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Effect of Aeration Rate on Nutrient Removal from Slaughterhouse Wastewater in Intermittently Aerated Sequencing Batch Reactors

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Abstract The effect of aeration rate on nutrient removal from slaughterhouse wastewater was examined in two 10-L laboratory-scale sequencing batch reactors (SBRs—SBR1 and SBR2) operated at ambient temperature. The contaminants in the slaughterhouse wastewater had average concentrations of 4,000 mg chemical oxygen demand (COD) L^{-1}, 350 mg total nitrogen (TN) L^{-1} and 26 mg total phosphorus (TP) L^{-1}. The duration of a complete SBR operation cycle was 8 h and comprised four operational phases: fill (7 min), react (393 min), settle (30 min) and draw/idle (50 min). During the react phase, the reactors were intermittently aerated four times at 50-min intervals, 50 min each time. DO, pH and oxidation–reduction potential (ORP) in the reactors were real-time monitored. Four aeration rates—0.2 L air min^{-1} in SBR1 for 70 days, 0.4 L air min^{-1} in SBR1 for 50 days, 0.8 L air min^{-1} in SBR2 for 120 days and 1.2 L air min^{-1} in SBR1 for 110 days—were tested. When the aeration rate was 0.2 L air min^{-1}, the SBR was continuously anaerobic. When the aeration rate was 0.4 L air min^{-1}, COD and TP removals were 90% but TN removal was only 34%. When the aeration rates were 0.8 and 1.2 L air min^{-1}, average effluent concentrations were 115 mg COD L^{-1}, 19 mg TN L^{-1} and 0.7 mg TP L^{-1}, giving COD, TN and TP removals of 97%, 95% and 97%, respectively. It was found that partial nitrification followed by denitrification occurred in the intermittently aerated SBR systems.

Keywords Aeration rate · Intermittent aeration · Nutrient removal · Slaughterhouse wastewater · Sequencing batch reactor

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1 Introduction

In Ireland, there are currently 306 licensed slaughterhouses comprising 270 slaughterhouses licensed for the domestic market and 36 approved bovine export slaughterhouses (Howlett et al. 2005). The amount of wastewater generated per cow is approximately 2 m^3 and mainly originates in the rendering department and holding yards of slaughterhouses (Johns et al. 1995). In pig slaughterhouses, 1.6–8.3 m^3 of water per tonne of carcase is generated (European Commission (EC) 2005). Depending on whether preliminary treatment is carried out and its efficiency, the concentrations of contaminants in slaughterhouse wastewater can be variable, with values ranging 250–5,000 mg suspended solids (SS) L^{-1}, 1,000–20,000 mg chemical oxygen demand (COD) L^{-1}, 150–10,000 mg total nitrogen (TN) L^{-1}, and 22–217 mg total phosphorus

(TP) L^{-1} (Fuchs et al. 2003; Cassidy and Belia 2005; Del Pozo and Diez 2005; Merzouki et al. 2005; Mittal 2006).

For large-scale slaughterhouses, on-site biological treatment is recommended by the EC to remove organic carbon and nutrients before the wastewater is discharged to surface waters or local wastewater treatment plants (EC 2005). The emission standards in Ireland for slaughterhouse wastewater are given in Table 1 (Irish EPA 2006). If the treated effluent is discharged to surface waters, it must satisfy other water quality standards. The EC also recommends that sequencing batch reactors (SBRs) be amongst the best available techniques (BATs) for slaughterhouse wastewater treatment, as SBRs are capable of removing organic carbon, nutrients and SS from wastewater, and have low capital and operational costs. Typical COD, TN and TP removals from slaughterhouse wastewater achieved in SBRs are 95%, 60–80% and 40%, respectively (EC 2005). SBRs are not able to remove nitrogen (N) as efficiently as to remove COD because slaughterhouse wastewater contains very high TN, with a typical biochemical oxygen demand (BOD_5) to TN ratio of 7–9:1.

Typically, biological N removal in SBRs is through pre-denitrification, which occurs during the fill phase (or an anoxic phase between the fill and the aerobic react phase). Anoxic heterotrophic denitrifiers reduce nitrate–nitrogen (NO_3–N) and/or nitrite–nitrogen (NO_2–N), which is produced in the preceding operational cycle and remains in the reactor after the draw phase, to N_2 gas. Denitrifiers consume the readily biodegradable COD (rbCOD). If the slaughterhouse wastewater has a low C/N ratio, external carbon sources, such as fermented waste sludge (Ra et al. 2000), should be added to enhance denitrification. This results in increased operational costs. If simultaneous phosphorus (P) and N removal is expected to be achieved in the reactor, P accumulating organisms (PAOs) will compete with denitrifiers for rbCOD for anaerobic P release. This competition between PAOs and denitrifiers will result in unstable biological P removal if the influent wastewater does not contain sufficient rbCOD. Therefore, tertiary treatment, such as chemical precipitation, is required to guarantee a low concentration of P in the effluent.

