

Landfill leachate treatment with a novel process: Anaerobic ammonium oxidation (Anammox) combined with soil infiltration system

Zhu Liang, Junxin Liu*

State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Science,
Chinese Academy of Sciences, Beijing 100085, PR China

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Abstract

A novel combined process was proposed to treat municipal landfill leachate with high concentrations of ammonium and organics. This process consisted of a partial nitrification reactor (PNR), an anaerobic ammonium oxidation (Anammox) reactor (AR) and two underground soil infiltration systems (USIS-1 and USIS-2). Based on the optimum operating conditions obtained from batch tests of individual unit, the combined process was continuously operated on a bench scale for 166 days. Partial nitrification was performed in a fixed bio-film reactor (PNR, working volume = 12 L). Ammonium nitrogen-loading rate (N_v) and DO were combined to monitor partial nitrification, and at $T = 30 \pm 1^\circ\text{C}$, $N_v = 0.27\text{--}1.2\text{ kg}/(\text{m}^3\cdot\text{d})$, $\text{DO} = 0.8\text{--}2.3\text{ mg}/\text{L}$, the ratios of nitrite nitrogen (NO_2^- -N) to ammonium nitrogen (NH_4^+ -N) were successfully kept close to 1.0–1.3 in the effluent. Nitrate nitrogen (NO_3^- -N) less than 43 mg/L was observed. The effluent of PNR was ideally suited as influent of AR. Sixty-nine percent COD_{cr} from the raw leachate was degraded in the PNR. Anammox was carried out in a fixed bio-film reactor (AR, working volume = 36 L). At $T = 30 \pm 1^\circ\text{C}$, $N_v = 0.06\text{--}0.11\text{ kg}/(\text{m}^3\cdot\text{d})$, about 60% NH_4^+ -N and 64% NO_2^- -N in the influent of AR were simultaneously removed. Inhibition of high-strength NO_2^- -N (up to 1011 mg/L) should be responsible for the low removal rate of nitrogen. About 35% aquatic humic substance (AHS) was degraded in the AR. With the same working volume (200 L), USIS-1 and USIS-2 were alternately performed to treat the effluent from AR at one cycle of about 30 days. At hydraulic loading rate (HLR) = 0.02–0.04 $\text{m}^3/\text{m}^3\cdot\text{d}$, pollutant loading rates (PLR) = NH_4^+ -N $\leq 14\text{ g}/\text{m}^3\cdot\text{d}$, TN $\leq 25\text{ g}/\text{m}^3\cdot\text{d}$, and $\text{COD}_{\text{cr}} \leq 13\text{ g}/\text{m}^3\cdot\text{d}$, average removal efficiencies of 88% NH_4^+ -N, 67% TN and 55% COD_{cr} were obtained. Overall, raw leachate with 1430–2720 mg NH_4^+ -N/L, 1524–2912 mg TN/L and 1165–2599 mg $\text{COD}_{\text{cr}}/\text{L}$, was treated by the process and the effluent with 22–58 mg NH_4^+ -N/L, 108–300 mg TN/L and 32–250 mg $\text{COD}_{\text{cr}}/\text{L}$ was obtained with average removal efficiencies of 97% NH_4^+ -N, 87% TN and 89% COD_{cr} . The test results indicated that the combined system could work stably over a long period under the operating conditions, and that the process was feasible for the leachate treatment. AR should be the key to the performance of the combined process.

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Keywords: Municipal landfill leachate; Partial nitrification; Anammox; Underground soil infiltration system

1. Introduction

Municipal landfill leachate is one of the types of high-strength wastewater with the greatest environmental impact. This is due to its pollutants: ammonium nitrogen (NH_4^+ -N), biodegradable and refractory organics and heavy metals [1–2]. At present, heavy metals are not at major concern because average metal concentrations are fairly low. Ammonium and organics are the most significant components of leachate for the long term [2–3].

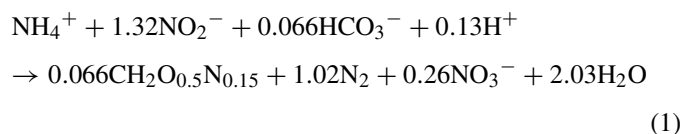
Satisfactory treatment of leachate is not an easy task for its high concentrations of ammonium nitrogen and refractory organics. Briefly, leachate can be treated by different methods: biological methods (aerobic, anaerobic) [4–7] and physicochemical methods: precipitation, oxidation, adsorption, stripping, reverse osmosis, etc. [8–10] to remove organic matter and ammonium nitrogen. Due to the operation costs and secondary pollution, physicochemical methods are mainly suitable for pretreatment or post-treatment to complement the biological treatment process [11]. Biological technologies for landfill leachate treatment have been shown to be the economic and effective methods to degrade organic matter and ammonium. No individual technology can guarantee particular treatment efficiencies due to high levels of NH_4^+ -N and COD in leachate,

* Corresponding author. Tel.: +86 10 62849133; fax: +86 10 62849133.
E-mail address: jxliu@mail.rcees.ac.cn (J. Liu).

therefore, combined processes should be adopted to improve treatment performance and to reduce overall running costs.

Conventional biological nitrogen removal process contains two stages: aerobic nitrification of ammonium to nitrate and anoxic denitrification of nitrate to nitrogen gas using readily biodegradable organic matter as electron acceptor. Due to low C/N ratio, high ammoniacal-nitrogen and refractory organic matter in landfill leachate, traditional biological technologies have encountered some problems, such as low removal efficiency of total nitrogen (TN), high-energy consumption and unstable running. Reducing oxygen and C-source requirement and enhancing the TN removal efficiency are the keys to the biological processes.

Anammox (anaerobic ammonium oxidation), an autotrophic nitrogen removal method, uses $\text{NH}_4^+\text{-N}$ as electron donor and nitrite nitrogen ($\text{NO}_2^-\text{-N}$) as electron acceptor to accomplish nitrogen removal (Eq. (1)) [12]. Without the need of organics, this technology has been developed to mainly treat ammonium rich wastewaters, such as landfill leachate, poultry manure and supernatant of digested sludge [13–16].



Prior to Anammox, partial nitrification (converting part of ammonium to nitrite) should be set in order to produce the appropriate ratio of nitrite/ammonium in the mixture [17,18]. Both nitrification stage and ammonium conversion efficiency must be controlled simultaneously in the partial nitrification process. On one hand, the oxidation of nitrite to nitrate must be prevented in order to acquire stable nitrite accumulation; on the other hand, the conversion efficiency of ammonium must be about 57% theoretically so that the nitrite/ammonium ratio produced is about 1.3. In this way, Anammox combined with partial nitrification (partial nitrification-Anammox), a completely autotrophic nitrogen removal technology is achieved. Compared with the conventional biological treatment technologies, the process may have promising technical and economic advantages for landfill leachate treatment because of less oxygen consumption, no organic source addition and low sludge production [19,20].

