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A novel anaerobic–anoxic/nitrifying-induced crystallization sequence batch reactor (A_2N-IC-SBR) process for enhancing phosphorus recovery and nutrient removal

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ABSTRACT

An anaerobic–anoxic/nitrifying-induced crystallization sequence batch reactor (A_2N-IC-SBR) process was developed for enhanced nutrient removal and phosphorus recovery. The performance of the A_2N-IC-SBR process was investigated in this study. Compared to the A_2N-IC continuous flow (CF) process, A_2N-IC-SBR provided important advantages, including minimal space requirements, ease of enhanced phosphorus recovery, and improved ammonia removal. Percentage of chemical phosphorus removal of total phosphorus removal was 14.9–17.1% in the A_2N-IC-SBR process, while it was 8.0–12.6% in the A_2N-IC-CF. The effluent ammonia concentrations were below 5 mg/L. The A_2N-IC-SBR process met the requirements of Urban Waste Water Treatment Directive 91/271/EEC. Furthermore, ammonia and nitrate concentrations could be simulated satisfactorily in each stage. In addition, an important feature called the self-adjustment characteristic was found, as the system has the ability to cushion the effect of increased or decreased chemical phosphorus removal amount during the process.

Keywords: Anaerobic–anoxic/nitrifying-induced crystallization sequence batch reactors process (A_2N-IC-SBR); Nutrient removal; Phosphorus recovery; Self-adjustment

1. Introduction

Elevated phosphorus has been one of the main nutrients responsible for eutrophication [1–4]. Enhanced biological phosphorus removal (EBPR) is one of the most economical and environmentally sustainable processes to remove phosphorus from wastewater; it is widely applied for the treatment of domestic wastewater [5–7]. The anaerobic–anoxic/nitrifying (A_2N) two-sludge system is an EBPR process [8,9] that uses denitrifying polyphosphate accumulating organisms (DNPAOs). To simultaneously recover phosphorus from wastewater, a continuous flow (CF) A_2N process coupled with induced crystallization (IC) called the A_2N-IC (A_2N-IC-CF) process was studied in our previous work [10]. It attained not only stable

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nutrient removal but also phosphorus recovery. However, its implementation is accompanied with a large footprint that should be taken into consideration in its design and operation. Additionally, from the perspective of economic benefit and resource sustainability, phosphorus recovery efficiency could be enhanced.

In this study, a new A_2N-IC sequence batch reactor (A_2N-IC-SBR) process, which consisted of anaerobic/anoxic/oxic-SBR (A/A/O-SBR) for biological denitrifying phosphorus removal, nitrifying-SBR (N-SBR) for nitrification, and IC-SBR for chemical phosphorus recovery, was proposed. In comparison with the A_2N-IC-CF system, the A_2N-IC-SBR process saved three settling tanks, and all of the biological phosphorus removal sections could be accomplished in the A/A/O-SBR [11,12]. Additionally, there was still the same advantages as SBR, such as ease of management, operation change [13], and possibility of modifications during trial phases through on-line control of the process [14–17].

Further, compared to the A_2N-IC-CF system, it was easier and more feasible to enhance phosphorus recovery efficiency in the A_2N-IC-SBR system. Phosphorus recovery could be strengthened by increasing the influent flow into the IC reactor (Q_{IC}) or by extending the hydraulic retention time (HRT) in the IC section. Unlike the A_2N-IC-CF system, no conflict between HRT and Q_{IC} existed in the A_2N-IC-SBR process. Moreover, calcium could be added continuously and equably during the chemical phosphorus recovery reaction stage, reducing high saturation for homogeneous precipitation. In particular, it was easy to add a settling period after the crystallization stage, which reduced the loss of the crystallization product and offered the possibility of recrystallization for crystal fragments and small particles that containing phosphorus.

The main objective of this study was to investigate nutrient removal and enhanced phosphorus recovery performances in the A_2N-IC-SBR process. Moreover, a new key feature of the A_2N-IC process, called the self-adjustment characteristic, was revealed.

2. Materials and methods

2.1. Experimental design

The A_2N-IC-SBR process (Fig. 1) was composed of A/A/O-SBR, N-SBR, and IC-SBR, which contained DNPAOs, nitrifiers sludge, and calcite seeds, respectively. The working volumes were 10, 10, and 1.3 L, respectively. A typical cycle consisted of five stages and is described in Table 1. For each cycle, 6.5 L of raw wastewater was introduced into the A/A/O-SBR. It was mixed with 3.5 L of sedimentary DNPAOs sludge from the last cycle, and phosphorus was released from the DNPAOs sludge under the anaerobic phase (step 1). After 3 h, the stirrer was stopped to allow sludge settling (step 2). Then, 1.3 L of supernatant rich in phosphorus went to the IC reactor for phosphorus recovery and the remaining supernatant (5.2 L) was led to the N-SBR (step 3). In the IC-SBR, aeration was utilized to supply sufficient contacts of seeds, calcium dosage, and wastewater (step 4). When the crystallization stage was finished, the aeration was stopped (step 5), and 1.56 L of supernatant (including 0.26 L of calcium dosage) flowed into the N-SBR (step 6). In the N-SBR, ammonia was transformed into nitrate with adequate oxygen and nitrifiers sludge (step 7). After settling (step 8), the supernatant of rich phosphorus and nitrate was pumped into A/A/O-SBR (step 9) for 4 h of denitrifying phosphorus removal (step 10) and 1 h of aerobic phosphorus removal (step 11). After a settling period (step 12), the supernatant flowed out of A/A/O-SBR (step 13). A typical cycle of A_2N-IC-SBR was, thus, completed. Then, the raw wastewater was introduced into A/A/O-SBR for the next cycle.

