The comparison of alkalinity and ORP as indicators for nitrification and denitrification in a sequencing batch reactor (SBR)

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Abstract

Selection of an easy-to-measure, well-correlated surrogate parameter is critical for ensuring the effective operation of a nitrification/denitrification process on a real-time basis. The study aimed at investigating alkalinity as a reliable indicator for effluent nitrogen concentration under a series of operational conditions (chemical oxygen demand (COD), NH_4^+, hydraulic retention time) and under allylthiourea (ATU, a chemical inhibited nitrification) shock. The accuracy of alkalinity indication was compared with redox potential (ORP) in a sequencing batch reactor (SBR). Although both ORP and alkalinity exhibited clear variations in a SBR cycle, alkalinity presented a better indication than ORP, especially when there was a progressive decease in nitrification/denitrification efficiency. Effluent alkalinity exhibited a linear reverse correlation with nitrogen concentration ($Alk = -4.26[N] + 180$, $R^2 = 0.92$), with alkalinity lower than 100 mg/L indicating insufficient denitrification, while alkalinity higher than 200–250 mg/L indicating insufficient nitrification. Furthermore, alkalinity difference between influent and effluent (ΔAlk), which reflected an overall result of alkalinity consumption in nitrification and alkalinity production in denitrification, was studied as another indicator. $\Delta Alk_{inf.-eff.}$ decreased with better denitrification ($\Delta Alk = 6.99[N] + 22$, $R^2 = 0.82$) but increased with better nitrification ($\Delta Alk = -5.54[N] + 126$, $R^2 = 0.76$). The strong correlations of alkalinity with effluent nitrogen concentration, and $\Delta Alk_{inf.-eff.}$ with nitrification/denitrification efficiency demonstrate that both alkalinity and $\Delta Alk_{inf.-eff.}$ can be used as indicators in nitrification/denitrification processes. In addition, the benefits and problems of alkalinity, ORP and pH indications for nitrogen removal were comprehensively compared in the paper.
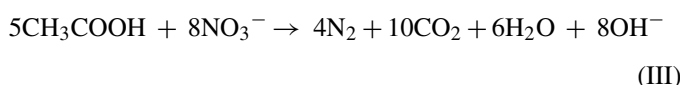© 2007 Published by Elsevier B.V.

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1. Introduction

Biological nitrogen removal, consisting of aerobic nitrification/anoxic denitrification, is generally regarded as the most economical and efficient means to remove nitrogen from wastewater. Nitrification is a two-step reaction: ammonium (NH_4^+) is first oxidized to nitrite (NO_2^-) by autotrophic ammonia oxidizers, nitrite is then oxidized to nitrate (NO_3^-) by autotrophic nitrite-oxidizers (Reactions (I) and (II)). In anoxic denitrification, nitrite/nitrate is reduced to nitrogen gas (N_2) by heterotrophic denitrifiers with the presence of extra carbon source (e.g. methanol or acetic acid) as electron donor (Reaction (III)). Nitrification can only be successfully operated under low chemical oxygen demand (COD), sufficient dissolved oxygen (DO) and long sludge retention time (SRT), while denitrification needs sufficient COD under anoxic condition. These different requirements pose challenges for nitrogen removal in sequencing batch reactor (SBR) systems, where nitrification and denitrification occur in the same tank:

$$2NH_4^+ + 3O_2 \rightarrow 2NO_2^- + 4H^+ + 2H_2O \tag{I}$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \tag{II}$$

$$5CH_3COOH + 8NO_3^- \rightarrow 4N_2 + 10CO_2 + 6H_2O + 8OH^- \tag{III}$$

Several operational parameters, such as oxidation–reduction potential (ORP) and pH, have been studied as indicators for nitrification/denitrification. However, conflicted results have been reported. ORP and pH breakpoints (e.g. nitrate knee, ammonia valley) indicating the start/end phases of nitrifica-

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tion/denitrification were detected in some tests [1–3], but not others [4]. Several studies reported ORP and pH had a good correlation [5,6], while Hamamoto et al. [7] found that pH remained stable while ORP changed substantially throughout aerobic/anoxic processes. In addition, although ORP breakpoints have been clearly identified for nitrification/denitrification control in bench-scale systems under well-controlled conditions [1,5,8], they are not easy to detect and apply in the practical operation of SBR systems. The accuracy of ORP probes was also in question due to the probe fouling after immersed in wastewater for certain period. So it is necessary to select a parameter easy to measure in real field and well-correlated with nitrogen removal efficiency and effluent quality.

Compared with ORP, alkalinity is directly related with nitrogen removal. Alkalinity is consumed at 7.14 g/g $N_{oxidized}$ during nitrification and generated at 3.57 g/g $N_{reduced}$ during denitrification. The easiness of measurement with test kits is another advantage for alkalinity. Alkalinity of secondary treated wastewater is normally regulated as higher than 80–100 mg/L to keep sufficient buffer capacity. Although the linkage of alkalinity and nitrification/denitrification has been known for decades on a scientific basis [9–12], very limited information is available about the indication of alkalinity for effluent nitrogen concentration. In addition, because the amount of alkalinity consumed in nitrification is greater than alkalinity generated in denitrification, the alkalinity variation throughout treatment processes ($\Delta Alk_{inf.-eff.}$) might be used as another indicator for the extent of nitrification/denitrification.