Organic materials in landfill leachates are typically volatile fatty acids and humic and fulvic compounds [2]. It is certain that biodegradable organic matters (volatile fatty acids) can be removed by heterotrophic bacteria in the partial nitrification stage, and that another measure must be taken to treat the remaining humic and fulvic compounds (refractory organics). Furthermore, there is a small amount of nitrite remaining in the Anammox effluent. Therefore, the residual refractory organics

and nitrite must be effectively removed in another process to meet the safe discharge requirements.

Underground soil infiltration system (USIS) with low construction and operation costs can achieve high purification efficiencies due to the complex interactions of hydraulic and purification processes: filtration, sorption, chemical reactions, biotransformation, predation and plant uptake [21]. Therefore, it is an effective and inexpensive treatment technology, and it can be an alternative technology of advanced treatment for landfill leachate.

Based on the above reviews, a novel integrated process was proposed to treat municipal landfill leachate in this study: partial nitrification-Anammox combined with USIS. In the partial nitrification stage, removal of biodegradable organic matter and acquirement of proper nitrite/ammonium ratio mixture (close to 1.0–1.3) were fulfilled. In the Anammox stage, TN was removed without organic carbon addition. In the USIS, the remaining nitrogen compounds and refractory organics from the Anammox effluent were further removed by the combination of biodegradation, filtration and adsorption.

In spite of much experimental work reported in the literature, a systematic investigation on the operating conditions of partial nitrification-Anammox for landfill leachate treatment and evaluation on the performance of the combined process over a long period are still scarce. Therefore, the three treatment units were operated independently in a batchwise fashion for determining the individual operating conditions. And then these optimum conditions were used to conduct the operations of three units in the combined sequence.

Based on the batch test results, the optimum operating conditions of three units have been acquired [22]. The focuses of this publication were to explore the feasibility of the combined process for the landfill leachate treatment and to evaluate the performance of the novel process for long-term running on a bench scale.

2. Materials and methods

2.1. Landfill leachate

The landfill leachate in this study was obtained from a municipal solid waste (MSW) sanitation landfill site in Beijing, China. Its $\text{NH}_4^+\text{-N}$ concentration was high, and C/N ratio ($\text{COD}_{\text{cr}}/\text{NH}_4^+\text{-N}$) was low (Table 1). The concentrations of heavy metals were fairly low (Table 2).

2.2. Experimental set-up

This process consisted of three major parts: a partial nitrification reactor (PNR), an Anammox reactor (AR) and two

Table 1
Characteristics of investigated leachate

Parameter	$\text{NH}_4^+\text{-N}$ (mg/L)	TN (mg/L)	COD_{cr} (mg/L)	Alkalinity (Na_2CO_3) (mg/L)	pH
Range	1400–2800	1500–3000	1100–2600	8000–15000	8.1–9
Average \pm S.D.	1972 \pm 408.2	2117 \pm 426.0	1703 \pm 393.5	11898 \pm 2639	8.5 \pm 0.3

Table 2
Average concentrations of metals in raw landfill leachate

Parameter	Na	K	Ca	Mg	Fe	Mn	Ba	Al
Value (mg/L)	2450.6	1881.6	7.23	625.8	0.95	0.01	0.06	0.38
Parameter	Cd	Cr	Cu	Pb	Zn	Ni		
Value (mg/L)	0.006	0.12	0.02	0.01	0.02	0.2		

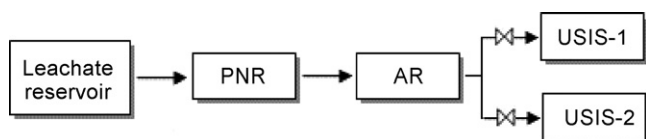


Fig. 1. The flow chart of the combined process.

underground soil infiltration systems (USIS-1 and USIS-2) for trade off. In the combined sequential treatment, the raw landfill leachate was first fed to the PNR for pretreatment. The effluent from that unit was then treated for nitrogen removal in the AR. Finally the Anammox effluent was fed to USIS for advanced treatment. The flow chart and experimental schematic diagram are shown in Figs. 1 and 2, respectively. After the start-up period, continuous running of the whole combined process was begun under the operating conditions from batch tests (Table 3).

2.2.1. Partial nitritation system and operative scheme

PNR was a bench scale up-flow fixed bed bio-film reactor with working volume of 12 L. Modified polypropylene balls (30 mm × 30 mm) were used as carriers with total sur-

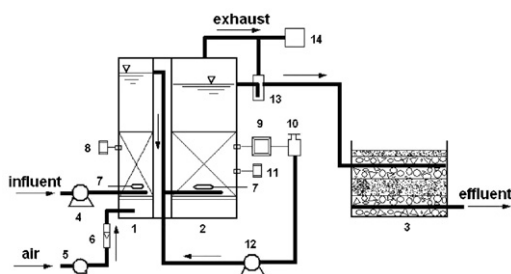


Fig. 2. Schematic diagram of the treatment process. 1, PNR; 2, AR; 3, USIS; 4, metering pump; 5, air pump; 6, flowmeter; 7, heater; 8, DO meter; 9, online control pH meter; 10, dosing device of NaHCO_3 or HCl ; 11, ORP meter; 12, metering pump; 13, water seal; 14, collection of gas.

Table 3
Operating conditions of three units in the continuous running of combined process

PNR	Nv: gradually increased from 0.27 to 1.2 $\text{kg H}_4^+\text{-N}/(\text{m}^3\cdot\text{d})$ DO: gradually increased from 0.8 to 2.3 mg/L T: $30 \pm 1^\circ\text{C}$
AR	Nv: changed along with the effluent from PNR T: $30 \pm 1^\circ\text{C}$ pH: 7.5–8.0
USIS	Hydraulic loading rate: 0.02–0.04 $\text{m}^3/(\text{m}^3\cdot\text{d})$

face areas of 4.12 m^2 . The desired dissolved oxygen (DO) concentration was acquired by adjusting the airflow. The desired ammonium nitrogen-loading rate (Nv) was acquired by adjusting the influent flow. Temperature in the reactor was maintained at $30 \pm 1^\circ\text{C}$ by heater. The start-up of reactor is shown in Table 4. The aerobic activated sludge from a landfill leachate plant was used as inoculum (19 g MLVSS).

2.2.2. Anammox system and operative scheme

AR was a bench scale up-flow fixed bed biofilm reactor with working volume of 36 L. Modified polypropylene balls (30 mm × 30 mm) were used as carriers with total surface areas of 11.3 m^2 . The desired Nv was acquired by adjusting the influent flow. Temperature in the reactor was maintained at $30 \pm 1^\circ\text{C}$ by heater. Online pH control meter with dosing device of chemicals was used to control the pH value at the range of 7.5–8.0. A novel culture method combining aerobic and subsequent anaerobic culture was used for the AR start-up in order to improve the culture of Anammox bacteria and accelerate start-up. Namely, nitritation biofilm was aerobically cultured in the AR in the first stage with aerobic activated sludge as inoculum (57 g MLVSS), and then anaerobic domestication of Anammox microorganism was begun in the second stage (Table 5).

