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High Rate Nitrogen Removal in an Alum Sludge-Based Intermittent Aeration Constructed Wetland

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ABSTRACT: A new development on treatment wetland technology for the purpose of achieving high rate nitrogen removal from high strength wastewater has been made in this study. The laboratory scale alum sludge-based intermittent aeration constructed wetland (AlS-IACW) was integrated with pre-denitrification, intermittent aeration and step-feeding strategies. Results obtained from 280 days' operation have demonstrated extraordinary nitrogen removal performance with mean TN removal efficiency of 90% under high N loading rate (NLR) of 46.7 g N $m^{-2}\cdot d^{-1}$. This performance was a substantial improvement compared to the reported TN removal performance in literature. Most significantly, partial nitrification and simultaneous nitrification denitrification (SND) via nitrite was found to be the main nitrogen conversion pathways in the AlS-IACW system under high dissolved oxygen concentrations (3-6 mg L^{-1}) without specific control. SND under high DO brings high nitrogen conversion rates. Partial nitrification and SND via nitrite can significantly reduce the demand for organic carbon compared with full nitrification and denitrification via nitrate (up to 40%). Overall, these mechanisms allow the system to maintaining efficient and high rate TN removal even under carbon limiting conditions.

INTRODUCTON

Although constructed wetlands (CWs) have been applied successfully in pollutants removal from various wastewaters, their capacity and efficiency is still low with regard to nutrient removal. With typical configurations (un-aerated surface flow and subsurface flow), removals of total nitrogen (TN) and total phosphorus (TP) remain around 50% in most cases under N loading rate (NLR) of 0.6-2 g N m^{-2} d^{-1} and P loading rate (PLR) of 0.02-0.2 g P m^{-2} d^{-1}.[1-3] This is mainly because that the most effective nutrient removal processes, such as enhanced biological phosphorus removal (EPBR) and biological nitrogen removal (BNR)[4] are limited in the conventional CWs.

Recently, a so-called alum sludge based-CWs (AlS-CWs) has been developed at University College Dublin, Ireland, which adopts dewatered alum sludge (DAS) as the main wetland medium. [5, 6] DAS is an inevitable by-product from drinking water treatment process when aluminium sulphate is used as the primary coagulant. Conventionally, DAS is regarded as a waste with unknown reuse value. However, this largely and locally available “waste” has been demonstrated as a low-cost adsorbent for P immobilization with high P retention capability.[7, 8] Accordingly, intensive efforts have been made by the authors’ research group to develop the AlS-CWs for nutrient removal. The results from laboratory and field trials have proven successful in P removal, [5, 6] thus making TN elimination remaining as the only challenge in AlS-CWs.

Complete TN elimination relies firstly on the complete nitrification. Most conventional CWs fail to fulfill this first step due to insufficient oxygen supply.[9-11] Hence, oxygen supply is the key issue to enhance nitrogen removal in CWs, and artificial aeration is the most effective alternative to guarantee sufficient oxygen supply [12-17]. In particular, when dealing with high strength wastewater, artificial aeration seems to be the only option to achieve complete nitrification. However, with the enhanced oxygen supply denitrification usually becomes the limiting step for effective TN elimination due to the lack of effective anoxic zone and the depletion of the influent carbon source. Consequently, TN removal might still be not desirable even if nitrification has been well conducted.[12, 14, 16] Hence, alternative wetland configuration and operational strategies are requested for efficient denitrification in aerated CWs.

A pre-denitrification stage is the most common adaptation in practice to make efficient utilization of the influent carbon source. And Batch mode is the most effective way to create such a pre-denitrification stage by keeping a certain stationary volume from the previous cycle and starting with an un-aerated phase. Moreover, multiple alternate anoxic/aerobic (An/A) phases and step-feeding can be easily employed in batch mode by intermittent aeration and introducing raw wastewater into each anoxic phase to further enhance the denitrification potential.[18] Significantly, simultaneous nitrification denitrification (SND) and partial nitrification denitrification have been well studied for the purpose of a better nitrogen removal.[19-22] It has been noted that both processes are likely to occur in a biofilm system.[19, 21] Therefore, they may also play an important role in nitrogen conversion in CWs.

Thus, the primary goal of the current study was to achieve high rate nutrient removal from high strength wastewater with a single stage alum sludge-based intermittent aeration CW (AlS-IACW) system. Since efficient P removal was guaranteed by DAS, the main focus was placed on TN elimination. Artificial aeration was employed to ensure complete nitrification under high NLR. Intermittent aeration, pre-denitrification and step-feeding were integrated to achieve efficient denitrification, which is a common problem limiting TN removal performance in aerated CWs.[12, 14, 16] Furthermore, special attention was paid on SND and partial nitrification/denitrification, which were expected to be the main mechanisms on N removal in the AlS-IACW system.

MATERIALS AND METHODS

System configuration and operation

The laboratory scale AlS-IACW system was constructed with plexiglass column (diameter 9.3 cm) (Fig. 1(a)). 10cm-depth gravel was filled into the bottom as the support medium and 60cm-depth air dried DAS (2 kg, moisture content 74%, particle size 1-3 cm) was filled as the main wetland medium layer, which gives a total volume of 4.75 L with initial porosity of 42% (2 L liquid contained). The source and characteristics of the DAS can be found from the authors' previous study.[23] Common reeds, *Phragmites australis*, were planted on the top of the column. Influent was introduced into the column from the top while effluent was drained from the bottom by peristaltic pumps. Aeration was supplied with a diffuser placed on the support layer and controlled with an air flow meter.

