

Comparison of SBR and SBBR: the effect of aeration DO, delay aeration, pre-denitrification, temperature, and inf. C/N on nitrogen removal from landfill leachate

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ABSTRACT

In this experiment, the pre-denitrification sequencing batch reactor (SBR) and pre-denitrification sequencing batch biofilm reactor (SBBR) biotechnologies were used to deal with landfill leachate. The experiment focused on the effects of operating factors (aeration dissolved oxygen (DO), delay aeration, pre-denitrification, temperature, and inf. C/N) on nitrogen removal from landfill leachate in both biotechnologies. The results of the experiment showed that when the initial influent concentration (inf.-con.) of chemical oxygen demand (COD) and total nitrogen (TN) were determined at approximately 4,500 and 1,100 mg/L, the final effluent concentration (eff.-con.) of COD and TN was 550 mg/L, <20 mg/L (in SBR) and 500 mg/L, <10 mg/L (in SBBR) after treatment. It was worth noting that the denitrification rate in both biotechnologies performed better than that of COD removal. As for TN, the denitrification rate (98%, <20 h) in SBBR was superior to (93%, <24 h) in SBR. The following five operating factors act on nitrogen removal. They are aeration DO \approx 3 mg/L mode, without delay aeration mode, pre-denitrification (60 min) mode, temperature (30°C) mode, and inf. C/N \approx 4:1 mode, which favors the operating because the denitrifying bacteria could store and utilize more polyhydroxyalkanoate to remove nitrogen in these modes. The ability of the SBBR system to resist severe operation mode was better than that of the SBR system due to the stability of biofilm.

Keywords: Landfill leachate treatment; Aeration DO; Delay aeration; Pre-denitrification; Temperature

1. Introduction

Landfill, which was prone to generate landfill leachate due to the combination of rainfall percolate and organic wastes decomposition, is widely used for solid waste treatment at present in China [1]. Landfill leachate is the dark brown toxic pollutant characterized by a high concentration of organics, $\text{NH}_4^+\text{-N}$, metal ions and other complex components [2,3]. Therefore, effective and reasonable treatment of landfill leachate for the avoidance of secondary pollution

to the surrounding environment has become an urgent problem to be solved in the urban environment.

The physical treatment technologies of landfill leachate included adsorption technology [4], membrane separation technology [5], advanced oxidation technology [6] and so on. The adsorption technology was suitable for treating the mature landfill leachate, but its high cost limits its application [7]. Although the membrane separation technology has certain advantages in the treatment of high concentration landfill leachate, it is not suitable for large-scale landfill

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leachate treatment due to its easy membrane pollution, concentration polarization, high investment and operation costs [8]. Advanced oxidation technology could degrade the refractory organics into the small molecular weight substances in the landfill leachate treatment. Nevertheless, it has the disadvantages of high equipment investment cost and secondary pollution [9].

Biological treatment technologies of landfill leachate are the most economical and effective technologies, which can be the sort of aerobic, anaerobic as well as bio-combination biotechnologies. The typical biotechnologies includes sequencing batch reactor (SBR) [10], sequencing batch biofilm reactor (SBBR) [11], membrane bio-reactor (MBR) [12], up-flow anaerobic sludge bed (UASB) [13], anaerobic sequencing batch reactor (ASBR) [14], anaerobic/aerobic (A/O) [15], denitrification-partial-nitrification-Anammox (DN-PN-Anammox) [16] and UASB-A/O [17]. Many researchers have studied the removal rates of COD and nitrogen with these biotechnologies. Boonnorat et al. [12] demonstrated that the removal rates of chemical oxygen demand (COD) and nitrogen were 80%–85% and 80%–95% respectively in MBR when sludge retention time was 90 d. Selvam et al. [18] observed that the removal rate of COD was higher than 80% in UASB. Li et al. [16] combined the DN-PN-Anammox process with a dual recycling system to remove nitrogen from mature landfill leachate. Although biotechnologies were more economical and environmentally friendly than physical and chemical technologies, there are still some shortcomings in biotechnologies. Most of all are that anaerobic biotechnologies can't remove ammonia efficiently [19]. However, the traditional biological aeration treatment alone can't deal with landfill leachate efficiently, and its effluent needs to be further treated by advanced treatment technology. Combined with aerobic and anaerobic biotechnologies, bio-combination technologies made up for the shortcoming of both to some extent, while their shortcomings are complex process operations and high infrastructure investment. Therefore, further upgrading and improving the operating modes or operating conditions of aerobic biotechnology are the key point for landfill leachate treatment.

Many studies indicated that different operating modes (pre-denitrification, delayed aeration) and operating conditions (temperature, DO, inf. C/N) would affect the effluent quality and operating efficiency in biotechnologies. For example, Zhu et al. [20] have studied the advanced treatment of landfill leachate by different inf. C/N in SBR; Zhang et al. [21] have used the simultaneous partial nitrification anammox and denitrification (SNAD) with intermittent aeration to treat old landfill leachate; Yin Wang and et al. [10,22] have employed pre-denitrification SBR and pre-denitrification SBBR respectively to achieve the advanced denitrification of landfill leachate without adding any additional carbon source; Wen et al. [23] have discussed the average total nitrogen removal efficiency under different dissolved oxygen levels (1.0, 2.0, 2.7 and 3.5 mg/L) in SBBR; Sun et al. [24] have investigated the effect of different temperatures on landfill leachate treatment in aerobic granules; Miao et al. [25] have discussed the nitrogen removal of landfill leachate by endogenous denitrification under different denitrification carbon sources. However, there is no report about the comparison between pre-denitrification

SBR and SBBR and various parameters optimization for the treatment of landfill leachate.

In this experiment, the pre-denitrification SBR and pre-denitrification SBBR biotechnologies were used to efficiently and economically treat landfill leachate to increase the utilization rate of raw water carbon sources. In addition, this experiment not only compared with their total nitrogen (TN) and COD removal rates of landfill leachate but also analyzed their removal mechanism. The effects of variables on nitrogen removal from landfill leachate such as aeration DO, delay aeration, pre-denitrification, temperature, and inf. C/N was discussed in detail for the seeking of optimal operating conditions.

2. Materials and methods

2.1. Landfill leachate and inoculation sludge

The landfill leachate obtained from the Jiyang landfill (Jinan, Shandong, China, 117°12'N, 36°58'E) was stored in the refrigeration house (−4°C) to inhibit the degradation of organics. The characteristics of landfill leachate were detected by detection methods of 2.4, and the conventional water quality indexes of landfill leachate were as follows: con. COD 6,500–7,000 mg/L, con. BOD₅ 4,510–5,000 mg/L, con. NH₄⁺-N 950–1,100 mg/L, con. NO₂⁻-N <1.0 mg/L, con. NO₃⁻-N <1.0 mg/L, con. TN 1,000–1,200 mg/L, and pH 8–8.5. The inoculation sludge was the whole-process-nitration-reaction sludge, obtained from everbright sewage treatment plant (Anaerobic-Anoxic-Oxic, A²O) in Jinan, China. The treated water quality indexes of the sewage plant were as follows: con. TN ≈ 63 mg/L and con. COD ≈ 500 mg/L. Other characteristics of inoculation sludge were MLSS (mixed liquid suspended solids) = 8.57 g/L, MLVSS (mixed liquor volatile suspended solids) = 6.22 g/L, and SVI (sludge volume index) = 105 mL/g.

2.2. Experimental equipment

As shown in Figs. 1a and b, the SBR and SBBR experimental equipment were laboratory-scale cylinders made of polymethyl methacrylate with an effective volume of 10 L (dimension: 20 cm (internal diameter) × 70 cm (height)). The equipment was equipped with a stirring system (stirrer, electric machine), aeration system (air diffuser, air compressor), temperature control system (heating belt, temperature control box) and monitoring system (pH, DO, oxidation-reduction potential (ORP), and temperature analyzer).

The carriers of the SBBR system were composed of the polyurethane and other polymer materials in Fig. 1c. The carriers' characteristics were as follows: edge length = 10 ± 1 mm, density = 12.5 ± 0.7 kg/m³, surface area = 4,000–5,000 m²/mg, and hanging film time = 3–7 d. The carrier fill ratio of the SBBR ($V_{\text{carrier}}/V_{\text{reactor}}$) was approximately 30%.