Many studies have been conducted for nitrification under influent shocks [13–16]. Ginestet et al. [17] and Gorska et al. [18] have found that allylthiourea (ATU) inhibited the oxidation of ammonium to nitrite (Reaction (I)), and 100% nitrification was inhibited at ATU of 5–10 mg/L. However, there has been no study for the recovery of nitrogen removal from ATU shock, though this would be important for nitrification stability. In addition, the study of the change of alkalinity during ATU shock could verify its feasibility for the indication of nitrification in the SBR systems.

The need for establishing a reliable correlation between alkalinity and nitrification/denitrification for practical operation motivated the study. The objective was to compare the accuracy of alkalinity and ORP as monitor tools for nitrogen removal in a SBR system under a series of operation conditions (COD, oxygen concentration, and retention time) and under ATU shock. Alkalinity difference between influent and effluent ($\Delta Alk_{inf.-eff.}$) was also tested for indicating the extents of nitrification/denitrification. Based on nitrogen removal under a series of operation conditions and ATU shock, mathematical equations to correlate alkalinity, $\Delta Alk_{inf.-eff.}$, and nitrogen concentration were developed.

2. Material and methods

2.1. SBR system and synthetic wastewater

A SBR system with an effective treatment capacity of 1.7 m³ was used in this study. There were three stages in the SBR:

fill, reaction, and settling, with the sequence being controlled by an auto-timer. Under standard (mid-level) operation, a cycle (4.75 h) consisted: 0.42 h aeration, 2.83 h anoxic mixing, 1.00 h settling and 0.5 h idle. The changes of dissolved oxygen (DO) concentration were achieved by adjusting aeration/anoxic duration. DO was maintained at 3.5–4.5 mg/L during aeration phase under mid-level operation.

Synthetic wastewater was prepared to obtain standard (mid-level) influent (COD: 700 mg/L, TKN 45 mg/L, NH_4^+: 35 mg/L, alkalinity: 200–230 mg/L as $CaCO_3$). The constituents were (per liter): milk powder 0.53 g, K_2HPO_4 0.04 g, urea 0.04 g, $(NH_4)_2SO_4$ 0.05 g, and CH_3COONa 0.02 g. The influent was pumped into the filling zone in the SBR system by a dosage pump. Hydraulic retention time (HRT) was 3.6 days (with flow rate of 0.47 m³/day) under mid-level operation. The main reason for this long HRT was that this SBR system was designed for single family use and wastewater was normally held 2–3 days in the system before being discharged. The sludge retention time (SRT) was 10–14 days throughout the experiment. Activated sludge was inoculated from Middletown Municipal Wastewater Treatment Plant. Mixed liquor suspended solid (MLSS) was 1000–1300 mg/L in the SBR system throughout the experiment.

2.2. Experiment set-up

Influent COD concentration, DO during aeration phase, and hydraulic retention time (HRT) were adjusted to get low-, mid-, and high- level conditions (Table 1). Only one parameter was changed each time with the other two remaining at mid-level. Thereby, the impact of each parameter on nitrogen removal could be tested individually without interference from other parameters.

2.3. ATU shock test

Alkalinity variation in nitrification was also examined under allylthiourea (ATU) shock. Before ATU was added into SBR feeding solution, batch tests were conducted to determine the dosage of ATU. In batch tests, activated sludge suspension was taken from the SBR system and put into 500 mL bottles with different ATU concentrations. The bottles were shaken at

Table 1
The levels of parameters changed in the SBR system (influent $[NH_4^+] = 35$–45 mg/L)

	COD (mg/L)	DO During aeration (mg/L)	HRT (days)
High COD-mid DO-mid HRT	1317	3.5–4.5	3.6
Mid COD-mid DO-mid HRT	700	3.5–4.5	3.6
Low COD (1)-mid DO-mid HRT	240	3.5–4.5	3.6
Low COD (2)-mid DO-mid HRT	103	3.5–4.5	3.6
Extremely low COD-mid DO-mid HRT	88	3.5–4.5	3.6
Mid-COD-high DO-mid HRT	700	5.2–5.5	3.6
Mid-COD-low DO-mid HRT	700	0.7–1.0	3.6
Mid COD-mid DO-long SRT	700	3.5–4.5	9
Mid COD-mid DO-short SRT	700	3.5–4.5	2.0

25 °C for 2 h. $[NH_4^+]$ and $[NO_3^-]$ were then measured. ATU inhibited nitrification by 42% at the dosage of 1 mg/L, and completely inhibited nitrification at 10 mg/L. ATU shock tests were performed when the SBR system was under mid-level operation.