After 37-day aerobic culture, removal efficiency of ammonium in the influent was more than 90%, and 90% removed ammonium was converted into nitrite in the PNR and AR. Here, cultures of nitritation biofilm were accomplished in the AR and PNR, and the anaerobic culture in the AR was subsequently begun. After 60-day anaerobic culture, Anammox performance of AR was gradually improved and stable nitrogen removal was acquired with the average removal efficiencies of 67% $\text{NH}_4^+\text{-N}$ and 77% $\text{NO}_2^-\text{-N}$. Total duration of start-up in the AR was 97 days.

2.2.3. USIS system and operative scheme

According to soil column test results in batch tests (not shown here), the feasible operational conditions (hydraulic loading rate and contaminant loading rate) and operational mode had been obtained. The operational mode was: two soil infiltration systems ran alternately to treat the effluent of AR, and one cycle was about 30 days. In the present study, these operational mode and conditions were used to conduct the continuous running of USIS. The USIS, working volume of 200 L, was filled with sandy loam soil. USIS-1 and USIS-2 were fed for trade off with 30-day cycle.

Table 4
Conditions of acclimation and culture of PNR

Duration (days)	Conditions		
	DO (mg/L)	T (°C)	Wastewater
7	2	30 ± 1	Mixture of leachate and domestic sewage (0.4–0.8, v/v)
30	1.0–1.5	30 ± 1	Raw leachate NH ₄ ⁺ -N: 1800–2700 mg/L; N _v ≤ 0.8 kg NH ₄ ⁺ -N/(m ³ ·d)

2.3. Analytic methods

The concentrations of NH₄⁺-N, NO₂⁻-N, NO₃⁻-N, and TN were determined according to the standard methods issued by the Environmental Protection Agency (EPA) of China. COD_{cr} measurement was based on digestion with potassium dichromate in concentrated sulphuric acid using a COD analyzer (CTL-12, China). TOC was measured using a TOC analyzer (Phoenix 8000, Tekmar Dohrmann, USA). Aquatic humic substance (AHS) was analyzed according to APHA (1992) (Method 5510C, 996) using XAD-7 resin (Rohmhaas, USA) [23]. Temperature and DO were online monitored by a DO meter (Oxi 330i WTW, Germany). The pH value was determined using glass electrodes connected to a pH meter (320-S, China). TSS was analyzed by drying the sample at 105 °C for at least 24 h. After burned at 600 °C for 1 h, the ash was measured. The difference between TSS and ash was termed as VSS. An ICP-OES analyzer (Perkin-Elmer Optima 2000DV, USA) was used for analyzing metals.

To determine the performance of nitrite build-up and inhibition of nitrate production in the PNR, percentage of nitrite accumulation (PNC) was brought forward in the study, which was calculated according to the Eq. (2).

$$\text{PNC} = \frac{C_{\text{NO}_2^- - \text{N, eff}}}{C_{\text{NO}_2^- - \text{N, eff}} + C_{\text{NO}_3^- - \text{N, eff}}} \times 100\% \quad (2)$$

where $C_{\text{NO}_2^- - \text{N, eff}}$ and $C_{\text{NO}_3^- - \text{N, eff}}$ represented the concentrations of NO₂⁻-N and NO₃⁻-N in the effluent from PNR, respectively.

Table 5
Conditions of acclimation and culture of AR

Stage	Duration (days)	Conditions		
		DO (mg/L)	T (°C)	Wastewater
Aerobic	7	2	30 ± 1	Mixture of leachate and domestic sewage (0.4–0.8 v/v)
	30	1.0–1.5	30 ± 1	Raw leachate NH ₄ ⁺ -N: 1800–2700 mg/L; N _v ≤ 0.8 kg NH ₄ ⁺ -N/(m ³ ·d)
Anaerobic	60	–	30 ± 1	Mixture of the effluent from PNR and tap water NO ₂ ⁻ -N/NH ₄ ⁺ -N ratio: 1–1.2 NH ₄ ⁺ -N: 220–480 mg/L N _v : 0.02–0.06 kg NH ₄ ⁺ -N/(m ³ ·d)

3. Results and discussion

3.1. Partial nitrification

Both DO and N_v were the key factors affecting partial nitrification [22]. In the study, their interaction impacts on the partial nitrification were investigated in a 166-day continuous running at 30 ± 1 °C. As shown in Fig. 3(a and b), along with the increase of N_v (from 0.27 to 1.2 kg NH₄⁺-N/m³·d), DO was adjusted from 0.8 to 2.3 mg/L. At the beginning of the change of N_v and DO, the running of PNR fluctuated, and after about 1 week, a stable treatment was achieved again. The raw leachate with NH₄⁺-N of 1400–2800 mg/L was treated, and the effluent with 506–885 mg NH₄⁺-N/L and 438–1011 mg NO₂⁻-N/L was acquired. Nitrite oxidation was successfully inhibited and produced NO₃⁻-N in the effluent was below 43 mg/L. Ammonium oxidation rate (AOR) increased with the N_v and was up to maximum (0.79 kg NH₄⁺-N/m³·d), indicating that ammonium oxidation was not inhibited under the operating conditions. According to Fig. 3(c), percentages of nitrite accumulation were more than 95%, and ammonium removal efficiencies varied from 54 to 73%. Ratios of NO₂⁻-N/NH₄⁺-N in the effluent varied from 0.56 to 1.26 and almost 80% ratios were close to 1.0–1.3. Relatively low ratios were produced at the times of adjustment of N_v and DO, especially at $t = 142$ days, when N_v was rapidly elevated from 0.68 to 0.83 kg NH₄⁺-N/m³·d, ammonium removal efficiency fell sharply, from 68 to 54%, resulting in the decrease of the ratio from 0.93 to 0.56. These results indicated that both nitrite build-up and ammonium removal efficiency were controlled simultaneously to obtain satisfying partial nitrification under applied conditions. Therefore, N_v and DO could be combined to control the partial nitrification for leachate treatment.

Stable nitrogen loss occurred in the PNR with average TN removal efficiency of 30% (Fig. 4), which resulted from the simultaneous nitrification and denitrification (SND) via nitrite