A conventionally operated SBR can be changed to an intermittently aerated SBR, where one complete operational cycle comprises four phases—fill, react (alternating aeration and mixing), settle and draw. In the react phase, aeration and mixing are alternatively applied. In an intermittently aerated SBR, during the aeration periods, DO is high and aerobic nitrifiers oxidize ammonium–nitrogen (NH_4–N) to oxidized nitrogen (NO_2–N and NO_3–N), and during the succeeding mixing periods, DO decreases to such a low level that anoxic denitrifiers reduce oxidized N to N_2 gas. The intermittent aeration strategy can also reduce the demand for rbCOD contained in the influent wastewater in the fill phase by minimizing the occurrence of N removal in the fill phase, so that PAOs will obtain sufficient rbCOD for anaerobic P release, which is beneficial to biological P removal. In addition, in an intermittently aerated reactor, the organic C stored by PAOs could be used by denitrifiers for denitrification in subsequent anoxic periods (Nazik and Derin 2005), resulting in less dependence of denitrification on the rbCOD content in the influent wastewater. Therefore, stable and efficient N and P removal can be achieved in intermittently aerated SBRs, which is an advantage over conventional SBRs. Laboratory studies have shown that when treating

Table 1 Performance of SBR1 and SBR2 at the four aeration rates

Parameter (mg L^{-1})	Emission standard[a]	0.2 L min^{-1}	0.4 L min^{-1}	0.8 L min^{-1}	1.2 L min^{-1}
SS	60	220±(73)[b]	100±(42)	33±(18)	24±(11)
COD	125–250 or >75% removal	1,500±(316) (68%)[c]	330±(165) (93%)	115±(13) (97%)	96±(27) (97%)
Total nitrogen	15–40 or >80% removal	343±(52) (<5%)	232±(22) (34%)	19±(8) (95%)	19±(7) (92%)
Total phosphorus	2–5 or >80% removal	16±(2.5) (43%)	1.8±(0.2) (94%)	0.7±(0.3) (97%)	0.6±(0.2) (97%)

[a] Emission standards given by Irish EPA (2006)

[b] Standard deviations

[c] Percentage removals

slaughterhouse wastewater at an influent organic loading rate of 1.2 g COD L^{-1} d^{-1}, average effluent concentrations of COD, TN and TP were 150 mg L^{-1}, 15 mg L^{-1} and 0.8 mg L^{-1}, respectively (Li et al. 2008). All parameters satisfied the emission standards required by Irish EPA. Corresponding removals of COD, TN and TP were 96%, 96% and 99%, respectively.

In this study, the performance of SBRs was examined at four aeration rates—0.2, 0.4, 0.8 and 1.2 L air min^{-1}—to obtain the optimum aeration rate. Meanwhile, the real-time data of DO, pH and oxidation–reduction potential (ORP) at various aeration rates were compared to provide information for the real-time automatic operation control of the system.

2 Materials and Methods

2.1 Laboratory-scale SBR Systems

Two identical laboratory-scale SBR systems were used in this study, so only one system is described here (Fig. 1). The cylindrical reactor tank was made from transparent Plexiglas and had a working volume of 10 L, with an inner diameter of 194 mm and a height of 400 mm. One MasterFlex® L/S peristaltic pump fed the reactor tank with slaughterhouse wastewater from the influent tank and the other pump drew the treated wastewater. A mechanical mixer with an 80-mm deep × 100-mm wide rectangular paddle was installed over the reactor. An air pump supplied air through a porous stone diffuser that was located at the base of the reactor. The air flow rate was manually regulated by an air flowmeter. The sequential operation of the reactor system, comprising fill, react, settle, draw and idle phases, was controlled by a programmable logic controller (PLC) (S7-222, Siemens, Germany).

DO, pH and ORP in the two reactors were real-time monitored using electrodes. The DO electrode (EC-DOTPII-S, Eutech, Singapore), pH electrode (Sentix 20, WTW, Germany) and ORP electrode (Sentix ORP, WTW, Germany) were connected to corresponding transmitters (Eutech, Singapore), which transformed the signals from the three electrodes into 4–20 mA analog signals. Then, a data acquisition card (USB-6009, National Instruments, USA) transformed the analog signals into digital signals that were pro-

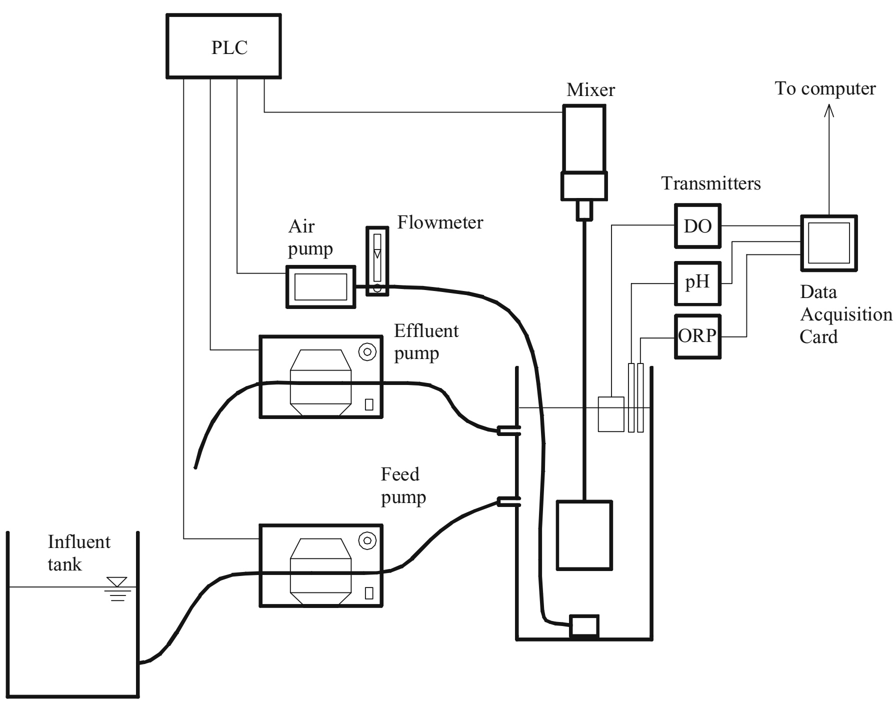


Fig. 1 Schematic diagram of the laboratory SBR system

cessed by LabVIEW software (National Instruments, USA).

