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Sequencing batch airlift reactor system for simultaneous removal of nitrogen and organic carbon from synthetic tannery wastewater

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ABSTRACT

Tannery wastewater has high organic carbon and nitrogenous compounds due to the raw hides/skins and chemicals used during leather processing. Conventional single stage activated sludge process is effective in reducing the organic but not nitrogenous load in the wastewater. In the present study, a sequencing batch airlift reactor system was investigated for the simultaneous removal of nitrogen and organic carbon from synthetic tannery wastewater. The reactor was operated at constant 50% volume exchange ratio at low dissolved oxygen concentration (DO 1–2 mg L^{-1}); different sludge retention times (SRTs) (7 and 20 d) and cycle times (CT's) (18, 12, 10, and 8 h) for 250 days. The organic and nitrogen loading rates were increased stepwise to 7.875 kg COD $m^{-3}d^{-1}$ (COD is abbreviated as chemical oxygen demand) and 0.531 kg NH_4–N m^{-3} d^{-1} respectively. Partial nitrification-denitrification was observed when the reactor was operated at SRT of 7 d, whereas complete nitrification-denitrification was observed when the reactor was operated at 20 d SRT. The total nitrogen (TN) removal efficiencies were observed to increase with the increase in the cycle time. In addition, the TN removals efficiency increased with cycle times. The optimum cycle time for (>90%) removal of COD and NH_4–N was found to be 8 h at SRT of 20 d. The remaining nitrogen in the effluent was more in the form of nitrate at higher cycle times and in the form of nitrite for lower cycle times.

Keywords: Sequencing batch airlift reactor; Cycle time; Sludge retention time; Nitrogen removal; Tannery wastewater

1. Introduction

Tannery wastewater is having high organic carbon (measured as chemical oxygen demand (COD)) and nitrogenous compounds due to the raw material (raw hides/skins) and chemicals used during leather processing. The major forms of nitrogen in tannery wastewater are organic nitrogen (ORG-N) and ammonium nitrogen (NH_4–N). They originated from the breakdown of nitrogenous compounds from processed hides and skins and ammonium nitrogen (NH_4–N) originated from ammonium salts used in deliming operation [1,2]. The common nitrogen compounds present in wastewaters are ammonium ions (NH_4^+), nitrite ions (NO_2^-) and nitrate ions (NO_3^-). The discharge of high

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nitrogen concentrations into the receiving waters without proper treatment causes dissolved oxygen depletion, toxicity, eutrophication, methemoglobinemia, deterioration of aesthetic quality and odor from decomposing algae [3].

Biological removal of nitrogen is the most economical option for industrial and municipal wastewater treatment [4]. Conventionally, it is carried out by nitrification and denitrification. Nitrification is the rate-limiting step in biological nitrogen removal and the wastewater C/N ratio is very important for effective nitrogen removal [5]. For wastewater having a low C/N ratio, an external carbon source is usually provided [6]. Short-cut partial nitrification–denitrification is possible where the ammonium nitrogen is first converted to nitrite (Eq. (1)) and then denitrified in the presence of organic carbon (Eq. (2)). This process helps significant savings in energy and cost of operations [7]. Anaerobic ammonia oxidation can also be possible under the anaerobic condition when the wastewater NH_4–N:NO_2 ratio is 1:1.31 (Eq. (3)) by chemoautotrophic anammox bacteria that use carbonate as the only carbon source [8]. This process is advantageous because it requires no external carbon source and dissolved oxygen and less energy, reactor footprint and greenhouse gas emission compared to denitrification [9].

$$NH_4^+ + 1.5\,O_2 \xrightarrow{\text{AOB}} NO_2^- + H_2O + 2H^+;\ \Delta G^\circ = -275\,\frac{\text{kJ}}{\text{M}} \tag{1}$$

$$\begin{aligned}&NO_2^- + 0.24\,NH_4^+ + H^+ + 0.975\,CH_3COO^- \xrightarrow{\text{HDB}} 0.24\,C_5H_7O_2N + \\ &\quad 0.015CO_2 + 0.5N_2 + 1.235H_2O + 0.735HCO_3^-\end{aligned} \tag{2}$$

$$\begin{aligned}&NH_4^+ + 1.31\,NO_2^- + 0.066\,HCO_3^- + 0.13H^+ \xrightarrow{\text{Anammoxbacteria}} \\ &\quad 1.02\,N_2 + 0.26NO_3^- + 0.066\,CH_2O_{0.5}N_{0.15} + 2.03H_2O; \\ &\quad \Delta G^\circ = -357\,\frac{\text{kJ}}{\text{M}}\end{aligned} \tag{3}$$

The sequencing batch reactor (SBR) system has been demonstrated as the most flexible and cost-effective biological treatment system. It involves a series of time-oriented operations, that is, fill, react, settle, decant and idle each lasting for a defined period during which wastewater is treated [10]. Advance in the online control system helped in detecting endpoints of biological reactions responsible for carbon and nitrogen removal thereby optimizing the process and improving effluent quality and cost of treatment [11]. Proper control of the SBR cycles, sludge retention time (SRT), pH, DO, ORP, conductivity, and temperature are important to influence the microbial populations and thereby the accompanying biological reactions responsible for the removal of organic carbon and nitrogen.

A low dissolved oxygen nitrification system resulted in unusually high ammonia-oxidizing bacteria (AOB) yield thereby increasing partial nitrification to nitrite. As a result, nitrogen removal via nitrite can be achieved [12] and this system results in a significant reduction of cost of treatment [13,14].

Studies on the application of SBR technology in laboratory, pilot and large-scale treatment systems for tannery wastewater have been reported [15–17]. However, the application of the sequencing batch airlift reactor (SBAR) for the treatment of tannery wastewater is not studied extensively. An SBAR can be used to selectively enrich ammonia oxidizers and help to improve nitrogen removal [18]. In this research study, the effect of SRT and cycle time (CT) on partial and complete nitrification-denitrification characteristics is investigated. Also, the study attempts to aid the nitrogen removal by the involvement of anammox which has a lot of advantages.

