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Effect of carbon-to-nitrogen ratio on high-rate nitrate removal in an upflow sludge blanket reactor for polluted raw water pre-treatment application

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Abstract

The drinking water treatment plants (DWTPs) in the developing countries urgently need an efficient pre-treatment for nitrate (NO_3^-) removal to cope with the increasing NO_3^- pollution in raw water. An upflow sludge blanket (USB) reactor applied for NO_3^- removal from domestic wastewater may be adopted by the DWTPs. However, studies on the optimal carbon-to-nitrogen ratio (C/N) and operation of USB reactor at short hydraulic retention times (HRT) for high-rate polluted raw water pre-treatment are lacking. In this study, we first investigated the optimal C/N for biological NO_3^- removal in a sequencing batch reactor (SBR). An USB reactor was then operated with the optimal C/N for pre-treating synthetic raw water contaminated with NO_3^- (40 mg N L^{-1}) to monitor the NO_3^- removal performance and to examine opportunities for reducing the HRT. After operating the SBR with designed C/N of 4, 3 and 2 g C g^{-1} N, we selected C/N of 3 g C g^{-1} N as the optimal ratio due to the lower carbon breakthrough and nitrite (NO_2^-) accumulation in the SBR. The USB reactor achieved complete NO_3^- and NO_2^- removal with a lower designed C/N of 2 g C g^{-1} N due to the longer sludge retention time when compared with that of SBR (10 d). The high specific denitrification rate (18.7 ± 3.6 mg N g^{-1} mixed liquor volatile suspended solids h^{-1}) suggested a possible HRT reduction to 36 min. We successfully demonstrated an USB reactor for high-rate NO_3^- removal, which could be a promising technology for DWTPs to pre-treat raw water sources polluted with NO_3^-.

Keywords: Denitrification, Hydraulic retention time, Nitrate contamination, Sequencing batch reactor, Sludge retention time

Introduction

Nitrate (NO_3^-) pollution is increasingly threatening the water quality in many developing countries undergoing rapid urbanization, mainly due to agricultural runoffs, livestock wastewater and discharge of inadequately treated domestic wastewater. For example, Malaysia is one these developing countries experiencing temporal elevated nitrate nitrogen (NO_3^--N) up to 35 mg L^{-1} in rivers [1, 2]. To prevent elevated NO_3^- pollution from causing public health concerns, World Health Organization [3] recommended that NO_3^--N in drinking water must not exceed 10 mg L^{-1}.

Most of the drinking water treatment plants (DWTPs) in the developing countries lack a treatment technology for NO_3^- removal from raw water because most of these plants are still using conventional process [4]. Thus, research study on a robust raw water pre-treatment technology for NO_3^- removal is urgently needed to protect the public health.

In recent years, biological denitrification treatment is gaining attention in NO_3^- removal rather than ion

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exchange, catalytic reduction, or reverse osmosis due to its high efficiency, low cost, and capability of converting NO_3^- into inert nitrogen gas [5, 6]. Biological denitrification was commonly reported for NO_3^- removal from domestic wastewater in activated sludge process [7–9]. Besides using activated sludge, using an upflow sludge blanket (USB) reactor for biological denitrification could encourage the agglomeration of sludge into granules. The sludge granulation occurred through the washout of light flocs, while sludge with good settleability remained in the USB reactor could agglomerate into granules [10, 11]. The granular sludge in the USB reactor may retain very high biomass concentration (7–130 g L^{-1}) to promote high-rate NO_3^- removal from the domestic wastewater [11–13]. For example, Watari et al. [11] reported granular sludge 3.8 mm in diameter with a biomass concentration between 7 and 8 g L^{-1} in an USB reactor after 15 d of operation using real domestic wastewater. The USB reactor influent was supplemented with sodium nitrate and operated at a NO_3^--N loading rate of 360 ± 90 mg L^{-1} d^{-1} [11]. Du et al. [12] applied USB reactor coupled with anaerobic ammonia oxidation (anammox) process to achieve 89% total nitrogen removal in treating synthetic wastewater rich in NO_3^- at a high NO_3^--N loading rate of 720 mg L^{-1} d^{-1}. Jin et al. [13] has also successfully operated an USB reactor with high biomass concentration (130 g L^{-1}) and granular sludge (1.5–3.5 mm in diameter) to achieve high denitrification efficiency (98%) at a nitrite nitrogen (NO_2^--N) loading rate of 1200 mg L^{-1} d^{-1}.

However, the use of USB reactor configuration for drinking water pre-treatment is still not well understood. A potential challenge of applying USB reactor for pre-treating raw water polluted with NO_3^- is the treatment capacity. USB reactor was typically operated with a hydraulic retention time (HRT) between 8 h and 24 h for domestic wastewater treatment [14, 15]. To meet the high treatment capacity of DWTPs, USB reactor must operate efficiently at lower HRTs, but the effect of HRT on the USB reactor performance for polluted raw water pre-treatment is still lacking in the literature. In contrast with wastewater, raw water contained very low concentration (< 5 mg L^{-1}) of organic carbon [2]. Biological denitrification requires sufficient organic carbon as electron donor, in theory 1.5 g of carbon is required to remove 1 g of NO_3^--N by denitrification [16, 17]. Thus, external carbon dosage was needed to enhance the denitrification performance. The common carbon sources commercially used include acetate, glucose, and methanol [18]. Methanol is the most widely used carbon source due to its high availability, biodegradability, and efficiency. However, methanol usage is hazardous as it is flammable, toxic, and highly reactive [19]. As an alternative solution, Peng et al. [20] suggested the use of acetate because it has low toxicity, high biodegradability and high NO_3^- utilization rate. An optimum dosage requirement expressed as carbon-to-nitrogen ratio (C/N) for raw water pre-treatment in the USB reactor is required to provide sufficient amount of carbon source for biological NO_3^- removal, at the same time over-dosage must be avoided to prevent carbon breakthrough in the effluent.