The system was operated in batch mode with 3 cycles per day. Incorporated pre-denitrification, intermittent aeration and step feeding was designed as illustrated in Fig. 1(b). Initially, each cycle started with a pre-denitrification stage (An1) by maintaining a stationary volume (V_S) from the previous cycle. V_S serves as NO_X-N (NO_2-N + NO_3-N) pool to form the first anoxic condition after filling. The degree of pre-denitrification is limited by the available NO_X-N, which is determined by the volume exchange ratio (VER) defined as V_S/V_F (V_F, the total filling volume per cycle). The higher the VER, the more NO_X-N is provided for pre-denitrification.[18] However, the hydraulic loading rate (HLR) is decreased if a high VER is adopted since the V_F has to be reduced for a certain total reactor volume (V_T=V_F+V_S). To obtain a high degree of pre-denitrification, a high VER of 9 was adopted with V_S of 1.8 L and V_F of 0.2 L, which results in a daily flow rate of 0.6 L d^{-1} and a HLR of 0.09 m^3 m^{-2} d^{-1}. Air was supplied intermittently with on/off control of the air compressor by a programmable timer. Three alternate An/A sub-cycles in sequence were then created, which provide post denitrification steps. Wastewater was step-fed into the system during the start of each anoxic phase for effective use of carbon substrate for denitrification, with distribution ratios of 60%, 30% and 10% for each feeding.

[Fig. 1]

The system was seeded with activated sludge collected from a local municipal wastewater treatment plant for two weeks before it was formally operated. The AlS-IACW was then operated for 280 days under room temperature, which can be divided into three periods according to the distribution of the An/A phases and the air flow rate. In general, air supply was increased from period 2 by extending the aerobic phases and/or increasing the air flow rate (Table S1).

Wastewater

Piggery wastewater, which is a typical representation of high strength wastewater, was used as the influent source. The raw wastewater was collected from an animal farm at Newcastle, Co. Dublin, Ireland. After collection, the raw wastewater was diluted 4-6 times with tap water to obtain appropriate loading rates and then served as the influent. The targeted influent range was set as COD 3000-6000 mg/l and TN 250-700 mg/l, which is the typical range after common pre-treatment (sedimentation & anaerobic digestion) and generally used in other studies. The characteristic of the influent and the loading rate for different periods were summarized in Table 1. The general trend was that the NLR increased while the organic loading rate (OLR) and the COD/TN ratio decreased over the operation periods.

[Table 1]

Overall performance and cyclic profile

Grab samples of the influent and effluent were collected 1-2 times per week and analyzed for COD, BOD_5, TN, NO_2-N, NO_3-N, NH_4-N, TP, PO_4-P, SS and pH. The overall performance in organic matters (OMs) and nutrient removal was evaluated with pollutants removal efficiency. In this case, nitrogen removal through plant uptake was considered to be neglectable due to the high NLR applied (32.5-46.7 g N m^{-2} d^{-1}, Table 1), which was far beyond the N uptake rate by plant of 0.03 g N m^{-2} d^{-1} [24].

To investigate the profiles of carbon and nutrient within a cycle, cyclic study was conducted on day 181 in period 3 when the system was considered in steady state which was indicated by the stable influent and effluent between day 175 and 200. Liquid samples were collected over time and analyzed for soluble COD (SCOD), PO_4-P, NH_4-N, NO_2-N and NO_3-N. DO was monitored online with an oxygen probe placed at the middle of the CW throughout the cycle. As the raw wastewater was introduced from the top of the column and it was not well mixed after the first filling, there was significant difference in concentrations among the different locations in the first subcycle (highest at the top and decreased downwards). Hence composite liquid samples were taken for the first subcycle. Then the following aeration provided strong mix and it was justified that the concentrations were more or less the same after the first aeration period. Therefore, only grab liquid samples from the middle were taken for the remaining sub-cycles.

SND efficiency

To estimate the SND efficiency, aerobic batch tests were conducted at the end of this study under room temperature. Representative DAS samples were obtained from the AlS-IACW and pretreated by washing several times with distilled water one day before the tests to remove the residual substrates and eliminate storage effect. Then three 100 mL pretreated DAS samples were mixed with 50 mL piggery wastewater in 250 mL beakers. The beakers were then filled to 200 mL with distilled water. Thereafter, glucose or ammonium chloride was added to adjust the initial COD/N ratio. The initial conditions were summarized in Table S2. In particular, the initial COD/N ratio was set at 6.3, 9.4 and 13.7, respectively, to reflect the influent variety during the system operation. Air was supplied with three diffusers placed at the bottom of the beakers, and DO was maintained between 4.7-6.3 mg L^{-1}. For each beaker, 15 liquid samples (3 mL each) were taken and analyzed for NH_4-N, NO_2-N and NO_3-N over a period of 35 hrs (minimum interval 1 h). At 24 hrs, inorganic carbon (IC) was supplemented to each beaker by adding 0.5 mL of $NaHCO_3$ solution (7.2 g C L^{-1}). The overall SND efficiency is defined as the amount of N denitrified divided by the amount of NH_4-N oxidized and expressed as a percentage (Eq. (1)). Specific rate of nitrification, NO_X-N production and denitrification is calculated according to Eq. (2) to Eq. (4), respectively, and expressed as mg N $LDAS^{-1}$ h^{-1}.

$$E_{SND}(\%) = 100 \times \frac{NH_{4_{Oxi.}} - (NO_2 + NO_3)_{Acc.}}{NH_{4_{Oxi.}}} \qquad (1)$$

$$r_{Nitri} = \frac{V_T \times (NH_{4,t1} - NH_{4,t0})}{\mathrm{V_{DAS}} \times (t_1 - t_0)} \qquad (2)$$

$$r_{NOx} = \frac{V_T \times (NO_{X,t1} - NO_{X,t0})}{\mathrm{V_{DAS}} \times (t_1 - t_0)} \qquad (3)$$

$$r_{Deni} = r_{Nitri} - r_{NOx} \qquad (4)$$

Where V_T is total volume, 0.2 L; V_{DAS} is the volume of the DAS sample, 0.1 L.