The SBAR system has a central draft tube arrangement as shown in Fig. 1. The draft tube provides adequate mixing by airlift movement and at the same time supplying dissolved oxygen. It is also provided with online monitoring and control of pH, DO, temperature CT. Thus, in this study, the effect of SRT and CT on the performance of SBAR on partial and complete nitrification-denitrification removals was investigated.

2. Materials and methods

2.1. Wastewater samples and seed sludge

A primary treated tannery wastewater sample was collected from the tannery common effluent treatment plant (CETP) located in Tamil Nadu, India. The sample was characterized for basic parameters (Table 1) and synthetic wastewater with C/N ratio similar to tannery wastewater was prepared based on the characteristics of real wastewater (Table 1) and the literature [19,20]. Commercial milk powder (Nestle Everyday) was used as the sole source of organic carbon and Org-N. The milk powder was selected to represent complex tannery effluent composition having both organic carbon and nitrogen generated during leather processing rather than choosing pure glucose and NH_4Cl. Further, to meet the COD/NH_4–N ratio of tannery effluent, ammonium sulfate was added. Hence, the composition of the synthetic wastewater used was: milk powder-2,500 mg L^{-1}; $(NH_4)_2SO_4$-1,378 mg L^{-1}; $MgSO_4{\cdot}7H_2O$-5 mg L^{-1}; $FeSO_4{\cdot}7H_2O$–20 mg L^{-1}; KH_2PO_4-88 mg L^{-1}; K_2HPO_4-90 mg L^{-1}; Na_2CO_3-66 mg L^{-1}; $NaHCO_3$-105 mg L^{-1}; $CaCl_2{\cdot}H_2O$–30 mg L^{-1}; and trace element solution (1 ml L^{-1}) [19]. Ten replica analyses were done for COD, soluble sCOD, total Kjeldahl nitrogen (TKN) and NH_4–N and the average values were found to be 5,250 ± 750, 3,300 ± 300, 425 ± 25and 270 ± 20 mg L^{-1}, respectively.

Aerobic sludge (5 L) from aeration tank and anoxic sludge (5 L) from an anoxic tank of the tannery CETP (A mixed culture of heterotrophic and nitrifying bacteria) were collected and 1.5 L of mixed sludge (3 aerobic: 1 anoxic) was used as seed sludge for the start-up of the reactor.

2.2. Sequencing batch airlift reactor

A cylindrical lab-scale SBAR was constructed with plexiglass having a nominal dimension of 80 cm height, the diameter of 10 cm, effective liquid depth of 64 cm and effective liquid holding capacity of 5 L. It had a 16 cm headspace and 60.5 cm long central draft tube with perforations for aeration at the bottom of the tube. Air was supplied through the top of the reactor down to the tip of the draft tube and released at the bottom. The draft tube was designed in such a way that there were uniform mixing, aeration, and ease of cleaning, without additional mixing arrangement during

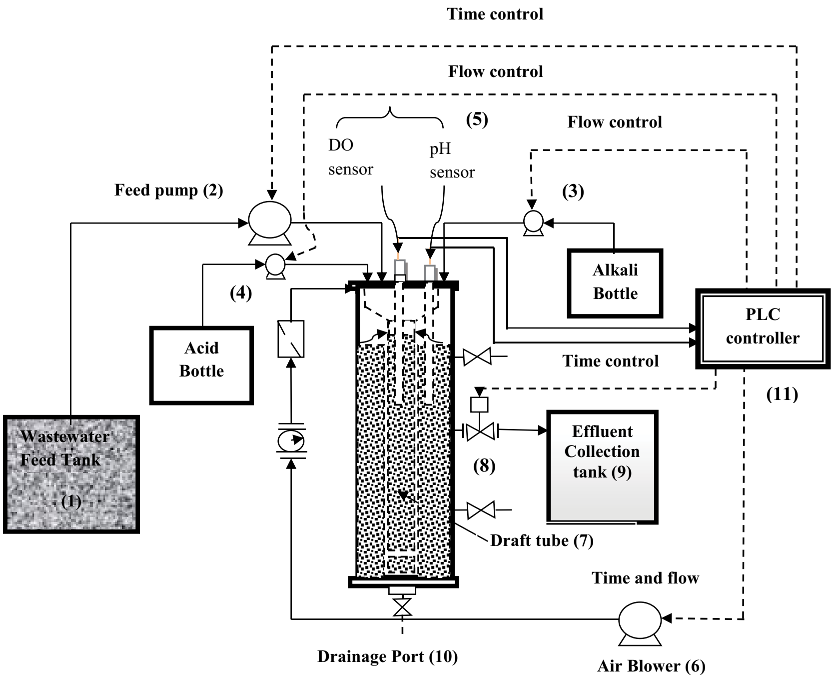


Fig. 1. Schematic diagram of the SBAR system.

Table 1
Characteristics of composite tannery wastewater

S/N	Parameters	Values[a]
1	pH	7–9
2	Suspended solids (mg L^{-1})	2,500–3,500
3	COD (mg L^{-1})	3,500–6,500
4	BOD$_5$, 20°C	1,400–3,000
5	Sulphate (mg L^{-1})	1,500–3,000
6	Sulphide (mg L^{-1})	20–40
7	TKN (mg L^{-1})	400–550
8	NH_4–N (mg L^{-1})	100–400
9	Chromium(III) (mg L^{-1})	50–70
10	Chloride (mg L^{-1})	5,000–8,500
11	TDS (mg L^{-1})	12,000–20,000

[a] Each parameter was analyzed 10 times.

aeration. The schematic diagram of the SBAR is depicted in Fig. 1. The reactor was equipped with wastewater collection tank (1), influent peristaltic pump (2), alkali feed pump (3), acid feed pump (4), pH, DO and temperature sensors (5), air blower (6), central draft tube (7), solenoid valve (8), effluent collection tank (9) and drainage port (10). The operation of the reactor was controlled by a PLC controller (11). The controller was linked with input measurements from pH, DO and temperature sensors and timer.