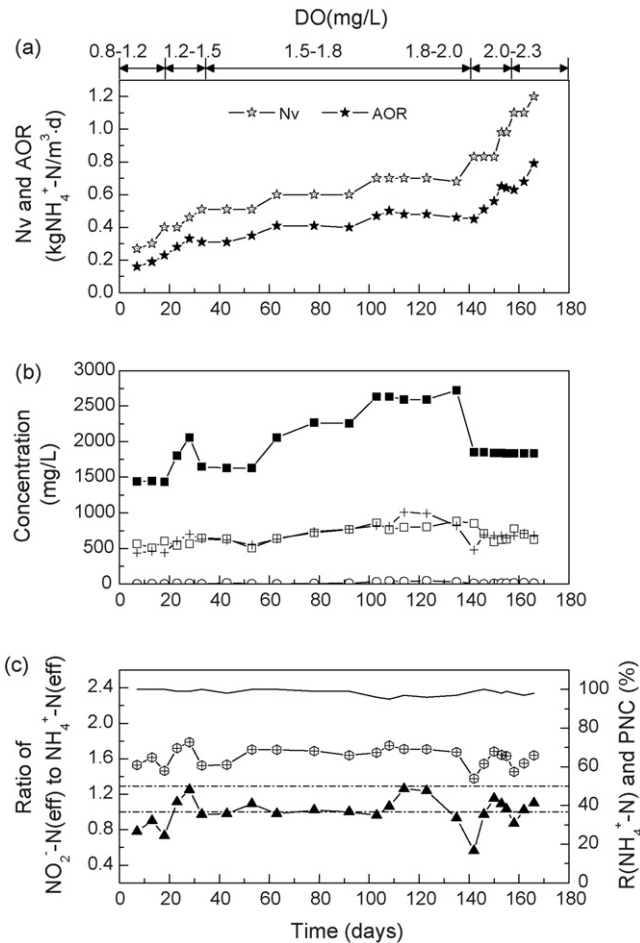


Fig. 3. Control results of partial nitritation in the PNR using Nv and DO (R represents removal efficiency) (■, NH₄⁺-N(in); □, NH₄⁺-N(eff); +, NO₂⁻-N(eff); ○, NO₃⁻-N(eff); ▲, ratio; ⊕, R; −, PNC).

at limited DO concentration [24]. SND resulted in a decrease of the NO₂⁻-N/NH₄⁺-N ratio because of the consumption of part nitrite, therefore, actual NH₄⁺-N removal efficiency should be more than its theoretical value (57%) in order to acquire favorite ratio of nitrite/ammonium mixture that will be fed into the following AR. In fact, the favorite ratios (close to

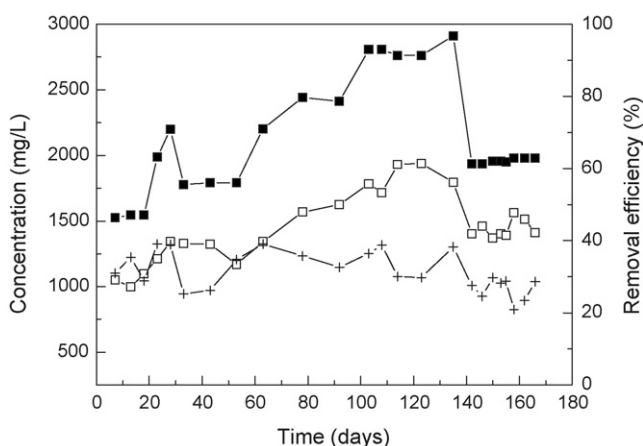


Fig. 4. Nitrogen loss in the PNR (■, TN(in); □, TN(eff); +, R(TN)).

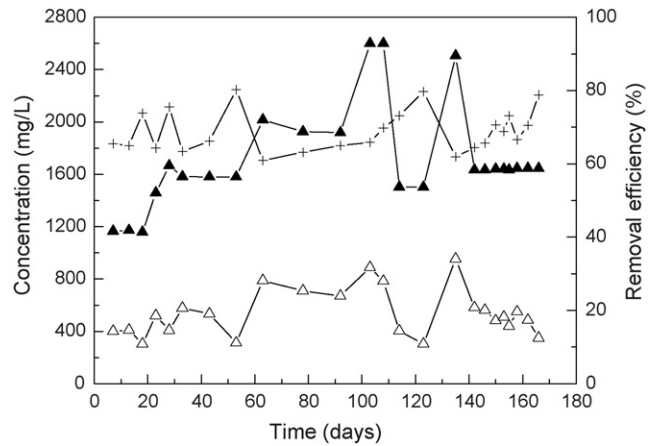


Fig. 5. Removal of COD_{cr} in the PNR (▲, COD_{cr}(in); △, COD_{cr}(eff); +, R(COD_{cr})).

1.0–1.3) were produced only when ammonium removal efficiencies were more than 60% (Fig. 3(c)). A substantial biological degradation of COD_{cr} also occurred with 60–81% removal efficiencies (Fig. 5), which resulted from biological oxidation of heterotrophic bacteria and C-resource consumption in denitrification. Biodegradable organic matter was removed and the residue was mainly fulvic-like organic matter.

Free ammonium (FA) and free nitrous acid (FNA) rather than ammonium and nitrite inhibit nitrifying bacteria, and the toxicities of FA and FNA depend on the environmental pH at certain temperature [25]. In this study, average alkalinity (Na₂CO₃) in the influent was 11898 mg/L, and all pH values in the effluent were all above 8.5 (its average value was 8.6). According to the average pH value, calculated values of FA and FNA were 160–260 mg/L and 0.007–0.019 mg/L, respectively [25]. More than 10–150 mg/L of FA will inhibit oxidation of ammonium and bring about failure of nitrite build-up [25]. However, in this study, the long-term stable partial nitritation was achieved at such high FA level. It was evident that oxidation of nitrite was inhibited, but oxidation of ammonium was not inhibited. It was in accordance with the observation of Princic et al., which reported that nitrifier strains adapted to high ammonium concentration (up to 3000 mg/L) at pH of 8.2 [26]. Owing to the high pH, FNA concentration was so low that its inhibition was ignored.

3.2. Anammox

According to the conclusions from batch tests of individual Anammox reactor (not shown here), Nv had been an important factor to influence the stable nitrogen removal, and Nv above 0.12 kg/(m³·d) had resulted in the decline of nitrogen removal rate. In the present study, Nv in the AR was changed along with the effluent quality from PNR and gradually increased from 0.06 to 0.16 kg/(m³·d) (Fig. 6(a)). Removal rates of both NH₄⁺-N and NO₂⁻-N were basically improved with the increase of Nv before *t* = 158 days, thereafter, elevation of Nv from 0.11 to 0.16 kg/(m³·d), resulted in an obvious fall of NH₄⁺-N removal rate from 0.07 to 0.065 kg/(m³·d) and a slight variation of NO₂⁻-N removal rate from 0.084 to 0.082 kg/(m³·d). At *t* = 166 day,

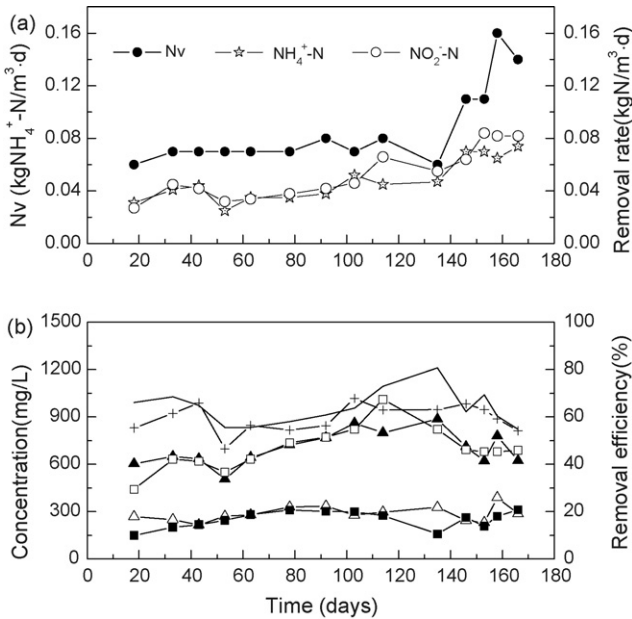


Fig. 6. Effects of Nv on the removals of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ in the AR (\blacktriangle , $\text{NH}_4^+\text{-N}$ (in); \triangle , $\text{NH}_4^+\text{-N}$ (eff); +, $R(\text{NH}_4^+\text{-N})$; \square , $\text{NO}_2^-\text{-N}$ (in); \blacksquare , $\text{NO}_2^-\text{-N}$ (eff); -, $R(\text{NO}_2^-\text{-N})$).