2.3. Batch experiment design

Batch experiments included: start-up experiment and stable operation experiment and effect experiment of different operational factors (aeration DO delay aeration,

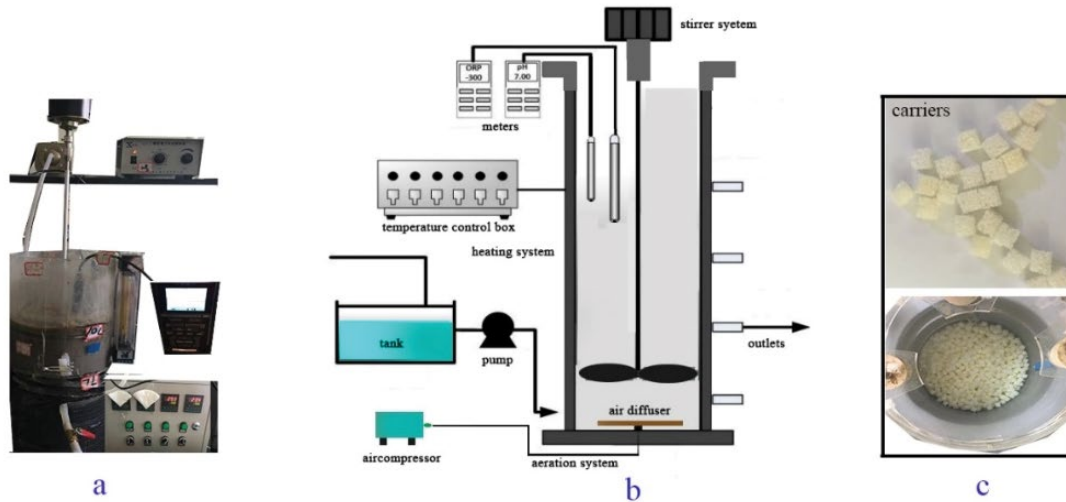


Fig. 1. Experimental equipment: (a) physical device, (b) model graph, and (c) carriers of SBBR.

pre-denitrification, temperature, and inf. C/N) on nitrogen removal. The operation mode (I–VI) of the batch experiments is shown in Fig. 2: filling stage → pre-denitrification stage → aeration stage → endogenous denitrification stage → settling stage → effluent stage. Each typical cycle was controlled within 24 h, and the operational time of the filling stage, the settling stage and effluent stage were 5, 30, and 5 min, respectively. The endpoints of the aeration stage (nitrification reaction), endogenous denitrification stage (endogenous denitrification reaction) were determined by ammonia valley point (A, pH variation), and nitrate knee point (B, ORP variation) are in Fig. 3 (Supplementary material) [11,26]. The volumetric exchange ratio of SBR and SBBR system was 30% and the stirring speed was controlled at around 200 rpm.

The start-up and stable operation experiment adopted operation mode I in Fig. 2a: pre-denitrification time = 60 min, aeration DO \approx 2.5 mg/L, delay aeration time = 0 min, temperature \approx 30°C, and inf. C/N \approx 4:1. The active sludge of the stable phase (in start-up and stable operation experiment) was used as an experimental sludge for effect experiment of different operational factors on nitrogen removal. The aeration DO effect experiment adopted operation mode II: (a) DO \approx 1; and (b) 3 mg/L in the aeration stage in Fig. 2b. The delay aeration effect experiment adopted operation mode III: (a) delay aeration (60 min) and (b) without delay aeration (0 min) in Fig. 2c. The pre-denitrification effect experiment adopted operation mode IV: (a) pre-denitrification (60 min) and (b) without pre-denitrification (direct aeration) in Fig. 2d. The temperature effect experiment adopted operation mode V: (a) temperature \approx 10°C and (b) temperature \approx 30°C in Fig. 2e. The inf. C/N effect experiment adopted operation mode V: inf. C/N \approx 5:1 (a) → 4:1 (b) → 3:1 (c) → 4:1 (d) in Fig. 2f.

2.4. Analytical methods

The pH, DO, ORP, and temperature were monitored using WTW 3620 oxygen and pH meters (WTW company, Germany). Water samples were filtered through 0.45 μ m

filter paper for the $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, COD analysis. The various indexes of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$, COD, MLSS, MLVSS, and SVI were conducted using standard methods [27]. TN was analyzed by using a TN analyzer (Multi N/C3000, Germany). The content of polyhydroxyalkanoate (PHA) was determined by gas chromatography, and the value was calculated using Eqs. (1) and (2) [28].

$$Y(\text{PHA}) = \frac{\text{PHA}(\text{mg OOD})}{X(\text{g OOD}) + \text{PHA}(\text{g OOD})} \quad (1)$$

$$X = \text{DW}(\text{g OOD}) - \text{PHA}(\text{g OOD}) \quad (2)$$

The three-sample *t*-test was used to evaluate the significant differences between the samples. It is considered to be statistically significant when the value of *P* is lower than 0.05.

3. Results and discussion

3.1. Start-up and stable operation

The toxic substances and high concentration pollutants contained in the landfill leachate would poison the activated sludge and biofilm directly. Thus, the start-up and stable operation experiment adopted the influent load progressive increase method to achieve advanced treatment of the raw landfill leachate in the SBR and SBBR system. The whole experiment operating period was 110 d, including the start-up period (I) and a stable period (II). As shown in Fig. 4, the SBR and SBBR systems finally achieved advanced denitrification of landfill leachate within 90–110 d.

The water quality indexes variations of start-up and stable operation periods in the SBR and SBBR system are shown in Fig. 4. As shown in Fig. 4a, the inf. con. COD gradually increased from 300 to 4,500 mg/L (inf. C/N \approx 4:1). There was a little difference between SBR and SBBR in the removal of organic matter. It can be seen that the final eff. con. COD was maintained at about 550 mg/L, and the effluent organics of

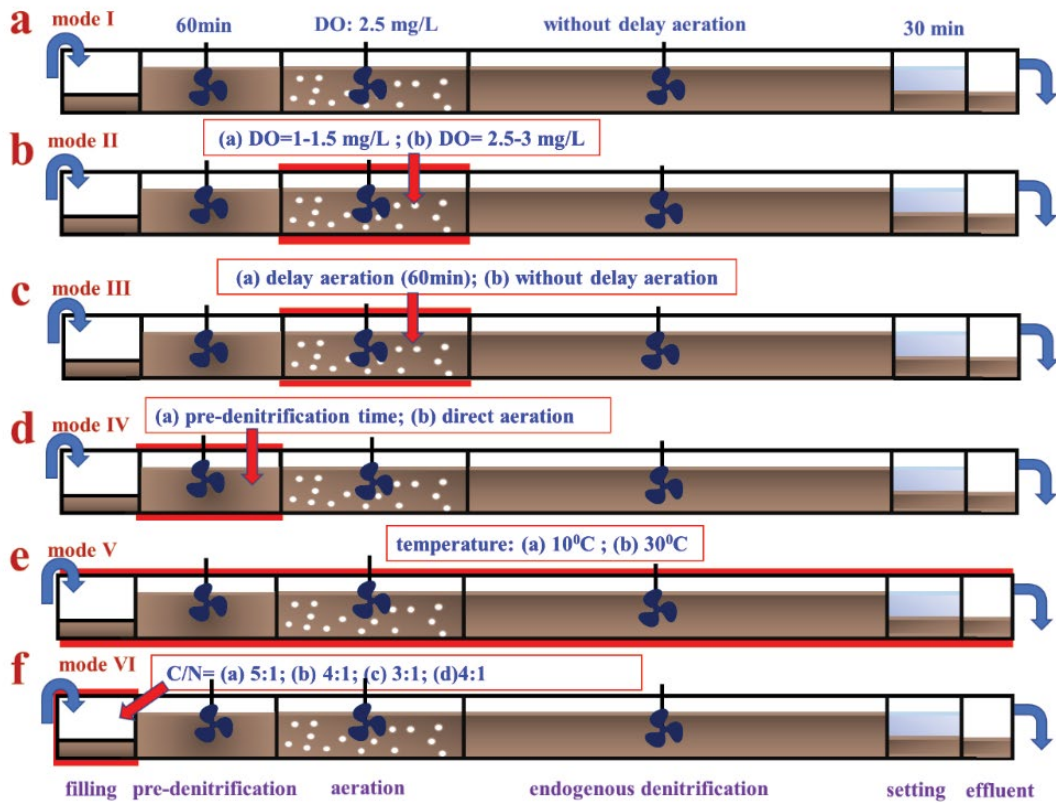


Fig. 2. Different operational modes: (a) startup-stability operation experiment mode I, (b) aeration DO affect experiment mode II, (c) delay aeration experiment mode III, (d) pre-denitrification effect experiment mode IV, (e) temperature effect experiment mode V, and (f) inf. C/N effect experiment mode VI.