2.3. Operation of the reactor

The reactor was inoculated with seed sludge and filled with synthetic wastewater, followed by immediate aeration. At the end of the aeration, the reactor mixture was allowed to settle and 2.5 L of the supernatant was withdrawn after decantation at the end of the cycle. The reactor was run in semi-continuous SBR mode for more than 250 d at different total cycle time (CT) of 18, 12, 10 and 8 h, and constant feed composition. The CT was calculated according to Eq. (4):

$$\mathrm{CT} = t_f + t_a + t_s + t_d \tag{4}$$

where t_f - feeding time, t_a - aeration time, t_s - settling time, t_d - decanting time.

The reactor was operated at a constant 50% Volume Exchange Ratio (VER). The hydraulic retention time (HRT) was calculated from CT and VER (Eq. (5)). The organic loading rate (OLR) and nitrogen loading rate (NLR) were varied by varying CTs as per determined values during the study period. The OLR and NLR were calculated according to Eqs. (6) and (7).

$$\mathrm{HRT} = \frac{V_r}{Q} = \frac{\mathrm{CT}}{\mathrm{VER}} \tag{5}$$

$$\mathrm{OLR} = \frac{Q \times C_0}{V_r} = \frac{C_0}{\mathrm{HRT}} \tag{6}$$

$$\mathrm{NLR} = \frac{QN_0}{V_r} = \frac{N_0}{\mathrm{HRT}} \tag{7}$$

where V_r is the volume of the reactor (L), Q is the flow rate (L d^{-1}), C_0 is feed COD (g L^{-1}), N_0 is feed TKN (g L^{-1}).

During the first 129 d, the reactor was operated at SRT of 10 d and CT of 18 h (day 1 to day 61) and 12 h (day 62 to day 129), respectively, maintaining mixed liquor suspended solids (MLSS) between 3.5 to 4 g L^{-1}. The SRT was calculated according to Eq. (8). The MLSS was measured every 2 d and the calculated amount of the excess sludge was withdrawn from the reactor.

$$\text{SRT} = \frac{V_r X_r}{Q_w X_w} \tag{8}$$

where X_r is the reactor mixed liquor volatile suspended solid (MLVSS) (g L^{-1}), W_w is the quantity of excess sludge wasted per day (L d^{-1}), X_w is the waste sludge MLVSS (g L^{-1}).

The reactor was operated at constant SRT of 20 d and MLSS of 10 to 11 g L^{-1} during the remaining period of 121 d. The operating conditions of the reactor are shown in Table 2. In addition, optimal values were taken by referring to the literature [6,21–23] as biological nitrogen removal is highly affected by operating temperature, pH and DO. The reactor was operated at room temperature (29°C–31°C) and a relatively alkaline pH [18]. The pH was monitored and controlled online throughout the operating days and 0.25 M $NaHCO_3$ and 0.25 M Hydrochloric acid (HCl) solutions were used to maintain the reactor pH in the range 7.25–7.30. The DO was controlled through an on-off control of the air blower.

The CT was also controlled by setting sequentially the time for feeding, aeration, settling and decanting. For all the CT's, the feeding time of 9 min, settling of 30 min and decanting for 6 min were maintained. The different CTs were carried out with different periods of aeration time. A total CT of 18, 12, 10, and 8 h were considered to study the effect of CT on the performance of the reactor.

2.4. Kinetics study

When the reactor showed stable performance, sampling was done weekly to study the kinetics by analyzing parameters for TCOD, sCOD, biochemical oxygen demand (BOD), TKN, NO_3–N, NO_2–N, alkalinity, pH, DO, and MLSS/MLVSS for all CT.

2.5. Sampling and analytical techniques

Initial mixed liquor samples (filtered) from the reactor and effluent samples (filtered) at the end of the SBR cycle were taken and analyzed immediately or preserved in refrigerator at 4°C till the analyses performed. The performance was evaluated in terms of COD, NH_4–N, NO_3–N, and NO_2–N concentrations and removal efficiencies.

All the physicochemical analyses were done as per Standard Methods [24]. Online pH measurement and input for controller were made by gel-filled autoclavable pH sensor (Broadley-James, USA) whereas online DO measurement was done with suspended solids polarographic DO sensor (Broadley-James, USA). Ammonium nitrogen was determined by titrimetric method following distillation of samples. TKN was determined by the Kjeldahl method by digesting the sample, ammonia distillation, and titration. COD was determined by the closed reflux method using the COD digester (Merk, Germany). NO_3–N, and NO_2–N were determined calorimetrically using a double beam spectrophotometer (U-2900/2910, Hitachi, Japan).

3. Results and discussion

3.1. Operation of the reactor during Phase I and II

During the first 7 d of startup period, the SBAR reactor was operated with HRT of 36 h by recycling back treated effluent and by changing the feed wastewater every 3 d. Recycling was done to properly acclimatize the seed sludge to the reactor condition and to prevent washout of seed sludge from the reactor. The recycling was stopped after one week and the reactor was operated with the operating conditions given in Table 2.

The operating conditions in Phase I and II were designed to study the startup of the reactor and the effect of HRT for constant low SRT (7 d) on the characteristics of nitrification and denitrification processes. Even if the wastewater under consideration has a high COD/N ratio, studies showed that the high COD/N ratio resulted in a high growth of heterotrophs but has a minor effect on the growth of nitrifiers [25]. The engineered system (SBAR) helped to manipulate the growth of these two important groups of bacteria involved in the simultaneous removal of organic carbon and nitrogen.

The operation of the SBAR reactor involved the control of pH, DO, HRT, SRT, and temperature. The control of the above parameters in the reactor has been reported to selectively inhibit NOB's or washout NOB's from the system [7,26]. Jubany et al. [27] demonstrated a total and stable washout of

Table 2
Operating conditions of the reactor

S/N	Phase	Days	CT (h)	DO (mg L^{-1})	SRT (d)	Process
1	Phase I (1–61)	61	18	2	7	Start-up, nitrite accumulation and denitrification via nitrite
2	Phase II (61–129)	68	12	2	7	Nitrite accumulation and denitrification via nitrite
3	Phase III (129–152)	23	18	1	20	Stable nitrification and denitrification
4	Phase IV (152–164)	12	10	1	20	Stable nitrification and denitrification
5	Phase V (164–186)	22	12	1	20	Stable nitrification and denitrification
6	Phase VI (186–250)	64	8	1	20	Stable nitrification and denitrification

*The feed composition was constant (TCOD = 5,250 ± 750, TKN = 350 ± 13, NH_4–N = 282 ± 8) where values are averages for 10 samples).
*The pH of the reactor was maintained in the range (7.25–7.3) throughout the operating period by the addition of 0.25 M $NaHCO_3$ and 0.25 M HCL.
*The airflow was maintained 3.5 L min^{-1} throughout the operating period.