Nitrogen conversion rates

Nitrogen conversion pathway is the main focus to explore in this study. There are two main pathways of nitrogen conversion, namely conventional nitrification/denitrification and partial nitrification/denitrification. When SND is significant, both conversion ways can occur concurrently in one reactor under aerobic condition. [25] The final route will be determined by three conversion rates: rate of ammonia oxidization (nitritation, r_{AOB}), rate of nitrite oxidization (nitratation, r_{NOB}) and rate of denitrification over nitrite ($r_{Deni-NO2}$). To determine these three rates, aerobic activity tests were conducted at the end of the trial under room temperature. Pretreated DAS samples (described in section "SND efficiency") of 100 mL were added into 250 mL beakers with different substrates (NH_4-N, NO_2-N or COD). Buffering solution [26] was supplied in r_{AOB} and r_{NOB} tests to avoid IC limitation. As such, ATU (Allylthiourea) and Azide [27], which are selective inhibitors for AOB (ammonia oxidation bacteria) and NOB (nitrite oxidation bacteria), respectively, were added in $r_{Deni-NO2}$ determination to ensure that all the NO_2-N reduction is caused by denitrification. The beakers were then filled to 200 mL with distilled water. pH was adjusted to 7.8 ± 0.1. DO was maintained between 5.8 and 7.0 mg L^{-1}. The detailed experimental conditions were summarized in Table S3. Liquid samples were taken every 15 min over a period of 2.5 hrs and analyzed for NH_4-N, NO_2-N and NO_3-N. Rates were determined as the slopes of the substrates reduction over time via linear regression, and expressed as mg N $LDAS^{-1}$ h^{-1}. DAS samples were prepared in duplicate.

Analysis

COD, NH_4-N, NO_2-N, NO_3-N, PO_4-P and SS were analyzed using a Hach DR/2400 spectrophotometer according to its standard operating procedures. BOD_5 was measured with a Hach BODTrak instrument. TP and TN were determined with ascorbic method and persulfate method, respectively.[28] pH was measured with a pH meter (Orion 920 A+, Thermo). DO was monitored with a microprocessor oximeter (Oxi 325, WTW).

RESULTS

Overall performance

Organic matters degradation:

Although this study is focused on the nitrogen removal, reduction of OMs in terms of BOD_5 and COD are highly related to nitrogen removal behavior. During period 1, both the COD and BOD_5 degradation were not well achieved with average removal of 74% and 82%, respectively (Figure S1). This is probably due to the insufficient oxygen supply, indicated by the high effluent BOD_5 (average 192 mg L^{-1}) and low DO (< 0.8 mg/l) at the end of A3. Air supply was accordingly increased at the beginning of period 2 (day 58) by extending the aerobic phases to 250 min in total and increasing the airflow rate to 3.16 mL h^{-1} L^{-1} (Table S1). Nine days after the action, effluent SCOD and BOD_5 decreased substantially with average of 223 and 45 mg L^{-1}, respectively. High COD and BOD_5 removal of 89% and 94% on average were obtained. The DO at the end of A3 was increased up to 4.3 mg/l accordingly. A drop in removal efficiency on day 145 was observed due to the air diffuser blockage, indicated by the visible decrease of air bubble and low DO (< 1 mg L^{-1}) during aeration. The air flow rate was further increased to 4.42 mL h^{-1} L^{-1} in period 3. Good performance was recovered steadily and nearly complete

BOD_5 removal (average 97%) was obtained with the enhanced air supply from day 175 (Figure S1). However, the COD removal (89%) remained more or less the same as period 2 regardless of the further increase of air flow. The low effluent BOD_5 (21 mg L^{-1}) and high residual SCOD (261 mg L^{-1}) suggested that there was significant part of inert SCOD in the influent, which could not be biologically degraded [29]. Consequently, the COD removal could not be further increased by increasing the air supply. Another drop in treatment efficiency was observed on day 220. The reason was identified as serious bed clogging. Action (backwash) was thus taken and treatment performance had been resumed very soon thereafter. Overall, a total aeration time of 250 min with air flow rate of 3.16 mL $h^{-1}\cdot L^{-1}$ seems to be adequate to obtain effective OMs removal under OLR of 0.32 kg COD $m^{-2}\cdot d^{-1}$.

Nitrogen removal:

Overall nitrogen removal performance is presented in Fig. 2. Nitrification in period 1 was quite poor. Only 56% NH_4-N removal (Fig. 2a, solid circle) was obtained on average. It was quickly increased to 85% with effluent NH_4-N of 51 mg L^{-1} (on average) after the enhancement of air supply in period 2 (Fig. 2b, solid diamond). Extreme nitrification was recorded in period 3 with average NH_4-N removal of 97% and effluent NH_4-N of 12 mg L^{-1}. Overall, a total aeration time of 250 min with air flow rate of 4.42 mL $h^{-1}\cdot L^{-1}$ could guarantee nearly complete nitrification under NLR of 46.7 g N $m^{-2}\cdot d^{-1}$ (Period 3). Similar to the removal of OMs, diffusor blockage and bed clogging seriously decreased the nitrification performance (Fig. 2a), which could be the major scale up issues. Diffusor blockage has been reported by Nivala et al., [14] while bed clogging is common problem in all CWs practice [30]. Total suspended solids (TSS) accumulation and biofilm development have been identified as the major causes for bed clogging, [30] which could be the main reasons for diffusor blockage as well. Hence, proper design and operation strategy are requested for further study.