This study aimed to investigate the effect of C/N on the NO_3^- removal performance of an USB reactor pre-treating synthetic raw water contaminated with NO_3^-. A sequencing batch reactor (SBR) was first operated to study the optimal C/N for biological denitrification pre-treating the synthetic raw water. Subsequently, we applied the optimal C/N in an USB reactor to monitor its denitrification performance and to examine opportunities to reduce the HRT of the reactor.

Materials and methods

SBR operation

A SBR of 1-L working volume was set up (Fig. 1). The SBR was inoculated with activated sludge obtained from a domestic wastewater treatment plant in Kuala Lumpur, Malaysia operating in SBR configuration with a pre-anoxic selector. Synthetic raw water contaminated with NO_3^- was prepared according to the composition listed in Table 1. Sodium acetate and sodium nitrate were used as the dissolved organic carbon (DOC) and NO_3^- sources, respectively. The synthetic raw water was autoclaved at 121 °C for 20 min immediately after preparation to prevent microbial consumption of DOC and NO_3^- for their growth.

Each SBR cycle consisted of five phases, including 15 min of filling phase, 300 min of reaction phase, 30 min of settling phase, 14 min of decanting phase and 1 min

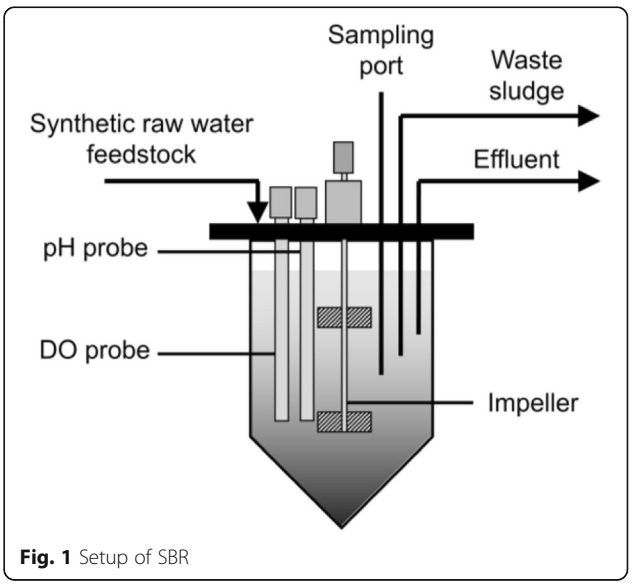

Fig. 1 Setup of SBR

Table 1 Composition of synthetic raw water feedstock for SBR

Macronutrient (mg L^{-1})		Micronutrient (mg L^{-1})	
Sodium acetate	228–456	Iron(II) sulfate heptahydrate	1.49
Sodium nitrate	202	Boric acid	0.17
Magnesium sulfate heptahydrate	101	Zinc sulfate heptahydrate	0.13
Sodium sulfite	100	Manganese (II) chloride tetrahydrate	0.11
Potassium hydrogen phosphate dibasic	29	Copper(II) sulfate pentahydrate	0.04
Calcium chloride dihydrate	18	Sodium molybdate dihydrate	0.01

of idling phase [21, 22]. Anoxic condition in the SBR was achieved through the addition of 0.1 g of sodium sulfite per liter of synthetic raw water [23]. Sodium sulfite was added to ensure a controlled anoxic environment in the lab-scale SBR. The addition of sodium sulfite will not be required in full-scale DWTPs operation due to lower dissolved oxygen (DO) concentrations in real raw water. Mixed liquor within the reactor was agitated using a single impeller operating at 90 rpm throughout the reaction phase. The sludge retention time (SRT) and HRT were set at 10 d and 10 h, respectively. The SBR was operated at ambient temperature (28 ± 2 °C). The DO and pH of the reactor was monitored on-line using a M300 Process 2-channel ¼ DIN transmitter coupled with an InPro6850i DO probe and a 405-DPAS-SC-K851200 combination pH/temperature probe (Mettler-Toledo, US).

We operated the SBR for 22 d in three operating phases (SP1, SP2 and SP3 in Table 2). The C/N of each operating phase was increased stepwise and operated for a week to monitor the denitrification performance at different C/N. Three sampling campaigns were carried out each week. In each sampling campaign, the mixed liquor samples were collected every 2 h for chemical analyses to monitor the evolution of DOC, nitrite (NO_2^-) and NO_3^- in the SBR.

USB reactor operation

We set up an USB reactor with a 2-L working volume (Fig. 2). The total height of the reactor was 100 cm with an internal diameter of 10 cm, the spacing between each sampling port was 15 cm. A purge gas recirculation line was installed to prevent floating sludge (Fig. 2). The nitrogen gas produced was recycled to the bottom of the USB reactor intermittently for 1 min every hour to purge the trapped nitrogen gas in the sludge flocs. We seeded the USB reactor with the same source of activated sludge for SBR as shown above. The synthetic raw water fed into the USB reactor was prepared by diluting the concentrated feedstock solution with tap water at a ratio of 1:5. Sodium acetate and potassium nitrate were used as the source of DOC and NO_3^- in the synthetic raw water, respectively. The macronutrient, micronutrient and phosphate feedstock solutions were mixed at a ratio of 1: 0.0004:1 in the feed tank. The compositions of the USB reactor influent were listed in Table 3. The synthetic raw water was fed into the USB reactor continuously using a peristaltic pump.