NOB's at a pH of 8.3 and DO of 1.2–1.9 mg L^{-1} in a nitrifying continuous activated system. In Phase I, the operating conditions was maintained at CT of 18 h, SRT of 7 d and controlled low dissolved oxygen concentration. The maximum DO of 2 mg L^{-1} was maintained considering the feed COD/N ratio and the economy of aeration. The pH in the range of 7.25–7.30 was ensured to accelerate the startup. Analysis results of the daily effluent profile for COD and NH_4–N (Fig. 2), showed the simultaneous removal of organic carbon and nitrogen. In phase II, the reactor was operated with an increased loading rate keeping all other parameters the same as phase I.

Fig. 3a shows the NH_4–N, NO_2–N and NO_3–N (NO_x–N) profile at steady-state operation. This profile clearly shows the ammonia conversion in one complete CT (18 h). The profile shows increasing NO_x–N concentrations, but the increase in NO_2–N is very high and NO_3–N is insignificant, while Fig. 3b shows the profile including NH_4–N and COD, respectively. This profile shows a decrease in both COD and NH_4–N and increases in NO_x–N as a result of the ammonia oxidation. The removal pattern of nitrogen species follows the typical pattern for incomplete nitrification reported [28]. The graphs clearly show nitrite accumulation and very little conversion to nitrate. This indicates a relatively higher startup period required for NOB compared to AOB and heterotrophs [16] and the relatively higher pH and low SRT maintained favor AOB more than NOB. The SRT was maintained in the range 7 d resulting in an MLSS of 3,500–4,000 mg L^{-1}. During partial nitrification, nitrogen and organic carbon removal was achieved. Denitrification seemed to play a role in organic carbon removal mainly during the anoxic feeding and initial period of aeration. During this phase of operation, the reactor shows 94.6% ± 2% COD removal, 80% ± 5% NH_4–N oxidation to nitrite and 35% ± 9.2% TN removal at steady state condition.

Phase II (day 61 to day 129) showed a similar trend of phase I, but there was aeration problem after the end of phase I and the reactor had taken some days to restore its nitrification efficiency. During this phase, the reactor again showed a good partial nitrification to nitrite. The COD, NH_4–N and TN removal were 93% ± 3%, 92.7% ± 2% and 40.4% ± 3%, respectively.

3.2. Operation of the reactor (Phase III-VI)

The effect of increasing the SRT on the removal efficiency and characteristics of the effluent was studied by maintaining

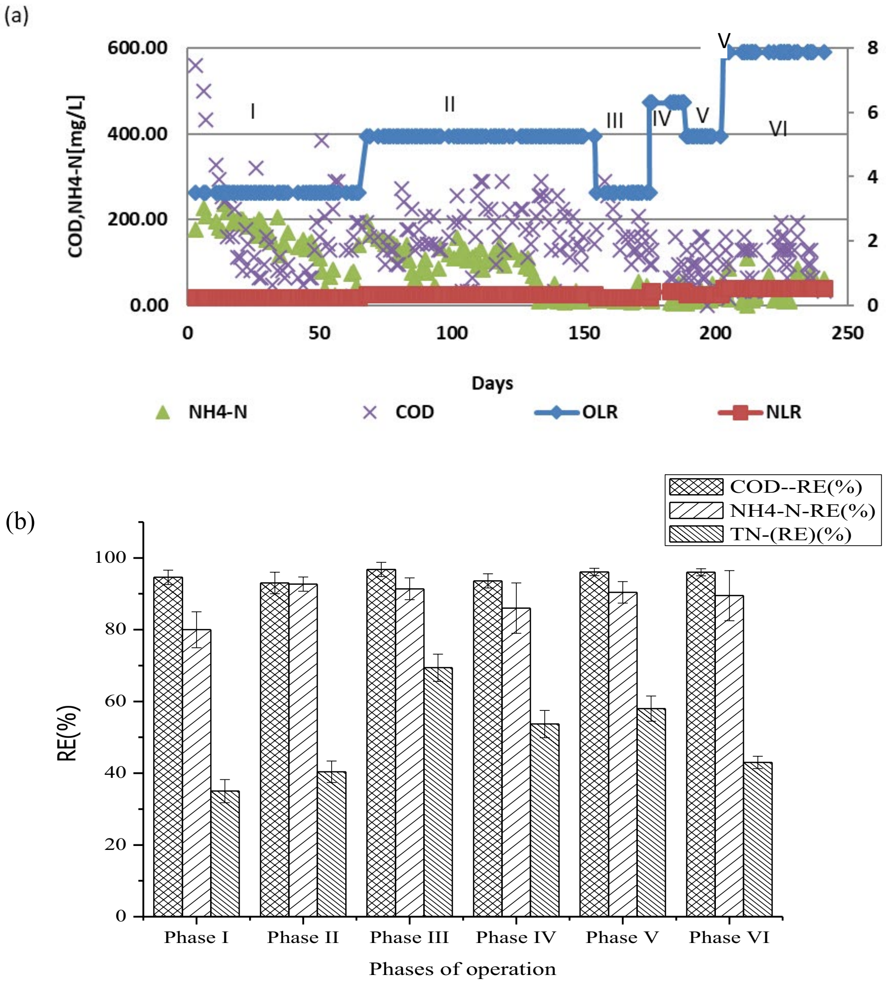


Fig. 2. Overall performance of the reactor (a) daily profile of final treated effluent COD and NH_4–N under varying OLR and NLR and (b) average removal efficiencies (RE-(%)) at steady state for NH_4–N, COD, and TN at each phase of operation.