2.4. Chemical analysis

After the SBR system was acclimatized to each operational condition for 15 days (Table 1), wastewater samples in each SBR cycle was collected once per two days within a 10–20 days stable operation period. Analysis of COD, MLSS, pH, total kjehldahl nitrogen (TKN), and alkalinity were performed following standard methods [19]. Ammonium and nitrate were measured by Orion ion selective membrane electrodes. Nitrite was measured by HACH colorimetric test kit. Dissolved oxygen (DO) was measured by an YSI oxygen meter equipped with an oxygen probe. Redox potential (ORP) was measured by Orion ORP probe. In this work, ORP, pH and alkalinity were measured at the end of each phase during a SBR cycle.

2.5. Alkalinity variation through nitrification and denitrification

Since nitrification and denitrification occurred in the same tank in the SBR system, effluent alkalinity was the overall result of alkalinity consumed in nitrification and alkalinity generated in denitrification. Theoretically, the difference between influent alkalinity and effluent alkalinity was 7.14−3.57 = 3.57 mg/L/mg/L $N_{removed}$. The theoretical values of alkalinity difference between influent and effluent were calculated as:

$$\Delta Alk_{theory} = 3.57([NH_4^+]_{inf.} + [NO_2^-]_{eff.} + [NO_3^-]_{eff.} - [NH_4^+]_{eff.}) \, (mg/L) \quad (1)$$

Because $[NO_2^-]$ and $[NO_3^-]$ were normally below the detection level in influent, they were not included in (1).

The experimental data of alkalinity difference were calculated as:

$$\Delta Alk_{exper.} = Alkalinity_{inf.} - Alkalinity_{eff.} \, (mg/L) \quad (2)$$

$\Delta Alk_{exper.}$ was compared with ΔAlk_{theory} for the accuracy of ΔAlk indicating nitrogen removal.

3. Results and discussion

3.1. COD and N removal under different operational conditions

A complete nitrification occurred over a broad range of influent COD concentrations (88–1317 mg/L), with effluent $[NH_4^+]$ and TKN less than 0.1 mg/L (Fig. 1a). It had not been expected that nitrification could occur well at high influent COD (1317 mg/L). The main reason for good nitrification was long retention time (HRT: 3.6 days), compared with 5–7 h in normal wastewater treatment process.
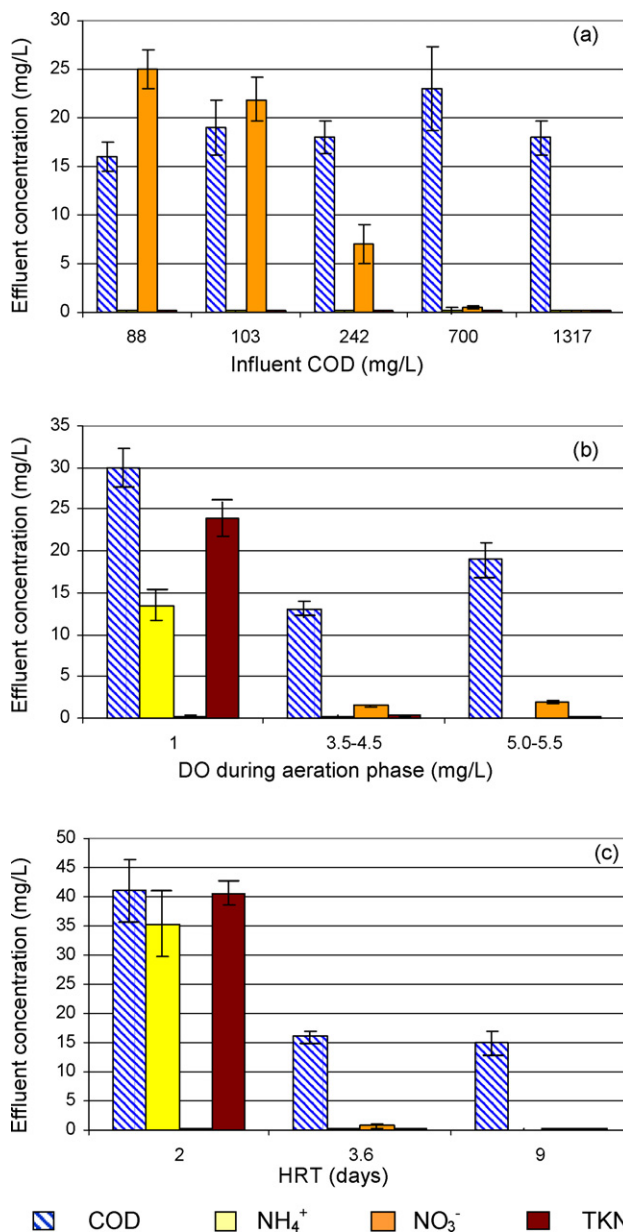

Fig. 1. COD and nitrogen removal in the SBR system at different COD, DO concentrations, and HRTs.

Denitrification failed when COD was less than 120 mg/L, with effluent $[NO_3^-]$ higher than 20 mg/L (Fig. 1a). Denitrification improved when COD increased to 242 mg/L, with effluent $[NO_3^-]$ lower than 7 mg/L. Effluent $[NO_3^-]$ further reduced to less than 0.2 mg/L at medium/high COD (740–1317 mg/L). This good removal of NO_3^- in the SBR system might be the result of complete denitrification with the presence of sufficient carbon source, or nitrogen uptake by excess cell growth at high influent COD.

