured leachate contains relatively lower concentration of organic matter but higher concentration of ammonia nitrogen (Zhang *et al.*, 2007). High concentration ammonia nitrogen is considered as the main reason for low efficiency in biological treatment of landfill leachate (Uygur and Kargi, 2004). Especially, with the release of new national standard for pollution control on the landfill site of municipal solid waste, the removal of total nitrogen (TN) and ammonia nitrogen from leachate becomes critical. In recent years, some studies have reported that leachate could be treated by biological methods and physicochemical methods. For instance, a

physicochemical treatment system using a up-flow anaerobic sludge blanket (UASB) and ultrafiltration (UF) + reverse osmosis (RO) was recommended as an effective process for the removal of organic compounds and nitrogen from leachate (Ozturk *et al.*, 2003). Although most chemical oxygen demand (COD) and ammonia nitrogen can be removed from leachate, the physicochemical treatments have many drawbacks such as high cost in the post treatment process and operational process, high energy consumption, low removal of TN. Due to operation costs and other reasons, biological technologies are major methods to treat landfill leachate, such as processes of UASB, anaerobic ammonium oxidation (Anammox), membrane biological reactor (MBR), sequencing batch reactor (SBR), anaerobic-aerobic combined (Calli *et al.*, 2005; Liang and Liu, 2008; Vassel *et al.*, 2004; Kim *et al.*, 2006; Im *et al.*, 2001). The anaerobic-aerobic combined process is considered the most economy and effective method to degrade ammonia for landfill leachate treatment by most of the researchers. In this study, a system consisting of a two-stage UASB, an anoxic/aerobic (A/O) reactor and a SBR was introduced to treat landfill leachate. The system was fully depended on biological treatment without any physicochemical process.

Biological denitrification is the fundamental solution to nitrogen-contamination of landfill leachate, and stable shortcut biological nitrogen removal is one of the most

* Corresponding author. E-mail: pyz@bjut.edu.cn

efficient methods for biological denitrification. The concept of direct nitrite reduction to nitrogen gas is utilized by the shortcut biological nitrogen removal (Peng *et al.*, 2008). Compared with traditional processes for biological nitrogen removal, shortcut biological nitrogen removal can reduce the consumption of oxygen by 25% for nitrification and carbon source by 40% for denitrification (Hellinga *et al.*, 1998; Christian *et al.*, 2002). Wang *et al.* (2007) reported that a stable short-cut nitrification was achieved with an A/O system to treat domestic wastewater. Yang *et al.* (2007) used a sequencing batch reactor to treat municipal wastewater, in which stable short-cut nitrification was achieved within 180 d and the average nitrite accumulation rate was above 95%. However, studies were seldom reported on processes that achieved complete nitrogen removal and stable short-cut nitrification simultaneously with the ammonia and total nitrogen removal efficiency above 90%, especially when the ammonia nitrogen concentration was above 1800 mg/L. Moreover, real wastewater is rarely used in current studies on stable short-cut nitrification. In this study, a shortcut biological nitrogen removal was achieved stably in treating real municipal landfill leachate with high strength ammonia nitrogen. The factors affecting the short-cut nitrification were also investigated. Therefore this study had good value of reference and application in engineering.

1 Materials and methods

1.1 Experimental lab-scale reactors and experimental procedure

In the experiment, a two-stage UASB+A/O+SBR system was used to treat landfill leachate. Raw leachate, as well as a part of the effluent from the clarifying tank, was pumped into the first stage UASB (UASB1). Nitrite and nitrate in recycled effluent was denitrified by organic compounds of raw leachate as carbon source in UASB1. Simultaneously the returned sludge from the clarifying tank was pumped into anoxic zone of A/O reactor, where denitrification was occurred. Organic matters were firstly used as carbon source by denitrification in UASB1. Most of the effluent COD in UASB1 was eliminated by methanogenesis in the second stage UASB (UASB2). Nitrification of high ammonia was carried out in the A/O reactor. The final effluent of the system was fed to SBR. UASB1 had a working volume of 4.25 L while that of UASB2 was 8.25 L. The A/O reactor with an effective volume of 15 L was divided into ten chambers, of which the first chamber was the anoxic zone. An effective volume of SBR was 8 L. For each cycle, 3 L of wastewater were fed to SBR. The reaction temperatures of UASB1 and UASB2 were controlled by a heater.