removal rate of $\text{NH}_4^+\text{-N}$ rose to $0.074 \text{ kg}/(\text{m}^3 \cdot \text{d})$ with the reduction of Nv. As illustrated in Fig. 6(b), 506–885 mg $\text{NH}_4^+\text{-N}/\text{L}$ and 441–1011 mg $\text{NO}_2^-\text{-N}/\text{L}$ from the effluent of PNR were continuously fed into the AR, and the AR effectively treated them to acquire the effluent with 216–388 mg $\text{NH}_4^+\text{-N}/\text{L}$ and 149–311 mg $\text{NO}_2^-\text{-N}/\text{L}$.

Overall, both removal rate and removal efficiency of $\text{NH}_4^+\text{-N}$ were less than those of $\text{NO}_2^-\text{-N}$ during the whole running period. Average removal rates of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were 0.049 and $0.053 \text{ kg}/(\text{m}^3 \cdot \text{d})$, respectively. Average removal efficiencies of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$ were 60 and 64%, respectively. Moreover, it seemed that the increase of Nv had greater impact on the removal of $\text{NH}_4^+\text{-N}$ than on that of $\text{NO}_2^-\text{-N}$. These results were all consistent with those in batch tests.

In Anammox process, a small quantity of $\text{NO}_2^-\text{-N}$ is converted to $\text{NO}_3^-\text{-N}$ to meet the possible need for electrons to reduce CO_2 for autotrophic growth, and produced $\text{NO}_3^-\text{-N}$ accounts for about 10% of the N-feed [27]. Fig. 7 demonstrates that nitrate was also produced in this study; however, its production was relatively low. Concentration of $\text{NO}_3^-\text{-N}$ was changed from 1.2 to 73 mg/L with average value of 29.3 mg/L, which averagely accounted for 3.2% of the converted nitrogen. The average ammonium and nitrite degradation and the nitrate production yielded a ratio of 1:1.09:0.07 and was less than the stoichiometric ratio given in Eq. (1) (1:1.32:0.26).

Fig. 8 shows the removal of TN in the AR, indicating that removal rate had growth with the Nv and also had a fall at $t = 158$ days. Average removal rate was $0.11 \text{ kg}/(\text{m}^3 \cdot \text{d})$.

Because autotrophic Anammox bacteria have relatively slow growth rate, the substrates and other compounds in the raw wastewater have possible toxicities to Anammox activity. Anammox process is not inhibited by $\text{NH}_4^+\text{-N}$ or $\text{NO}_3^-\text{-N}$ up to concentrations of at least 1000 mg/L; however, $\text{NO}_2^-\text{-N}$ of more

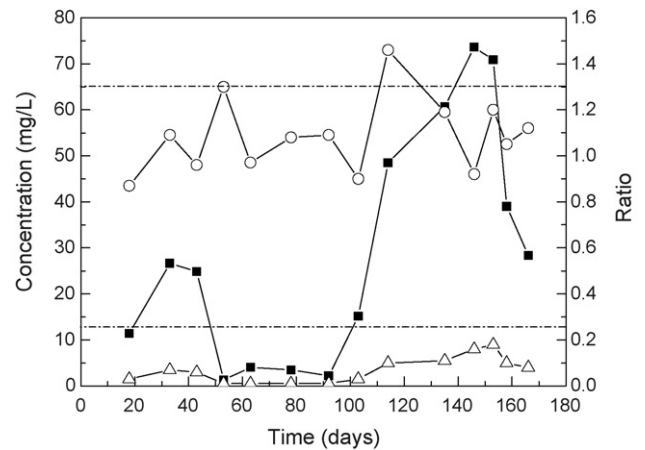


Fig. 7. Ratios of ammonium and nitrite degradation and the nitrate production (\blacksquare , $\text{NO}_3^-\text{-N}$ (eff); \circ , ratio of removed $\text{NO}_2^-\text{-N}$ to removed $\text{NH}_4^+\text{-N}$; \triangle , ratio of produced $\text{NO}_3^-\text{-N}$ to removed $\text{NH}_4^+\text{-N}$).

than 100 mg/L can completely inhibit the process [28]; at concentrations of nitrite more than 18 mM the Anammox activity is completely inhibited [14]; 25 mM nitrite corresponds to the 50% inhibition concentration and 50 mM acetate results in 70% inhibition percentage [29]; phosphate (5–50 mM) has strong inhibition of Anammox activity, and 50 mM KCl or 40 mM KHCO_3 has no effect on Anammox [27]; low oxygen concentrations have reversible inhibition of Anammox, but higher oxygen concentrations have irreversible inhibition (18% of oxygen saturation) [14]; 2 mM sulfide and 1 mM sulfite have active effect [27]. From these results, it has been suggested that nitrite exerts the highest inhibitory effect on the activity of Anammox microorganisms, and the nitrite concentration in an Anammox reactor must be strictly controlled to avoid inhibition of the process [29].

Based on the above literature, the following analyses suggested that nitrite made greatest adverse effect on the Anammox process in this study: (1) average concentration of $\text{NO}_2^-\text{-N}$ in the influent of AR was 698 mg/L, and sometimes it was as high as 1011 mg/L; (2) fulvic-like compound was the main organic matter in the influent of AR, which should have little adverseness to Anammox activity; (3) alkalinity (Na_2CO_3) in the raw leachate

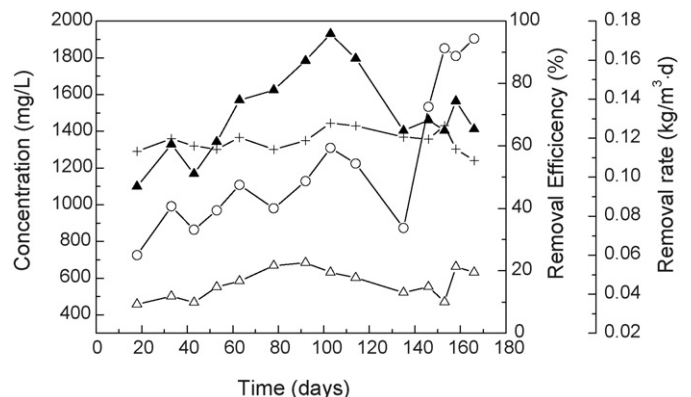


Fig. 8. Removal of TN in the AR (\blacktriangle , TN(in); \triangle , TN(eff); +, $R(\text{TN})$; \circ , removal rate).