Proper duration for aeration/anoxic phases is necessary for good nitrification and denitrification in a SBR system. It takes longer time for oxygen to drop to zero if oxygen concentration is too high in aeration phase, which might lead to incomplete denitrification. Nitrification did not proceed well under low DO

(1 mg/L) with effluent [NH_4^+] higher than 13 mg/L (Fig. 1b), though complete denitrification occurred with effluent [NO_3^-] below detection level. Nitrification was complete when DO concentration was higher than 5.0 mg/L during aeration, but incomplete denitrification caused effluent [NO_3^-] higher than 2.0 mg/L.

Both COD and nitrogen removal were adversely affected by short HRT. Effluent COD was lower than 20 mg/L at HRT of 3.6 and 9 days, but above 40 mg/L at short HRT (2.0 days) (Fig. 1c). Two reasons caused high effluent COD. First, microorganisms did not have sufficient time to degrade organic matter from wastewater. Second, lower amount of NO_3^- produced from the deteriorated nitrification consumed less organic carbon source in denitrification. Nitrogen removal efficiency substantially declined at short HRT, with effluent [NH_4^+] as high as 34 mg/L, indicating nitrification barely occurred. Denitrification, carried out by heterotrophic denitrifiers, was not affected by HRT, with effluent [NO_3^-] below detection level. The results agree with the previous study that nitrification at short HRT/SRT failed if continuous feeding of nitrifiers stopped [20,21].

3.2. ORP changes in the SBR operation at different conditions

On-line ORP values were in a reverse correlation with influent COD in the SBR system. During anoxic period, ORP dropped to −104 mV under high COD condition (1317 mg/L), while ORP was still as high as 178 mV under low COD condition (88 mg/L) (Fig. 2a). Good denitrification occurred at low ORP with sufficient carbon source present, while low carbon source (indicated by high ORP) caused the failure of denitrification.

ORP values increased in aeration phase and then decreased in anoxic phase in all DO tests (Fig. 2b). The extent of ORP decrease in anoxic phase became gradual at high DO (5.0–5.5 mg/L), caused by certain amount of oxygen still present in wastewater even aeration stopped after high aeration phase. Although effluent ORP values at mid-DO (173 mV, DO: 3.0–4.5 mg/L) and high-DO (175 mV, DO: 5.0–5.5 mg/L) were higher than that at low DO (123 mV, DO: 1.0 mg/L), there was no detectable difference between ORP values at mid- and high-DO levels. The possible reason was that DO was critical for
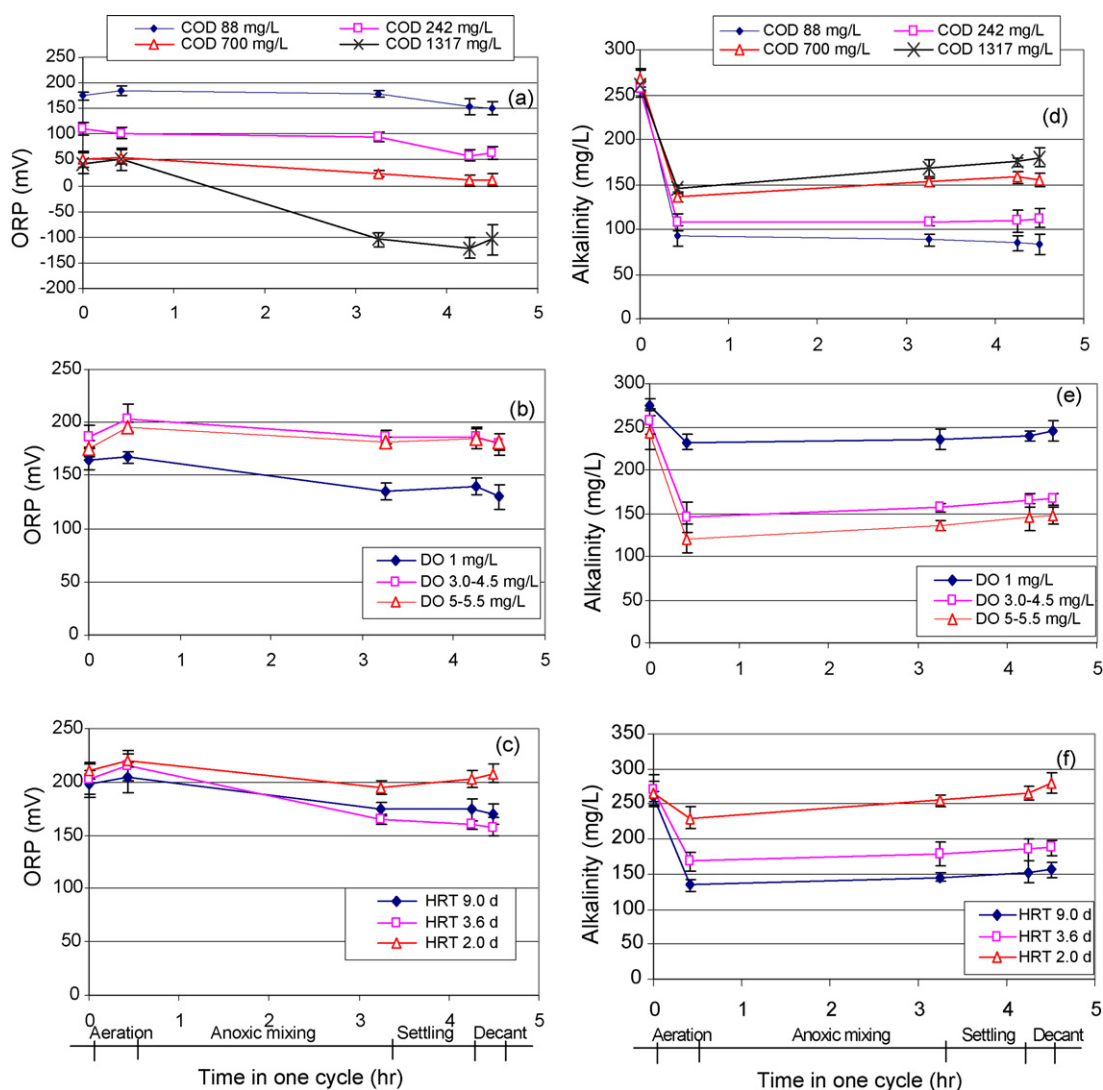