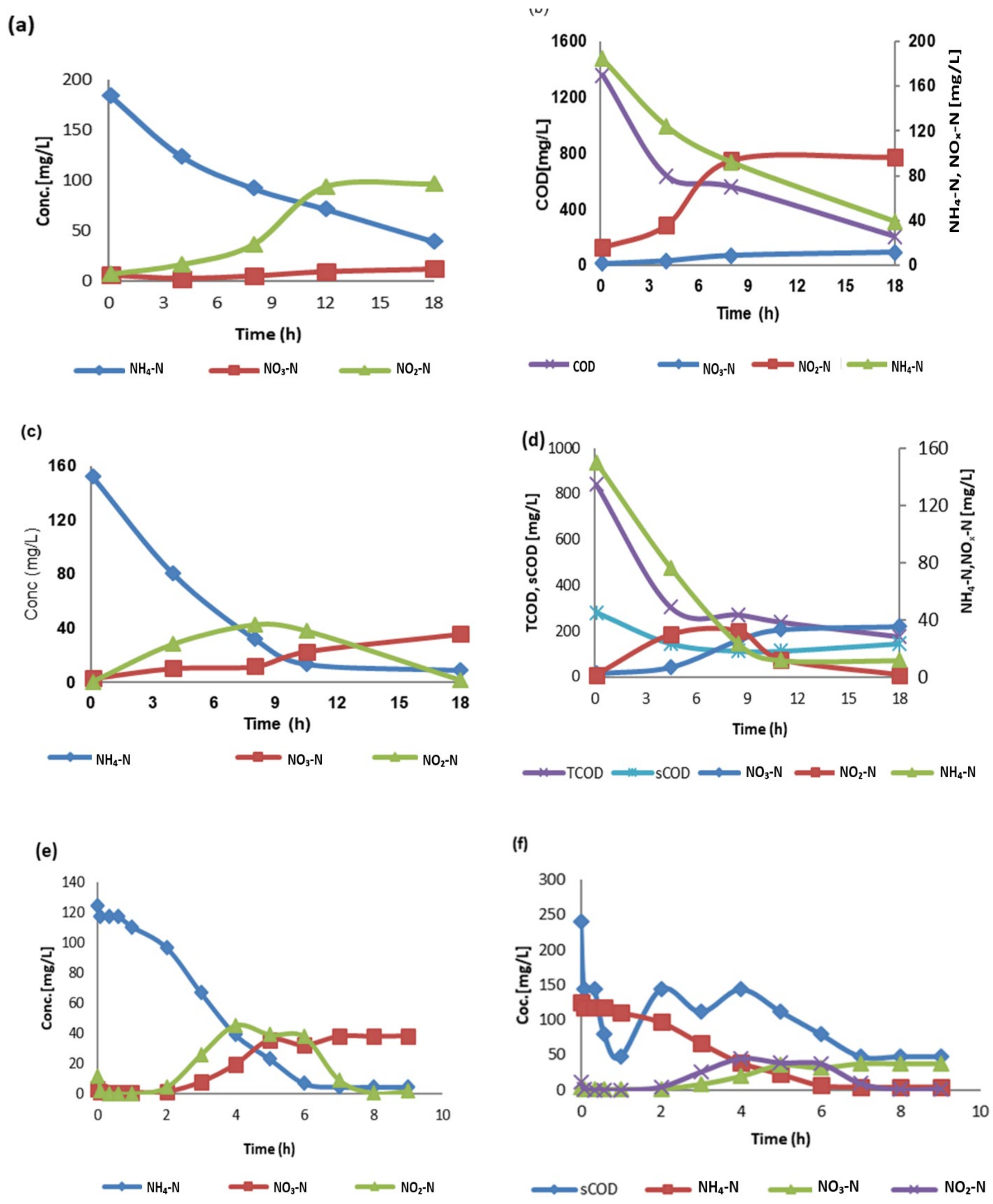


Fig. 3. Typical steady-state profiles for NH_4–N, NO_x–N and COD (a) Phase I and II, NH_4–N and NO_x–N profile, (b) Phase I and II, NH_4–N, NO_x and COD profiles, (c) Phase(III), NH_4–N and NO_x–N profile, (d) Phase III, NH_4–N, NO_x, and COD profiles, (e) Phase IV, NH_4–N and NO_x–N profile, and (f) Phase IV, NH_4–N, NO_x, and COD profiles.

the SRT at 20 d but by setting different values for the total CTs (i.e. 18, 12, 10, and 8 h). During this period, the COD and NH_4–N removals were also very high and complete oxidation of ammonia to nitrate was observed at the end of the CT. This shows that higher SRTs favor the growth of both nitrifiers (AOB and NOB). Figs. 3c and d display the NH_4–N, NO_x–N, and COD profiles for different operating days at 18 h CT. The results clearly show that the ammonia oxidation was taking place as in phases I and II but the NO_2–N and NO_3–N profiles were changed significantly and effluent had more of nitrate than nitrite. From Figs. 3c and d, it was observed that the NH_4–N removal shows a logarithmic correlation; thatNO_2–N conversion shows parabolic correlation; and that NO_3–N conversion shows linear correlation. A similar kinetics study was conducted for 10 h CT. The results are plotted in Figs. 3e and f for NH_4–N, NO_x–N and COD profiles on 181st day. The profiles show optimized forms of Figs. 3c and d where unnecessary aeration time was cut down to 10 h and still gave the same performance. Figs. 4a–d show the NH_4–N, NO_x–N and COD profiles for 8 h complete CT on 200th day. The profile again shows that under controlled conditions, the CT can be further reduced to 8 h.

3.3. Performance of the reactor

3.3.1. Organic carbon removal

The composition of the feed synthetic tannery wastewater was kept constant throughout the operation of the reactor. The average feed concentrations of TCOD was 5,250 ± 750 mg L^{-1}, TKN was 350 ± 13 mg L^{-1} and NH_4–N was 282 ± 8 mg L^{-1}. The operating condition, Phase I, was mainly for biomass acclimatization and the development of nitrifying biomass. During the whole study, the daily COD and nitrogen removal efficiencies and effluent characteristics were evaluated. The OLR was increased during the course of operation by decreasing the HRT. Very good removal efficiencies were obtained in all the loading rates as observed in Fig. 2b. At a maximum OLR of 7.875 kg COD $m^{-3}d^{-1}$, the reactor showed very good organic carbon removal in terms of COD. The result showed that the overall COD removal was not affected by increasing the OLR of the system.