The experiment went through two phases within 120 d. In phase I, a system consisting of a two-stage UASB and A/O reactor was used to achieve the short-cut nitrification stably (60 d). In phase II, the effluent of phase I was treated by the SBR (60 d). The system of a two-stage UASB-A/O-SBR reactor was used to treat landfill leachate thoroughly.

The process flow diagrams of the two phases are shown in Fig. 1.

Operational conditions were as follows: during a 120-d operation, the influent flow rate was 3 L/d. The influent of UASB1 was a mixture of raw leachate and a part of the effluent from the clarifying tank. The effluent recycle ratio was 300%. The sludge return ratio was 100%. Dissolved oxygen (DO) concentrations varied from 0.5 to 5 mg/L crossing the second to the tenth chamber. The temperatures of UASB1 and UASB2 were controlled at 32°C and 35°C, respectively. The temperature of A/O reactor and SBR was maintained at 27–29°C by heaters. The solution pH was 8–9 from the first to the tenth chamber in the A/O reactor. The mixed liquor suspended solid (MLSS) was maintained at approximately 3000–5000 mg/L. The solids retention time (SRT) was about 30–40 d. Each SBR cycle consisted of 3 min feeding, aerobic reaction, anoxic reaction (sodium acetate anhydrous added), 1 h of settling, 6 min of decanting, and idling. The DO concentration in the aerobic reaction was maintained at 3 mg/L in SBR. The MLSS was controlled at about 4000–5000 mg/L. SRT was about 30 d. The reaction time of nitrification and denitrification was controlled by online monitoring parameters (DO, oxidation-reduction potential (ORP) and pH). Samples were collected from raw leachate (raw), the influent of UASB1 which was the mixed liquid of raw leachate and recycled effluent (mix), the effluent of UASB1(U1e), the effluent of UASB2 (U2e), the anoxic zone of A/O reactor (A1), and the individual chambers of aerobic zone of A/O reactor (O2–O10). The sampling points were arranged according to the sequence of SBR.

1.2 Characteristics of landfill leachate

The real municipal landfill leachate discharged from a Liulitun landfill site, at Haidian District of Beijing, China was collected monthly for the study. The characteristics of the leachate are shown in Table 1. During the experiment, COD, NH₄⁺-N, NO₂⁻-N, NO₃⁻-N, TN and MLSS were measured according to the standard methods (APHA, 1998). The TN concentration was measured by multi N/C 3000 TOC (Analytik Jena AG, Germany). DO, ORP, pH and temperature were measured online using a dissolved oxygen meter (WTW DO 330i, Germany), an ORP meter (WTW ORP 340i) and a pH meter (WTW pH 340i), respectively.

Table 1 Characteristics of raw leachate

Parameter	Range	Mean
COD (mg/L)	8000–11000	9500
NH ₄ ⁺ -N (mg/L)	1500–2500	2000
pH	7.2–7.9	7.5
SS (mg/L)	3000–3400	3200
TN (mg/L)	2000–3000	2500
TP (mg/L)	9–15	12
NO _x ⁻ -N (mg/L)	0.5–15	7.75
BOD ₅ (mg/L)	4030–5000	4515

COD: chemical oxygen demand; SS: suspended solids; TN: total nitrogen; TP: total phosphorus; BOD₅: five day biochemical oxygen demand.