The aeration flow for all SBRs was 150 L/h. A volume of 0.26 L of calcium chloride solution (3.8–10.0 mmol/L) was added into IC-SBR continuously during stage II by a peristaltic pump, and the Ca/P mole ratio in IC-SBR was maintained at about 1.67. pH was not controlled during chemical phosphorus removal and the value was 8.2–8.6 in the IC-SBR. The sludge in A_2N-IC-SBR was taken from the excess sludge of the A_2N-IC-CF process, when the influent wastewater contained 250 mg/L of chemical oxygen demand (COD), 7.8 mg/L of total phosphorus (TP), and 45 mg/L of ammonia. Mixed liquid suspended solid (MLSS) was maintained at 4,200–5,000 mg/L. The influent phosphorus loading was 1.47 mg-P/g-MLSS (Run B, listed in Table 2).

The A_2N-IC-CF process consisted of ten tanks: an anaerobic tank for phosphorus release, a stripping tank for alkalinity reduction and pH increase, a reagent tank for supplying calcium dosage, a crystallization reactor for phosphorus recovery, an aerobic tank for nitration, an anoxic tank for denitrifying phosphorus removal, a post-aerobic tank for further phosphorus uptake, and three settlers for separating sludge with water. The influent flow was 25 L/h. The ratio of flow rate into the crystallization reactor to influent flow was 0.2, which was the same with the A_2N-IC-SBR process. The SRT of DNPAOs was 15 d for both CF and SBR systems.

2.2. Wastewater composition

Synthetic wastewater used as the influent consisted of 250 mg/L of COD (carbon source: CH_3COONa),

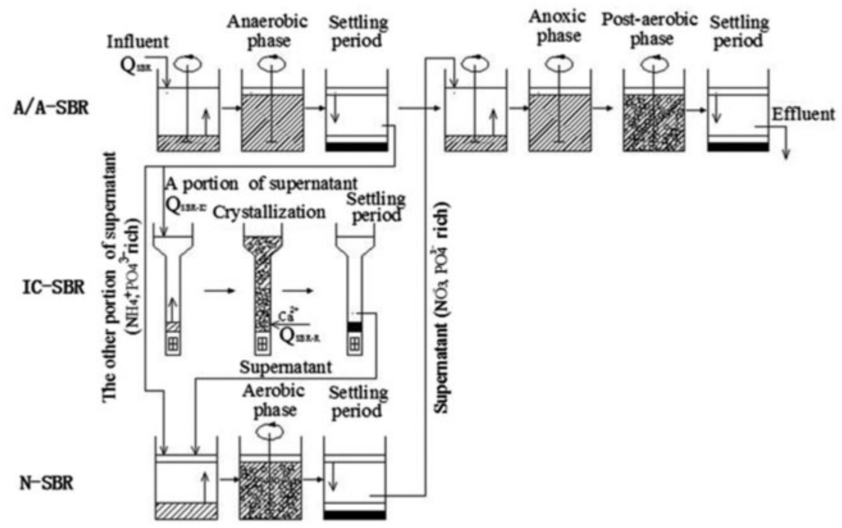

Fig. 1. Schematic diagram of the A_2N-IC-SBR process.

Table 1
Operating procedure for the A_2N-IC-SBR process

Stage	Step	SBR	Phase	Time (h)
1. Phosphorus release	1	A/A/O	Phosphorus release	3
	2	A/A/O	Settling	1
	3	$A/A/O_{1.3L}$→IC^a; $A/A/O_{5.2L}$→N	Supernatant exchange	0.5
2. Phosphorus recovery	4	IC	Induced crystallization	5
	5	IC	Settling	0.5
	6	$IC_{1.56L}$→N	Supernatant exchange	0.5
3. Nitrification	7	N	Nitrification	4.5
	8	N	Settling	1
	9	$N_{6.76L}$→A/A/O	Supernatant exchange	0.5
4. Phosphorus uptake	10	A/A/O	Denitrifying phosphorus removal	4
	11	A/A/O	Aerobic phosphorus removal	1
	12	A/A/O	Settling	1
5. Effluent and influent	13	$A/A/O_{6.76L}$→eff; $Inf_{6.5L}$→A/A/O	Effluent and influent	1.5

[a] 1.3 L supernatant in the A/A/O-SBR was flowed to the IC-SBR.

Table 2
Operation conditions for the experiment

Run or Set	Process	Influent phosphorus loading (mg-P/g-MLSS)
Run A	A_2N-IC-CF	0.70
Run B	A_2N-IC-CF	1.47
Run C	A_2N-IC-CF	2.30
Set A	A_2N-IC-SBR	0.60
Set B	A_2N-IC-SBR	1.22
Set C	A_2N-IC-SBR	2.19

3.9–15 mg/L of TP (KH_2PO_4), 40–43 mg/L of ammonia (NH_4HCO_3), and 0.3 ml/L of trace solution. The trace solution (per liter) was composed of 1.5 g $FeCl_3·6H_2O$, 0.15 g H_3BO_3, 0.03 g $CuSO_4·5H_2O$, 0.18 g

KI, 0.12 g $MnCl_2{\cdot}4H_2O$, 0.06 g $Na_2MoO_4{\cdot}2H_2O$, 0.12 g $ZnSO_4{\cdot}7H_2O$, 0.15 g $CoCl_2{\cdot}6H_2O$, and 10 g ethylenediamine tetraacetic acid. The temperature was maintained at 20˚C by heaters.