TN removal was mainly dependent on nitrification and the availability of carbon source for denitrification. During period 1, incomplete nitrification showed as the limiting factor for TN elimination. The major N component in the effluent was NH_4-N (average 128 mg L^{-1}) (Fig. 2b, solid diamond). Effluent NO_X-N (NO_2-N and NO_3-N) was neglectable (average 1.7 mg L^{-1}) (Fig. 2b, open circle and triangle). After effective nitrification was achieved from period 2, carbon deficiency became the key limiting factor for TN removal, and NO_3-N accounted for the major part of the effluent TN (Fig. 2b, triangle). It has been found that the influent COD/TN ratio controlled the NO_X-N accumulation (NO_X-N/NH_4-$N_{Oxi.}$) (Figure S2). When this ratio was around or below 5, there was great chance of substantial NO_X-N accumulation. If the ratio was above 6, both the NO_2-N and NO_3-N accumulation rarely exceeded 4%.

Overall, effective TN removal was achieved after sufficient oxygen (total aeration time of 250 min with air flow rate of 4.42 mL h^{-1} L^{-1}, Table S1) was supplied in the proposed system. TN removal up to 97% with mean removal efficiency of 90% (from 528 mg L^{-1} to 52 mg L^{-1}, NLR 46.7 g N $m^{-2}\cdot d^{-1}$) was obtained in period 3 (Fig. 2a). Even under carbon limiting conditions (influent COD/N around 3), TN reduction was still maintained above 80%. This performance is a substantial improvement in both treatment efficiency and capacity (NLR) compared with the reported TN removal efficiency of 51% under NLR of 6 g N $m^{-2}\cdot d^{-1}$ [12] and 67% under NLR of 3.3 6 g N $m^{-2}\cdot d^{-1}$ [15] in the literature, which properly reflected the effectiveness of the enhanced aeration and process design of the proposed system.

[Fig. 2]

Cyclic nitrogen profile

A cyclic nitrogen profile is illustrated in Fig. 3. The nitrogen profile was quite different with the typical profiles in BNR processes. Generally, NH_4-N is oxidized in aerobic phase. Accordingly, buildup of NO_X-N is expected along with the decrease of NH_4-N. The reduction of NO_X-N (denitrification) can only be expected in the un-aerated phases [4, 18]. However, no notable NO_X-N buildup (circle and triangle) was observed throughout the whole cycle in this study regardless of the substantial decrease of NH_4-N (square) and the high DO (red line) during the aerobic phases. This suggests that most of the oxidized N was denitrified once produced, i.e. a very effective SND process in the AlS-IACW system. The effective SND has a great impact on the process design. As stated in section 2.1, a high VER of 9 was adopted at the cost of a low HLR. This adoption was based on the assumption that SND was not significant. In such case, the degree of pre-denitrification determines the extent of the overall denitrification process. [18] However, such a design rationale was confounded by the effective SND, because the major part of the oxidized N had been denitrified already during the aeration periods and thus the pre-denitrification stage lost its significance. For this reason, the treatment capacity of AlS-

IACW could be extended by increasing HLR, i.e. by adopting low VER without notable decline of the overall nitrogen removal performance.

[Fig. 3]

DISCUSSION

Controlling factors for SND

The profiles of NH_4-N, NO_2-N and NO_3-N under aerobic condition are shown in Fig. S3. Specific rates of nitrification, NO_X-N production and denitrification during different reaction phases are summarized in Table 2. The overall SND efficiencies are compared with other studies in Table 3. Fig. S3 and Table 3 demonstrate that the SND performance was controlled by carbon substrate. Under low COD/N ratio (6.3), substantial NO_X-N accumulation (up to 22 mg L^{-1}) was observed along the NH_4-N decrease (Fig. S3), resulting in a relative low SND efficiency (72.9%, Table 3). With the increase of COD/N ratio (9.4 and 13.7), NO_X-N accumulation decreased (Fig. S3), and a higher SND efficiency was achieved (80.8% and 89.4% respectively, Table 3). These results are consistent with the previous studies (Table 3). It is believed that a high COD/N ratio can promote SND efficiency mainly through three mechanisms: (1) to provide sufficient reducing power for denitrification;[36, 37] (2) to reduce the oxygen penetration depth under certain oxygen supply, thus to create more micro anoxic zone for denitrification;[34] (3) to lower the nitrification rate due to the competition for DO between nitrifiers and heterotrophic organisms, therefore, to bring more balanced nitrification and denitrification rates.[31, 32, 34] In this case, the COD/N played its role mainly through the mechanism (3), which is revealed by the decrease of nitrification rate along the increase of COD/N (Table 2). Accordingly, a more balanced equilibrium between nitrification and denitrification (higher r_{Deni}/r_{Nitri} ratio) was obtained under high COD/N situation (Table 2). This led to the less accumulation of NO_X-N and a more effective SND (Fig. S3 and Table 3).