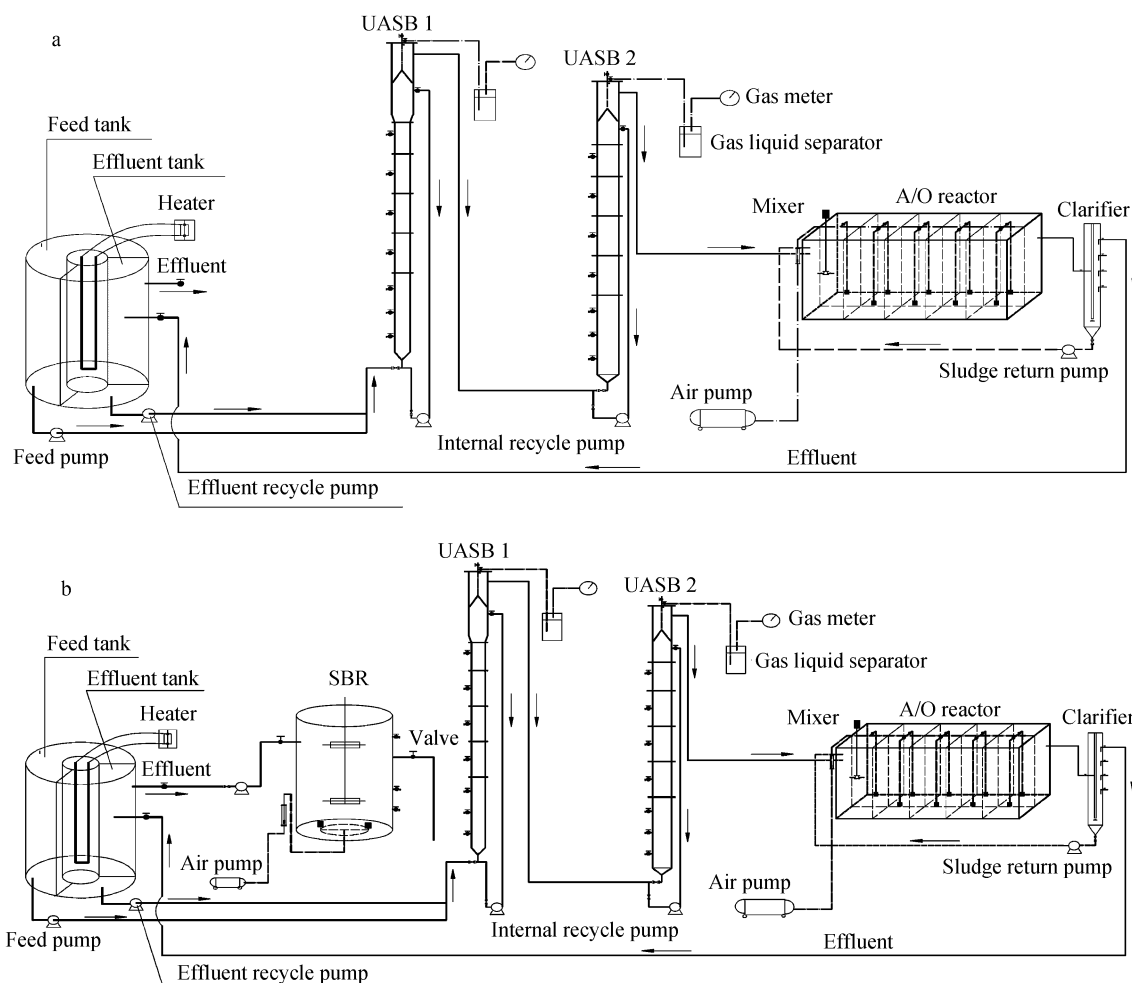


Fig. 1 Flow diagram of the two-stage UASB-A/O system in phase I (a) and two-stage UASB-A/O-SBR system in phase II (b).

2 Results and discussion

2.1 Two-stage UASB and A/O reactor system

The $\text{NH}_4^+\text{-N}$ concentration of raw leachate was high with mean value 2000 mg/L, which may inhibit the activity of the bacteria, especially at high pH (Wang *et al.*, 2008). The variation of nitrogen in the system during phase I is shown in Fig. 2. When $\text{NH}_4^+\text{-N}$ concentration of raw leachate was about 2000 mg/L, its concentration in UASB1 influent was less than 700 mg/L because of the dilution of the final recycled effluent of the system. The $\text{NH}_4^+\text{-N}$ concentration of A/O reactor influent was only 250 mg/L because of the further dilution of the returned sludge. Nitrification occurred in the second chamber (the first chamber in the aerobic zone) of A/O reactor, and the short-cut nitrification was almost completed. The $\text{NH}_4^+\text{-N}$ concentration in the final effluent of the system was 60 mg/L. The $\text{NH}_4^+\text{-N}$ removal efficiency was about 97%. The $\text{NO}_2^-\text{-N}$ concentration in the final effluent of the system was about 218 mg/L, while the $\text{NO}_3^-\text{-N}$ was about 28 mg/L. The stable short-cut nitrification was obtained with 89% nitrite accumulation in this study.