2.3. *Experimental procedure*

The experiment had Runs A-C for the A_2N-IC-CF process and Sets A-C for the A_2N-IC-SBR process. To compare nutrient removal and enhanced phosphorus recovery performances in the two systems, Runs and Sets with the same letters had nearly the same phosphorus loadings, which are in Table 2. In the A_2N-IC-SBR process, samples were taken once per cycle, during the unsteady state to a steady state, which lasted more than 30 d in each Set.

2.4. *Analytical methods*

Determination of COD, TP, NH_4^+-N, NO_3^--N, NO_2^--N, MLSS, and alkalinity were performed in accordance with Standard Methods [18]. After Cycle 35, calcite seeds were removed from the crystallization reactor and then dried at room temperature. The crystallization product of Set B was analyzed using scanning electron microscopy (SEM) in conjunction with energy dispersive X-ray spectroscopy.

3. Results and discussion

3.1. *Enhanced phosphorus recovery in A_2N-IC-SBR*

Phosphorus concentrations in each phase of SBR-cycle 1–29 are presented in Fig. 2. The effluent TP concentration was always below 0.5 mg/L, which met the goals of Urban Waste Water Treatment Directive 91/271/EEC. Because of the cooperation between biological phosphorus removal and chemical phosphorus recovery, effluent TP was always satisfactory. This stable performance could be found in many systems which had combined chemical and biological phosphorus removal [19–21].

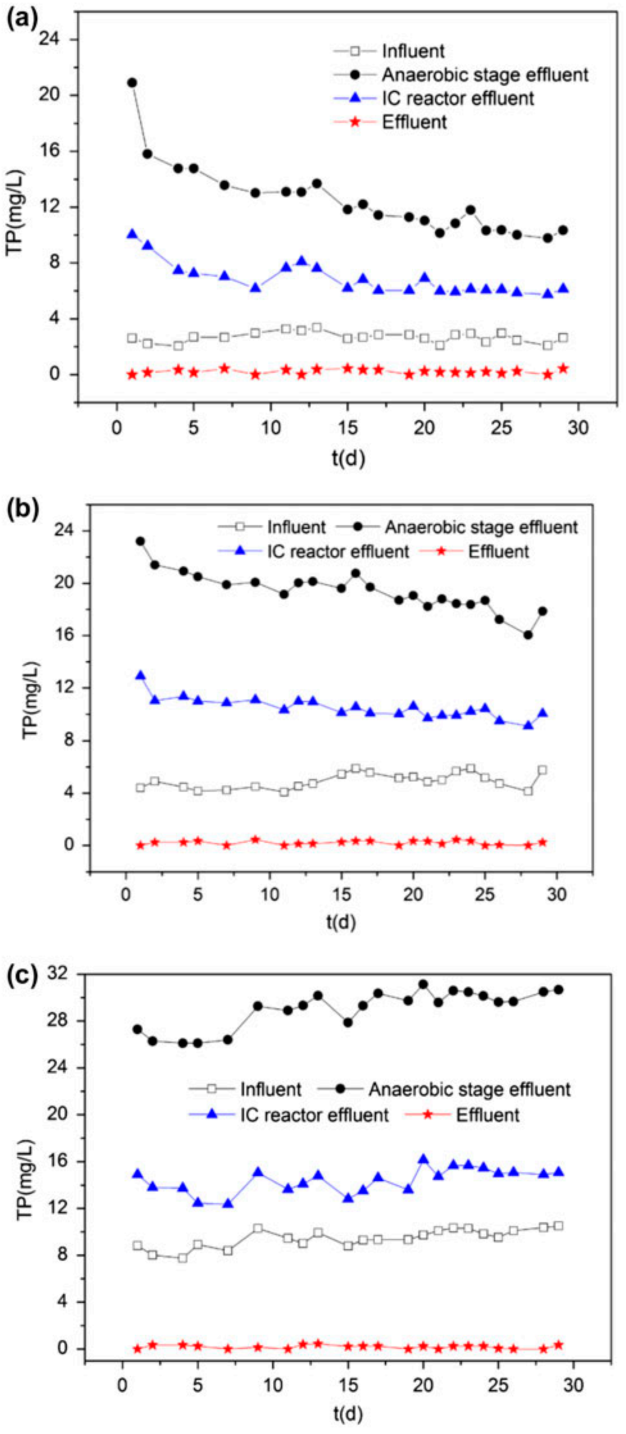

Fig. 2. Phosphorus variations of Set A (a), B (b), and C (c) in the A_2N-IC-SBR process during Cycle 1–29.

As shown in Table 2, Runs A, B, and C had similar phosphorus loadings as Sets A, B, and C, respectively. Compared to A_2N-IC-CF, phosphorus recovery efficiency significantly increased in the A_2N-IC-SBR process. In the IC reactor, the TP removal rate (the percentage of chemical phosphorus removal amount to phosphorus amount of IC reactor influent) was 9.9–13.6% in the IC reactor of the A_2N-IC-CF process, while it was 41.2–49.9% in A_2N-IC-SBR. Correspondingly, as shown in Table 3, the percentage of chemical phosphorus removal to TP removal was higher in A_2N-IC-SBR. The improvement was attributed to the increment of calcium dosage and the settling period (step 5) in the A_2N-IC-SBR system. In the A_2N-IC-CF process, increased calcium had a negative effect on heterogeneous crystallization, while in A_2N-IC-SBR, calcium was added continuously and equably during chemical phosphorus recovery stage, reducing the need for high saturation required for homogeneous precipitation. Even if homogeneous precipitation occurred, the settling period could maintain them in IC-SBR. However, in the CF system, the homogeneous precipitation could likely flow into the aerobic tank, which could not be recovered.