Fig. 2. ORP and alkalinity change with operational conditions (COD, DO, and HRT) in the SBR system.

ORP values at low concentration (<1 mg/L), but after there was sufficient oxygen in wastewater (DO > 3.0 mg/L in this study), further increasing DO did not lead to a higher ORP value.

ORP values did not follow a clear trend with HRTs. ORP values (208 mV) at short HRT (2.0 days) were higher than that of long/mid HRTs (158–170 mV, HRT 3.6–9.0 days) (Fig. 2c), although nitrification failed at short HRT (Fig. 1c). These findings were different from previous studies, which reported that low ORP corresponded to poor effluent quality [1,3,6,8] and nitrification failed when ORP values were lower than 50–150 mV [7,22]. The contribution of DO (as oxidant) in ORP values may explain this discrepancy. DO was still maintained at mid-level (3.5–4.5 mg/L) during aeration phase in the HRT tests (Table 1). With sufficient oxygen available in wastewater and less oxygen consumed by poor nitrification at short HRT, effluent ORP values were still high even though $[NH_4^+]$ might be as high as 35 mg/L. This could pose an obstacle to interpret ORP values in nitrogen removal systems, especially when poor nitrification occurred at high DO.

A variation in ORP values at the settling period was observed, with 50% of measured ORP values increase and 50% of ORP values decrease from anoxic section. This ORP variation indicated although most biochemical reactions finished during aerobic/anoxic phases, the separation of biomass from wastewater still generated the changes of redox status.

3.3. Alkalinity changes in the SBR operation at different conditions

Nitrification (alkalinity consumption) and denitrification (alkalinity production) at different COD concentrations led to the variation of alkalinity in the SBR system (Fig. 2d). The greatest alkalinity drop in aerobic nitrification phase occurred at lowest COD (COD: 88 mg/L) with effluent alkalinity of 86 mg/L. Alkalinity started increasing in anoxic denitrification phase when COD was higher than 700 mg/L. Effluent alkalinity was 185 mg/L at high COD concentration (COD: 1317 mg/L), as the result of more alkalinity generated in denitrification at high COD. Alkalinity gradually increased during settling phase in most tests (except at low COD), indicating residual denitrification continued if there was carbon source available after anoxic mixing phase.

Incomplete nitrification at low DO and short HRT correlated with high effluent alkalinity. Alkalinity only dropped 50 mg/L in aerobic phase at low DO (<1 mg/L, Fig. 2e), with effluent alkalinity of 250 mg/L. With better nitrification at mid/high DO, alkalinity underwent a greater drop from 230–254 mg/L in influent to 120–140 mg/L after aeration phase. Less alkalinity consumed by the deteriorated nitrification at short HRT (2.0 days) led to the highest effluent alkalinity (285 mg/L), compared with effluent alkalinity of 152–189 mg/L at long/mid HRT (Fig. 2f). Based on the experimental data of SBR cycles, alkalinity exhibited good correlations with nitrification/denitrification at a series of COD, DO, and HRT tests.