In the experiment, TN concentrations were also monitored. As shown in Fig. 3, when the TN concentration of raw leachate was about 2500 mg/L, the TN concentration

of final effluent was approximately 400 mg/L due to existence of nitrite and nitrate. The TN removal efficiency was 80%–85%. Because the total organic nitrogen (TON) concentration was very low, the TN concentration was nearly about the sum of ammonia, nitrite and nitrate. Thus the TN removal efficiency was nearly equal to the total inorganic nitrogen (TIN) removal efficiency.

The COD/TN and biochemical oxygen demand (BOD)/TN ratios of raw leachate were very low. The

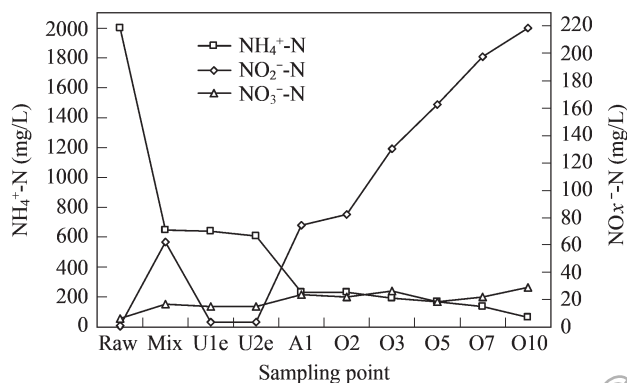


Fig. 2 Variation of nitrogen in the system during phase I. U1e: effluent of UASB1; U2e: effluent of UASB2; A1: anoxic zone of A/O reactor; O2-O10: individual chambers of aerobic zone of A/O reactor.

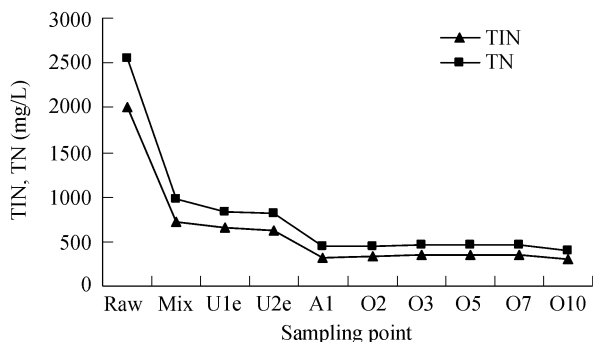


Fig. 3 Variation of total inorganic nitrogen (TIN) and total nitrogen (TN) in the system during phase I.

average COD/TN ratio was less than 4 and the average BOD/TN ratio was only 2. Hence, carbon source for denitrification was not sufficient and external carbon source was required to remove nitrogen thoroughly. Therefore, a SBR was added as the second stage to complete the process.

2.2 Two-stage UASB+A/O+SBR system

In order to reduce the TN concentration further, the process was improved phase II. The final effluent of phase I was further treated by SBR. Because nitrification was not accomplished thoroughly phase I, aeration was carried out for 3 h at first in SBR to remove residual $\text{NH}_4^+\text{-N}$. Aeration was switched off after 3 h and denitrification could then take place. External carbon source was not added during the first hour of the denitrification (the 4th hour of the whole reaction) and organic carbon phase I effluent was fully utilized. At the 2nd hour of denitrification (the 5th hour of the whole reaction), the external carbon source was added. Denitrification was ceased after the 13th hour (the 16th hour of the whole reaction). Then aeration was introduced for 1 h to remove the residual COD. Subsequently, settling, decanting, and idling would be carried out.