Compared to other systems that consisted of biological and chemical phosphorus removal, the phosphorus removal rate of the chemical part in the A_2N-IC-SBR was lower. There are two possible reasons. First, in some other systems, TP concentration of the anaerobic supernatant was much higher than that in the A_2N-IC-SBR process [22,23]. Second, different precipitate or crystallization methods, such as struvite, were used for chemical phosphorus recovery. This approach could be applied for high ammonia wastewater, which was not appropriate for the A_2N-IC-SBR process [24,25].

There were two ways to remove phosphorus in this system: chemical phosphorus recovery and biological phosphorus removal. The interactions between them were complex. They were not only cooperators, but also competitors. They worked together to remove phosphorus from wastewater. However, if chemical phosphorus recovery was beyond an appropriate range, the system might lose its phosphorus release and uptake capacities, which would result in a collapse of the system. This conflict also existed in other systems consisting of chemical phosphorus removal and biological phosphorus removal [19,23].

Under constant influent phosphorus loading, more chemical phosphorus recovery means that less phosphorus could be utilized by DNPAOs. Therefore, in the A_2N-IC-SBR, biological phosphorus release and uptake declined compared to that in the CF process under nearly the same TP loading (Table 3).

3.2. Nitrogen removal in the A_2N-IC-SBR

In A_2N-IC-SBR, nitrification and denitrification rates were both more than 98%, in agreement with Wang et al. [13] for the A_2N-SBR system. The ammonia, nitrates, and total nitrogen (TN) variations of Set B during Cycle 1–29 was shown in Figs. 3 and 4(b). Ammonia and nitrate concentrations were similar to results from the A_2N-IC-CF process.

In order to understand the ammonia and nitrate removal characteristic in the A_2N-IC-SBR, the mass balance equations were performed with several assumptions taking into account: (1) the influent ammonia concentration was the same in each cycle; (2) the nitrification rate was 100% in the N-SBR, and nitrification was the only way for ammonia transformation. The ammonia for the bacteria growth was considered negligible [26]; (3) in the A/A/O-SBR, 100% nitrate was denitrified by DNPAOs, without any other approach for nitrate removal; (4) the dilution in the IC-SBR by the calcium dosage (0.26 L) was ignored; (5) the small amount of ammonia removal by stripping in the IC-SBR was not calculated into the following equations:

$$S_n = 0.35X_n \tag{1}$$

$$P_n = Y_n + Z_n \tag{2}$$

$$Y_n = 0.65X_n \tag{3}$$

$$X_{n+1} = 0.65C_{\text{inf}} + 0.35S_n \tag{4}$$

$$Z_{n+1} = 0.35P_n \tag{5}$$

$$X_1 = 0.65C_{\text{inf}} \tag{6}$$

$$Z_1 = 0 \tag{7}$$

Table 3
Phosphorus removal in A_2N-IC-CF and A_2N-IC-SBR at different influent phosphorus loadings

Run or Set	Influent phosphorus loading[a] (mg-P/g-MLSS)	Phosphorus release (mg-P/g-MLSS)	Phosphorus uptake (mg-P/g-MLSS)	Chemical phosphorus removal/ total phosphorus removal (%)
Run A	0.70	4.65	5.21	12.6
Run B	1.47	4.72	5.90	9.1
Run C	2.30	5.33	7.24	8.0
Set A[b]	0.60	1.82	2.29	17.1
Set B	1.22	2.82	3.80	14.9
Set C	2.19	4.36	6.18	15.7

[a] For the influent phosphorus loading data, the dilutions of the DNPAO sludge were taken into consideration in both the CF and SBR systems.

[b] The data in three SBR Sets were the average values of Cycle 24–29 under the steady state.

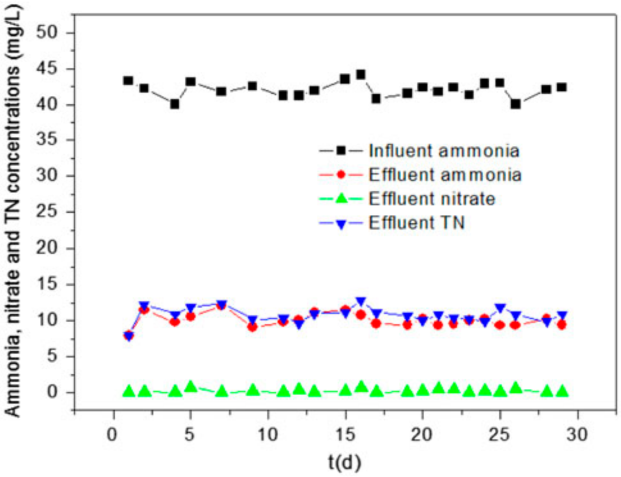

Fig. 3. Influent and effluent ammonia, nitrate, and TN concentrations in Set B during Cycle 1–29.