Effluent ORP and alkalinity were then assessed for indicating effluent $[NH_4^+] + [NO_3^-]$ (Fig. 3). Effluent ORP did not have a clear correlation with nitrogen concentra-

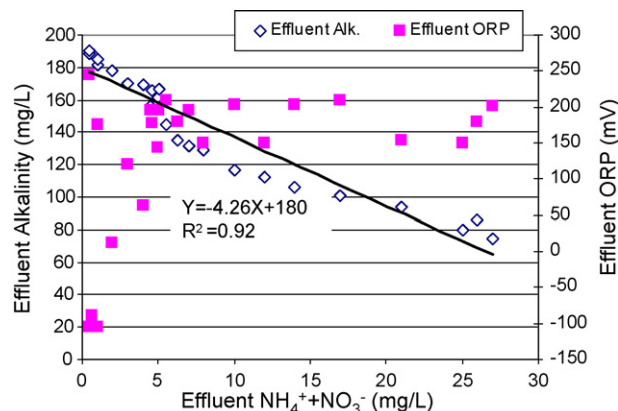Fig. 3. The correlation of effluent ORP and alkalinity (as $CaCO_3$) with effluent total nitrogen ($NH_4^+ + NO_3^-$) at COD level tests.

tion. ORP values ranged from −150 mV (at high COD) to 250 mV (at mid-DO) at good nitrogen removal (with effluent $[NH_4^+] + [NO_3^-] < 5$ mg/L), while ORP values were still 180–250 mV at poor nitrogen removal (with effluent $[NH_4^+] + [NO_3^-] = 10–27$ mg/L). It was assumed that the involvement of several factors (COD as reductant, DO as oxidant) in ORP values caused this non-clear correlation. Nitrogen removal was good at both high COD and mid/high DO (Fig. 1a and b), but ORP was negatively related with COD while positively related with DO (Fig. 2a and b). Nitrogen removal decreased at both low COD and short HRT (Fig. 1a and c), but ORP were still 200–250 mV due to low COD concentration and low oxygen consumption (Fig. 2a and c). These interferences from COD and DO hindered ORP as an indictor for effluent nitrogen concentration.

In contrast, alkalinity exhibited a linear reverse relationship with effluent $[NH_4^+] + [NO_3^-]$ (Alk = −4.26[N] + 180, $R^2 = 0.92$) (Fig. 3). The incomplete denitrification at low COD concentration led to high effluent $[NO_3^-]$ (23 mg/L), and alkalinity produced in denitrification could not make up for alkalinity consumed in nitrification, resulting in low alkalinity (<100 mg/L) in effluent. Effluent alkalinity steadily improved with more carbon source available, and was higher than 160 mg/L at effluent $[NH_4^+] + [NO_3^-]$ lower than 5 mg/L.

Alkalinity difference between influent and effluent ($\Delta Alk_{inf.-eff.}$) was also studied as an indicator for nitrogen removal efficiency (Eq. (2)). Since alkalinity is consumed at 7.14 g/g $N_{oxidized}$ during nitrification and generated at 3.57 g/g $N_{reduced}$ during denitrification, effluent alkalinity was expected to be lower than influent alkalinity. A greater ΔAlk presents a higher extent of nitrification (alkalinity consumption) and a lower extent of denitrification (alkalinity production). Effluent [N] linearly increased with ΔAlk ($\Delta Alk = 6.99[N] + 22$, $R^2 = 0.82$) while reversely correlated with COD (Fig. 4). At low COD (COD < 300 mg/L), $\Delta Alk_{inf.-eff.}$ was 140–161 mg/L and effluent [N] was higher than 12 mg/L. This big drop of alkalinity was caused by less alkalinity produced by incomplete denitrification with insufficient carbon source present in wastewater. $\Delta Alk_{inf.-eff.}$ decreased with COD increase, and was −2 mg/L at COD of 1317 mg/L, indicating that sufficient
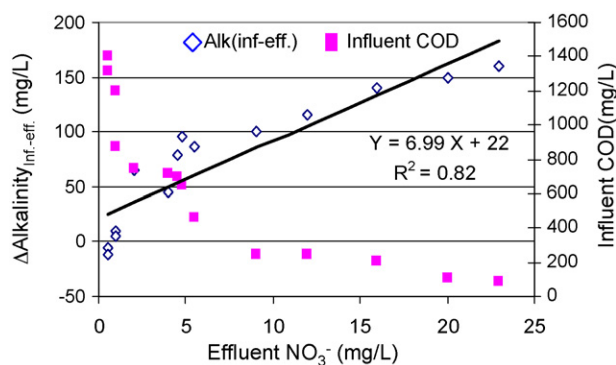
Fig. 4. The correlation of alkalinity difference between influent and effluent (ΔAlk) and influent COD with effluent NO_3^- concentration (with good nitrification, effluent [NH_4^+]: 0.2–4 mg/L).

Fig. 6. The theoretical and experimental alkalinity difference between influent and effluent in the SBR system under ATU shock (with good denitrification, effluent [NO_3^-] < 0.2 mg/L).

alkalinity produced by complete denitrification at high COD compensated alkalinity consumed in nitrification. Fig. 4 showed that ΔAlk$_{inf.-eff.}$ should be less than 50 mg/L in order to achieve complete denitrification (effluent [N] < 5 mg/L).