Since the VER was 50%, the theoretical initial mixed liquor COD was taken as half the sum of effluent COD from the previous cycle and the feed COD. The actual initial COD in the mixed liquor was however lower than the theoretical value as there is rapid uptake of COD by cells due to starvation and absorption to cell surface. The daily COD removal efficiency of the reactor, except for very few days of the initial periods of the reactor operation, was very high and showed 95% ± 1.8% of average removal efficiency. The average effluent total COD (TCOD) value was 158 ± 31 mg L^{-1}. These data seem to signify the reactor provided a consistently high COD removal efficiency.

In phases I and II, the DO in the reactor was maintained at 2 mg L^{-1}, the reactor showed an increase in the COD removal efficiency and reached a maximum in few days of operation. During the active partial nitrification to nitrite, the reactor showed very low effluent COD which shows nitrification and denitrification plays a role in COD removal. After day 129, the reactor DO was maintained 1 mg L^{-1} at SRT of 20 d, the change of DO did not affect the COD removal.

Variation of the reactor COD with respect to time in 8h complete CT operated at 20 d SRT is shown in Fig. 4b, and showed a sudden drop of COD during the first 5min of aeration after feeding fresh feed. The COD removal rate was very high in the first 2 h. Denitrification would also play a major role during the initial period of the reactor operation as DO demand would be very high. Thus, during this time, DO in the bulk liquid will be made very low (0–0.4 mg L^{-1}). This condition creates favorable environment for denitrifiers to utilize the available NO_x and organic carbon for denitrification. In fact, the lactose in milk solution is complex substrate (higher molecular weight) and which must first be hydrolyzed by extracellular metabolism before utilization by the bacteria. Therefore, the oxidation rate of lactose would be less than simpler molecule such as glucose and acetate. The remaining COD in the effluent was mainly composed of soluble refractory substance from the feed synthetic tannery wastewater itself and from the refractory substances released from starvation by the microorganisms themselves in the sludge.

3.3.2. Ammonia removal by nitrification

The feed wastewater contains both Org-N and NH_4–N. The Org-N is readily converted to NH_4–N by ammonification process contributing to the total ammonia in the system [29]. Ammonia removal happened due to assimilation by biomass, due to nitrification by nitrifiers and anaerobic oxidation by anammox bacteria as the reactor was operated at low dissolved oxygen concentration. The assimilation of ammonia by hetrotrophs happens in preference to nitrification and anammox conversion. The addition of organic matter provokes the growth of hetrotrophs and inhibits ammonia oxidation. This could be due to the mass transfer limitation of ammonia from bulk liquid to the cells of nitrifieres as a result of the crowded cells of hetrotrophs [30].

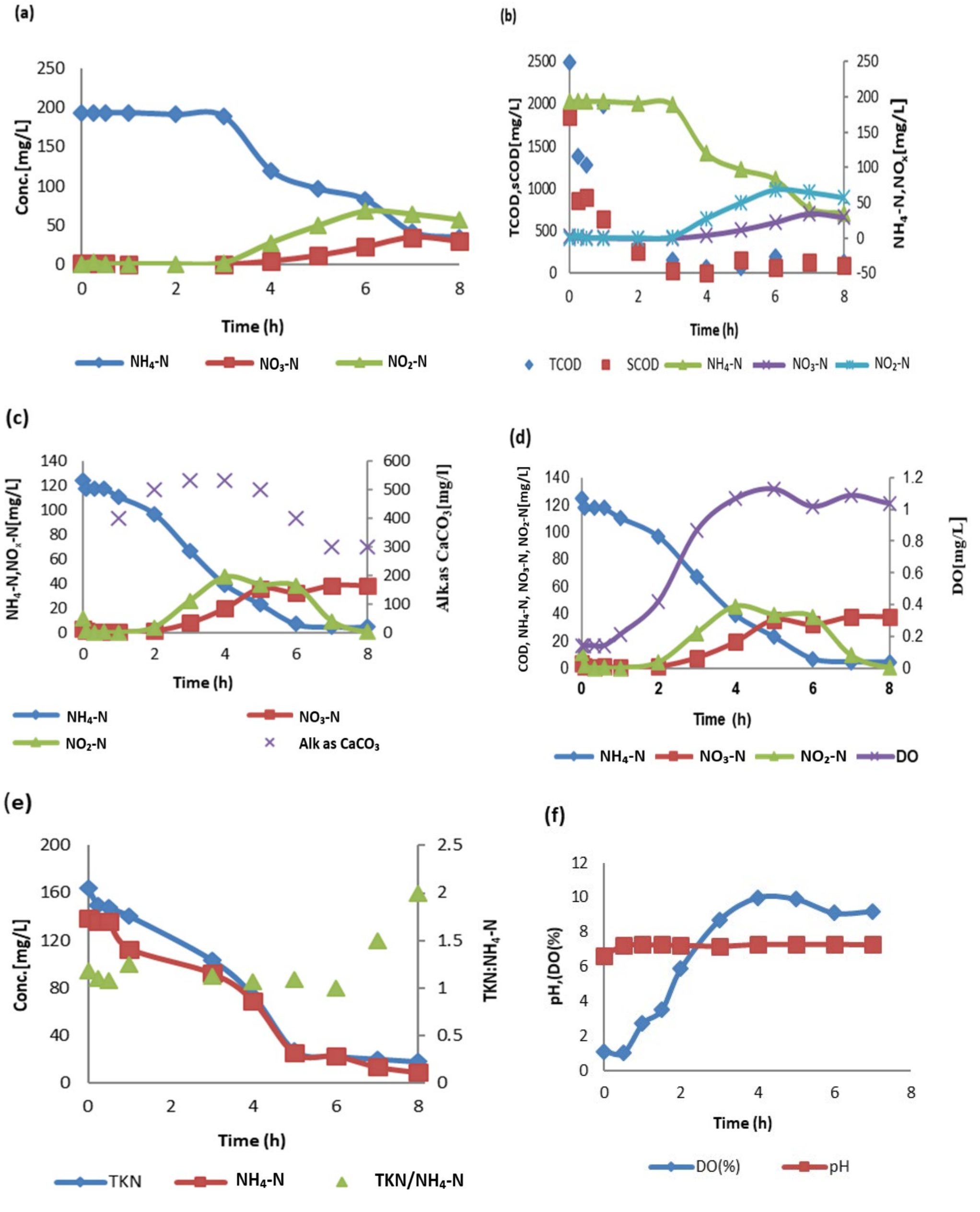
Fig. 4e shows the NH_4–N and TKN profiles in 8 h optimum CT. The result showed that the TKN: NH_4–N ratio is greater than one during the initial 2 h; closer to one during the next 4 h; and increase to above one during the last 2 h. This indicates that the initial organic nitrogen is getting converted to ammonium nitrogen during the initial 2 h. The effluent ratio signifies the discharge of biomass contributing to higher TKN.