[Table 2]

[Table 3]

DO is another controlling factor for SND.[34, 35] The main cause of SND is the stratification of the biofilm/floc due to the oxygen diffusion limitation.[34] In the outer layer of the biofilm/floc, nitrification takes place. DO decreases along the penetration depth and finally micro anoxic zone exist inside the biofilm/floc, where denitrification occurs. Obviously, the degree of SND relies on the size of the micro anoxic zone, which decreases with the increase of the bulk DO.[38, 39] That is why low DO favors SND (Table 3). To achieve a high SND efficiency, low DO (0.5-1 mg L^{-1}) is generally recommended at the cost of a lower SND rate.[20, 34] However, comparable SND efficiency was obtained under much higher DO (4.7-6.3 mg L^{-1}) in this study. A high oxygen transfer resistance in the biofilm system (this study) could be the explanation. Under the same bulk DO concentration, thick biofilm/large floc could promote the formation of a larger anoxic zone (Table 3). [32, 36] The relative high substrate loading rate applied in this study might result in a thick biofilm (indicated by the clogging phenomenon), [40] which allowed the system to achieve the effective SND under high DO. This is of great significance for practice, since high SND efficiency and high SND rate can be obtained simultaneously.

It's also very interesting to explore the SND characteristics during different reaction phases (Table 2). Nitrification rate of the first two hours was much higher than that of the later phases, which induced the most serious imbalance between nitrification and denitrification (r_{Deni}/r_{Nitri}, Table 2) and thus high NO_X-N accumulation (Fig. S3). Thereafter, nitrification rate decreased markedly and a more balanced equilibrium was established and maintained in phase 2. Denitrification rate could even exceed the nitrification rate in this phase, such as at 11-18 hrs for COD/N of 6.3, 7-18 hrs for COD/N of 9.4 and the whole phase 2 for COD/N of 13.7 (Table 2). This suggests that the organic substrate can be preserved for a long period to support SND. Third et al.[34] and Zeng et al.[35] attribute this phenomenon to the storage of soluble organic substrate in the form of polyhydroxybutyrate (PHB), which is degraded more slowly than the soluble form and thus preserves reducing power for denitrification. These characteristics provide good evidence that a more delicate aeration scheme should be considered to bring achieve more efficient SND. For example, air flow rate in the first aerobic phase can be reduced to bring more balanced nitrification and denitrification rates.

Partial nitrification and SND via nitrite

During the SND batch tests, transient nitrite buildup was observed especially with low COD/N ratio (Figure S3). It implies that the rate of ammonia oxidization is faster than the nitrite oxidization, i.e. partial nitrification might be the major conversion way of ammonia oxidization. The degree of partial nitrification is usually evaluated by nitrite accumulation ratio (NAR, effluent NO_2-N/NO_X-N).[41] However, this is not adequate if SND is significant because the major part of the NO_2-N could be reduced via SND already. A comparison of $r_{AOB,}$ r_{NOB} and $r_{Deni\text{-}NO2}$ can give a better assessment of the nitrogen conversion pathway (Table 4). The results revealed that nitritation (r_{AOB}=14.67±1.24 mg N LDAS^{-1} h^{-1}) was much faster than nitratation (r_{NOB}=4.47±0.82 mg N LDAS^{-1} h^{-1}). If there is no nitrite reduction via SND, substantial nitrite buildup after complete nitrification could be expected. However, this phenomenon was not observed in the aerobic batch tests (Fig. S3). This was because that the denitrification rate via nitrite was comparable to nitratation (Table 4), so that the major part of nitrite was denitrified once produced. The percentage of nitrite denitrified via SND can be estimated by the ratio of $r_{Deni\text{-}NO2}/(r_{NOB}+r_{Deni\text{-}NO2})$, and the result is illustrated in Fig. 4. It shows that 65% of nitrite was removed through SND under high COD/N (14) condition. Even with low COD/N of 6, the proportion of nitrite reduction via SND was still above that of nitratation. Hence, a conclusion that partial nitrification and SND via nitrite (instead of nitrate) is the main nitrogen conversion pathway in the AlS-IACW can be drawn accordingly.

Typically the rate of nitratation is faster than the rate of nitritation and nitrite is rarely accumulated during the BNR processes unless specific process control is adopted. The advantages of BNR via nitrite, such as lower oxygen consumption, higher denitrification rate and particularly significant reduction (40%) of COD demand, aroused persistent efforts to achieve and maintain stable partial nitrification. [22] Yoo et al.[25] summarized the controlling factors for partial nitrification, which include high free ammonia (FA); high temperature (30-36 ℃); lag-time during the transition from anoxic to aerobic; low DO and free hydroxylamine (FH). They claimed to achieve SND via nitrite by controlling DO concentration, DO increase rate, length of aeration and FA level. In this study, however, partial nitrification has been achieved without any specific controlling actions listed above. On the contrary, the operational condition is actually adverse to partial nitrification with the high DO (3-6 mg L^{-1}). Instead, the partial nitrification that occurred in this study might be an outcome of long-term competition between nitratation and SND via nitrite. Because of the effective SND via nitrite, NOB consistently lost its substrate (nitrite) and was out-competed after long-term operation. By keeping this in mind, it seems that effective SND via nitrite is the cause of partial nitrification, rather than the result of partial nitrification.

[Table 4]

[Fig. 4]

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Supporting information

System operation periods and conditions; Initial conditions for the SND efficiency tests and nitrogen conversion rates determination; Overall performance in organic matter removal; Effects of influent COD/TN ratio on NO_X-N accumulation; Nitrogen profiles under aerobic tests with different initial COD/N ratio. These materials are available free of charge via the internet at http://pubs.acs.org.