Table 2 Designed operating conditions of SBR

Operating phase	SP1	SP2	SP3
Days	1–9	10–15	16–22
C/N (g C g^{-1} N)	4	3	2
DOC (mg L^{-1})	80	60	40
NO_3^--N (mg L^{-1})	20	20	20

The HRT of the reactor was 3 h. We operated the USB reactor at ambient temperature (28 ± 2 °C). We started up the reactor for 22 d to reach a stable denitrification performance with a C/N of 3 g C g^{-1} N. The reactor was subsequently operated in two consecutive operating phases (UP1 and UP2) to monitor the NO_3^- removal performance of the USB reactor (Table 4). Three sampling campaigns were performed per week to collect the influent and effluent samples at the bottom and top of the USB reactor, respectively. Additionally, detailed sampling campaign were conducted biweekly to show the evolution of carbon and nitrogen species along the vertical flow length of the reactor by collecting influent sample, effluent sample and mixed liquor samples from each of the sampling port (Fig. 2).

Chemical analyses

The pH of mixed liquor samples obtained from the USB reactor was measured using an 827 pH Lab with Primatode (Metrohm, Switzerland). We filtered all the mixed liquor samples from the SBR and the USB reactor through a 0.2-μm membrane filter for anion analysis (NO_2^- and NO_3^-) using an 861 Advanced Compact Ion Chromatograph (Metrohm, Switzerland). The DOC of the samples was measured using a TOC-V CSN total organic carbon analyzer (Shimadzu, Japan) after filtration through a 0.45-μm membrane filter. The concentrations of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were determined according to the Standard Methods [24].

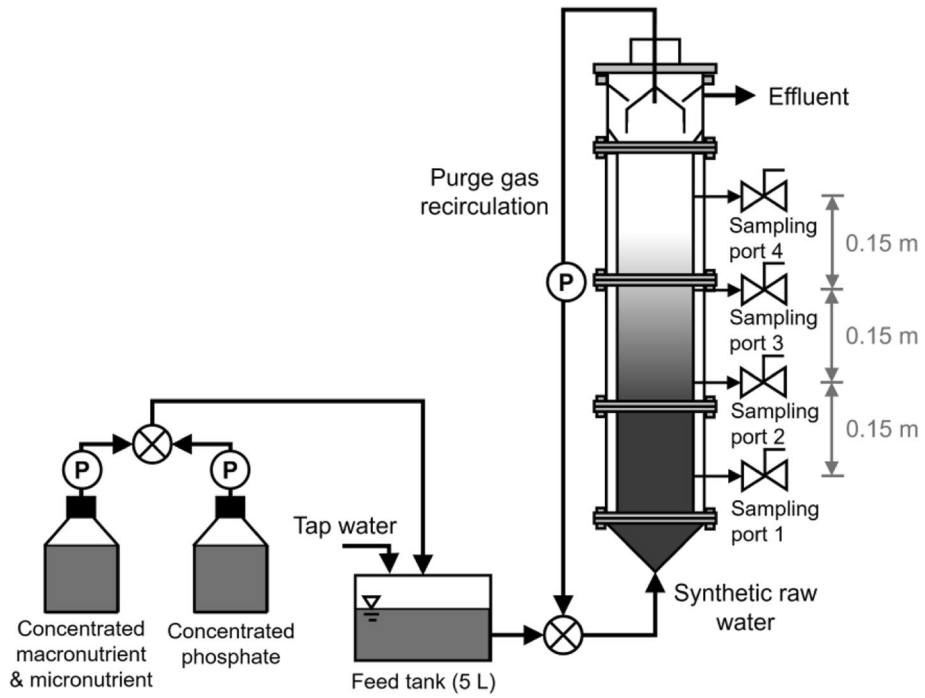

Fig. 2 Setup of USB reactor

Specific denitrification rate (SDNR) calculation

The SDNR was calculated using Eq. (1).

$$\mathrm{SDNR} = \frac{\Delta \mathrm{NO_x}^- - \mathrm{N}}{\mathrm{HRT} \times \mathrm{MLVSS}} \quad (1)$$

where ΔNO_x^--N (mg L^{-1}) was the sum of NO_3^--N and 0.6 times NO_2^--N removed in the reactor to account for the lower oxygen equivalent of NO_2^- when compared with NO_3^- [25]. MLVSS and HRT were in the unit of g L^{-1} and h, respectively.

Results and discussion

Effect of C/N on denitrification performance in SBR

The SBR was operated for 22 d (Table 2). The pH, DOC, NO_3^- and NO_2^- profiles under different C/N in SP1, SP2 and SP3 are shown in Fig. 3. The C/N was calculated from DOC, which was a normalized parameter for the measurement of organic carbon concentration from sodium acetate. The use of DOC allows fair comparison of reactor performance with other studies using different types of carbon source, such as methanol and ethanol, under similar C/N. In SP1 operated with a designed C/N of 4 g C g^{-1} N, the pH of the SBR (Fig. 3a)

Table 3 Composition of synthetic raw water for USB reactor

Macronutrient (mg L^{-1})		Micronutrient (×10^{-3} mg L^{-1})	
Sodium acetate	273–410	Ethylenediaminetetraacetic acid	12
Potassium nitrate	289	Iron(III) chloride hexahydrate	1.8
Magnesium chloride hexahydrate	121	Potassium iodide	0.22
Magnesium sulfate heptahydrate	68	Boric acid	0.18
Potassium hydrogen phosphate monobasic	18	Cobalt(II) chloride hexahydrate	0.18
Calcium chloride dihydrate	32	Manganese (II) chloride tetrahydrate	0.14
		Zinc sulfate heptahydrate	0.14
		Sodium molybdate dihydrate	0.07
		Copper(II) sulfate pentahydrate	0.04