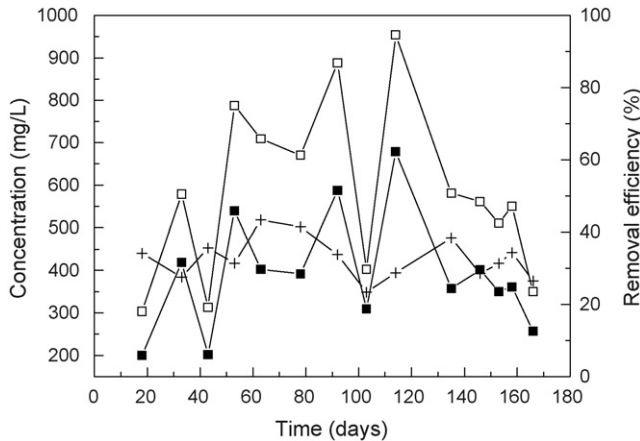


Fig. 9. Removal of COD_{Cr} in the AR (\square , $\text{COD}_{\text{Cr}}(\text{in})$; \blacksquare , $\text{COD}_{\text{Cr}}(\text{eff})$; $+$, $R(\text{COD}_{\text{Cr}})$).

was consumed a lot in the PNR, and the remaining Na_2CO_3 should be inorganic C-resource of Anammox microorganism; (4) the AR was fully airproofed to maintain the anaerobic condition; (5) concentration of phosphate in the leachate was fairly low; (6) concentrations of heavy metals in the raw leachate were so low as to have little inhibitions.

Anammox process is used to treat synthetic wastewater with 70–840 $\text{mg NH}_4^+\text{-N/L}$ and 70–840 $\text{mg NO}_2^-\text{-N/L}$, and maximum nitrogen conversion capacity (0.7 $\text{kg NH}_4^+\text{-N}/(\text{m}^3\cdot\text{d})$ and 1.5 $\text{kg TN}/(\text{m}^3\cdot\text{d})$) is obtained [30]. In an Anammox fluidized bed reactor at maximum loading rate of 0.43 $\text{kg NH}_4^+\text{-N}/(\text{m}^3\cdot\text{d})$, influent with 267 $\text{mg NH}_4^+\text{-N/L}$ and 227 $\text{mg NO}_2^-\text{-N/L}$ is treated, and about 0.33 $\text{kg NH}_4^+\text{-N}/(\text{m}^3\cdot\text{d})$ removal rate is acquired [31]. Compared with these results, both loading rate and removal rate of nitrogen in the AR were relatively low in this study. That high-strength nitrite made great inhibition of Anammox activity should be the main reason.

No matter how much COD_{Cr} was in the influent of AR (from 303 to 954 mg/L), part of COD_{Cr} was removed with removal efficiencies of 23–41% during the 166-day operating period (Fig. 9).

Furthermore, COD_{Cr} removal seemed to have no correlation with the nitrogen removal and variation of N_v . There was no doubt that almost all biodegradable organics could be degraded in the PNR, and that there should be only refractory organics like fulvic compound remaining in the effluent. Therefore, it could be inferred that removed organics in the AR should mainly be fulvic-like material. Because fulvic-like material is aquatic humic substance (AHS) [32], it can be determined by means of the analysis of AHS. Because the analysis of AHS was time-consuming, only six sets of samples were analyzed. Six sets of data were ranked according to the concentration (Fig. 10(a)). As illustrated in Fig. 10(a and b), both AHS and TOC in the effluent from PNR always were partly removed in the AR with average removal efficiencies of 35 and 36%, respectively, which suggested that the removed AHS was certainly mineralized, if not, TOC could not simultaneously removed. Furthermore, the percentages of the AHS removed/the TOC removed were all above 75% (Fig. 10(c)), suggesting that the removed TOC was mainly AHS in the AR.

Denitrifier could not directly use fulvic-like material for denitrification, and Anammox microorganism, autotrophic bacterium, did not need it. Therefore, other microorganism might biodegrade it. There were two possible mechanisms for the mineralization of fulvic-like material: (1) it was directly mineralized by some kinds of heterotrophs; (2) it was firstly degraded into readily biodegradable organic matter by some kinds of heterotrophs, and then was utilized by denitrifier. According to the nitrogen removal (Figs. 6 and 7), average removed $\text{NO}_2^-\text{-N}$ was 449.3 mg/L ; average removed $\text{NH}_4^+\text{-N}$ was 414.7 mg/L and average produced $\text{NO}_3^-\text{-N}$ was 29.3 mg/L . $\text{NH}_4^+\text{-N}$ removal was certainly ascribed to Anammox, which needed 414.7 $\text{mg NO}_2^-\text{-N/L}$ as electron receiver and converted 29.3 $\text{NO}_2^-\text{-N mg/L}$ into $\text{NO}_3^-\text{-N}$. Therefore, only 5.3 $\text{mg NO}_2^-\text{-N/L}$ was possibly denitrified (needing 9.1 mg/L C-resource), which accounted for 1.2% of total removed $\text{NO}_2^-\text{-N}$. Based on the average TN removal efficiency of 62% (Fig. 8) and average $\text{NH}_4^+\text{-N}$ removal efficiency of 60% (Fig. 6), it could be inferred that the removed TN ascribed to Anammox accounted for 97%.

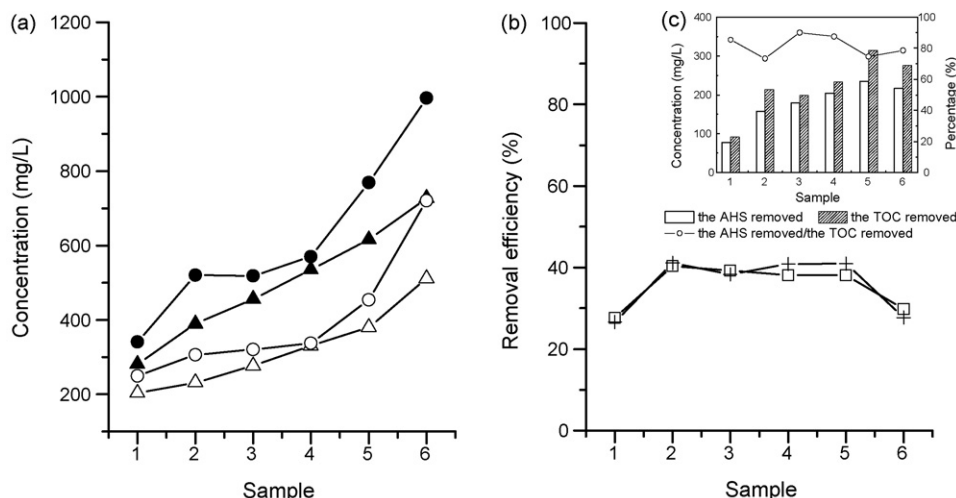


Fig. 10. Removals of AHS and TOC in the AR (\blacktriangle , AHS(in); \triangle , AHS(eff); \bullet , TOC(in); \circ , TOC(eff); \square , $R(\text{AHS})$; $+$, $R(\text{TOC})$).