The operation sequence of the SBR system is given in Fig. 2. The duration of a whole cycle was 480 min, giving three cycles per day. During the fill phase, 1.0 L slaughterhouse wastewater was pumped from the influent tank into the reactor tank. From the 50th minute, the reactor was intermittently aerated with a constant air supply four times at 50-min intervals, 50 min each time. The mechanical mixer was operated continuously with a rotational velocity of 100 rpm during the fill and react phases. During the draw phase, the supernatant liquid was withdrawn from the reactor until the liquid volume in the reactor decreased to 9.0 L. The sludge retention time (SRT) was controlled by the manual daily discharge of a certain amount of mixed liquor from the reactor immediately prior to the commencement of the settle phase.

2.2 Slaughterhouse Wastewater

The wastewater was collected from the conditioning tank in the wastewater treatment plant of a local slaughterhouse in western Ireland. Prior to entering the conditioning tank, the raw wastewater was preliminarily treated by means of screening and dissolved air floatation (DAF). The wastewater was collected from the slaughterhouse with 10-L plastic containers and stored in a refrigerator at approximately 4°C up to 10–20 days before use. The influent wastewater used in this study was prepared daily by filtering the raw wastewater through a 0.6-mm mesh screen to remove large particles. A pump was submerged in the influent tank to continuously stir the wastewater.

The average wastewater quality in the influent tank over the study period is given in Table 2.

2.3 Operation of the Reactors

The two SBR reactors (SBR1 and SBR2) were seeded with the recycle sludge taken from the secondary clarifier of the local slaughterhouse's wastewater treatment plant. The aeration tanks of this plant were operated at an average organic loading rate (OLR) of 0.5 kg COD m^{-3} d^{-1}, a SRT of 20–30 days, and a mixed liquor suspended solids (MLSS) concentration of 5,000–6,000 mg L^{-1}. The volatile suspended solids (VSS)/SS ratio of the seed sludge was 0.86. After seeded, the two SBR reactors had an initial MLSS of about 3,500 mg L^{-1}.

SBR1 was operated at 0.2 L air min^{-1} during Days 1–70, 0.4 L air min^{-1} during Days 71–120 and 1.2 L air min^{-1} during Days 121–230. SBR2 was operated at 0.8 L air min^{-1} during Days 1–120. During Days 1–120, COD and SS in the influent wastewater fluctuated greatly and had average influent COD and SS concentrations of 4,700 and 1,400 mg L^{-1}, respectively, giving an average OLR of 1.4 g COD L^{-1} d^{-1}. TN was relatively stable during this period and had an average value of 350 mg TN L^{-1}. During Days 121–230, raw slaughterhouse wastewater contained lower COD, SS and TN. Therefore, when SBR1 was operated at an aeration rate of 1.2 L air min^{-1}, the average OLR was 0.86 g COD L^{-1} d^{-1} and the average N loading rate (NLR) was 0.075 g N L^{-1} d^{-1}.

At aeration rates of 0.2 and 0.4 L air min^{-1}, relatively high SRTs of 30 and 20 days were used in order to maintain MLSS in the reactors in the range of 4,000–6,000 mg L^{-1} (5,100±400 mg L^{-1} at the aeration rate of 0.2 L min^{-1} and 5,700±100 mg L^{-1} at the aeration rate of 0.4 L min^{-1}). During the periods when 0.8 and 1.2 L air min^{-1} aeration rates were applied, SRTs in the reactors were kept at 14.5 days. The average MLSS during the 0.8 L min^{-1} aeration rate was 4,400±550 mg L^{-1}. Due to the low influent

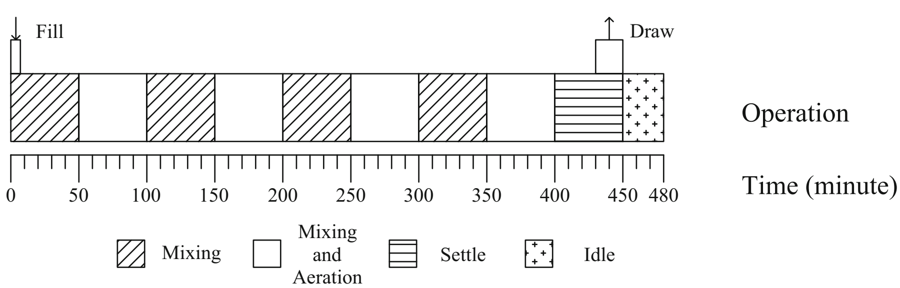


Fig. 2 A complete operational cycle of the laboratory-scale SBR system

Table 2 Characteristics of the slaughterhouse wastewater filled in the reactor tanks

Parameter	Unit	Days 1–120 (runs 1, 2, 3)	Day 121–230 (run 4)
pH	–	7.0–8.0	7.0–8.0
Suspended solids	mg L^{-1}	1,400±600	720±160
COD	mg L^{-1}	4,700±950	2,850±780
BOD_5	mg L^{-1}	2,900±600	1,000±150
Total nitrogen	mg L^{-1}	350±45	250±45
Total phosphorus	mg L^{-1}	28±5	20±5

SS and COD concentrations over the period when the 1.2 L air min^{-1} aeration rate was applied, MLSS was around 3,900±850 mg L^{-1}.