Table 4 Designed operating conditions of USB reactor

Operating phase	UP1	UP2
Days	1–6	7–34
C/N (g C g^{-1} N)	3	2
DOC (mg L^{-1})	120	80
NO_3^--N (mg L^{-1})	40	40

increased from 8.9–9.3 in the influent to 9.4 in the effluent due to the production of alkalinity during the denitrification process [26]. The initial DOC concentration in the SBR was 118.2 ± 4.8 mg L^{-1}, which was higher than the designed initial DOC concentration of 80 mg L^{-1} (Table 2). The higher measured initial DOC concentration in the SBR was caused by DOC carryover from the previous SBR cycle. Based on the average unremoved DOC at the end of the cycle (66.1 ± 7.1 mg L^{-1}) in Fig. 3b and a SBR volume exchange ratio of 0.6, the DOC concentration in the feedstock before entering the SBR (133 mg L^{-1}) will be diluted to [(133.0 mg L^{-1} × 0.6 L) + (66.1 mg L^{-1} × 0.4 L)]/1 L = 106.2 mg L^{-1} ≈ 110 mg L^{-1} in the SBR. Since the estimated DOC concentration at the start of cycle (110 mg L^{-1}) agreed with our measured DOC concentration (118.2 ± 4.8 mg L^{-1}), we may reason that the higher initial DOC concentration in the SBR was caused by the carryover of unremoved DOC from the previous SBR cycle. The NO_x^--N removed, which was defined as the sum of NO_3^--N and 0.6 times NO_2^--N, during SP1 was 21.7 ± 0.4 mg L^{-1}, with negligible NO_3^--N and NO_2^--N at the end of SBR cycle (Fig. 3c and d). A small amount of NO_2^--N (1.3 ± 0.5 mg L^{-1}) was present at the start of the SBR reaction phase (Fig. 3d) because some NO_3^- could be reduced to NO_2^- by the heterotrophs during the anoxic filling phase. Based on the difference between the DOC at the beginning and at the end of the SBR reaction phase in SP1 (Fig. 3b), approximately 52.1 ± 0.6 mg L^{-1} of DOC was consumed for both denitrification and cell synthesis. The theoretical concentration of DOC required to remove the NO_x^--N present at the start of the SBR reaction phase (21.7 ± 0.4 mg L^{-1}) was only 32.6 mg L^{-1} using a C/N (expressed as a ratio between carbon and nitrogen) of 1.5 g C g^{-1} N [16]. The remaining DOC consumed (19.5 mg L^{-1}) may be attributed to the cell synthesis. Thus, the high DOC concentration at the beginning of SBR cycle in SP1 (118 ± 5 mg L^{-1}, Fig. 3b) resulted in excess DOC supplied and significant carbon breakthrough in the effluent.

To reduce the carbon breakthrough in the effluent, we decreased the designed C/N to 3 g C g^{-1} N in SP2

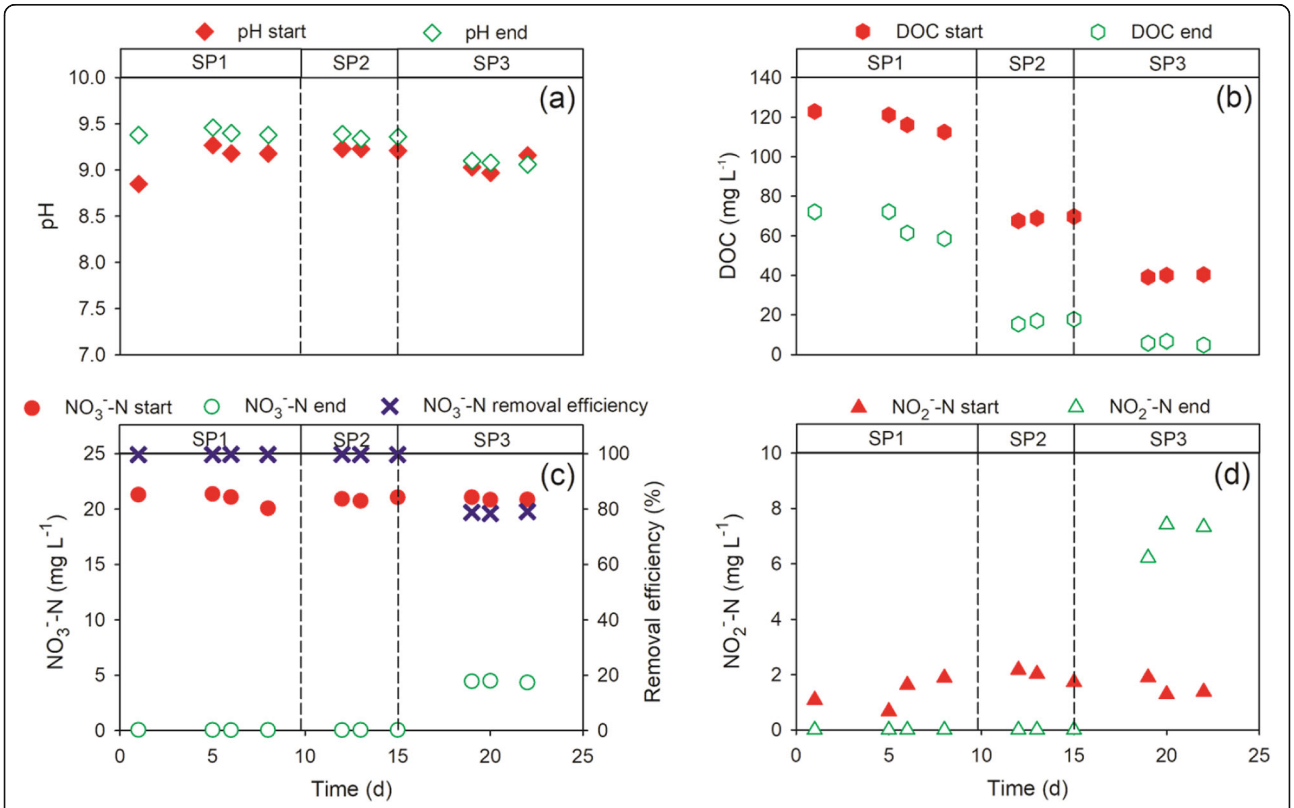

Fig. 3 The SBR profiles during SP1, SP2 and SP3. pH (**a**), DOC (**b**), NO_3^--N (**c**) and NO_2^--N (**d**). The suffixes "start" and "end" refer to the beginning and end of the reaction phase, respectively