These results implied that Anammox was dominant over denitrification for the nitrogen removal in the AR, and that organic matter consumed for denitrification was in a quite small quantity. Therefore, the AHS removal should be ascribed to the first possible mechanism.

3.3. USIS

According to batch tests of soil column (not shown here), hydraulic loading rate (HLR) and pollutant loading rate (PLR) were important factors influencing performance of soil treatment system. Relatively high loading rates could not maintain stable running for the long term; relatively low loading rates would demand much soil. The feasible HLR was below $0.05 \text{ m}^3/(\text{m}^3 \cdot \text{d})$ (3.2 cm/d) and PLRs were as follows: $\text{NH}_4^+ \text{-N} \leq 9.9 \text{ g}/(\text{m}^3 \cdot \text{d})$, $\text{TN} \leq 21 \text{ g}/(\text{m}^3 \cdot \text{d})$, and $\text{COD}_{\text{cr}} \leq 9.9 \text{ g}/(\text{m}^3 \cdot \text{d})$. The operational mode was that two soil infiltration systems ran alternately to treat the effluent of AR, and the cycle was 1 month. In this study, these operational conditions and operational mode were applied and verified in the 166-day continuous running.

During the whole running period (Fig. 11), both USIS-1 and USIS-2 ran two cycles. In the first cycle, HLR was maintained at $0.02 \text{ m}^3/(\text{m}^3 \cdot \text{d})$, and PLRs varied with the effluent quality from the AR: (1) the loading rates of both $\text{NH}_4^+ \text{-N}$ and TN were relatively steady, and were about 5.0 and $9.5 \text{ g}/(\text{m}^3 \cdot \text{d})$, respectively; (2) the COD_{cr} loading rate varied at $3.4\text{--}9.8 \text{ g}/(\text{m}^3 \cdot \text{d})$. In the second cycle, HLR increased gradually from 0.2 to $0.4 \text{ m}^3/(\text{m}^3 \cdot \text{d})$; the loading rates of both $\text{NH}_4^+ \text{-N}$ and TN were gradually elevated from 4.5 and 9.1 to 14.0 and $24.8 \text{ g}/(\text{m}^3 \cdot \text{d})$, respectively,

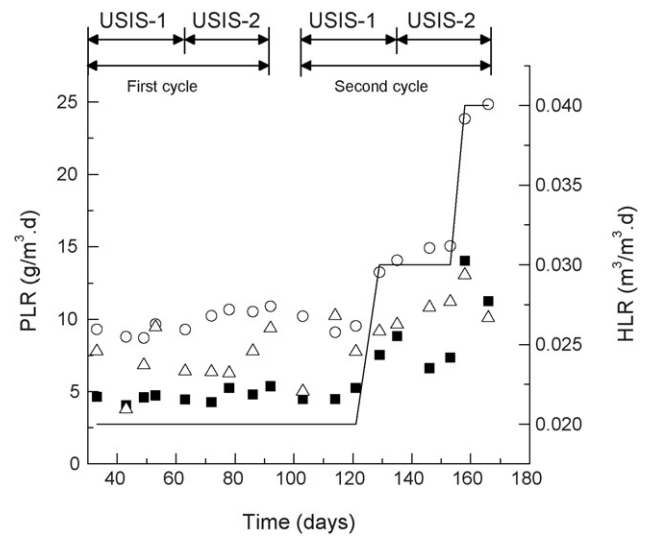


Fig. 11. HLR and PLR in the USIS during the running period (■, $\text{NH}_4^+ \text{-N}$; ○, TN; △, COD_{cr} ; —, HLR).

the COD_{cr} loading rate varied at $5\text{--}13 \text{ g}/(\text{m}^3 \cdot \text{d})$. According to Fig. 12(a and b), during the two cycles, the removals of $\text{NH}_4^+ \text{-N}$ and $\text{NO}_2^- \text{-N}$ were quite steady with high removal efficiencies, and $\text{NH}_4^+ \text{-N}$ and $\text{NO}_2^- \text{-N}$ in the effluent were averagely 32 and 3.9 mg/L with average removal efficiencies of 88 and 98% , respectively. However, the treatment capabilities for TN and COD_{cr} were weakened in the second cycle. Average concentration of TN in the effluent increased from 176 mg/L in the first cycle to 211 mg/L in the second cycle; average concentra-

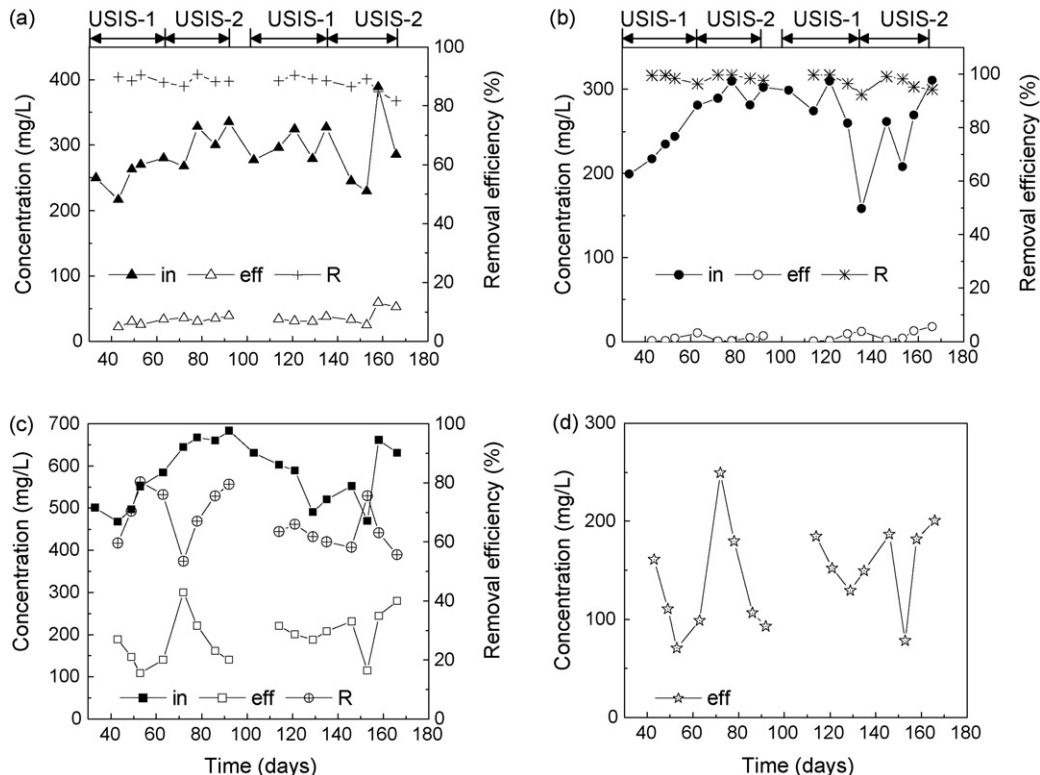


Fig. 12. Variation of nitrogen in the effluent of USIS. (a) $\text{NH}_4^+ \text{-N}$; (b) $\text{NO}_2^- \text{-N}$; (c) TN; (d) $\text{NO}_3^- \text{-N}$.