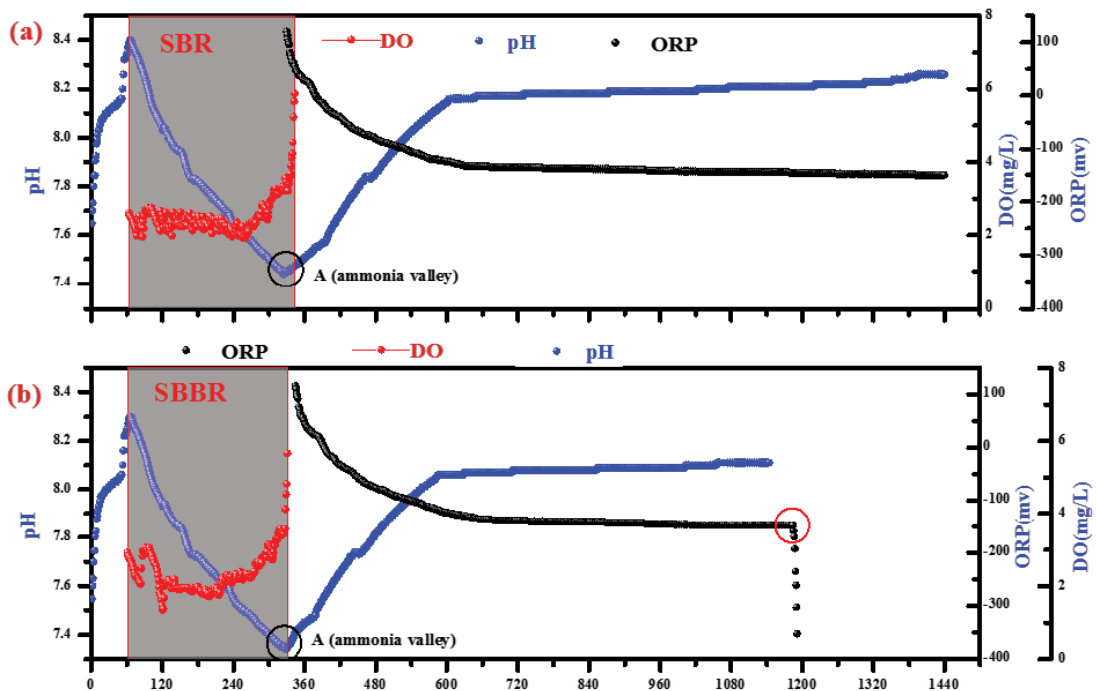


Fig. 3. Ammonia valley and nitrate knee of a typical cycle in (a) SBR and (b) SBBR.

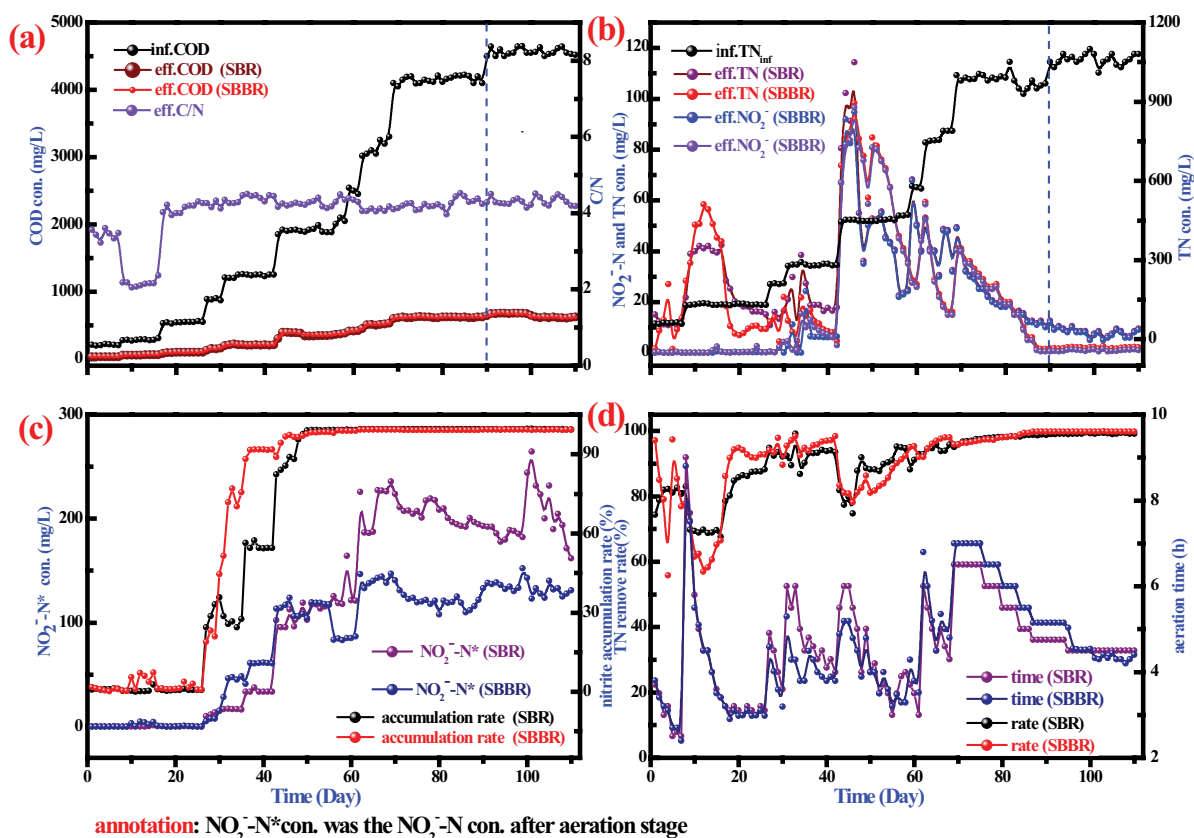


Fig. 4. Water quality indexes variations of start-up and stable operation periods in SBR and SBBR systems: (a) COD con. (mg/L) vs. C/N, (b) NO₂-N and TN con. (mg/L) vs. TN con. (mg/L), (c) NO₂-N* con. (mg/L) vs. nitrite accumulation rate (%) and (d) TN remove rate (%) vs. aeration time (h).

the system at this moment may come from refractory organics of landfill leachate such as humus [29].

It can be known from Fig. 4b that the inf.-con. TN was finally maintained at approximately 1,100 mg/L. The trends of eff.-con. NO₂-N in SBR and SBBR systems increased firstly and then decreased. The reasons can be mainly ascribed to the following: (1) the con. NO₂-N* (NO₂-N after aeration stage) was extremely low because the nitrification reaction at the preliminary stage of the start-up period (I) was the whole-run nitrification reaction; (2) the con. TN, con. FA (free ammonia) [30] and con. poisonous substances [31] increased with the landfill leachate inf. load and ammonia-oxidizing bacteria (AOB) gradually eliminated as well as nitrite-oxidizing bacteria became the dominant nitrobacterium [32]. In addition, short-range nitrification gradually replaced the whole-run nitrification reaction and became the leading nitrification reaction. Therefore, as the con. NO₂-N* gradually increased to nearly 100% owing to the accumulation of nitrite, the con. NO₃-N* (NO₃-N after aeration stage) gradually decreased to approximately 0 mg/L in Fig. 4c; (3) the steady denitrification reaction reduced eff.-con. NO₂-N. The final-eff.-con. TN was gradually maintained below 20 mg/L (in SBR (< 20 mg/L) and SBBR (< 10 mg/L) system). It is obvious that the TN removal rate of SBBR (≈98%) was higher than that of SBR (≈3%) in a stable period (II) from Fig. 4d. The reason may be that simultaneous nitrification and denitrification (SND) in the biofilm

anaerobic zone resulted in the lower con. NO₂-N* of SBBR than that of SBR [33,34].

The mechanism of nitrogen removal in SBBR was shown in Fig. 5. Firstly, the special denitrifying bacteria with the PHA synthesis function [35] (denitrifying bacteria*) could convert organics into intracellular PHA in the pre-denitrification stage. Secondly, the short-range nitrification (removal of ammonia nitrogen) and SND (removal of NO₂-N) would occur simultaneously in the aeration stage. Lastly, the denitrifying bacteria* that stored PHA could remove NO₂-N* by endogenous denitrification reaction [36] in the endogenous denitrification stage. Hereto, the SBBR system finally realized the advanced denitrification of leachate. In conclusion, SBBR was better than SBR in treating landfill leachate because there was no biofilm anaerobic zone in the SBR system compared with the SBBR system. The variations of nitrogen and carbon during in the typical cycle of the stable period (II) in Fig. 6 also showed that the nitrogen removal rate and denitrification rate of SBBR was better than that of SBR.