(Table 2). The pH increased from 9.2 to 9.4 (Fig. 3a), indicating active denitrification in the SBR. The DOC concentration at the start of cycle was 68.8 ± 1.1 mg L^{-1}, which was slightly higher than the designed concentration of 60 mg L^{-1} due to the carryover of unremoved DOC from the previous cycle. The DOC at the end of cycle in SP2 (16.7 ± 1.3 mg L^{-1}; Fig. 3b) was 4 times lower than that in SP1 (66.1 ± 7.1 mg L^{-1}; Fig. 3b), thus indicating a significantly lower carbon breakthrough in the effluent during SP2 when compared with that during SP1. This implied that a designed C/N of 3 g C g^{-1} N may be a suitable C/N to be adopted for NO_3^- removal from polluted raw water, while ensuring minimal carbon breakthrough in the effluent. Similar to SP1, the effluent NO_3^--N and NO_2^--N were negligible and the NO_x^--N removed was 22.1 ± 0.1 mg L^{-1} (Fig. 3c and d). From the DOC, NO_3^- and NO_2^- profiles in SP1 and SP2, the ratio of DOC to NO_x^--N consumed (DOC/NO_x^--N) to achieve complete denitrification was 2.4 ± 0.1 g DOC g^{-1} NO_x^--N. The calculated DOC/NO_x^--N agreed with the C/N range of 1.7 to 2.9 g C g^{-1} N typically applied for denitrification systems [17, 20, 27], which should be slightly higher than the theoretical C/N of 1.5 g C g^{-1} NO_x^--N removed reported in the literature [16].

To validate that DOC/NO_x^--N of 2.4 g C g^{-1} N was required for complete denitrification, we operated the SBR with a slightly lower designed C/N of 2 g C g^{-1} N in SP3 (Table 2). The pH of the reaction mixture did not increase (Fig. 3a), which indicated a reduction in denitrification activity. The DOC concentration at the start of cycle in SP3 was 39.9 ± 0.7 mg L^{-1}, while its concentration reduced to 5.8 ± 0.9 mg L^{-1} at the end of cycle (Fig. 3b). The NO_3^--N and NO_2^--N at the end of cycle were 4.4 ± 0.1 and 7.0 ± 0.7 mg L^{-1}, respectively (Fig. 3c and d), which was comparatively higher than the negligible NO_3^--N and NO_2^--N at the end of cycle during SP1 and SP2. The high NO_2^- concentration in the reactor exceeded the limit for drinking water (3.0 mg L^{-1}) recommended by World Health Organization [3], which may cause lethal methemoglobinemia amongst infants. Thus, higher C/N (> 2.4 g C g^{-1} N) should be applied to prevent NO_2^- accumulation.

From the investigation of different C/N (2, 3 and 4 g C g^{-1} N) in the SBR, we deduced that a designed C/N of 3 g C g^{-1} N was the optimal ratio that should be applied for the subsequent USB reactor operation. By using a designed C/N of 3 g C g^{-1} N, the carbon breakthrough could be minimized while ensuring complete NO_3^- and NO_2^- removal from the synthetic raw water.

Denitrification efficiency and SDNR in USB reactor

After a stabilization period of 22 d, the USB reactor was operated in UP1 (designed C/N = 3 g C g^{-1} N) for 6 days (Table 4). Figure 4 shows the pH, DOC, NO_3^- and NO_2^-profiles of the USB reactor. The pH of the reaction mixture in USB reactor increased from 7.3–8.6 in the influent to 8.7–9.5 in the effluent during UP1 (Fig. 4a). The larger magnitude of pH increases in the USB reactor when compared with that in the SBR was caused by the higher designed influent NO_3^--N (40 mg L^{-1}) in the USB reactor in comparison to 20 mg NO_3^--N L^{-1} in the SBR. The influent pH in the USB reactor (7.3–8.6) was also lower than that in the SBR after influent addition (9.1) because potassium hydrogen phosphate monobasic was used as the phosphate buffer during the USB reactor operation, while potassium hydrogen phosphate dibasic was used for the SBR operation. In UP1, the DOC concentration reduced from 98.9 ± 23.5 mg L^{-1} in the influent to 62.1 ± 12.9 mg L^{-1} (Fig. 4b). The influent DOC on day 6 was lower due to reactor operation error that caused denitrification along the transport tube from the feed tank to the USB reactor. Based on the ratio of the difference between the designed and measured influent DOC and NO_x^--N on day 6, the C/N for denitrification along the transport tube was 2.3 g DOC g^{-1} NO_x^--N. The C/N was similar to the ratio calculated from the SBR operation, which explained the partial denitrification of NO_3^- in the influent into NO_2^- at the entrance of the USB reactor. During UP1, Fig. 4c showed that only 15.1 ± 2.4 mg L^{-1} of NO_3^--N was present in the influent, while the influent NO_2^--N was 17.8 ± 6.3 mg L^{-1} (Fig. 4d). Thus, the sum of influent NO_2^--N and NO_3^--N was 32.9 ± 8.4 mg L^{-1}, which was close to the designed influent NO_3^--N (40 mg L^{-1}). Both NO_3^- and NO_2^- was completely removed from the synthetic raw water with a low effluent NO_3^--N (0.5 ± 0.1 mg L^{-1}) and NO_2^--N (≈ 0). Based on the concentrations of DOC (36.9 ± 17.2 mg L^{-1}) and NO_x^--N (25.3 ± 6.0 mg L^{-1}) removed in UP1, the calculated DOC/NO_x^--N was 1.4 ± 0.4 g DOC g^{-1} NO_x^--N. The ratio was lower than the calculated ratio in the SBR (2.4 ± 0.1 g DOC g^{-1} NO_x^--N) and along the transport tube on day 6 during UP1 (2.3 g DOC g^{-1} NO_x^--N). A probable reason for the lower DOC/NO_x^--N was the long SRT operation of USB reactor because the sludge in the reactor was not wasted regularly, when compared with a SRT of 10 d in the SBR. Nonetheless, the true SRT of the USB reactor should be evaluated in the future works considering small amount of the floating sludge that discharged together with the effluent. The longer SRT of USB reactor could promote sludge hydrolysis that supplemented the carbon source [28, 29], thus the DOC supplied to the reactor may not be fully utilized for denitrification. We may further reduce the C/N of the USB reactor influent due to the lower required DOC/NO_x^--N. The reduction in the influent C/N could lower the carbon breakthrough observed in UP1 (62.1 ± 12.9 mg L^{-1}).