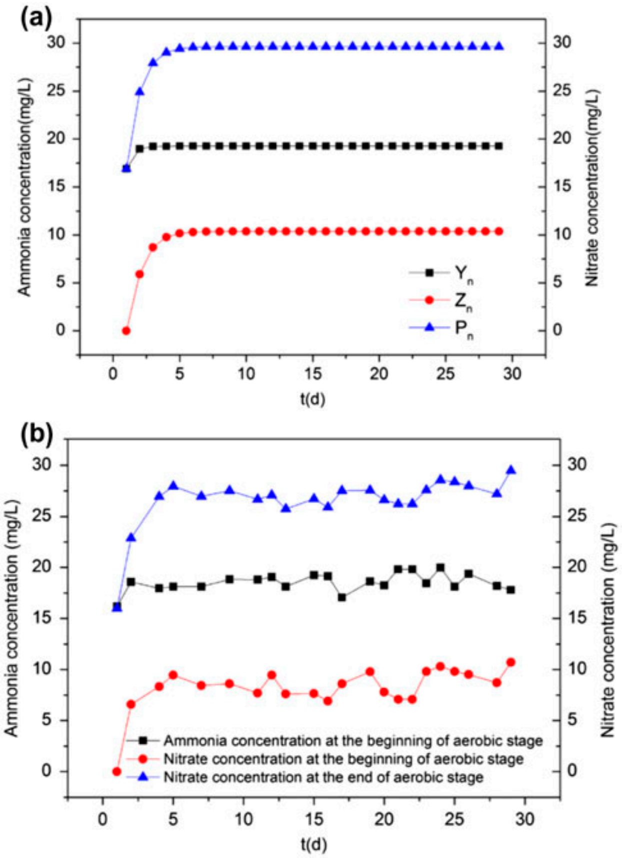

Fig. 4. The calculated (a) and monitored (b) ammonia and nitrate concentrations in N-SBR.

According to Eqs. (1), (4), and (6), X_n can be calculated in the following equation:

$$\begin{aligned} X_n &= 0.65C_{\inf}(1-0.35^{2n})/(1-0.35^2) \\ &= C_{\inf}(1-0.35^{2n})/1.35 \end{aligned} \tag{8}$$

Eqs. (9) and (10) were obtained on the basis of Eqs. (1), (3), and (8).

$$S_n = 0.35C_{\inf}(1-0.35^{2n})/1.35 \tag{9}$$

$$Y_n = 0.65C_{\inf}(1-0.35^{2n})/1.35 \tag{10}$$

In accordance with Eqs. (2) and (5), Eq. (11) was created, which could be simplified as Eq. (12) based on Eq. (10).

$$\begin{aligned} P_n &= Y_n + 0.35Y_{n-1} + \ldots + 0.35^{n-m}Y_m + \ldots + 0.35^{n-1}Y_1 \\ &= \sum_{i=1}^{n} 0.35^{n-i}Y_i \end{aligned} \tag{11}$$

$$\begin{aligned} P_n &= 0.65C_{\inf}\left(\sum_{i=1}^{n} 0.35^{n-i} - \sum_{i=1}^{n} 0.35^{n+i}\right)/1.35 \\ &= C_{\inf}(1-0.35^{n+1})(1-0.35^{n})/1.35 \end{aligned} \tag{12}$$

According to Eqs. (5) and (12), Z_n should satisfy the following equation consequently.

$$Z_n = 0.35C_{\inf}(1-0.35^{n})(1-0.35^{n-1})/1.35 \tag{13}$$

Ammonia and nitrate concentrations at different stages calculated by the above equations are listed in Table 4. It was obvious that after Cycle 4, ammonia and nitrate concentrations were consistent regardless of cycle and experimental results confirmed the simulations (Fig. 4). Consequently, when influent ammonia concentration and removal efficiencies were stable, ammonia and nitrate concentrations at different stages and cycles could be predicted.

In the A_2N-IC-SBR process, although both the nitrification rate in N-SBR and denitrification rate in A/A/O-SBR were satisfactory, the effluent ammonia concentration under the steady stage was about 9.3–10.2 mg/L, a little higher than that of A_2N-IC-CF, owing to the volume exchange of supernatant between the two SBRs. In A_2N-IC-CF, the ratio of bypass sludge flow to the influent flow ratio was only 0.2, whereas due to the settling limitation in A_2N-IC-SBR, the proportion of settling volume to working volume was 0.35. To solve this problem,

Table 4
The calculated ammonia and nitrate concentration in different stages and cycles (Unit: mg/L)

Cycle	X_n[a]	Y_n[b]	Z_n[c]	P_n[d]	S_n[e]
$n = 1$	26.00	16.90	0.00	16.90	9.10
$n = 2$	29.19	18.97	5.92	24.89	10.21
$n = 3$	29.58	19.22	8.71	27.93	10.35
$n = 4$	29.62	19.25	9.78	29.03	10.37
$n = 5$	29.63	19.26	10.16	29.42	10.37
$n = 6–29$	29.63	19.26	10.30	29.56	10.37

[a] Ammonia concentration at the initial anaerobic stage in A/A/O-SBR of Cycle *n*.

[b] Ammonia concentration at the initial aerobic stage in N-SBR of Cycle *n*.

[c] Nitrate concentration at the start of aerobic stage in N-SBR of Cycle *n*.

[d] Nitrate concentration at the end of aerobic stage in N-SBR of Cycle *n*.