3.4. Nitrification and alkalinity change under ATU shock

Nitrification under ATU shock was tested at low ATU dosage (1 mg/L) and high ATU dosage (10 mg/L). About 20–30% nitrification was inhibited when the SBR system was under low ATU shock, with effluent [NH_4^+] increase to 10 mg/L (Fig. 5). Fifty to 70% nitrification was inhibited at high ATU dosage with effluent [NH_4^+] increase to 20 mg/L. ATU shock was stopped on 15th day, and the SBR system started recovery with effluent [NH_4^+] gradually decreasing to 0.2 mg/L at 23rd day. This indicated ATU only inhibited nitrifying bacterial activity, but not killed them and nitrifying bacteria started to recover after ATU shock period. Effluent alkalinity followed the same trend as nitrification throughout ATU shock tests. Alkalinity increased from 190 mg/L at normal status to 230 mg/L at ATU of 1 mg/L, and further increased to 292 mg/L at ATU of 10 mg/L. During the recovery period, alkalinity steadily dropped and stabilized at 190 mg/L seven days after ATU shock. By combining ATU shock tests (Fig. 5) and operational condition results (Fig. 3), effluent alkalinity should be around 130–190 mg/L for good effluent nitrogen quality ([NH_4^+] + [NO_3^-] < 5 mg/L). Alkalinity lower than 100 mg/L indicated insufficient denitrification (e.g. low COD), while alkalinity higher than 200–250 mg/L
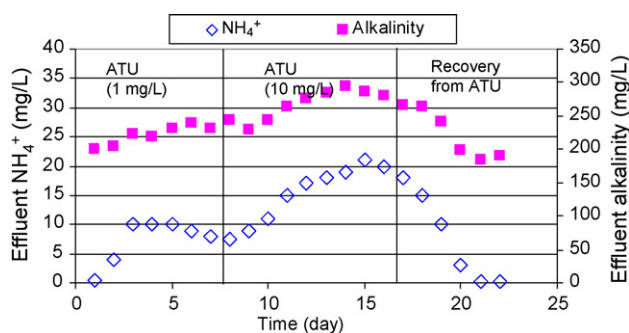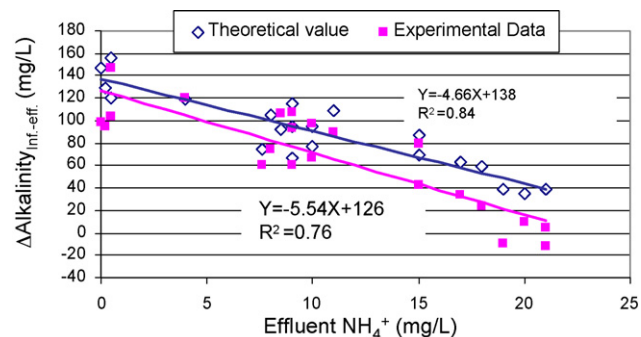
indicated insufficient nitrification (e.g. low DO, short HRT, and influent shock).

Alkalinity difference between influent and effluent (ΔAlk$_{exper.}$) under ATU shock was compared with theoretical values (ΔAlk$_{theory}$). Both ΔAlk$_{exper.}$ and ΔAlk$_{theory}$ had good linear reverse correlations with effluent [NH_4^+] ($R^2 > 0.75$) (Fig. 6). ΔAlk was 100–150 mg/L when effluent [NH_4^+] was lower than 1 mg/L without ATU shock. It decreased to 50–110 mg/L when effluent [NH_4^+] increased to 7–12 mg/L at low ATU dosage, indicating less alkalinity was consumed at the inhibited nitrification. ΔAlk further dropped to −9 to 40 mg/L when effluent [NH_4^+] increased to 17–22 mg/L under high ATU dosage. It was found that ΔAlk$_{exper.}$ values were about 10–20 mg/L lower than ΔAlk$_{theory}$. The possible reason was that the occurrence of alkalinity consumption (nitrification) and alkalinity production (denitrification) in the same tank in the SBR system might reduce the alkalinity variation from influent and effluent.

It is important to note that although ΔAlk exhibited a strong correlation with effluent nitrogen concentration, the correlation under ATU shock (ΔAlk versus [NH_4^+], Fig. 6) was opposite to that in the series of operational parameter tests (ΔAlk versus [NO_3^-], Fig. 4). ATU shock inhibited nitrification and led to low alkalinity consumption, so a low ΔAlk indicated high effluent [NH_4^+] from the inhibited nitrification. However, nitrification occurred well in most of series of operational parameter tests (Fig. 1), a high ΔAlk indicated high effluent [NO_3^-] from incomplete denitrification at lower COD. Therefore, it is derived from ATU shock and operational parameter tests that ΔAlk was 120–140 mg/L in order to get good nitrification, while ΔAlk was −10–60 mg/L for good denitrification.