The average settling volume index (SVI) of activated sludge in this study ranged from 90 to 140 mL g^{-1}, indicating that the sludge had a good settling property.

2.4 Analytical Methods

COD, BOD_5 and SS were measured in accordance with the standard APHA methods (APHA 1995). The pore size of the filter paper for SS test was 0.45 µm. TN and TP were measured with TN and TP kits (Hach, USA). NH_4–N, NO_2–N, NO_3–N and PO_4–P concentrations were measured with a nutrient analyzer (Konelab 20, Thermo, USA). All filtered samples were obtained by filtering the water sample through 0.8-µm filter papers.

3 Results and Discussion

3.1 Effects of the Aeration Rate on the Overall Performance of Intermittently Aerated SBRs

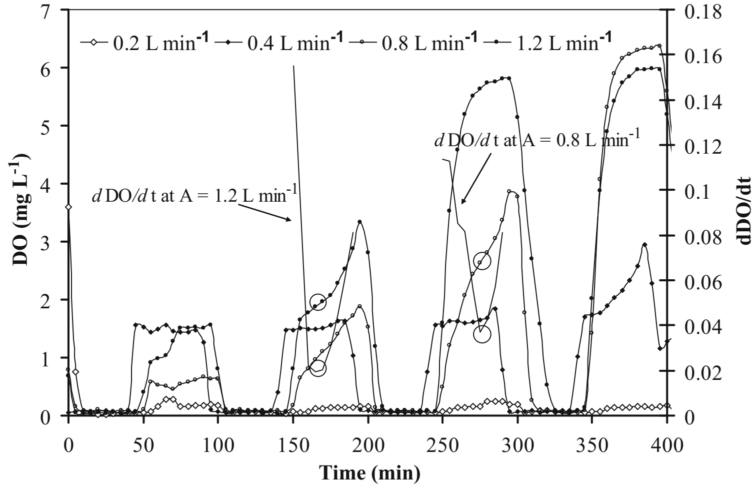
The performance of the intermittently aerated SBRs at the four aeration rates is given in Table 1. At aeration rates of 0.2 and 0.4 L min^{-1}, the effluent contained high concentrations of COD and nutrients and the effluent quality did not reach the emission standards required by Irish EPA (Table 1). The effluent quality at the 0.4 L min^{-1} aeration rate was much better than that at the 0.2 L min^{-1} aeration rate and produced lower effluent COD, TN and TP concentrations. Enhanced biological phosphorus removal (EBPR) did not occur at the 0.2 L min^{-1} aeration rate but took place when the aeration rate was increased to 0.4 L min^{-1}. This was because no phosphorus release occurred during the non-aeration periods at the aeration rate of 0.2 L min^{-1}. At 0.4 L air min^{-1}, effluent PO_4–P was less than 0.6 mg L^{-1} and effluent TP was around 1.8 mg L^{-1}.

At high aeration rates of 0.8 and 1.2 L air min^{-1}, the effluent quality met the emission standards (Table 1). COD removals were up to 97% and effluent SS concentrations were less than 60 mg L^{-1}. Biological nitrification and denitrification reduced TN in the effluent to 19 mg L^{-1}, representing TN removals up to 95% and 92%, respectively. Effluent PO_4–P and TP was less than 0.2 mg L^{-1} and 1.0 mg L^{-1}, respectively. TP removals were up to 97%. Filali-Meknassi et al. (2005) applied a step-feed SBR to treat slaughterhouse wastewater and the average PO_4–P concentration in the effluent was 10 mg L^{-1}; consequently, ferric chloride was required to further reduce effluent PO_4–P. The present study illustrates the possible advantages of intermittently aerated SBRs over step-feed SBRs in enhanced biological phosphorus removal.

The effects of the aeration rate on the performance of the SBRs were due to different DO concentrations during the aerobic periods in the reactors at the four aeration rates (Fig. 3). Since the cyclic analysis associated with individual aeration rates was carried out at different influent wastewater conditions, the absolute values of DO at the four aeration rates were not comparable. At the 0.2 L min^{-1} aeration rate, DO was negligible during the react phase (0–400 min). Because of the almost completely anaerobic conditions in the bulk water phase in the reactor, processes that required oxygen, including carbonaceous oxidation, nitrification and enhanced biological P uptake, were unable to occur. The constant ORP value of −12 mV during the whole react period (Fig. 4) revealed that the bulk wastewater in the reactor remained anaerobic.