3.2. Effect of different operating factors on nitrogen removal

The aeration DO, delay aeration, pre-denitrification, temperature, and inf. C/N were the important factors affecting the nitrogen removal from landfill leachate in the SBR and SBBR systems, so the study of the nitrogen removal effect experiment by different operational factors was of great

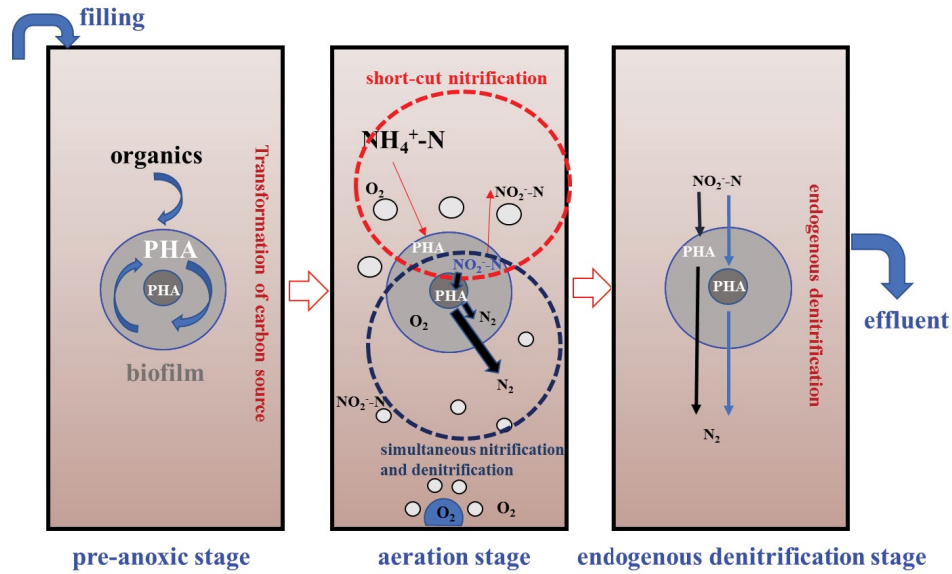


Fig. 5. Mechanism of nitrogen removal in the SBBR system.

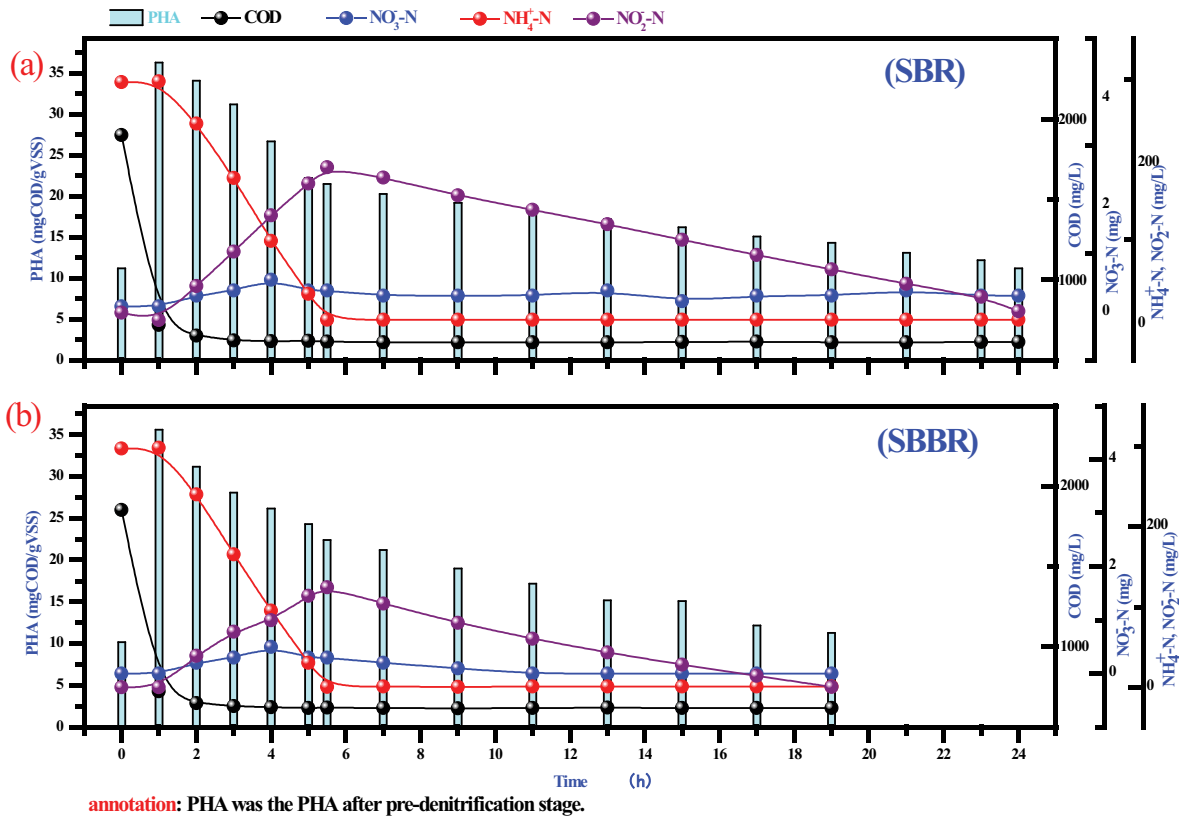


Fig. 6. The variations of nitrogen and carbon during in typical cycle of the stable period (II): (a) SBR and (b) SBBR.

significance. The activated sludge with stable denitrification effect (after 110 d of start-up and stable operation periods) was used in the batch tests. According to different operational factors in SBR and SBBR systems, the nitrogen removal effect experiment was explored by investigating the changes of $\text{NH}_4^+\text{-N}$, $\text{NO}_2^-\text{-N}$ and PHA* content in sludge.

3.2.1. Aeration DO

Different aeration DO correspond to different aeration duration, which also has a certain impact on nitrogen removal, [37]. Therefore, the change of aeration duration and the effect of aeration duration on nitrogen removal under

different DO modes (mode (II)-a: DO = 1 mg/L; mode (II)-b: DO = 3 mg/L) were investigated by controlling the aeration amount. The effects of different aeration DO on nitrogen removal in SBR and SBBR systems are shown in Fig. 7. In the SBBR system, the PHA* content in mode (II)-b was greater than that of in mode (II)-a, while the con. $\text{NO}_2^- \text{-N}^*$, eff.-con. $\text{NO}_2^- \text{-N}$ and aeration duration in mode (II)-b were lower than that of in mode (II)-a. Moreover, as for removal time, the SBBR system has achieved advanced nitrogen removal in mode (II)-b within the 20th h compared with mode (II)-a. The above results can be explained by the following reason. Longer aeration time would consume PHA stored in denitrifying bacteria* cells, and further, inhibit the endogenous denitrification reaction at the end phase of the endogenous denitrification stage due to the lack of carbon sources. The variations of PHA* content, $\text{NO}_2^- \text{-N}^*$ and other parameters in the SBR system also proved that mode (II)-a was not conducive to remove nitrogen from landfill leachate, and the reasons were similar to those in the SBBR system. Compared with the differences between SBBR and SBR systems in mode (II)-a, the eff. con. $\text{NO}_2^- \text{-N}$ of the SBBR system was lower than that of the SBR system, which may be because that biofilm contains abundant biomass (for example, nitrifying bacteria), and SND was found in biofilm anaerobic zone of SBBR system [38].

To sum up, mode (II)-b: DO = 3 mg/L was beneficial to the nitrification reaction, which ensures the PHA* content for endogenous denitrification reaction and further facilitates the advanced nitrogen removal in the SBR and SBBR systems.

3.2.2. Delay aeration

Delayed aeration can not only inhibit the nitrification reaction but also can consume the internal carbon source (PHA) stored in denitrifying bacteria*. Thus, it is significant to study the delay aeration effect on nitrogen removal

(mode (III)-(a): delay aeration (60 min)/mode (III)-(b): without delay aeration) in the SBR and SBBR systems. As shown in Fig. 8, the PHA* content in mode (III)-(b) was greater than that in mode (III)-(a). However, the con. $\text{NO}_2^- \text{-N}^*$ and eff. con. $\text{NO}_2^- \text{-N}$ in mode (III)-(b) was lower than in mode (III)-(a) in the SBBR system. The above results can be explained by the following two reasons: (1) delayed aeration had an adverse effect on nitrification reaction; (2) delayed aeration consumed the PHA content stored in denitrifying bacteria*. The variations of PHA* content, con. $\text{NO}_2^- \text{-N}^*$ and other parameters in the SBR system also proved that delayed aeration was not conducive to the advanced nitrogen removal, and the reasons were similar to those in the SBBR system. Meanwhile, the anti-delay aeration ability of the SBBR system was better than that of the SBR system in mode (III)-(a). The reason can be ascribed to the existence of the anaerobic zone in the SBBR biofilm system, which could promote the nitrogen removal by SND in mode (III)-(a) [23,39].