Fig. 3a shows the typical ammonia conversion profile in phase I. This graph shows that ammonia was being oxidized mainly to nitrite and only lesser concentrations of nitrate are present at the end of 18 h CT. Fig. 3c shows the ammonia conversion profile for phase III, Phase IV to VI have similar profile as phase III; Fig. 3f and phase IV Fig. 4c. These profiles clearly showed that the SRT maintained in the reactor affects the nitrification efficiency and characteristics of nitrogen species present at the end of CT. As reported in literature, low SRT resulted in reduced nitrification efficiency and increased N_2O emission rate in oxic reactors [31]. The nitrite accumulation rate also increased with decrease in SRT [32]. Also higher SRT, generally enhanced the nitrification efficiency and reduced nitrous oxide N_2O emission [33] Figs. 4c and d show the nitrification kinetics with alkalinity and DO profiles, respectively, when the reactor was operated at 20 d SRT and 8 h CT. The reactor was operated within the pH range of 7.25–7.30 by continuously feeding with 0.25 M $NaHCO_3$ and 0.25 M HCL and a maximum DO value of 1 mg L^{-1} by automatic on-off control of the air pump.

NLR from 0.236 to 0.531 kg NH_4–N m^{-3} $d^{-1}$was gradually increased, during operation; (Fig. 2a). It was observed that the OLR and NLR variation had little impact on ammonia removal within the range of values studied. However, the results showed that NH_4–N removal was highly affected by the process aeration, DO and alkalinity as can be seen during phase II. After Phase II, the process was restored and showed good performance. A total CT of 8 h and 20 d SRT were found to be the optimum conditions for effective removal of ammonium nitrogen.

3.3.3. Total nitrogen (TN) removal

Analysis of the removal kinetics in the reactor showed that nitrogen was simultaneously removed with organic



* (Note that 100% DO saturation is equal to 8mg/L)

Fig. 4. Typical steady-state profiles for NH_4–N, NO_x–N and alkalinity, pH and DO in phase VI (a) NH_4–N and NO_x–N profiles, (b) NH_4–N and NO_x–N, TCOD, sCOD profiles, (c) NH_4–N and NO_x–N and alkalinity profiles, (d) NH_4–N and NO_x–N and DO profiles, (e) variation of NH_4–N and TKN, and (f) time variation of pH and DO.

carbon at the start of every cycle due to the instant very high COD exerted and the presence of NO_x from the previous cycle. The results in Fig. 4d show the DO profile of the reactor in one CT (8 h). It was observed that the DO was below 0.4 mg L^{-1} during the initial 2 h of aeration and simultaneous removal of nitrogen and organic carbon observed mainly due to denitrification. This process significantly reduces the oxygen requirement for COD reduction in the aerobic reactor as the NO_x–N was used instead of DO as a terminal electron acceptor instead of DO [34,35]. The process of denitrification was confirmed by the increase in alkalinity and pH as shown in Figs. 4c and f, respectively, during the start of aeration. Fig. 4c also shows the alkalinity profile where the alkalinity was increased to 500 mg L^{-1} as $CaCO_3$ in the first 2 h and later decreased to 300 mg L^{-1} as $CaCO_3$ at the end of 8 h CT. The increase in alkalinity at the start of the cycle could be due to denitrification while the decrease in alkalinity at the end of the cycle was due to nitrification [6].

It has been reported that the wastewater COD/N ratio significantly affects the TN removal efficiency and lack of suitable organic substrate may result in poor denitrification [36]. Further, it has been reported that 3.3–5.0 g of the COD/NO_3–N ratio is required to achieve complete denitrification [37]. The production of some alkalinity was noticed during pre-denitrification which resulted in net savings in alkalinity requirements for the nitrification reaction [38]. The organic matter was not a significant factor in the total nitrogen removal as the feed COD: TKN ratio was 15. The TN removal efficiency was affected by the nitrification efficiency, SRT and HRT maintained.

Figs. 4c and d also show that ammonia oxidation started at the early stage where the DO was very less (DO < 0.2 mg L^{-1}); where DO > 0.4 mg L^{-1}, NO_x–N accumulation started after 2 h of operation; and between DO 0.2–0.4 mg L^{-1} where any NO_x–N produced was denitrified. In every kinetic data, it has been observed that the NO_3–N was accumulated after the COD was removed and thereby favoring the C/N ratio for anammox to be active. This nitrate accumulation could be due to the action of anammox bacteria. It is reported by Anjali and Sabumon [20,39] that anammox could be maintained in the presence of COD at lower C/N ratios.