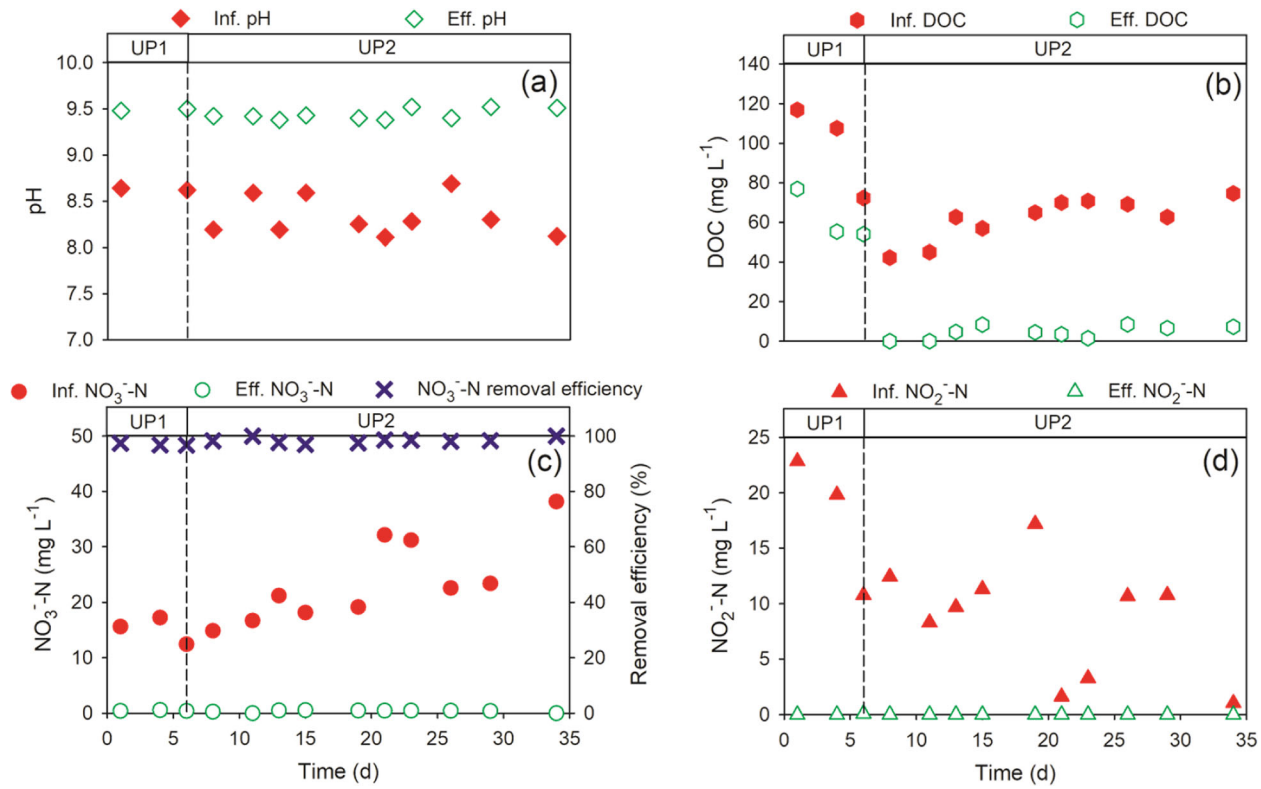

Fig. 4 The USB reactor profiles during UP1 and UP2. pH (**a**), DOC (**b**), NO_3^--N (**c**) and NO_2^--N (**d**). The abbreviations "Inf" and "Eff" stand for influent and effluent, respectively