[e] Ammonia concentration at the end of anoxic stage in A/A/O-SBR of Cycle *n*.

two stages were added after the phosphorus uptake stage (Table 5). In the improved procedure, steps 1–12 were the same as in Table 1. From step 13, measures were taken as in Table 5. When step 12 was finished, the supernatant from A/A/O-SBR was introduced into N-SBR again for removal of ammonia by nitrifiers sludge (step 13). After settling (step 14), the supernatant went back to A/A/O-SBR (step 15) for aerobic phosphorus removal (step 16) again in order to avoid the residual phosphorus in the N-SBR flowing out the system. After the improvement, A_2N-IC-SBR was stable enough to attain 5 mg/L ammonia concentrations in the effluent. Although the effluent nitrate concentration increased, TN concentration could reach the Urban Waste Water Treatment Directive 91/271/EEC. Thus, the unsatisfactory effluent ammonia concentration in the CF system [27] could be easily solved in the SBR system, which was an additional advantage of A_2N-IC-SBR.

3.3. The self-adjustment characteristic

To evaluate the effect of enhanced chemical phosphorus recovery in the A_2N-IC-SBR system, the equilibrium procedure from the unsteady state to the steady state in Set B was investigated. The start of the equilibrium procedure was the time when chemical phosphorus recovery was enhanced or decreased by operations. As described in Materials and Methods, the sludge in A_2N-IC-SBR was taken from the excess sludge of the A_2N-IC-CF process. The influent TP loadings were nearly the same in Run B and Set B, but phosphorus recovery efficiency was improved in Set B.

Because of the enhanced phosphorus recovery rates in A_2N-IC-SBR during the equilibrium procedure, phosphorus release reduced from 187.9 mg (at SBR-cycle 1) to 120.8 mg (at SBR-cycle 29) in Set B. Meanwhile, chemical phosphorus removal amount also declined with SBR-cycle (Fig. 5). Correspondingly, the value of $k_{(n)}$ gradually increased during the equilibrium procedure (Fig. 6). This could be explained as follows.

According to the principles of mass balance, in the A_2N-IC-SBR system, the phosphorus was removed either by the biological way or the chemical way. With respect to the biological phosphorus removal, it depended on two aspects. One was the phosphorus release under the anaerobic stage, and the other was the phosphorus uptake under the anoxic and aerobic stage. Consequently, Eqs. (14) and (15) were created. Therefore, ${M_{\mathrm{upt}(n)}}^P$ could be expressed as Eqs. (16), and (17) was created correspondingly. Hence, in accordance with Eq. (17), when ${M_{\mathrm{chem}(n)}}^P$ and ${M_{\mathrm{rel}(n)}}^P$ both decreased, the value of $k_{(n)}$ should increase. Conversely, if chemical phosphorus recovery rate decreased in a steady-state A_2N-IC-SBR system or even by removing the chemical crystallization reactor, the value of $k_{(n)}$ would decrease during the equilibrium procedure.

$$ {M_{\mathrm{inf}(n)}}^P - {M_{\mathrm{eff}(n)}}^P = {M_{\mathrm{biol}(n)}}^P + {M_{\mathrm{chem}(n)}}^P \tag{14} $$

Table 5
The procedure for ammonia removal improvement in A_2N-IC-SBR

Stage	Step	SBR	Phase
5. Nitrification	13	N	Nitrification
	14	N	Settling
	15	$N_{6.76L} \rightarrow$ A/A/O	Supernatant exchange
6. Phosphorus uptake	16	A/A/O	Aerobic phosphorus removal
	17	A/A/O	Settling
7. Effluent and influent	18	$A/A/O_{6.76L} \rightarrow$ Eff; $Inf_{6.5L} \rightarrow$ A/A/O	Effluent and influent

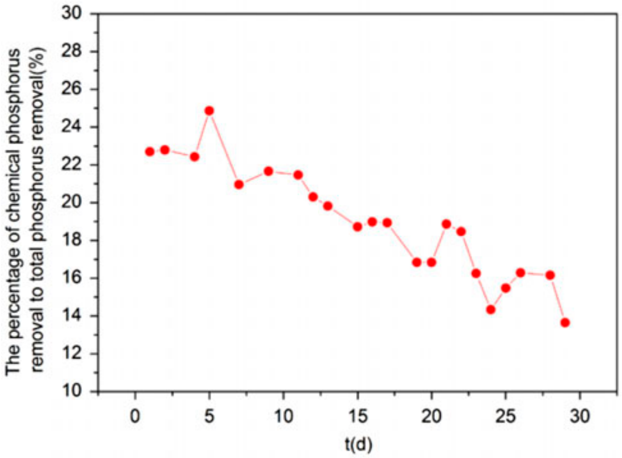

Fig. 5. The percentages of chemical phosphorus removal to TP removal with cycles in Set B.

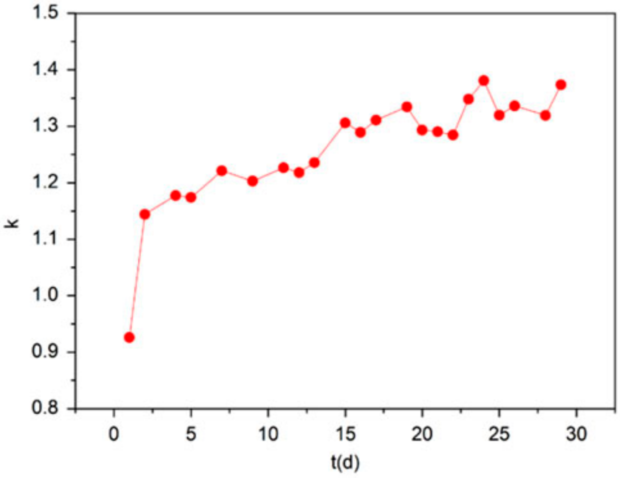

Fig. 6. *k*-values with cycles in Set B.