When the 0.4 L air min^{-1} aeration rate was applied, during the first, second and third aeration periods, DO concentrations were relatively stable at 20% saturation (1.76 mg L^{-1}). In the last aeration period (350–400 min), DO gradually rose from 20% to 40% saturation (1.76–3.52 mg L^{-1}). Although the DO concentrations were supposed to be good for nitrification, high concentrations of organic matter in the water phase—330 mg COD L^{-1} at the end of the react

Fig. 3 Typical cycle profiles of DO at different aeration rates

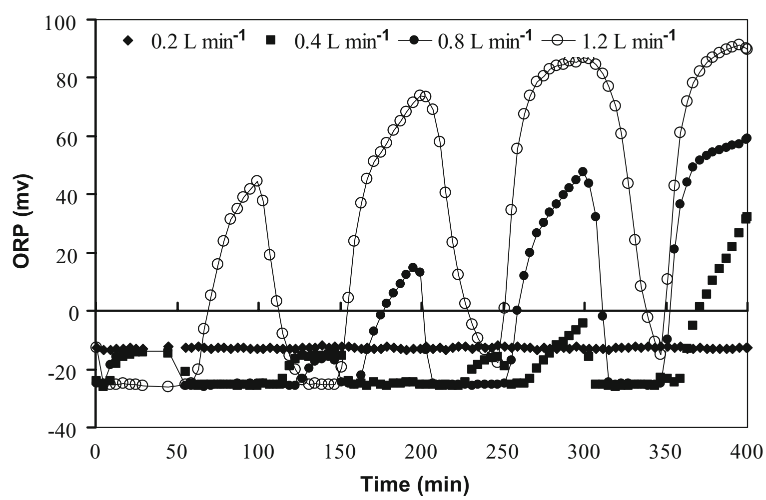


phase (at the 400th minute)—inhibited nitrification. A stable pH in the reactor (between 7.7 and 7.8) indicates that no significant nitrification occurred during the react phase (Fig. 5). The low DO concentration during aeration periods resulted in PO_4–P uptake and anaerobic conditions during the non-aeration periods contributed to P removal. This can explain the difference in P removal during the 0.2 and 0.4 L air min^{-1} aeration rates.

At the 0.8 L air min^{-1} aeration rate, the average DO concentrations during the four aeration periods were 0.7, 1.3, 2.6 and 6.0 mg L^{-1} (Fig. 3). During the non-aeration but mixing periods, DO was rapidly decreased to nearly zero. The high DO fostered nitrification and the NH_4–N concentration in the third aeration period was less than 5 mg L^{-1}.

During the 7-min fill phase, the remaining NO_2–N and NO_3–N from the preceding cycle were rapidly removed by means of denitrification, with a denitrification rate over 1.25 mg N L^{-1} min^{-1} (Fig. 6). After the fill phase, a soluble TN (TNs) of 35 mg L^{-1} was measured in the bulk mixed liquor phase. NH_4–N decreased during the aeration periods, resulting from nitrification and biomass synthesis. A release of around 7 NH_4–N mg L^{-1} was observed during the second anoxic period (100–150 min), probably because of ammonification of organic N. After P uptake was complete, NO_2–N appeared in the reactor

Fig. 4 Typical cycle profiles of ORP at different aeration rates



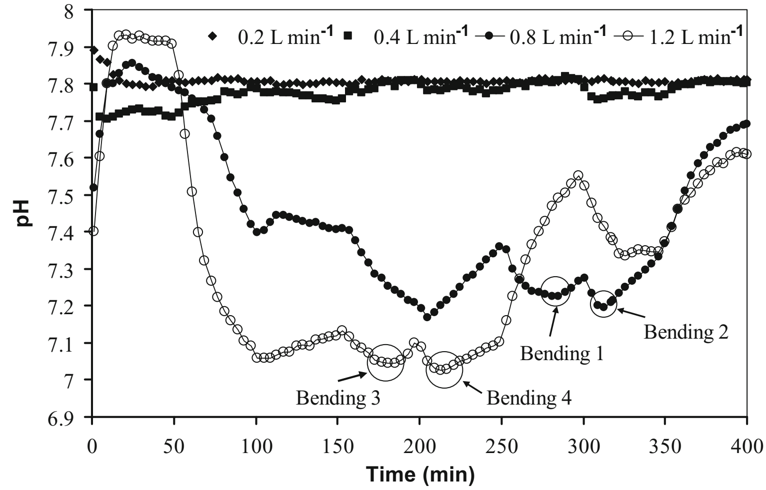


Fig. 5 Typical cycle profiles of pH at different aeration rates

tank from Minute 71. NO_2–N increased linearly in the first three aeration periods (50–100 min, 150–200 min and 250–300 min, respectively) and NO_2–N production rates were 0.065, 0.207 and 0.178 mg L^{-1} min^{-1}. During the last aeration period (350–400 min), the nitrification rate was close to zero due to the depletion of NH_4–N in the bulk reactor tank. NO_2–N did not decrease during the last aeration period.

P release occurred during the first non-aeration period, and a maximum PO_4–P concentration of 11.8 mg L^{-1} was reached at the 50th minute. Given an influent PO_4–P concentration of 27 mg L^{-1}, it is calculated that 91 mg PO_4–P was released from the sludge. P uptake commenced at the start of the first aeration period and was completed after 20 min. Throughout the cycle, the average P uptake rate was 0.54 mg P L^{-1} min^{-1}. Soluble COD (CODs) decreased during the fill phase and the first non-aeration period, and it levelled to around 100 mg L^{-1} until the end of the cycle.