Subsequently, we operated the USB reactor for 28 d in UP2 (designed C/N = 2 g C g^{-1} N; Table 4). In UP2, the pH of the USB reactor increased from 8.1–8.7 in the influent to 9.4–9.5 in the effluent (Fig. 4a). Figure 4b shows that the carbon breakthrough in UP2 significantly improved with an effluent DOC (4.5 ± 3.2 mg L^{-1}), or 12 times lower than that in UP1 (62.1 ± 12.9 mg L^{-1}), which may serve as a practical guideline for the DWTPs' operators to adopt a lower designed C/N of 2.0 g C g^{-1} N when pre-treating raw water contaminated with NO_3^- using an USB reactor. At the same time, the USB reactor achieved complete denitrification with effluent NO_3^--N and NO_2^--N of 0.2 ± 0.1 mg L^{-1} and close to 0, respectively (Fig. 4c and d). The corresponding NO_3^- and NO_2^- removal efficiencies were 99 ± 1% and near 100%, respectively. The USB reactor operation in UP2 implied a designed C/N of 2 g C g^{-1} N was sufficient for an USB reactor system pre-treating synthetic raw water with NO_3^--N loading rate of 320 mg L^{-1} d^{-1} to achieve a high denitrification efficiency with a HRT of 3 h. The HRT applied in this study was relatively shorter than other denitrification reactors with a similar or lower NO_3^--N loading rate and C/N (all expressed in g C g^{-1} N) in Table 5 [5, 11, 16, 30, 31]. For instance, Her et al. [30] reported a NO_3^- removal efficiency of 97–99% in a batch denitrification system treating synthetic wastewater (C/N = 1.9 g C g^{-1} N, HRT = 12 h, NO_3^--N loading rate = 100 mg L^{-1} d^{-1}). Chen et al. [5] needed a HRT of 24 h for complete NO_3^- removal in a freshwater batch denitrification system operated with a C/N of 3.0–5.0 g C g^{-1} N and a NO_3^--N loading rate of 5 mg L^{-1} d^{-1}. Similarly, a batch biofilm reactor with a C/N of 1.1 g C g^{-1} N and a NO_3^--N loading rate of 4 mg L^{-1} d^{-1} required a HRT of 24 h to remove 82% of the total nitrogen from the synthetic polluted water [31]. Dahab et al. [16] also reported an upflow packed bed reactor operated with a C/N and a NO_3^--N loading rate of 1.5 g C g^{-1} N and 267 mg L^{-1} d^{-1}, respectively, but needed a longer HRT of 9 h to achieve near complete NO_3^- removal from their synthetic raw water. In contrast, Watari et al. [11] reported that a HRT of 3 h in an USB reactor operated at a C/N and a NO_3^--N loading rate of 1.4 g C g^{-1} N and 360 ± 90 mg L^{-1} d^{-1}, respectively, attained a poor NO_3^- removal efficiency (35%). The poor denitrification performance was attributed to the decreasing wastewater temperature from 27 to 10 °C during the winter months in Japan [11].

Table 5 Comparison of reactor configuration, operating conditions, influent compositions and denitrification efficiency between the USB reactor and other studies

Reactor configuration	HRT (h)	Carbon source	Influent NO_3^--N (mg L^{-1})	Influent C/N (g C g^{-1} N)	NO_3^--N loading rate (mg L^{-1} d^{-1})	NO_3^--N removal efficiency (%)	Reference
USB	3	Sodium acetate	40	2–3	320	99 ± 1	This study
Batch denitrification experiment	12	Acetic acid	50	1.9	100	97–99	[30]
Batch denitrification experiment	24	Sodium acetate	5	3–5	5	> 99	[5]
Batch biofilm reactor	24	Sodium acetate with rice straw/rice husk	4	1.1	4	82	[31]
Upflow packed bed column	9	Acetic acid	100	1.5	267	> 99	[16]
USB	3	Raw sewage	32.9 ± 11.0	1.4	360 ± 90	35	[11]

To explore opportunities for HRT reduction to achieve the high treatment capacity required for raw water pre-treatment, we examined the detailed pH, NO_x^- and DOC profiles of the USB reactor during UP2 (Fig. 5). The detailed profile indicated that the denitrification reaction was completed by the first sampling port (flow length = 0.15 m). The pH of the reaction mixture increased from 8.2 to 9.4, after which the pH remained constant from the first sampling port to the effluent outlet (flow length = 0.75 m). In line with the increasing pH trend, we observed concomitant removal in DOC and NO_x^- in the USB reactor from the influent inlet to the first sampling port. The DOC and NO_x^--N at the first sampling port were 16.2 ± 3.1 and 0.4 ± 0.1 mg L^{-1} (Fig. 5). The concentrations of DOC and NO_x^- remained relatively constant from the first sampling port to the effluent outlet. The effluent DOC and NO_x^--N were 6.9 ± 0.5 and 0.3 ± 0.2 mg L^{-1}, respectively (Fig. 5). Thus, the HRT may be reduced to 36 min, which was one-fifth of the HRT of our USB reactor. By using Eq. (1) and a HRT of 36 min, the SDNR of the USB reactor was 18.7 ± 3.6 mg N g^{-1} MLVSS h^{-1}. The calculated SDNR for our USB reactor was within the range reported in the literature (10–24 mg N g^{-1} MLVSS h^{-1}) [12, 13, 32]. The high SDNR of USB reactor could lead to potential reduction in HRT, which could be a promising technology for DWTPs to pre-treat raw water contaminated with NO_3^-.