$$M_{\mathrm{biol}(n)}{}^{P} = M_{\mathrm{upt}(n)}{}^{P} - M_{\mathrm{rel}(n)}{}^{P} \tag{15}$$

$$M_{\mathrm{upt}(n)}{}^{P} = M_{\mathrm{inf}(n)}{}^{P} - M_{\mathrm{eff}(n)}{}^{P} + M_{\mathrm{rel}(n)}{}^{P} - M_{\mathrm{chem}(n)}{}^{P} \tag{16}$$

$$\begin{aligned} k_{(n)} &= M_{\mathrm{upt}(n)}{}^{P}/M_{\mathrm{rel}(n)}{}^{P} \\ &= 1 + (M_{\mathrm{inf}(n)}{}^{P} - M_{\mathrm{eff}(n)}{}^{P} - M_{\mathrm{chem}(n)}{}^{P})/M_{\mathrm{rel}(n)}{}^{P} \end{aligned} \tag{17}$$

It was assumed that the effluent TP was approximately equal to zero ($M_{\mathrm{eff}(n)}{}^{P} \approx 0$) in a steady A_2N-IC-SBR system, so that Eq. (18) could be utilized [10]. If the chemical phosphorus rate was enhanced, the value of m increased to $m_{(0)}$ at the initial stage of the equilibrium procedure. As the results above, $k_{(n)}$ would decrease gradually. For decreasing phosphorus release, $m_{(0)}$ could decline with cycle until reaching the new steady state [27]. Therefore, $M_{\mathrm{chem}(n)}{}^{P}/M_{\mathrm{biol}(n)}{}^{P}$ would decrease with cycle during the equilibrium procedure. In other words, the equilibrium procedure weakened the effect of enhanced chemical phosphorus

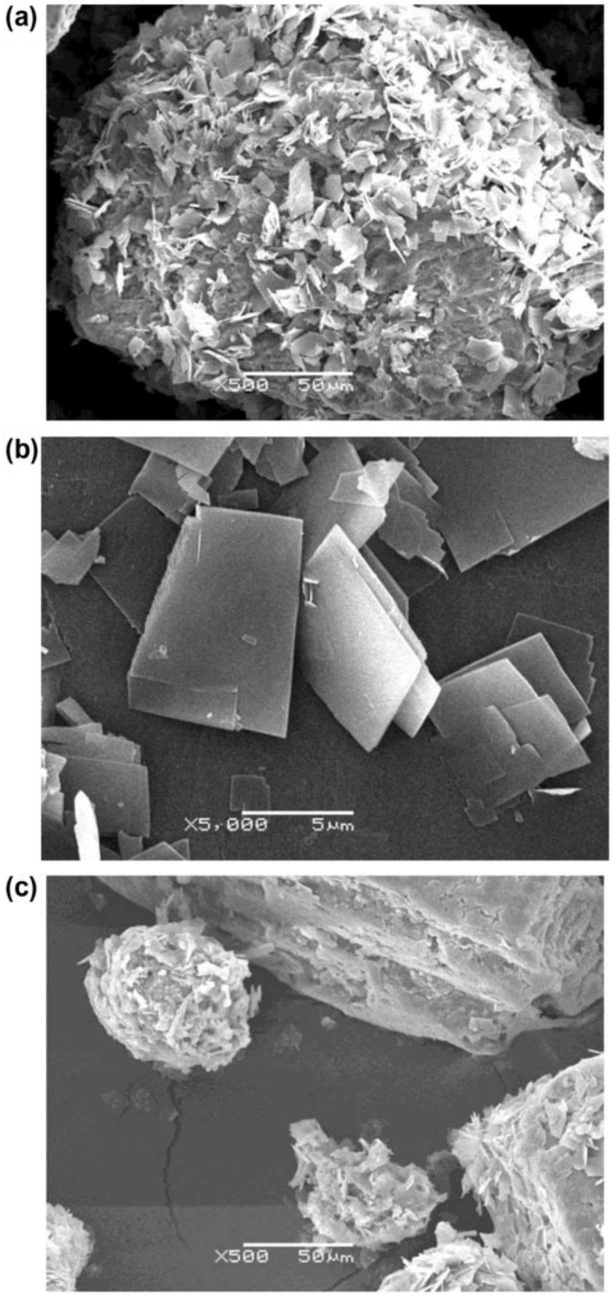

Fig. 7. SEM images of the phosphorus recovery product: (a) the seed after crystallization (b) the flake phosphorus recovery product, and (c) small particles contained phosphorus.

removal to the system. Conversely, if chemical phosphorus removal declined suddenly, $M_{\mathrm{chem}(n)}{}^{P}/M_{\mathrm{biol}(n)}{}^{P}$ would go up during the equilibrium procedure. That is to say, the equilibrium procedure alleviated the declined chemical phosphorus removal impact to the A_2N-IC-SBR system. In summary, A_2N-IC-SBR has a self-adjustment characteristic, which is the ability to cushion and weaken the impact of increased or decreased chemical phosphorus removal amount on the system. The self-adjustment characteristic provides a significant guideline for optimizing the design and operation of the novel A_2N-IC-SBR process.