At the 1.2 L min^{-1} aeration rate, during the first aeration period, the DO concentration increased dramatically from 0 to around 25% saturation within 20 min, and then remained higher than 30% saturation from the first aeration period. During this period, most of the oxidized N produced was NO_2–N. NO_2–N was around 6 mg L^{-1} (60% of TON) (Fig. 7). The

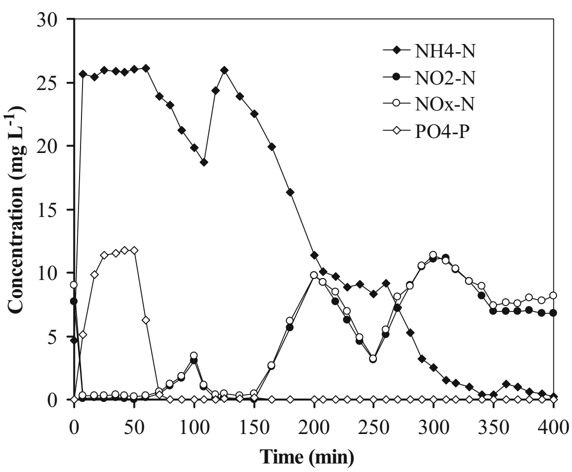


Fig. 6 Cycle profiles of N and P at the aeration rate of 0.8 L air min^{-1}

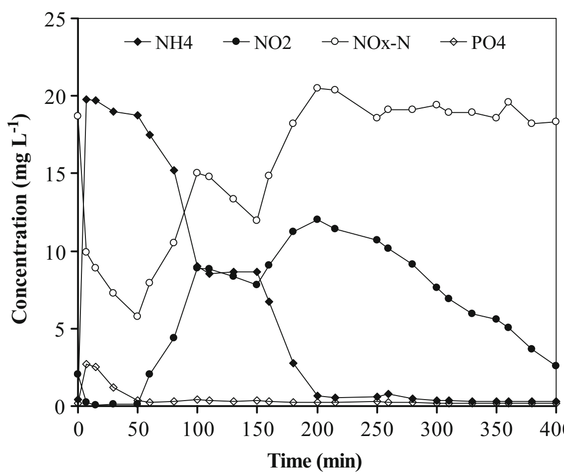


Fig. 7 Cycle profiles of N and P at the aeration rate of 1.2 L air min^{-1}

post-denitrification during 100–150 min was not as effective as in the same period in the aeration rate of 0.8 L air min^{-1} case. During the second aeration period of 150–200 min, NO_2–N and NO_3–N concentrations increased. From the 160th minute, NH_4–N was less than 5 mg L^{-1}. From 200 to 400 min, NO_2–N decreased from 12 mg L^{-1} to 2.5 mg L^{-1} and NO_3–N increased to 16 mg L^{-1}. NO_3–N was the main form of oxidized N present in the effluent.

Because high NO_3–N remained from the previous cycle, the pre-denitrification occurring in the first 50 min was not complete. During the fill period, 2 mg L^{-1} of NO_2–N and 17 mg L^{-1} of NO_3–N rapidly decreased to 0 and 9 mg L^{-1}, respectively. Highest PO_4–P concentrations of 2.7 mg L^{-1} appeared at the end of the fill period. From 8 to 50 min, around 4.0 mg L^{-1} NO_3–N was depleted by means of denitrification, while 2.4 mg L^{-1} of PO_4–P was simultaneously removed. With no or little anaerobic/anoxic P release, anoxic P uptake occurred during this period. The phenomenon of simultaneous denitrification and P uptake has also been found by other researchers (Kuba et al. 1997; Meinhold et al. 1999). However, NO_3–N reduced P release during the fill phase. The P uptake rate under anoxic conditions was 0.054 mg P L^{-1} min^{-1}, which was only 10% of the P uptake rate during the same period at the aeration rate of 0.8 L air min^{-1}.

The profiles of the ratio of NO_2–N to total oxidized nitrogen (TON) are given in Fig. 8. At the aeration rate of 0.8 L min^{-1}, NO_2–N/TON was over 80% during most of the operational cycle. When the aeration rate was 1.2 L min^{-1}, the highest ratio was around 65% and took place during the period of 100–250 min. The ratio decreased in the subsequent periods and was equal to 15% at the end of the operational cycle. This was because NO_2–N was oxidized by nitrite oxidizing bacteria to NO_3–N:

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad (1)$$

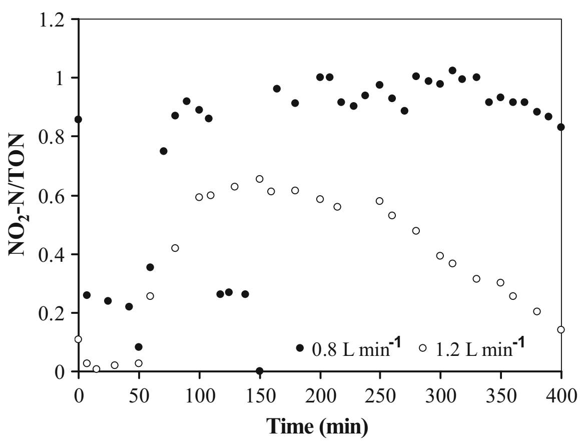


Fig. 8 Variation of NO_2–N/TON in a complete cycle at the aeration rates of 0.8 and 1.2 L min^{-1}

At the aeration rate of 0.8 L min^{-1}, in the first and second non-aeration periods (0–50 min and 100–150 min, respectively), NO_2–N/TON was reduced to 8% and 26%, respectively, indicating that removal of NO_2–N by means of denitrification was faster than the removal of NO_3–N in the anoxic condition. This phenomenon also appeared during the first non-aeration period (0–50 min) at the aeration rate of 1.2 L min^{-1}.