The typical variations of pH and ORP of a cycle in the SBR are shown in Fig. 4. In this cycle, nitrification was carried out with in the first 3 h. As shown in Fig. 4a, because acid was produced by nitrification, pH decreased gradually until it reached the lowest point, which is known

as “ammonia valley”. At ammonia valley, nitrite concentration reached the peak because ammonia was depleted. After that, pH began to increase. Therefore, ammonia valley represented the end of the short-cut nitrification. In order to ensure that pH would reach the ammonia valley, aeration was continued to be carried out for some time until it reached point A. Meanwhile, O_2 was supplied in nitrification, and ammonia was reduced while nitrite was increased. Thereby, ORP began to increase until it reached point C, as shown in Fig. 4b. At point C, ammonia was depleted and nitrite concentration reached the peak value. If aeration was continued, ORP would not change. This ORP platform indicated oxidizers (nitrite and nitrate) were not produced in the system any more, and nitrification ended. Aeration was stopped at point C.

Under anoxic period, because nitrite and nitrate were reduced in denitrification and alkalinity was produced, pH increased gradually. When nitrite and nitrate was depleted, pH began to decrease and the peak point appeared on the pH curve which is known as “nitrate apex”. At nitrate apex, the alkalinity produced in denitrification reached the peak. Nitrate apex indicated the completion of denitrification. In order to ensure that pH could reach nitrate apex, stirring was continued for a while until it reached point B. As shown in Fig. 4b, when pH increased during denitrification, ORP decreased gradually because nitrite and nitrate were reduced to nitrogen gas which caused the decrease in oxidizers amount. ORP decreased gradually until it reached “nitrate knee”, where it presented as platform. In the mean time, pH rose to the peak (nitrate apex). Nitrate apex on the pH curve and nitrate knee on the ORP curve indicated the end of denitrification. In order to ensure that ORP reached nitrate knee, stirring was continued for a while until points B and D. The denitrification was accomplished. Because aeration was again carried out at point E to remove the residual COD, ORP increased. Therefore, the process of the short-cut nitrification could be grasped by measuring pH and ORP online. According to the characteristic points on the pH and ORP curves, the aerobic and anoxic durations could be controlled with real-time feed back. The stable treatment was achieved after several cycles of operation. The results are shown in Fig. 5.

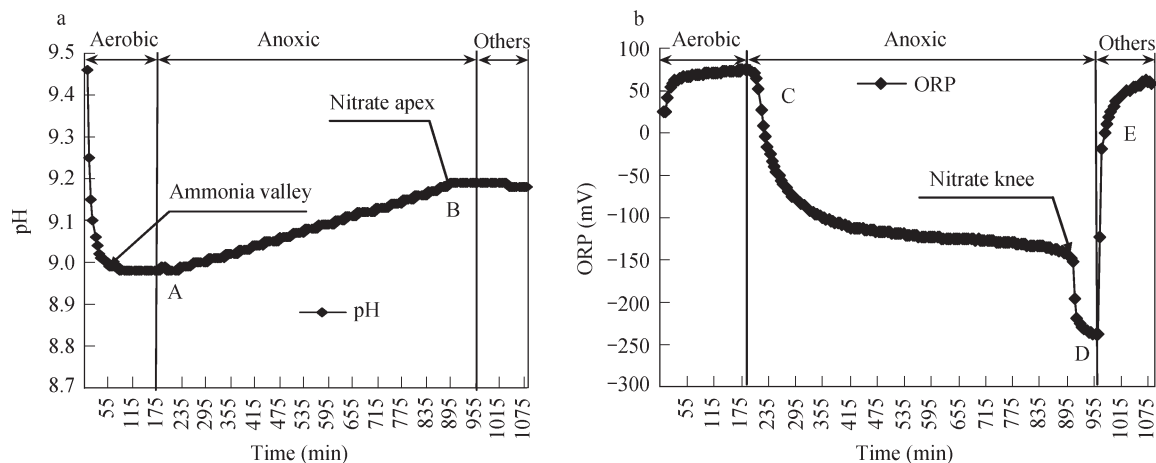


Fig. 4 Variation of pH and ORP in the SBR during phase II.