In conclusion, the endogenous denitrification time in mode (III)-(a) was far greater than that in mode (III)-(b). It can be seen that the adoption of real-time control and timely stop aeration system could not only save the aeration amount but also has important significance for the realization of advanced nitrogen removal in the SBR and SBBR systems.

3.2.3. Pre-denitrification

The denitrifying bacteria* can not only convert organics into intracellular PHA under hypoxia or anaerobic conditions but also can perform SND and endogenous denitrification by using PHA as carbon sources [25,40]. Compared with the traditional SBR and SBBR processes which the filling stage was followed directly by the aeration stage, the SBR and SBBR systems reported in this paper can make reasonable use of organics in raw landfill leachate under the condition of no additional carbon sources added. Due to the great merits

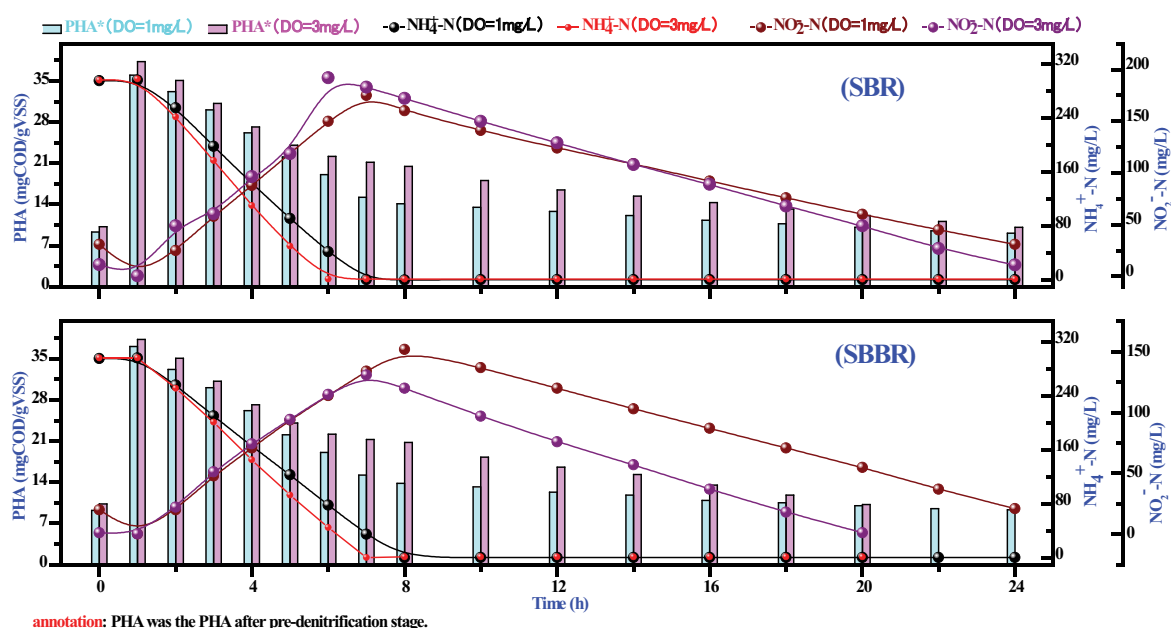


Fig. 7. Effect of different aeration DO on nitrogen removal.

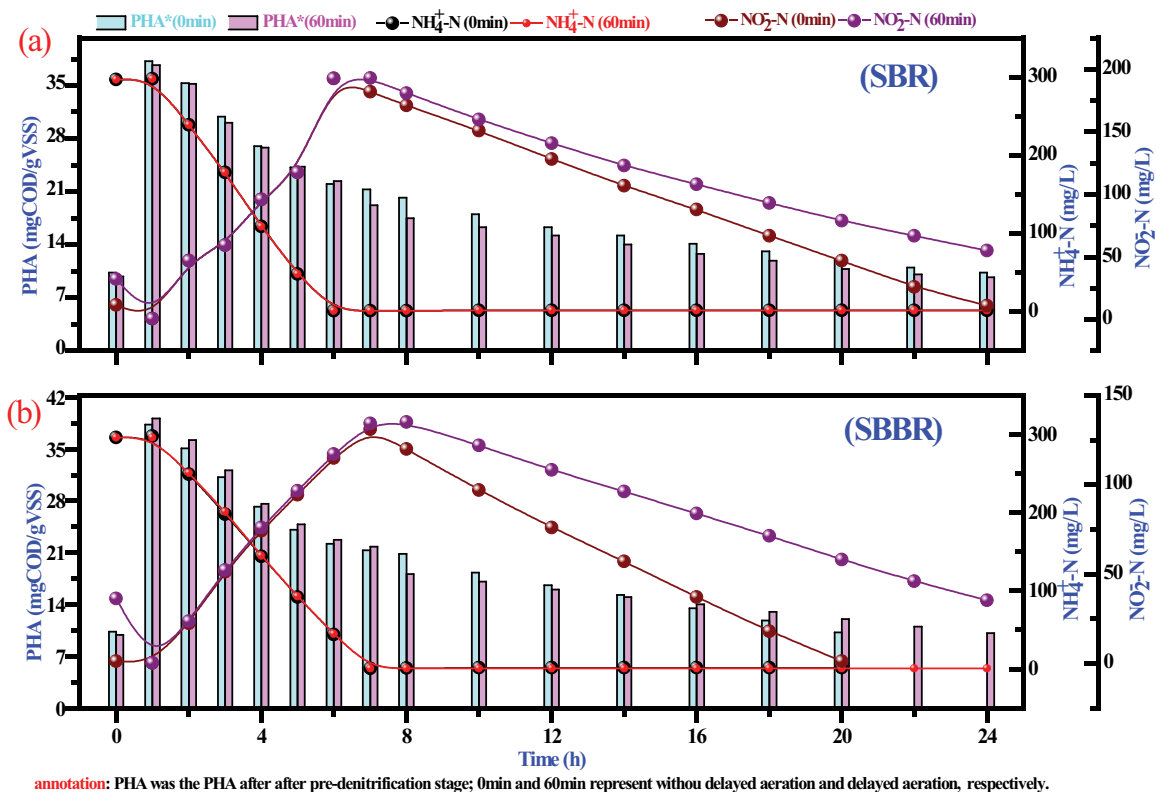


Fig. 8. Effect of delay aeration on nitrogen removal: (a) SBR and (b) SBBR.

of denitrifying bacteria*, the effect of pre-denitrification on nitrogen removal (mode (IV)-(a): pre-anoxic time (60 min)/ mode (IV)-(b): direct aeration) was investigated in the SBBR and SBR systems.

The effect of pre-denitrification on nitrogen removal in SBR and SBBR systems is shown in Fig. 9. In SBBR system, the aeration time of aeration phase in mode (IV)-(a) was later than that mode (IV)-(b), while the PHA content (before aeration phase) in mode (IV)-(a) was approximately 2.5 times than that of mode (IV)-(b). After aeration, the PHA* content in mode (IV)-(a) was about 40% higher than that in mode (IV)-(b), while the con. NO₂⁻-N* in mode (IV)-(a) was about 50 mg/L lower than that of in mode (IV)-(b). Therefore, the low PHA* content eventually led to the failure to realize the deep denitrification from landfill leachate in mode (IV)-(b). The reasons for the above results can be ascribed that the denitrifying bacteria* adsorbed a large number of organics in the pre-denitrification stage and converted them into PHA as well as a stored carbon source in the cell body. Owing to the less organics in the aeration stage, the heterotrophic bacteria were gradually eliminated by the dominant ammonia-oxidation bacteria and further made the nitrification reaction occurred rapidly [32,41]. In addition, it is more important than the decrease of PHA content at the end of the previous cycle would directly affect the nitrogen removal in the next cycle. Hence, the next operation cycle will be longer and longer. As a result, the system was unable to achieve deep denitrification in mode (IV)-(b).

The variations of parameters (PHA*, NO₂⁻-N) in the SBR system also proved that the mode (IV)-(b) was not conducive

to the deep denitrification of landfill leachate, and the reasons were similar to those of the SBBR system in Fig. 9b. Compared with the differences between SBR and SBBR systems in mode (IV)-(b), it can be found that the eff. con. NO₂⁻-N in the SBBR system was lower than that in the SBR system. The reason may impute that the biofilm had a stronger ability to absorb organics than the activated sludge, and the denitrifying bacteria* in the biofilm anaerobic zone could store more PHA, which could be basically used as carbon sources for endogenous denitrifying and SND to remove nitrogen.