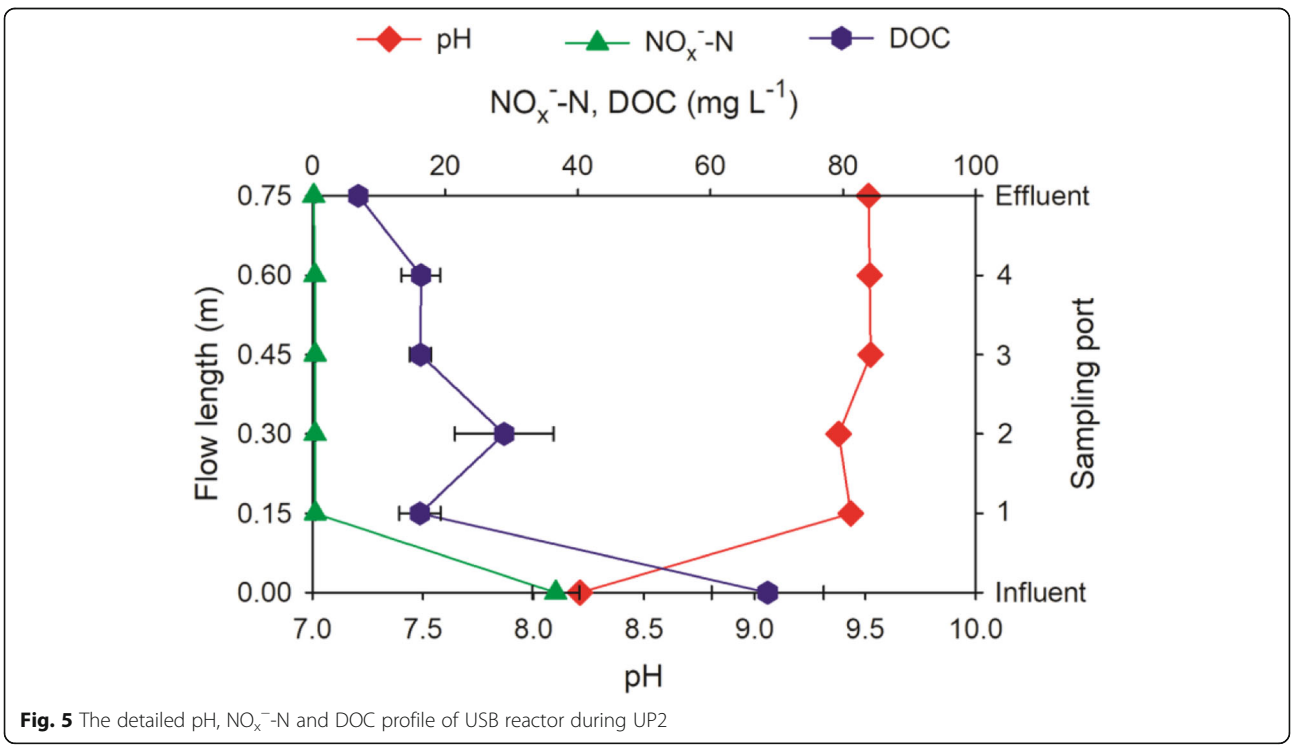

Fig. 5 The detailed pH, NO_x^--N and DOC profile of USB reactor during UP2

Implications on the design of DWTPs

Most of the DWTPs in the developing countries are currently using conventional treatment processes consisting of physical and chemical process (precipitation, sedimentation, sand filtration and chlorination) [4], which necessitated a robust pre-treatment technology to remove NO_3^- from the raw water during pollution. Biological denitrification was the most effective and economical method for NO_3^- removal from polluted raw water [33]. Besides the USB reactor proposed in this study, biofilm reactor is another common biological denitrification technology reported for polluted raw water pre-treatment [31, 34]. A major advantage of the USB reactor proposed in this study was the relatively shorter HRT (3 h) required for near complete removal of NO_x^- from the synthetic raw water contaminated with NO_3^- when compared with other biofilm reactors (24 h) [31, 34]. Since near complete NO_3^- and NO_2^- removal was surprisingly achieved at one-fifth of the total reactor flow length, we recommend a tracer study to gain a better understanding on the hydrodynamics inside the USB reactor and the HRT may be further reduced to 36 min or shorter. Thus, the USB reactor may be a promising pre-treatment process necessary for high-rate NO_3^- removal in DWTPs operating with a high treatment capacity.

We also found that the DOC/NO_x^--N of the USB reactor (1.4 ± 0.4 g DOC g^{-1} NO_x^--N) was slightly lower than the theoretical C/N for denitrification (1.5 g C g^{-1} N) [16, 17]. The long SRT of USB reactor could have promoted sludge hydrolysis to supplement carbon source for denitrification [28, 29]. Thus, adopting USB reactor for polluted raw water pre-treatment may require smaller amount of external carbon sources than the amount calculated based on theoretical C/N to save cost.

In addition, NO_3^- pollution in raw water sources occurred seasonally [1, 2]. Therefore, further investigations are required to study the resilience of USB reactor to recover its denitrification performance after a prolonged period of low NO_3^--N (< 1 mg L^{-1}) in the raw water source [2]. The prolonged low NO_3^- in the raw water source may cause a lower biomass concentration than those reported for USB reactors treating domestic wastewater (7–130 mg MLVSS L^{-1}) [11–13]. The impact of potentially lower biomass concentration in the USB reactor for pre-treating raw water should be investigated during the prolonged exposure to low influent NO_3^-.

Conclusions

An USB reactor for pre-treating synthetic raw water contaminated with NO_3^- was successfully started up in this study. A SBR was first operated to determine a suitable C/N for biological denitrification pre-treating synthetic raw water, a designed C/N of 3 g C g^{-1} N was the optimum ratio to achieve complete denitrification. An USB reactor was then operated at designed C/N of 3 and 2 g C g^{-1} N, a designed C/N ratio of 2 g C g^{-1} N was more suitable for USB reactor to prevent carbon breakthrough. The USB reactor achieved a high SDNR (18.7 ± 3.6 mg N g^{-1} VSS h^{-1}), which suggested opportunities to reduce the HRT (≤ 36 min). Future studies should investigate the USB reactor performance at shorter HRTs to achieve a high treatment capacity required for raw water pre-treatment. We also recommend to address the resilience of USB reactor system to cope with prolonged low NO_3^- in the raw water in future research. Overall, the USB reactor was a promising pre-treatment technology necessary for DWTPs in the developing countries to polish up polluted raw water with NO_3^- prior to entering the drinking water treatment process train, thereby ensuring uninterrupted supply of safe drinking water.

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Authors' contributions

SWH prepared and revised the manuscript draft, and also involved in methodology development, formal analysis and presentation of reactor performance data. CXT, JYY and CYK contributed equally to the conceptualization of reactor study, methodology development, experiment investigation and formal analysis of reactor performance data. CKT and WY were involved in reviewing the data presentation in the manuscript and provided supervisions on the experiment planning. KS provided supervision on reactor operation, project administration and funding acquisition for the study. ASMC was the project principal investigator who contributed to experiment supervision, project administration and funding acquisition. All authors reviewed and approved the final manuscript.

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Availability of data and materials

The data used to support the findings of this study are available from the corresponding author upon request.

Declarations

Competing interests

The authors declare they have no competing interests.

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