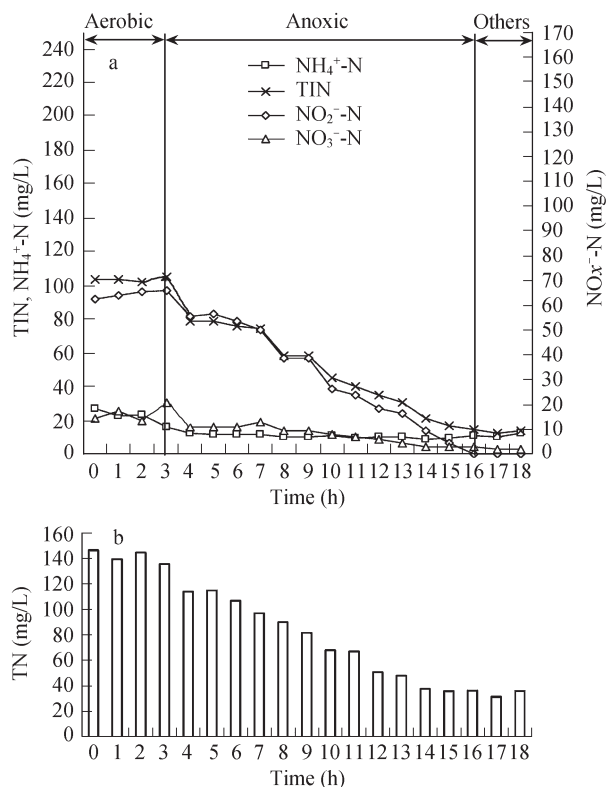


Fig. 5 Variation of nitrogen (a) and TN (b) in the SBR during phase II.

The SBR had an effective volume of 8 L, and 3 L of wastewater was fed to each cycle. Because of dilution, nitrogen concentration and other indices of SBR influent were less than that of the effluent from the previous phase. The variation of nitrogen in a typical cycle of SBR is shown in Fig. 5a. The $\text{NH}_4^+\text{-N}$ concentration of final effluent at the first phase was 60 mg/L and was 30 mg/L in the SBR influent due to the dilution. After 3 h of aeration in SBR, the $\text{NH}_4^+\text{-N}$ concentration decreased to 15 mg/L. The nitrite nitrogen concentration was decreased to 65 mg/L in the influent of SBR, mainly due to the dilution. After denitrification, the nitrite nitrogen and nitrate nitrogen concentrations of effluent were less than 1 mg/L.

The study showed that the reaction time of denitrification was as long as 13 h, although the external carbon source was added excessively. The aims of future investigation are as follows: how to domesticate the effective denitrifiers; and how to enhance the efficiency of denitrification; and how to reduce the amount of external carbon source and the reaction time.

As shown in Fig. 5b, the TN concentration in the influent of SBR was 146 mg/L and was always less than 40 mg/L in the SBR effluent.

3 Conclusions

Based on the experimental results, several conclusions could be made. (1) A system consisting of a two-stage UASB and A/O reactor is able to be adopted to treat landfill leachate. Ammonia nitrogen concentration of raw influent could be reduced from about 2000 mg/L to 60 mg/L.

The ammonia nitrogen removal efficiency could reach about 97%. The stable short-cut nitrification was achieved with 89% nitrite accumulation. The total nitrogen removal efficiency was about 80%. The nitrite nitrogen and the total nitrogen concentrations in the final effluent were still about 218 and 400 mg/L, respectively. Although the system could remove high strength ammonia nitrogen by biological treatment without any physicochemical pretreatment, the total nitrogen removal efficiency was not very high. (2) The system of a two-stage UASB-A/O-SBR was utilized to treat landfill leachate to remove nitrogen thoroughly. The effluent of phase I was treated in SBR by stable nitrification and denitrification. Several cycles were carried out and the stable treatment was obtained. The ammonia nitrogen concentration in the effluent of SBR was 15 mg/L. The nitrite nitrogen and nitrate nitrogen concentrations in the effluent were no more than 1 mg/L. The TN concentration was nearly 39 mg/L. Therefore, the two-stage UASB-A/O-SBR system was a highly efficient process to treat landfill leachate. (3) ORP and pH were adopted as the real-time control parameters in nitrification and denitrification. The parameters could facilitate to grasp the processes of the short-cut nitrification and denitrification, and save the reaction time and energy as well.