To make a long story short, the pre-anoxic phase was added before the aeration stage in the traditional SBR and SBBR systems, which could improve the nitrogen removal rate and denitrification rate of the whole system.

3.2.4. Temperature

Temperature is one of the important influencing factors of biological denitrification, especially reflecting on the type of nitrification reaction. It has been reported that the short-range nitrification reaction can be realized and stabilized at high temperature conditions [42]. Therefore, the effect of nitrogen removal by different temperatures (mode (V)-(a): temperature = 10°C and mode (V)-(b): 30°C) was investigated in the SBR and SBBR systems.

Figs. 10c and d reveal that the con. NO₂⁻-N* and of PHA* content decreased with the increase of aeration time in the aeration stage in the SBBR system, which indicated that the nitrification time in mode (V)-(a) was more than that in mode (V)-(b). Studies have shown that the growth rate and

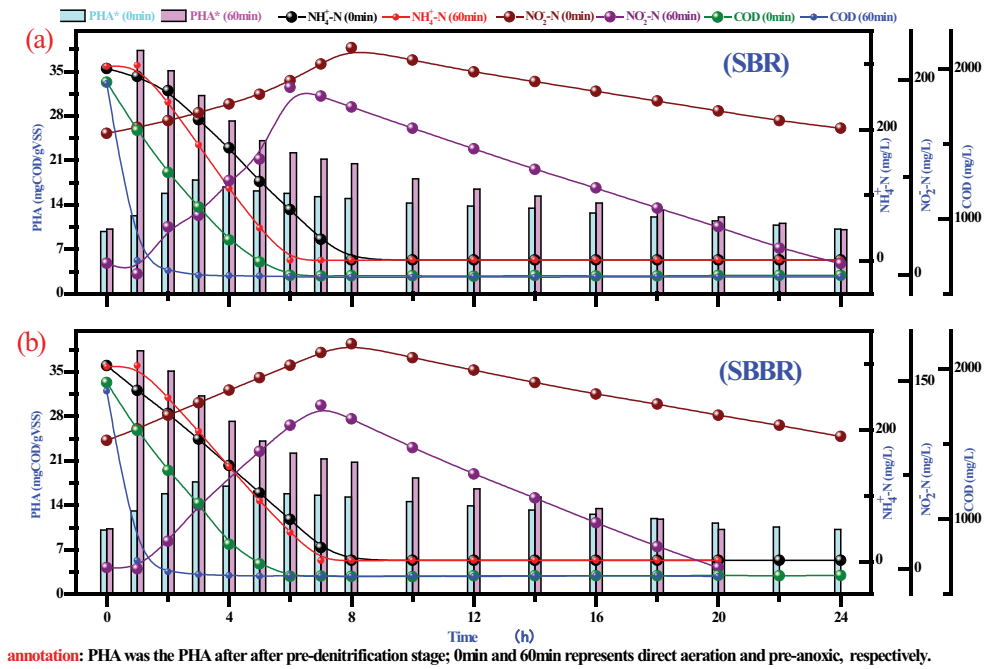


Fig. 9. Effect of pre-denitrification on nitrogen removal: (a) SBR and (b) SBBR.

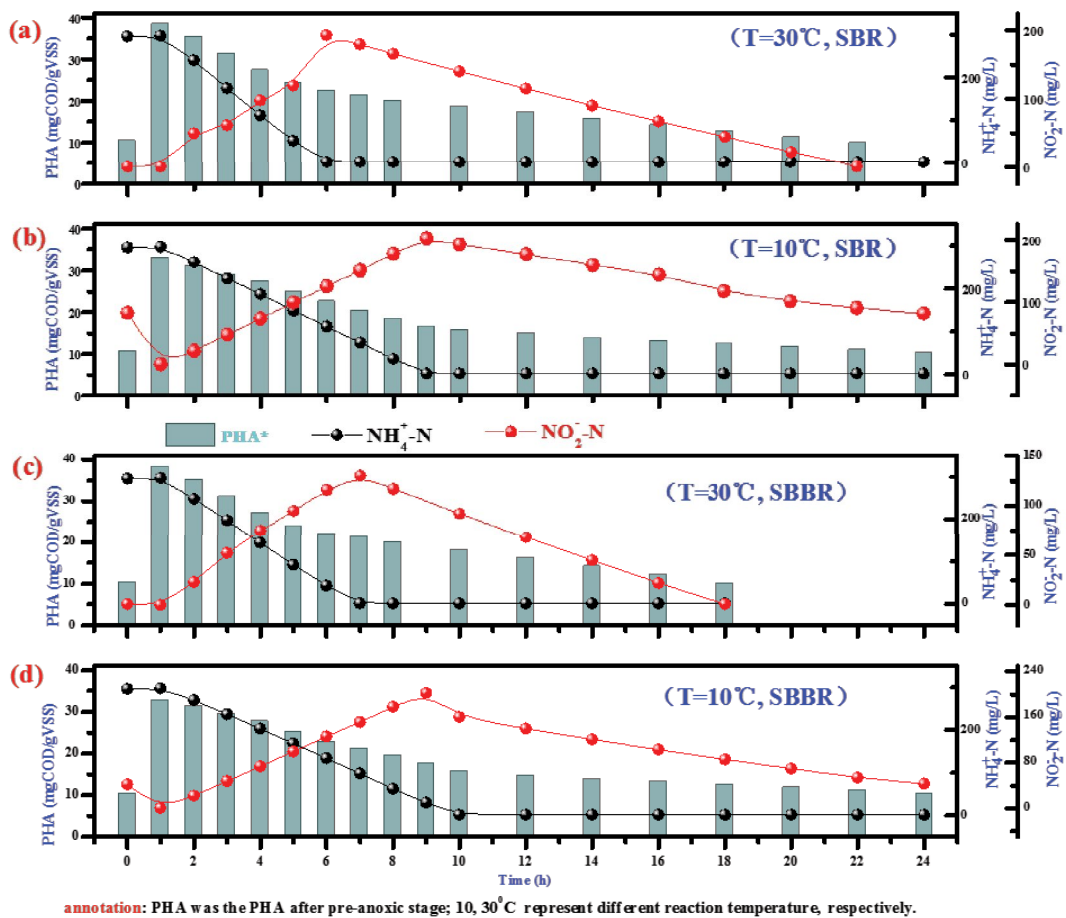


Fig. 10. Effect of different temperature on nitrogen removal: (a) $T = 30^{\circ}\text{C}$, SBR; (b) $T = 10^{\circ}\text{C}$, SBR; (c) $T = 30^{\circ}\text{C}$, SBBR; and (d) $T = 10^{\circ}\text{C}$, SBBR.

metabolic capacity of AOB is a positive correlation to temperature. In other words, the increase in temperature would increase the growth rate of ammonia-oxidizing bacteria and further promote the efficiency and rate of nitrification reaction [43]. The endogenous denitrification reaction time was prolonged due to the decrease of PHA* content, so the SBBR system was ultimately unable to realize advanced nitrogen removal because of the lack of PHA in the endogenous denitrification stage. At the same time, the increase of eff.-con. $\text{NO}_2\text{-N}$ in the previous cycle inhibited the organic matter transformation reaction in the pre-anoxic stage of the next cycle. This can be attributed to the influent organics were first used to treat the residual nitrogen in the previous cycle. Furthermore, low temperature also inhibited the activity of denitrifying bacteria [24]. Therefore, low temperature is not conducive to the advanced nitrogen removal of the system.

The variations of parameters (PHA*, $\text{NO}_2\text{-N}$) in the SBR system also proved that the mode (V)-(a) (temperature = 10°C) was not conducive to the deep denitrification of landfill leachate, and the reasons are similar to those of the SBBR system in Figs. 10a and b. Compared with the differences between SBR and SBBR systems in mode (IV)-(b), the eff.-con. $\text{NO}_2\text{-N}$ in the SBBR system was lower than that in the SBR system. Because the biofilm was more resistant than that of activated sludge, and the con. $\text{NO}_2\text{-N}^*$ was decreased by the SND in the aeration stage, the nitrogen removal efficiency of the SBBR system was better than that of the SBR system in mode (V)-(a).

All in all, the improvement of nitrogen removal can be ascribed to the characters of the activity and growth rate of

nitrifying bacteria and denitrifying bacteria with the increase of temperature.