The high NO_2–N/TON in the react phase at the aeration rates of 0.8 and 1.2 L min^{-1} indicates that partial nitrification occurred. However, the 0.8 L min^{-1} aeration rate favored partial nitrification, in comparison with the 1.2 L min^{-1} aeration rate. Low DO concentrations, ranging from 0.2 to 0.7 mg L^{-1}, favor partial nitrification (Ruiz et al. 2003; Chuang et al. 2007). It also has been found that when DO concentrations were in the medium range of 1.4 mg L^{-1}, NO_2–N accumulation can still take place (Ciudad et al. 2005). In biofilm reactors, the DO concentration at which the maximum NO_2–N accumulation was achieved was as high as 3.5 mg L^{-1} (Oyanedel-Craver et al. 2005). However, in the present SBR system, the average DO levels during the four aeration periods were 0.7, 1.3, 2.6 and 6.0 mg L^{-1} and NH_4–N concentrations were 23.4, 17.5, 5.9 and 0.6 mg L^{-1}. Both DO and NH_4–N concentrations were not consistent with the findings of the other researchers mentioned above. NO_2–N/TON ratios were 96% and 89% in the third and fourth aeration periods, respectively. These were higher than the ratios during the first and second aeration periods—64% and 72%, respectively.

It is possible that the intermittent aeration pattern applied in the SBR system caused the partial nitrification (Mota et al. 2005a, b; Li et al. 2008). Further research should be conducted to study the mechanisms triggering NO_2–N accumulation in the SBR system.

3.2 Automatic Control of SBRs Using DO, pH and ORP Real-time Data

Studies on automatic control of conventional SBR systems using DO, pH and ORP probes have been carried out to enhance N and P removal and to reduce operational costs (Tilche et al. 1999; Casellas et al. 2006; Lee et al. 2001; Lee and Oleszkiewicz 2003; Marsili-Libelli 2006). In the present study, the application of DO, pH and ORP real-time data to control the operation of intermittently aerated SBRs was studied.

DO data are always used to identify the end point of nitrification. The early identification of the end point of nitrification can save the operation cost on aeration. Marsili-Libelli (2006) proposed that DO probe data be used to identify the end of the nitrification phase: when the curve of DO concentrations with respect to time levels off, i.e., $\frac{dDO}{dt} = 0$, nitrification ends. From Fig. 3, it is found that at the aeration rate (A) of 0.8 L min^{-1}, an ammonium breakpoint appeared during the period of 250–300 min, since NH_4–N was almost completely depleted during this period; at A=1.2 L min^{-1}, an ammonium breakpoint appeared during the aeration period of 150–200 min, corresponding to the almost complete depletion of NH_4–N. However, the two ammonium breakpoints were not easily found on the profile of DO curves (Fig. 3). At the two points, DO curve did not level off, which is different to the findings of Marsili-Libelli (2006). It is found that at the two ammonium breakpoints, $\frac{d^2DO}{dt^2} = 0$. The reason could be due to the difference in wastewater used in the present study and in Marsili-Libelli's study. If using the ammonium breakpoints to identify the end of nitrification points, at A=0.8 L min^{-1}, the fourth aeration period (350–400 min) can be omitted. Hence, the aeration ratio (the ratio of the total aeration duration to the total cycle duration) would be reduced from 42% to 31%. At A=1.2 L min^{-1}, the third and the fourth aeration periods (250–300 min and 350–400 min) can be saved, which would reduce the aeration ratio from 42% to 21%.

The pH profile can be used to indicate the end of nitrification (Kim and Hao 2001), end of denitrification (Casellas et al. 2006) and end of P release (Marsili-Libelli 2006). A minimum pH variation ("ammonia valley") indicates the end of nitrification; a maximum pH value indicates the end of denitrification ("nitrate apex") and pH levels off in the anaerobic phase indicated the end of P release.

In Fig. 5, there were two bending points on the curves of pH in a complete cycle at aeration rates of 0.8 L min^{-1} and 1.2 L min^{-1}. The first bending points (Bending Point 1 at around Minute 280 at A= 0.8 L air min^{-1} and Bending Point 3 around Minute 180 at 1.2 L air min^{-1}) corresponded to the low ammonium concentrations (ammonia valley) in the aeration periods. The explanation of the ammonia valley is that the nitrification process in the aerobic periods drove pH decreasing

$$55NH_4^+ + 76O_2 + 109HCO_3^- \rightarrow C_5H_7NO_2 + 54NO_2^- + 57H_2O + 104H_2CO_3 \quad (2)$$

$$400NO_2^- + NH_4^+ + 195O_2 + HCO_3^- + 4H_2CO_3 \rightarrow C_5H_7NO_2 + 400NO_3^- + 3H_2O \quad (3)$$

and that the air stripped carbon dioxide from the wastewater, which caused pH to increase