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Tables

Table 1 Influent wastewater characteristic (Average ± SD)

	Period 1 (0-58 days)	Period 2 (59-145 Days)	Period 3 (146-280 Days)
COD (mg L^{-1})	4007±2337	3644±2738	2823±1060
TN (mg L^{-1})	368±102	431±97	528±142
NH_4-N (mg L^{-1})	312±106	358±111	435±136
TP (mg L^{-1})	27±15	35±25	56±26
SS (mg L^{-1})	2141±1612	1979±2651	941±954
pH	7.9±0.2	8.0±0.4	7.7±0.4
OLR (kg COD $m^{-2}\cdot d^{-1}$)	0.35	0.32	0.25
NLR(g N $m^{-2}\cdot d^{-1}$)	32.5	38.1	46.7
PLR(g P $m^{-2}\cdot d^{-1}$)	2.4	3.1	4.9
COD/TN	11	9	5

Table 2 Rate of nitrification, NO_X-N production and denitrification during SND with different initial COD/N ratio (Unit: mg N $LDAS^{-1} \cdot h^{-1}$)

	Phase 1 (0-2 hrs)			Phase 2 (3-18 hrs)			Phase 3 (24-35 hrs)		
COD/N	6.3	9.4	13.7	6.3*	9.4	13.7	6.3	9.4	13.7
r_{Nitri}	22.3	7.7	9.0	8.1	2.5	2.0	4.2	1.5	1.6
r_{NOx}	19.8	6.8	4.9	2.1	0.5	-0.2	2.3	0.6	0.6
r_{Deni}	2.5	0.9	4.1	6.1	2.1	2.2	1.9	0.9	1.0
r_{Deni}/r_{Nitri}	0.11	0.12	0.46	0.75	0.81	1.10	0.44	0.61	0.63

*Phase 2 for COD/N=6.3 is 3-9 hrs.

Table 3 Comparative evaluation of SND performance

System	COD/N	DO ($mg\ L^{-1}$)	Particle size (mm)	E_{SND} (%)	Controlling factors	Reference
Biofilm (AS-IACW)	6.3	4.7-6.3		72.9	COD/N ratio	This study
	9.4			80.8		
	13.7			89.4		
Biofilm (Suspended carrier)	3	1.5-2.5		83.3	COD/N ratio	31
	5			84.5		
	10			87.2		
Biofilm (Aerobic granular)	5.8	2-3	<0.18	≈0	Particle size	32
			0.18-0.45	19.1		
			0.45-0.9	31.9		
			>0.9	49.3		
Suspension (AIC-MBR)	4.77	1		53.6	COD/N ratio	33
	10.04			98.2		
	15.11			97.4		
Suspension (SBR)	10.4	0.5		78	DO	34
		1.0		61		
		1.5		55		
		5.0		31		
Suspension (SBR)	10	0.5		98	DO	35
		1.5		62		
		2.5		51		
Suspension (SBR)	10.4	0.3-2.5	0.04-0.05	21	Particle size	36
			0.08	52		

Table 4 Rate of nitritation (r_{AOB}), nitratation (r_{NOB}) and denitrification via NO_2-N ($r_{Deni-NO2}$) under aerobic condition (Unit: mg N LDAS^{-1}·h^{-1})

	No.1	R^2	No.2	R^2	Mean	S.D.
r_{AOB}	13.79	0.938	15.55	0.966	14.67	1.24
r_{NOB}	5.05	0.788	3.89	0.807	4.47	0.82
$r_{Deni-NO2}$, COD/N 6	4.66	0.967	4.49	0.968	4.57	0.12
$r_{Deni-NO2}$, COD/N 14	8.11	0.941	8.18	0.969	8.15	0.05

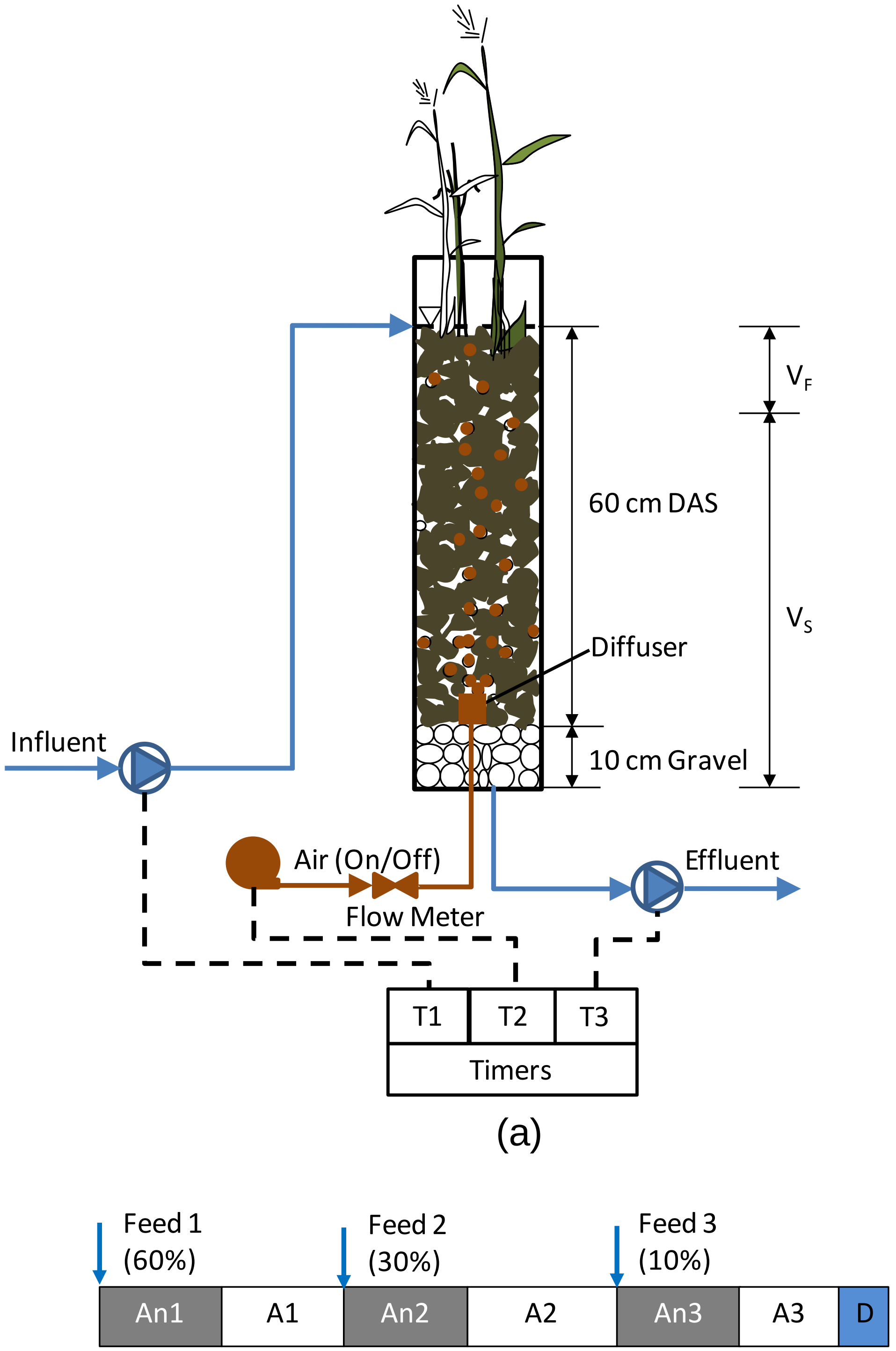
Figure caption:

Fig. 1 Laboratory alum sludge-based IACW (a) System set-up (b) Aeration and feed scheme within a cycle

Fig. 2 Overall performance of nitrogen removal (a) Influent NH_4-N/TN and NH_4-N/TN removal (b) Effluent N and influent COD/TN ratio

Fig. 3 Cyclic nitrogen and DO profiles (Influent COD/TN=8. Data: An1/A1 – average of top, middle and bottom of the reactor; others – middle of the reactor)

Fig. 4 Nitrogen conversion pathway determined by COD/N ratio during SND


Influent
V_F
60 cm DAS
V_S
Diffuser
10 cm Gravel
Air (On/Off)
Flow Meter
Effluent
T1
T2
T3
Timers
Feed 1 (60%)
Feed 2 (30%)
Feed 3 (10%)
An1
A1
An2
A2
An3
A3
D

(a)

(b)

Fig. 1

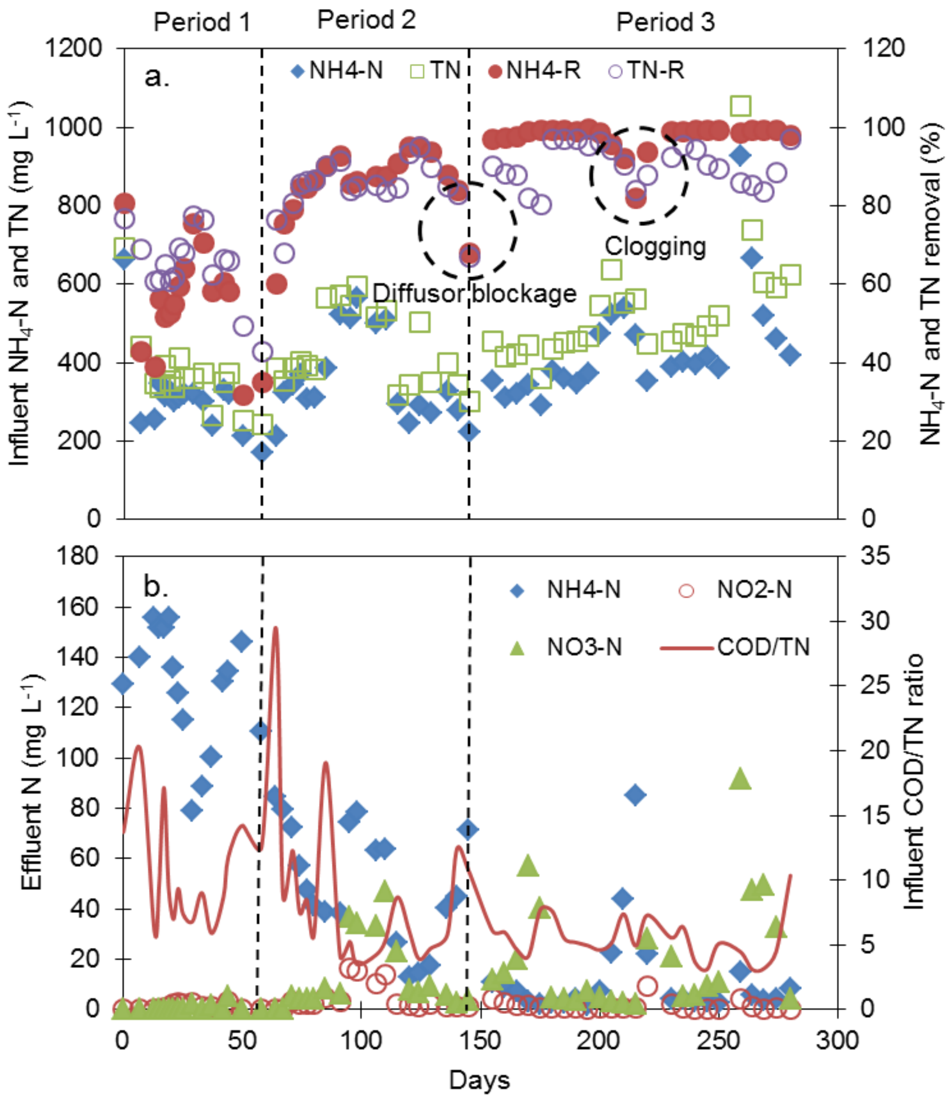

Period 1
Period 2
Period 3
a.
NH4-N
TN
NH4-R
TN-R
Diffusor blockage
Clogging