3.2.5. Inf. C/N

The water quality of landfill leachate varies with the landfill age, especially the change of C/N ratio [3]. In this experiment, inf.-con. TN of landfill leachate was maintained at approximately 1,100 mg/L, and the inf. C/N was set as 5:1 (mode VI-a), 4:1 (mode VI-b), 3:1 (mode VI-c) and 4:1 (mode VI-d) to investigate the effects of inf. C/N on nitrogen removal. The experimental results were shown in Fig. 11. For mode VI-a, it can be seen that the PHA** and PHA* content increased from approximately 35 mg COD/gVSS to about 40 mg COD/g VSS, approximately 20 mg COD/g VSS to about 25 mg COD/g VSS, respectively. At this moment, the aeration time and eff. TN was maintained at approximately 5.5 h and less than 10 mg/L, respectively. The adequate carbon sources of landfill leachate could improve the PHA content stored in the biofilm and further facilitate the nitrogen removal in the SBBR system. For mode VI-c, the PHA**, PHA* and PHA*** content decreased when the inf. C/N of landfill leachate was adjusted to 3:1. Besides, the aeration time was slightly shortened, and the eff. TN gradually increased to about 100 mg/L with the total operating time increasing. The reason can be attributed to that the denitrifying bacteria in the system could not store enough carbon sources to synthesize PHA in the cell body when the inf. C/N was lower than 4:1, so stable advanced nitrogen removal could not be achieved in mode VI-c. For mode VI-b and mode VI-d, the PHA content

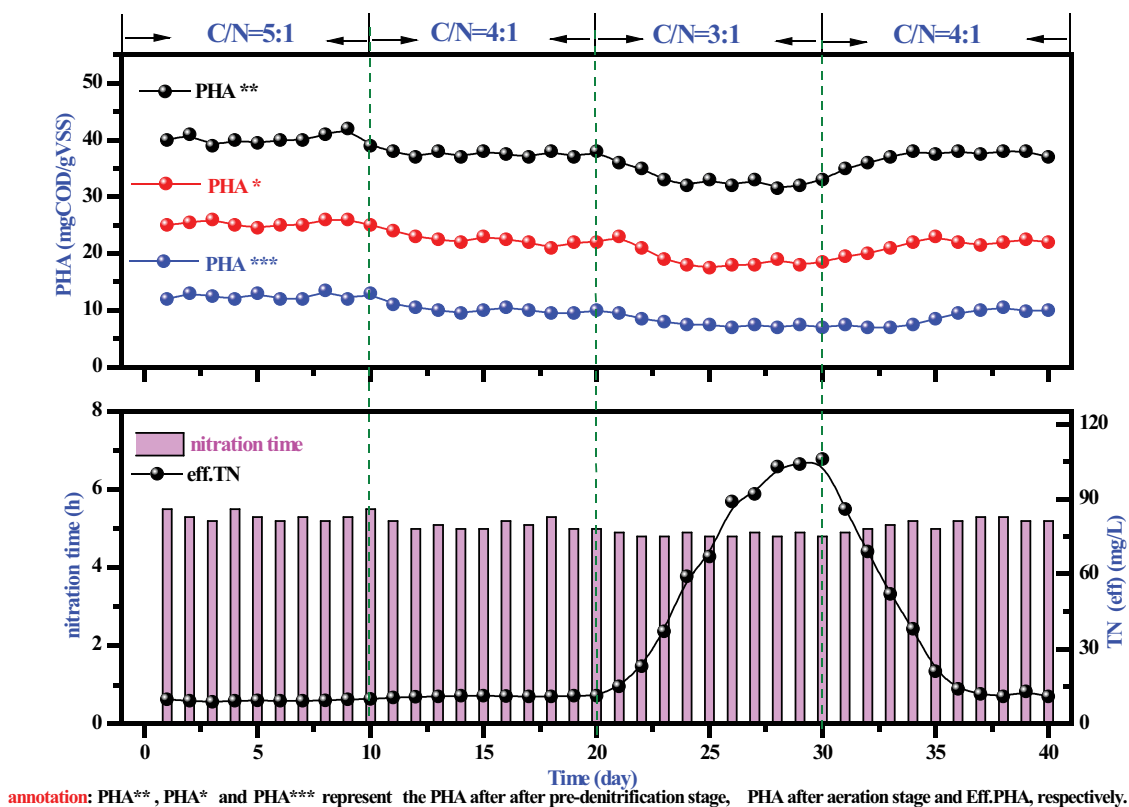


Fig. 11. Effect of inf. C/N on nitrogen removal.

was gradually increased or decreased rather than suddenly increased or decreased with the changes of inf. C/N, and eff. con. TN didn't change immediately with the change of inf. load. Both two points indicated that the biofilm had certain adaptability and buffering ability to the change of inf. C/N in the SBBR system.

4. Conclusion

Based on the observed effects of aeration DO, delay aeration, pre-denitrification, temperature, and inf. C/N on nitrogen removal from landfill leachate in the pre-denitrification SBR and pre-denitrification SBBR biotechnologies, the following three conclusions could be drawn:

- The final eff.-con. COD and eff.-con. TN was approximately 500 mg/L, <20 mg/L (<20 mg/L in SBR; <10 mg/L in SBBR) under the condition that the final inf.-con. COD and inf.-con. TN was approximately 4,500 and 1,100 mg/L.
- The aeration favorable operating modes: DO \approx 3 mg/L mode, without delay aeration mode, pre-denitrification (60 min) mode, temperature (30°C) mode, and inf. C/N \approx 4:1.
- The nitrogen removal rate and denitrification rate in the SBBR system (98%, <20 h) were better than that in the SBR system (93%, <24 h), and the ability of the SBBR system to resist severe operation mode was better than that of SBR system due to the stability of biofilm.