$$\begin{aligned} M_{\mathrm{chem}(n)}{}^{P}/M_{\mathrm{biol}(n)}{}^{P} &= [m_{(n)}/(1-m_{(n)})]\cdot[k_{(n)}/(k_{(n)}-1)] \\ &= [-1+1/(1-m_{(n)})][1+1/(k_{(n)}-1)] \end{aligned} \tag{18}$$

The key operation parameters such as the Q_{IC}/Q ratio and calcium dosage could affect the A_2N-IC system. By the explanations above, three aspects of data should be taken into consideration for predicting the threshold values of these parameters: (1) the $M^{P}_{\mathrm{upt}(n)}/M^{P}_{\mathrm{rel}(n+1)}$ value variation during the unstable stage for estimating phosphorus release amount in the next cycle; (2) the relationship between k and the supplied phosphorus for biological system, which is to determinate the steady condition of the system; (3) the m value variations under different conditions, such as different HRT and dosage. According to the above data, the phosphorus release and uptake amount could be evaluated for the steady state by iterative method. Correspondingly, threshold values of the parameters could be predicted.

3.4. Crystallization product analysis in IC-SBR

Compared to the A_2N-IC-CF process, calcium could be added continuously in the A_2N-IC-SBR system, reducing the high saturation for homogeneous precipitation, which was the in favor of heterogeneous crystallization. A plate-shaped crystallization product, confirmed by SEM (Fig. 7), was found in IC-SBR and was similar to previous results [28,29].

Some smaller particles, containing the high amount of phosphorus, were also found in the crystallization product. There were three possible explanations for their formation. First, due to the aeration-mix, the product formed on the seed surface falls off, becoming the new seed and calcium phosphorus formed on the new seed with time. Second, it was unavoidable that homogeneous precipitation would occur. Tiny homogeneous precipitations were used as the new seeds or contacted with each other by aeration-mix then created the aggregation. Third, calcite seeds coated with phosphorus recovery product were eroded by water and gas.

4. Conclusions

In this work, the novel A_2N-IC-SBR process was studied, which consisted of three SBRs for biological denitrifying phosphorus removal, nitrification, and chemical phosphorus recovery. Compared to A_2N-IC-CF, it used three less settling tanks and saved post-aerobic tank.

Furthermore, it was easier and feasible to enhance phosphorus recovery efficiency in the A_2N-IC-SBR system. Phosphorus recovery efficiency increased significantly in the A_2N-IC-SBR process. The removal rate of TP was 9.9–13.6% in the IC reactor of the A_2N-IC-CF process, while it was 41.2–49.9% in A_2N-IC-SBR. Calcium was added continuously and equably during the chemical phosphorus recovery stage, reducing the need for high saturation required for homogeneous precipitation. The plate-shaped crystallization product was formed in the IC-SBR. For nitrogen removal, it was stable enough to attain 5 mg/L ammonia concentrations in the effluent. TN could meet the Urban Waste Water Treatment Directive 91/271/EEC.

According mass balance equations, ammonia and nitrate concentrations at different stages and cycles could be predicted. Moreover, A_2N-IC-SBR has an important characteristic called a self-adjustment characteristic, which is the ability to cushion and weaken the impact of increased or decreased amount of chemical phosphorus removal on the system.

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List of symbols

C_{inf} — influent ammonia concentration (mg/L)

X_n — ammonia concentration at the initial anaerobic stage in A/A/O-SBR of Cycle n (mg/L)

X_1 — ammonia concentration at the initial anaerobic stage in A/A/O-SBR of Cycle 1 (mg/L)

X_{n+1} — ammonia concentration at the initial anaerobic stage in A/A/O-SBR of Cycle $(n+1)$ (mg/L)

Y_n — ammonia concentration at the initial aerobic stage in N-SBR of Cycle *n* (mg/L)

Y_i — ammonia concentration at the initial aerobic stage in N-SBR of Cycle *i* (mg/L)

Z_n — nitrate concentration at the start of the aerobic stage in N-SBR of Cycle *n* (mg/L)

Z_1 — nitrate concentration at the start of the aerobic stage in N-SBR of Cycle 1 (mg/L)

P_n — nitrate concentration at the end of the aerobic stage in N-SBR of Cycle *n* (mg/L)

S_n — ammonia concentration at the end of the anoxic stage in A/A/O-SBR of Cycle *n* (mg/L)

${M_{\mathrm{inf}(n)}}^P$ — influent phosphorus amount of Cycle *n* (mg)

${M_{\mathrm{eff}(n)}}^P$ — effluent phosphorus amount of Cycle *n* (mg)

${M_{\mathrm{rel}(n)}}^P$ — phosphorus release amount of Cycle *n* in the anaerobic stage (mg)

${M_{\mathrm{upt}(n)}}^P$ — phosphorus uptake amount of Cycle *n* in the anoxic and aerobic phase (mg)

${M_{\mathrm{biol}(n)}}^P$ — biological removal amount of Cycle *n*, which equals ${M_{\mathrm{upt}(n)}}^P - {M_{\mathrm{rel}(n)}}^P$ (mg)

${M_{\mathrm{chem}(n)}}^P$ — chemical removal amount of Cycle *n* (mg)

$m_{(n)}$ — $m_{(n)} = \frac{{M_{\mathrm{chem}(n)}}^P}{{M_{\mathrm{rel}(n)}}^P + {M_{\mathrm{inf}(n)}}^P}$, chemical phosphorus removal coefficient in IC-SBR

$k_{(n)}$ — the ratio of ${M_{\mathrm{upt}(n)}}^P$ to ${M_{\mathrm{rel}(n)}}^P$

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