Acknowledgments

This work was supported by the Project of Beijing Natural Science Foundation (No. 8091001), the National Natural Science Foundation of China (No. 50978003), the Higher Learning under the Jurisdiction of Beijing Municipality (No. PHR20090502), and the State Key Laboratory of Urban Water Resource and Environment (HIT) (No. QAK200802).

References

- APHA (American Public Health Association), 1998. Standard Methods for the Examination of Water and Wastewater. Baltimore: Port City Press.
- Calli B, Mertoglu B, Inanc B, 2005. Effects of high free ammonia concentrations on the performances of anaerobic bioreactors. *Process Biochemistry*, 40(3): 1285–1292.
- Christian F, Marc B, Philipp H, Irene B, Hansruedi S, 2002. Biological treatment of ammonium-rich wastewater by partial nitrification and subsequent anaerobic ammonium oxidation (anammox) in a pilot plant. *Journal of Biotechnology*, 99(3): 295–306.
- Hellinga C, Schellen A A J C, Mulder J W, van Loosdrecht M C, Heijnen J J, 1998. The sharon process: An innovative method for nitrogen removal from ammonium-rich wastewater. *Water Science and Technology*, 37(9): 135–142.
- Im J H, Woo H J, Choi M W, Han K B, Kim C W, 2001. Simultaneous organic and nitrogen removal from municipal landfill leachate using an anaerobic-aerobic system. *Water Research*, 35(10): 2403–2410.
- Kim D J, Lee D I, Keller J, 2006. Effect of temperature and free ammonia on nitrification and nitrite accumulation in landfill leachate and analysis of its nitrifying bacterial community by FISH. *Bioresource Technology*, 97(3): 459–468.
- Liang Z, Liu J X, 2008. Landfill leachate treatment with a novel process: Anaerobic ammonium oxidation (Anammox)

- combined with soil infiltration system. *Journal of Hazardous Materials*, 151(1): 202–212.
- Ozturk I, Altinbas M, Koyuncu I, Arikan O, Gomec Y C, 2003. Advanced physico-chemical treatment experiences on young municipal landfill leachates. *Waste Management*, 23(5): 441–446.
- Palma L D, Ferrantelli P, Merli C, Petrucci E, 2002. Treatment of industrial landfill leachate by means of evaporation and reverse osmosis. *Waste Management*, 22(8): 951–955.
- Peng Y Z, Zhang S J, Zeng W, Zheng S W, Mino T, Satoh H, 2008. Organic removal by denitrification and methanogenesis and nitrogen removal by nitrification from landfill leachate. *Water Research*, 42(4/5): 883–892.
- Renou S, Givaudan J G, Poulain S, Dirassouyan F, Moulin P, 2008. Landfill leachate treatment: Review and opportunity. *Journal of Hazardous Materials*, 150(3): 468–493.
- Uygun A, Kargi F, 2004. Biological nutrient removal from pretreated landfill leachate in a sequencing batch reactor. *Journal of Environmental Management*, 71(1): 9–14.
- Vasel J L, Jupsin H, Annachatre A P, 2004. Nitrogen removal during leachate treatment: comparison of simple and sophisticated systems. *Water Science and Technology*, 50(6): 45–52.
- Wang S L, Wu X H, Wang Y S, Li Q F, Tao M J, 2008. Removal of organic matter and ammonia nitrogen from landfill leachate by ultrasound. *Ultrasonics Sonochemistry*, 15(6): 933–937.
- Wang X L, Ma Y, Peng Y Z, Wang S Y, 2007. Short-cut nitrification of domestic wastewater in a pilot-scale A/O nitrogen removal plant. *Bioprocess and Biosystems Engineering*, 30(2): 91–97.
- Yang Q, Peng Y Z, Liu X H, Zeng W, Mino T, Satoh H, 2007. Nitrogen removal via nitrite from municipal wastewater at low temperatures using real-time control to optimize nitrifying communities. *Environmental Science and Technology*, 41(23): 8159–8164.
- Zhang S J, Peng Y Z, Wang S Y, Zheng S W, Guo J, 2007. Organic matter and concentrated nitrogen removal by shortcut nitrification and denitrification from mature municipal landfill leachate. *Journal of Environmental Sciences*, 19(6): 647–651.