References

- [1] N. Remmas, S. Ntougias, M. Chatzopoulou, P. Melidis, Optimization aspects of the biological nitrogen removal process in a full-scale twin sequencing batch reactor (SBR) system in series treating landfill leachate, *J. Environ. Sci. Health*, 53 (2018) 847–853.
- [2] L. Miao, G. Yang, T. Tao, Y. Peng, Recent advances in nitrogen removal from landfill leachate using biological treatments—a review, *J. Environ. Manage.*, 235 (2019) 178–185.
- [3] S. Morling, Nitrogen removal and heavy metals in leachate treatment using SBR technology, *J. Hazard. Mater.*, 174 (2010) 679–686.
- [4] T.H. Martins, T.S. Souza, E. Foresti, Ammonium removal from landfill leachate by clinoptilolite adsorption followed by bioregeneration, *J. Environ. Chem. Eng.*, 5 (2017) 63–68.
- [5] D. Dolar, K. Košutić, T. Strmecky, Hybrid processes for treatment of landfill leachate: coagulation/UF/NF-RO and adsorption/UF/NF-RO, *Sep. Purif. Technol.*, 168 (2016) 39–46.
- [6] G. Wang, G. Lu, P. Yin, L. Zhao, Q.J. Yu, Genotoxicity assessment of membrane concentrates of landfill leachate treated with Fenton reagent and UV-Fenton reagent using human hepatoma cell line, *J. Hazard. Mater.*, 307 (2016) 154–162.
- [7] J. Ayala, B. Fernández, Treatment of mining waste leachate by the adsorption process using spent coffee grounds, *Environ. Technol.*, 40 (2018) 1–15.
- [8] Q.-Q. Zhang, B.-H. Tian, X. Zhang, A. Ghulam, C.-R. Fang, R. He, Investigation on characteristics of leachate and concentrated leachate in three landfill leachate treatment plants, *Waste Manage.*, 33 (2013) 2277–2286.
- [9] T. Zhou, T.-T. Lim, S.-S. Chin, A. Fane, Treatment of organics in reverse osmosis concentrate from a municipal wastewater reclamation plant: feasibility test of advanced oxidation processes with/without pretreatment, *Chem. Eng. J.*, 166 (2011) 932–939.
- [10] W. Yin, K. Wang, D. Wu, J. Xu, X. Gao, X. Cheng, C. Luo, C. Zhao, Variation in bacterial communities during landfill leachate treatment by a modified sequencing batch reactor (SBR), *Desal. Water Treat.*, 140 (2019) 365–372.
- [11] W. Yin, K. Wang, J. Xu, D. Wu, C. Zhao, The performance and associated mechanisms of carbon transformation (PHAs, polyhydroxyalkanoates) and nitrogen removal for landfill leachate treatment in a sequencing batch biofilm reactor (SBBR), *RSC Adv.*, 8 (2018) 42329–42336.
- [12] J. Boonnorat, C. Chiemchaisri, W. Chiemchaisri, K. Yamamoto, Kinetics of phenolic and phthalic acid esters biodegradation in membrane bioreactor (MBR) treating municipal landfill leachate, *Chemosphere*, 150 (2016) 639–649.
- [13] T. Lu, B. George, H. Zhao, W. Liu, A case study of coupling up-flow anaerobic sludge blanket (UASB) and ANITA™ Mox process to treat high-strength landfill leachate, *Water Sci. Technol.*, 73 (2016) 662–668.
- [14] S.A. Mousavi, A. Almasi, Z. Kamari, F. Abdali, Z. Yosefi, Application of the central composite design and response surface methodology for the treatment of Kermanshah landfill leachate by a sequencing batch reactor, *Desal. Water Treat.*, 56 (2015) 622–628.
- [15] H. Sun, Y. Peng, X. Shi, Advanced treatment of landfill leachate using anaerobic-aerobic process: organic removal by simultaneous denitrification and methanogenesis and nitrogen removal via nitrite, *Bioresour. Technol.*, 177 (2015) 337–345.
- [16] X. Li, Y. Yuan, F. Wang, Y. Huang, Q.-t. Qiu, Y. Yi, Z. Bi, Highly efficient of nitrogen removal from mature landfill leachate using a combined DN-PN-Anammox process with a dual recycling system, *Bioresour. Technol.*, 265 (2018) 357–364.
- [17] M. Liu, Q. Yang, Y. Peng, T. Liu, H. Xiao, S. Wang, Treatment performance and N₂O emission in the UASB-A/O shortcut biological nitrogen removal system for landfill leachate at different salinity, *J. Ind. Eng. Chem.*, 32 (2015) 63–71.
- [18] S.B. Selvam, S. Chelliapan, M.F.M. Din, R. Shahperi, M.A.M. Aris, Performance of an up-flow anaerobic sludge bed (UASB) reactor treating landfill leachate containing heavy metals and formaldehyde, *Desal. Water Treat.*, 86 (2017) 51–58.
- [19] J. Liu, P. Zhang, H. Li, Y. Tian, S. Wang, Y. Song, G. Zeng, C. Sun, Z. Tian, Denitrification of landfill leachate under different hydraulic retention time in a two-stage anoxic/oxic combined membrane bioreactor process: performances and bacterial community, *Bioresour. Technol.*, 250 (2018) 110–116.
- [20] R.L. Zhu, S.Y. Wang, J. Li, K. Wang, L. Miao, B. Ma, L.X. Gong, Y.Z. Peng, Effect of influent C/N ratio on nitrogen removal using PHB as an electron donor in a post-denitrification SBR, *J. Chem. Technol. Biotechnol.*, 88 (2013) 1898–1905.
- [21] F. Zhang, Y. Peng, L. Miao, Z. Wang, S. Wang, B. Li, A novel simultaneous partial nitrification Anammox and denitrification (SNAD) with intermittent aeration for cost-effective nitrogen removal from mature landfill leachate, *Chem. Eng. J.*, 313 (2017) 619–628.
- [22] K. Wang, S. Wang, R. Zhu, L. Miao, Y. Peng, Advanced nitrogen removal from landfill leachate without the addition of external carbon using a novel system coupling ASBR and modified SBR, *Bioresour. Technol.*, 134 (2013) 212–218.
- [23] X. Wen, J. Zhou, J. Wang, X. Qing, Q. He, Effects of dissolved oxygen on microbial community of single-stage autotrophic nitrogen removal system treating simulating mature landfill leachate, *Bioresour. Technol.*, 218 (2016) 962–968.
- [24] H. Sun, Y. Peng, S. Wang, J. Ma, Achieving nitrification at low temperatures using free ammonia inhibition on Nitrobacter and real-time control in an SBR treating landfill leachate, *J. Environ. Sci.*, 30 (2015) 157–163.
- [25] L. Miao, S. Wang, B. Li, T. Cao, F. Zhang, Z. Wang, Y. Peng, Effect of carbon source type on intracellular stored polymers during endogenous denitrification (ED) treating landfill leachate, *Water Res.*, 100 (2016) 405–412.
- [26] R. Zhu, S. Wang, J. Li, K. Wang, L. Miao, B. Ma, Y. Peng, Biological nitrogen removal from landfill leachate using anaerobic-aerobic process: denitrification via organics in raw leachate and intracellular storage polymers of microorganisms, *Bioresour. Technol.*, 128 (2013) 401–408.
- [27] W.E. Federation, A.P.H. Association, Standard Methods for the Examination of Water and Wastewater, American Public Health Association (APHA), Washington DC, 2005.

- [28] R.J. Zeng, R. Lemaire, Z. Yuan, J. Keller, Simultaneous nitrification, denitrification, and phosphorus removal in a lab-scale sequencing batch reactor, *Biotechnol. Bioeng.*, 84 (2003) 170–178.
- [29] J. Beun, F. Paletta, M. Van Loosdrecht, J. Heijnen, Stoichiometry and kinetics of poly- β -hydroxybutyrate metabolism in aerobic, slow-growing, activated sludge cultures, *Biotechnol. Bioeng.*, 67 (2000) 379–389.
- [30] M. Saleem, A. Spagni, L. Alibardi, A. Bertucco, M.C. Lavagnolo, Assessment of dynamic membrane filtration for biological treatment of old landfill leachate, *J. Environ. Manage.*, 213 (2018) 27–35.
- [31] L. Miao, Q. Zhang, S. Wang, B. Li, Z. Wang, S. Zhang, M. Zhang, Y. Peng, Characterization of EPS compositions and microbial community in an Anammox SBBR system treating landfill leachate, *Bioresour. Technol.*, 249 (2018) 108–116.
- [32] R. Nogueira, L.s.F. Melo, U. Purkhold, S. Wuertz, M. Wagner, Nitrifying and heterotrophic population dynamics in biofilm reactors: effects of hydraulic retention time and the presence of organic carbon, *Water Res.*, 36 (2002) 469–481.
- [33] A. Ozturk, A. Ahmet, N. Bilgehan, Application of sequencing batch biofilm reactor (SBBR) in dairy wastewater treatment, *Korean J. Chem. Eng.*, 36 (2019) 248–254.
- [34] K. Dong-Seog, N.-S. Jung, Y.-S. Park, Characteristics of nitrogen and phosphorus removal in SBR and SBBR with different ammonium loading rates, *Korean J. Chem. Eng.*, 25 (2008) 793–800.
- [35] S. Zeng, F. Song, P. Lu, Q. He, Improving PHA production in a SBR of coupling PHA-storing microorganism enrichment and PHA accumulation by feed-on-demand control, *AMB Express*, 8 (2018) 97.
- [36] J. Zhao, X. Wang, X. Li, S. Jia, Y. Peng, Combining partial nitrification and post endogenous denitrification in an EBPR system for deep-level nutrient removal from low carbon/nitrogen (C/N) domestic wastewater, *Chemosphere*, 210 (2018) 19–28.
- [37] J. Boog, T. Kalbacher, J. Nivala, N. Forquet, M. van Afferden, R.A. Müller, Modeling the relationship of aeration, oxygen transfer and treatment performance in aerated horizontal flow wetlands, *Water Res.*, 157 (2019) 321–334.
- [38] K.A. Third, N. Burnett, R. Cord-Ruwisch, Simultaneous nitrification and denitrification using stored substrate (PHB) as the electron donor in an SBR, *Biotechnol. Bioeng.*, 83 (2003) 706–720.
- [39] J. Zhang, L. Zhang, Y. Miao, Y. Sun, X. Li, Q. Zhang, Y. Peng, Feasibility of in situ enriching anammox bacteria in a sequencing batch biofilm reactor (SBBR) for enhancing nitrogen removal of real domestic wastewater, *Chem. Eng. J.*, 352 (2018) 847–854.
- [40] J. Zhu, Q. Tian, Y. Zhu, J. Yang, M. Wang, Factors for promoting polyhydroxyalkanoate (PHA) synthesis in bio-nutrient-removal and recovery system, *IOP Conf. Ser.: Earth and Environ. Sci.*, 178 (2018) 012021.
- [41] H. Zhang, H. Zhai, M. Ji, X. Su, Z. Du, J. Liu, Long-term effect of Cr (VI) on ammonia-oxidizing and nitrite-oxidizing bacteria in an activated sludge system, *Desal. Water Treat.*, 54 (2015) 1981–1989.
- [42] Q. Yang, Y. Peng, X. Liu, W. Zeng, T. Mino, H. Satoh, Nitrogen removal via nitrite from municipal wastewater at low temperatures using real-time control to optimize nitrifying communities, *Environ. Sci. Technol.*, 41 (2007) 8159–8164.
- [43] J. Guo, Y. Peng, H. Huang, S. Wang, S. Ge, J. Zhang, Z. Wang, Short-and long-term effects of temperature on partial nitrification in a sequencing batch reactor treating domestic wastewater, *J. Hazard. Mater.*, 179 (2010) 471–479.