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (4)$$

The other two bending points in the non-aeration periods (Bending Point 2 at around Minute 310 at A= 0.8 L air min^{-1} and Bending Point 4 around Minute 220 at A=1.2 L air min^{-1}; Fig. 5) were due to the end point of complete nitrification during the non-aeration period, which was represented by the peak of the NO_x–N concentration and the level off of the NH_4^+–N concentration. At the start of the non-aeration periods, the DO concentration was still high enough to support nitrification, causing pH to reduce. When DO was consumed and nitrification was complete, denitrification occurred, resulting in an increase in pH:

$$\frac{1}{70}C_{18}H_{19}O_9N + \frac{1}{5}NO_3^- + \frac{1}{5}H^+ \rightarrow \frac{1}{10}N_2 + \frac{17}{70}CO_2 + \frac{1}{70}HCO_3^- + \frac{1}{70}NH_4^+ + \frac{1}{5}H_2O \quad (5)$$

ORP can be also used as the control parameter for wastewater treatment. It can provide more flexibility than the DO profile, since it provides a much wider monitoring range than DO, using both positive and negative data to represent the changes in aerobic, anaerobic and anoxic conditions. Comparatively, DO only gives positive data corresponding to aerobic conditions. Bending points found on the real-time ORP curves can reveal the beginning of denitrification, end of denitrification and end of nitrification (Shimabukuro et al. 2004). The absolute values of ORP depend on the characteristics of wastewater, DO concentrations and the biomass concentration, but the relative values of ORP can show the reduction and oxidation conditions in wastewater. Generally, in aerobic conditions, ORP values are positive, showing oxidation conditions; in anaerobic and anoxic conditions, ORP values are negative, showing reduction conditions.

The profiles of OPR at the four aeration rates are given in Fig. 4. In the wastewater, there were three typical oxidation–reduction states. At A=0.2 L air min^{-1}, in the bulk wastewater, the ORP value was close to −12 mV during the entire operational cycle. The reason was that the DO concentrations were nearly zero, showing that anaerobic conditions existed during all the phases. The concentrations of NO_x–N were low, showing that nitrification did not occur at A=0.2 L min^{-1}.

There was an interesting finding concerning ORP in the present study. At aeration rates of 0.2, 0.4, 0.8 and 1.2 L air min^{-1}, when the wastewater was anaerobic and DO and NO_x–N were close to zero, ORP was −12 mV. At aeration rates of 0.4, 0.8 and 1.2 L air min^{-1}, when the wastewater was anoxic, i.e., DO was zero and NO_x–N was present, ORP was close to −26 mV. In the aerobic phase, ORP increased from negative values to positive values from the onset of aeration. The three states are summarized in Fig. 9. The variation of ORP was different from that observed by other researchers in typical SBRs; this was possibly due to the complex composition of real slaughterhouse wastewater, which contributed to ORP greatly with the depletion of DO and NO_x–N in the anaerobic periods.

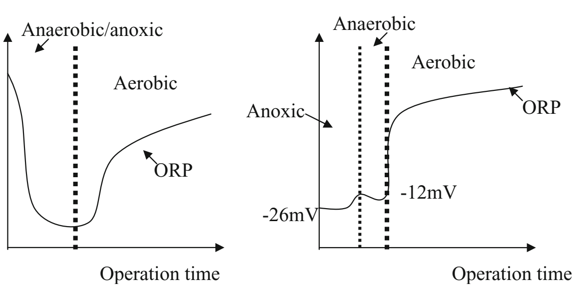


Fig. 9 ORP profiles for a typical anoxic/oxic SBR reactor and for the present study

When NO_x–N was removed by means of denitrification during non-aeration periods, ORP values rose from −26 mV to −12 mV. This was found at aeration rates of 0.4 and 0.8 L air min^{-1} during the periods of 0–50 min and 100–150 min. This finding indicates that the end point of denitrification can be detected by measuring an ORP of −12 mV during non-aeration periods.

In this study, the bending points for denitrification are not found in ORP profiles during the non-aeration periods (Fig. 4). This could be due to the short anoxic time, and incomplete denitrification prior to the onset of aerobic conditions.

4 Conclusion

The study examined the effects of aeration rates on the performance of intermittently aerated SBRs and investigated the profiles of real-time DO, pH and ORP data. The following results were obtained:

1. The optimum aeration rate of 0.8 L air min^{-1} produced the best system performance. Removals of COD, TN and TP were up to 97%, 94% and 97%, respectively. The average effluent was 115±13 mg L^{-1} COD, 19±8 mg L^{-1} TN and 0.7±0.3 mg L^{-1} TP and it reached the Irish emission standards.
2. Partial nitrification followed by denitrification occurred in the intermittently aerated SBR systems at aeration rates of 0.8 and 1.2 L air min^{-1}. At the aeration rate of 0.8 L min^{-1}, NO_2–N/TON during most of the operational cycle was over 80%. When the aeration rate was 1.2 L min^{-1}, NO_2–N/TON ranged from 15% to 65%. The cyclic operation could be the cause of partial nitrification.
3. The end of nitrification can be identified from DO and pH real-time data using $\frac{d^2DO}{dt^2} = 0$ and $\frac{dpH}{dt} = 0$.
4. There were three stages of ORP variation. ORP was around −26 mV in anoxic conditions, around −12 mV in anaerobic conditions and

was positive in aerobic conditions. The end point of denitrification in non-aeration periods can be set at an ORP value of −12 mV.

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