Table 6
Average removal efficiencies of landfill leachate by the combined process

Reactor	Removal efficiency			Percentage of nitrite accumulation (%)
	NH ₄ ⁺ -N %	TN %	COD _{cr} %	
PNR	64	30	69	>95
AR	60	62	32	
USIS	88	67	55	
Combined process	97	87	89	

tion of COD_{cr} in the effluent increased from 174 mg/L in the first cycle to 194 mg/L in the second cycle (Figs. 12(c) and 13). The increases of HLR and PLR in the second cycle should be the main reasons, and the results were consistent with those in batch tests, indicating that feasible operating conditions obtained from soil column tests should be followed. These results also suggested that the increases of HLR and PLR had obviously negative influences on the removals of TN and COD_{cr} and had little influences on the removals of NH₄⁺-N and NO₂⁻-N. Therefore, the removals of TN and COD_{cr} seemed to be the keys to the USIS. Almost all NO₂⁻-N from the AR effluent was removed and converted to NO₃⁻-N to obtain safe discharge (Fig. 12(d)). However, denitrification of NO₃⁻-N was limited because of the insufficiency of biodegradable C-resource, resulting in relatively low removal efficiency of TN.

After being fed, soil firstly adsorbed refractory organic matter, and then adsorbed organic matter was gradually converted into low-molecular-weight matter by microorganism, which was easily utilized by denitrifier and other heterotrophs; therefore, removal efficiency of COD_{cr} always gradually decreased because of adsorption saturation. Herein, after being fed for 30 days, one USIS stopped running, and then adsorbed refractory organic matter was degraded in another 30 days in order to acquire the resume of adsorption capability. As shown in Fig. 13, removal efficiency of COD_{cr} in USIS-1 was about 50% at the end of the first cycle ($t = 63$ days), and after 30-day rest, it was

resumed to 66% at the beginning of the second cycle ($t = 114$ days); removal efficiency in USIS-2 was 42% at the end of the first cycle ($t = 92$ days), and after 30-day rest, it was resumed to 64% at the beginning of the second cycle ($t = 146$ days).

3.4. Treatment for leachate by the combined process

Treatment results of the combined process for landfill leachate are listed in Table 6. About 86% NH₄⁺-N, 73% TN and 79% COD_{cr} in landfill leachate were removed in partial nitrification-Anammox process, and the purification of the remaining pollutants was accredited to the USIS. Overall, the raw leachate with 1430–2720 mg NH₄⁺-N/L, 1524–2912 mg TN/L and 1165–2599 mg COD_{cr}/L was treated by the combined system, and the effluent with 22–58 mg NH₄⁺-N/L, 108–300 mg TN/L and 32–250 mg COD_{cr}/L was obtained. Average removal efficiencies were 97% NH₄⁺-N, 87% TN and 89% COD_{cr}. Effective treatment for the landfill leachate was accomplished.

The test results showed that the advisable operating conditions could ensure stable work of the system over a long period. Certainly, these conditions would be expected to vary with leachates of different landfill sites and different ages. Compared with the other processes, the system offered effective removals of high concentrations of ammonium and organics with relatively low energy consumption, however, removals of TN and COD_{cr} should be improved. Therefore, further studies should be made for full-scale implementation of the combined process.

4. Conclusions

The municipal landfill leachate obtained from an old-aged landfill site was treated using a combined process including partial nitrification-Anammox and underground soil infiltration system. The test results from 166-day continuous running revealed the following information.

- (1) Under the conditions of this study, it was possible to operate the combined process on a long-term basis and to accomplish the effective treatment for the leachate. Average removal efficiencies with 97% NH₄⁺-N, 87% TN and 89% COD_{cr} were obtained.
- (2) Ammonium loading rate and DO were excellent parameters for monitoring partial nitrification. An anticipant of nitrite/ammonium ratio close to 1.0–1.3 in the effluent could

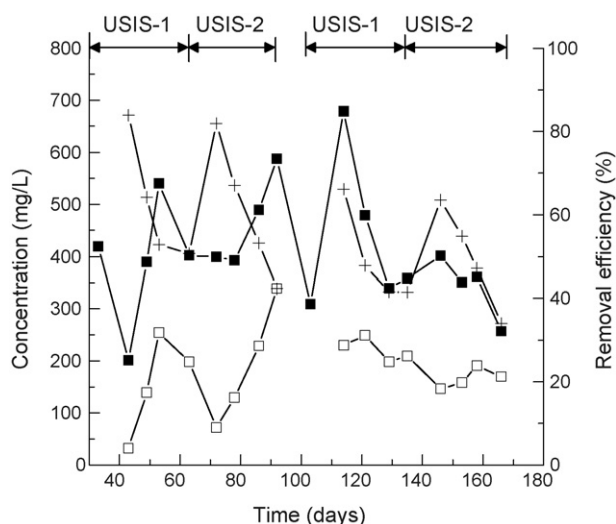


Fig. 13. Removal of COD_{cr} in the USIS (■, in; □, eff; +, R).

be acquired by controlling them. Ammonium oxidizing bacteria in the PNR seemed to be acclimated to high FA level of 160–260 mg/L so that nitrification was not inhibited.

- (3) About 60% $\text{NH}_4^+\text{-N}$ and 64% $\text{NO}_2^-\text{-N}$ were simultaneously removed in the AR. Although denitrification might occur in the AR, 97% of the removed TN was ascribed to Anammox. Nv up to 0.16 kg/(m³·d) could result in obvious fall of nitrogen removal rate. Inhibition of high-strength $\text{NO}_2^-\text{-N}$ (as high as 1011 mg/L) should be responsible for the relatively low removal rate of nitrogen. It was interesting that average 35% removal efficiency of AHS was obtained in the AR.
- (4) Two soil infiltration systems ran alternately to treat the effluent of AR, and one cycle was about 30 days. On an average, 88% $\text{NH}_4^+\text{-N}$ and 98% $\text{NO}_2^-\text{-N}$ in the effluent from AR were converted into $\text{NO}_3^-\text{-N}$ in the USIS, and safe discharge was acquired. Increases of HLR and PLR exerted more influence on the removals of TN and COD_{Cr} than on those of $\text{NH}_4^+\text{-N}$ and $\text{NO}_2^-\text{-N}$, indicating that removals of TN and COD_{Cr} were the key in the USIS.
- (5) Of the three units, AR should be the key to the performance of the combined process. For the purpose of full-scale application of the integrated process, two major issues remained to be solved in the further studies: how to reduce inhibition of high-concentration $\text{NO}_2^-\text{-N}$ to Anammox microorganism and how to improve the loading rate and removal rate in the AR.

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