Influent NH_4-N and TN (mg L^{-1})
NH_4-N and TN removal (%)
1200
1000
800
600
400
200
0
120
100
80
60
40
20
0
b.
NH4-N
NO2-N
NO3-N
COD/TN
Effluent N (mg L^{-1})
Influent COD/TN ratio
180
160
140
120
100
80
60
40
20
0
35
30
25
20
15
10
5
0
0
50
100
150
200
250
300
Days

Fig. 2

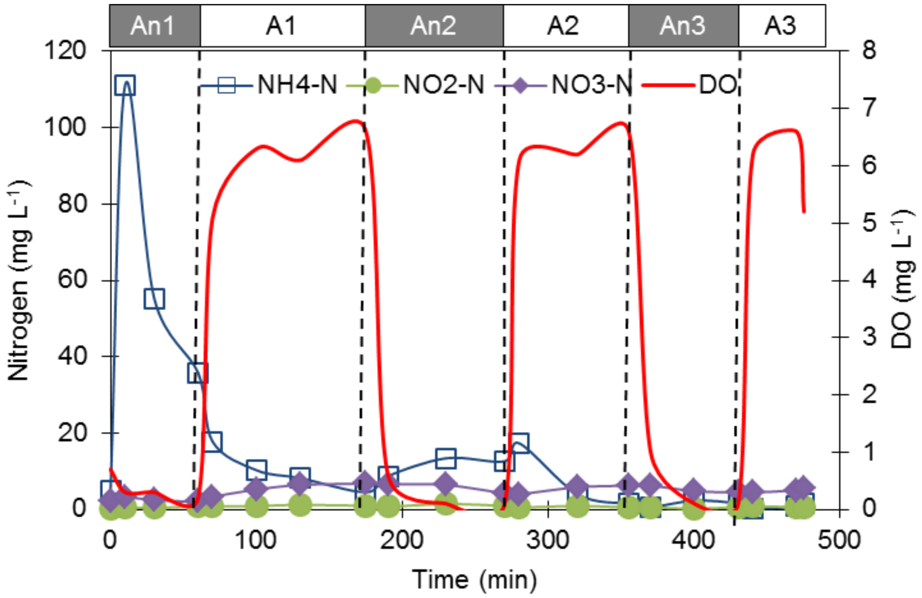

An1
A1
An2
A2
An3
A3
NH4-N
NO2-N
NO3-N
DO
Nitrogen (mg L-1)
DO (mg L-1)
Time (min)
120
100
80
60
40
20
0
8
7
6
5
4
3
2
1
0
0
100
200
300
400
500

Fig. 3

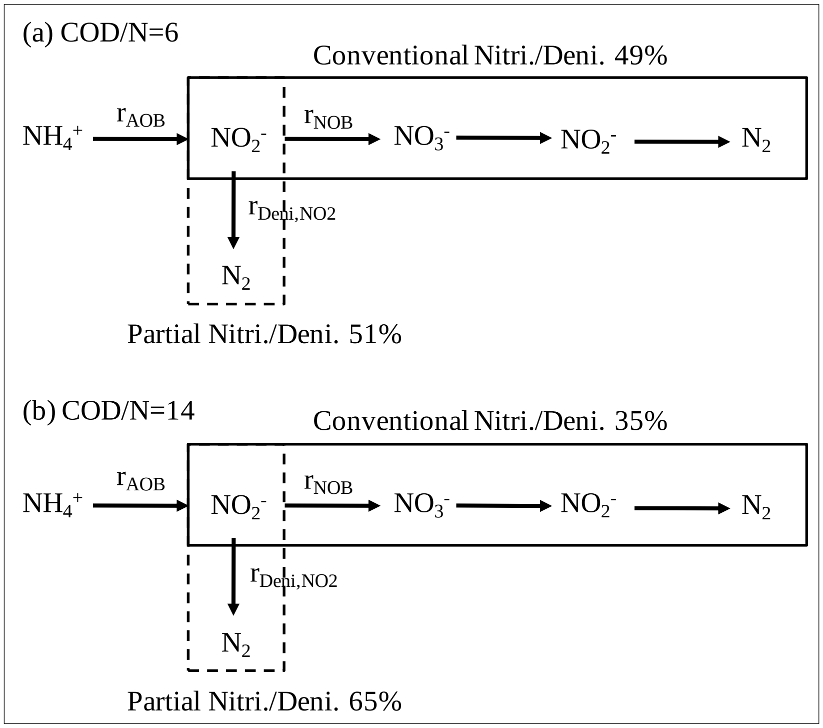

(a) COD/N=6
Conventional Nitri./Deni. 49%
NH_4^+
r_{AOB}
NO_2^-
r_{NOB}
NO_3^-
NO_2^-
N_2
$r_{Deni,NO2}$
N_2
Partial Nitri./Deni. 51%
(b) COD/N=14
Conventional Nitri./Deni. 35%
NH_4^+
r_{AOB}
NO_2^-
r_{NOB}
NO_3^-
NO_2^-
N_2
$r_{Deni,NO2}$
N_2
Partial Nitri./Deni. 65%

Fig. 4