3.5. The application of alkalinity for monitoring nitrogen removal process

The tests of alkalinity variation in the SBR system clearly showed its accuracy for indicating the completion of nitrification and denitrification. We also compared alkalinity and pH in the SBR system and found that pH values exhibited clear decrease in nitrification (aerobic phase) and increase in denitrification (anoxic phase) (data not shown). Although effluent pH was higher than 7 at incomplete nitrification (effluent
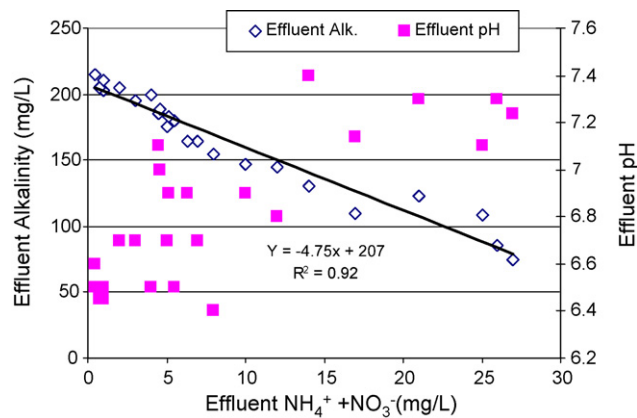

Fig. 5. Nitrification in the SBR system at low ATU dosage (1 mg/L), high ATU dosage (10 mg/L) and recovery period.

Fig. 7. The correlation of effluent pH and alkalinity (as $CaCO_3$) with effluent total nitrogen ($NH_4^+ + NO_3^-$) at COD level tests.

$[NH_4^+] > 10$ mg/L) and lower than 6.5 at complete nitrification (effluent $[NH_4^+] < 5$ mg/L), its variation with nitrogen concentration in effluent was not as clear as alkalinity (Fig. 7), some pH values were the same even though nitrogen concentration varied more than 10 mg/L. This could be explained by pH logarithmic order of $[H^+]$. Couple magnitudes of $[H^+]$ variation might not lead to a clear measurable change of pH values. On the other hand, alkalinity based on $CaCO_3$ can clearly reflect $[H^+]$. When water pH is 6–8, alkalinity changes at a magnitude of 20–30 mg $CaCO_3$/L per 1.5–2 times of $[H^+]$ variation. The tests also showed that ORP values increased at aerobic phase and decreased at anoxic phase, but they were not well related with effluent nitrogen concentration.

The close correlation between alkalinity and each step of nitrification/denitrification also provides advantages for its indication. In nitrification, alkalinity is consumed at 7.14 g as $CaCO_3$ per gram of NH_4^+ oxidized to NO_2^-. There is no further alkalinity consumption at the oxidation of NO_2^- to NO_3^-. In denitrification, alkalinity is generated at 3.57 g $CaCO_3$ per gram of NO_3^-/NO_2^- reduced to N_2. Therefore, a good/poor nitrogen removal and short-cut nitrification/denitrification (via NO_2^-) can be indicated or validated by alkalinity values and alkalinity difference between influent and effluent. Compared with ORP and pH, alkalinity values can not only monitor the system operational status, but also indicate the completion of nitrification/denitrification. Unlike the break points in ORP and pH curves that are difficult to detect and follow in real operation, alkalinity values are easy and simple to obtain and interpret.

However, real-time measurement of alkalinity is currently not available. Wastewater samples have to been taken from treatment facilities and measured off-line by titration, which caused a time lag of several minutes. On-line ORP and pH monitor have been extensively studied [1–8] and applied in treatment processes. However, because of the difficulties to identify breakpoints in ORP profiles, the involvement of many factors in ORP values, and the low sensitivity of pH to nitrogen concentrations, the accuracy for their on-line monitor was below expectation in engineering application. Based on the good correlation of alkalinity and nitrification/denitrification observed in this study, it is suggested that more efforts should be put on the develop-

ment of on-line analysis techniques for alkalinity measurement. At current stage, couple months measurements need to be conducted for a treatment process in order to get a clear correlation of alkalinity and nitrogen concentration. Afterwards, wastewater alkalinity will be tested and fit into the alkalinity–nitrogen curve to obtain nitrogen removal efficiency. It is feasible to use ORP, DO and pH as on-line parameters and use alkalinity as off-line confirmative parameter.

4. Conclusion

The following conclusions can be drawn from the investigation of alkalinity and ORP in the SBR system:

1. Both alkalinity and ORP exhibited clear variations in a SBR cycle under different operating conditions (COD, DO, and HRT), but alkalinity presented a better indication for effluent nitrogen concentration than ORP did. The involvement of COD and DO in ORP hindered its clear correlation with effluent nitrogen concentration. Alkalinity exhibited a linear reverse correlation with effluent nitrogen concentration ($Alk = -4.26[N] + 216$, $R^2 = 0.92$). Alkalinity lower than 100 mg/L indicated insufficient denitrification, while alkalinity higher than 200–250 mg/L was related with insufficient nitrification.
2. As an overall result of alkalinity consumption in nitrification and alkalinity production in denitrification, alkalinity difference between influent and effluent ($\triangle Alk$) clearly reflected nitrification/denitrification efficiency. $\triangle Alk$ decreased with better denitrification ($\triangle Alk = 6.99[N] + 22$, $R^2 = 0.82$), but increased with better nitrification ($\triangle Alk = -5.54[N] + 126$, $R^2 = 0.76$). $\triangle Alk$ was about 120–140 mg/L in order to get good nitrification, while $\triangle Alk$ was -10–60 mg/L for good denitrification.

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