Fig. 5a shows the total influent and effluent nitrogen profile with associated removal efficiency profile. The result showed that high nitrogen removal efficiency in phase (III–VI) and the average removal efficiency increased with an increase in operating CT at constant SRT of 20 d (Fig. 5b). At 20 d SRT, TN efficiencies (TN-RE) were 43.10% ± 1.7%, 53.74% ± 8.8%, 58.05% ± 10.5% and 69.35% ± 3.8% for CT

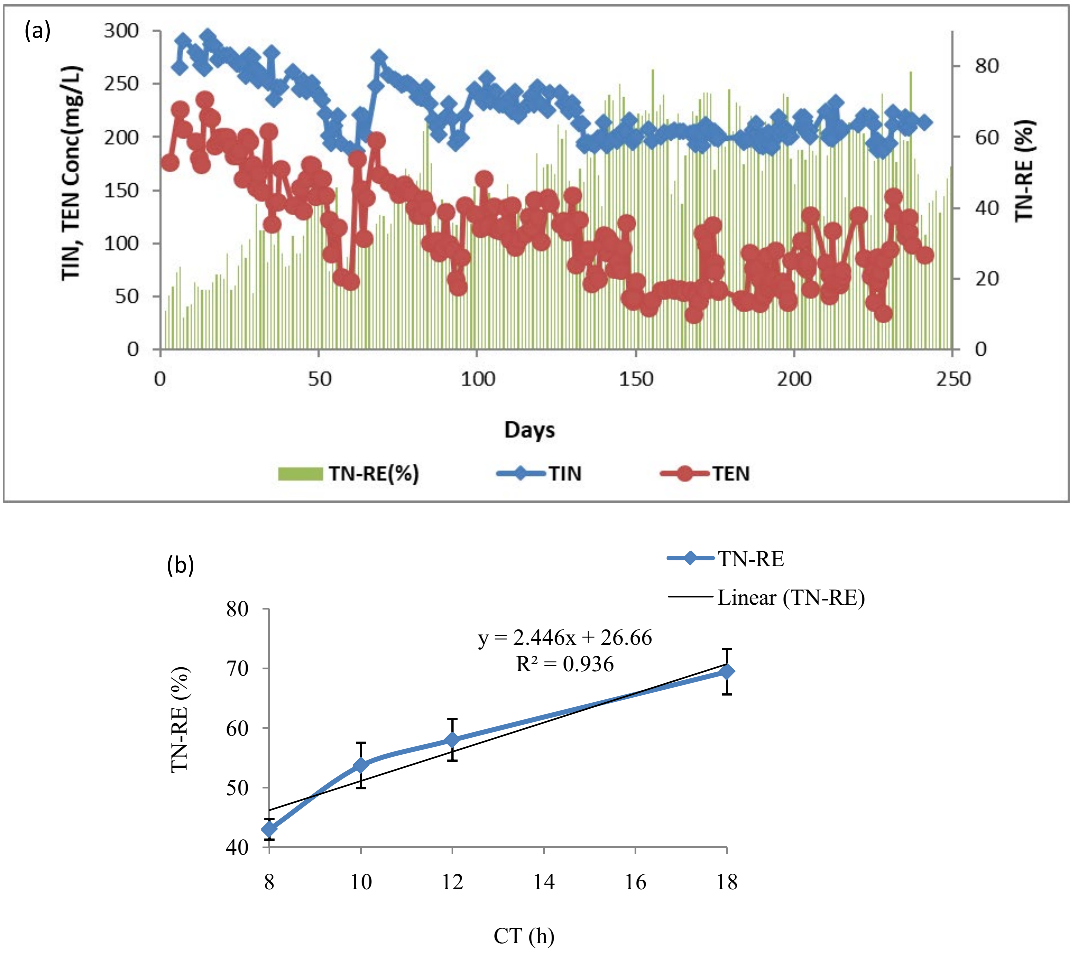


Fig. 5. Daily nitrogen removal and respective cycles average TN removal (a) Daily initial TN (TIN) and effluent TN (TEN) with corresponding removal efficiency and (b) average TN removal efficiency for phase (III–VI) at different operating CT.

$$\mathrm{TN-RE}(\%)=\frac{[\mathrm{TIN}-\mathrm{TEN}]\times 100}{[\mathrm{TIN}]}$$
$$=\frac{[\mathrm{Initial}(\mathrm{NH_4-N+NO_2-N+NO_3-N})-\mathrm{final}(\mathrm{NH_4-N+NO_2-N+NO_3-N})]}{\mathrm{Initial}[\mathrm{NH_4-N+NO_2-N+NO_3-N}]}$$

N.B.: TN removal efficiency was calculated based on the above equation and considering TN concentrations in initial mixed liquor after 5 min of aeration and TN concentrations in final effluent samples. TN removal is observed during the initial anoxic feeding and 5 min of aeration, this can be justified as the NO_x–N profiles show near zero value at the start of CT.

values of 8, 10, 12, and 18 h, respectively. The TN-RE showed a linear correlation with CT and removal increased with increasing CT and removal was affected at very low CT.

4. Conclusion

From the results of the study, it was observed that SRT and CT have a significant effect on the removal efficiency organic carbon (COD) and nitrogen and the quality of final treated effluent. Operating at low SRT resulted in partial nitrification and denitrification mainly through via nitrite. At higher SRT, complete nitrification was observed while partial nitrification was observed in a short period as compared to low SRT. Denitrification took place in the course of the anoxic feeding and initial period of mixing and aeration. Under this condition with low dissolved oxygen, nitrate and/or nitrite from previous cycles can be used as an alternative electron acceptor for denitrification. The TN removal was also found to be dependent on the operating SRT and CT. From this research study, it is concluded that the optimum CT for (>90%) removal of both organic carbon and nitrogen was 8 h at SRT of 20 d.

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Symbols

AOB — Ammonia oxidizing bacteria
C_0 — Influent COD concentration, g/L
CT — Cycle time, *h*
DO — Dissolved oxygen, mg/L
HRT — Hydraulic retention time, h
MLSS — Mixed liquor suspended solids, g/L
MLVSS — Mixed liquor volatile suspended solids, g/L
N_0 — Influent nitrogen concentration (gNH$_4$–N/L)
NOB — Nitrite oxidizing bacteria
NLR — Nitrogen loading rate (gNH$_4$–N/L d)
OLR — Organic loading rate (gCOD/L d)
ORP — Oxidation-reduction potential
PLC — Programmable logic controller
Q — Flow rate, L/d
$\mathbf{Q}_w$ — Quantity of excess sludge wasted per day, L/d
SRT — Sludge retention time, *d*
t_a — Time for aeration, min
t_d — Time for decanting, min
t_f — Time for feeding, min
t_s — Time for settling, min
TN — Total nitrogen
TN-RE — Total nitrogen removal efficiency
VER — Volume exchange ratio
V_r — Volume of reactor, L
X_r — MLVSS (g/L) in the reactor
X_w — MLVSS (g/L) in Waste sludge

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