New operational strategy for SBR technology for total nitrogen removal from industrial wastewaters highly loaded with nitrogen

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Abstract The present work deals with the upgrading of conventional Sequential Batch Reactor (SBR) technology for treating industrial wastewater. The aim is to obtain total nitrogen removal in a single SBR by implementing short aeration cycles. The operational strategy of conventional SBR consisting of a sequence of five phases (filling, aeration, stirring, settling and withdrawing) is simplified into a four phases sequence (filling, short cycled aeration, settling and withdrawing). This operational sequence has been proven to be adequate for total nitrogen removal from high strength wastewater containing nitrogen (up to 700 mg TKN/L) and organic matter (up to 2,000 mg COD/L). Short-cycled aeration allowed for a more efficient use of the oxygen supply for nitrification and the organic carbon content present in the wastewater for denitrification. The results here reported show that initially the tested technology is feasible and can report significant cuts in operation and maintenance when compared with conventional SBR processes. Total nitrogen removal up to 79% was attained treating the effluent of an UASB process designed for treating the wastewater of a potato starch factory. Total nitrogen removal capacities ranging between 0.2 and 0.65 kg of nitrogen per cubic metre per day are reported.

Keywords SBR; cycled aeration; industrial wastewater; nitrification; denitrification; total nitrogen removal

Introduction

The progressive application of more severe regulations (EU Directive 271/91) limiting the discharge of total nitrogen and phosphorus to 15 mg N/L and 2 mg P/L, respectively, is demanding the updating of conventional nutrient removal technologies to fulfill these discharge limits at the lowest cost. Some strategies have been reported to improve, at low cost, total nitrogen removal in continuous and discontinuous flow processes. These strategies are based on achieving co-current nitrification-denitrification (N/D) controlling the addition and/or consumption of any of the substrates intervening in the nitrification or denitrification process (Goronszy, 1992, Hasselblad and Hallin, 1998, Wareham et al., 1993).

In this sense the application of aeration cycles to achieve total nitrogen removal has been already applied in continuous flow reactors based on ORP control which resulted in aeration cycles of several hours (Hao and Huang, 1996). In discontinuous processes, the implementation of short aeration cycles based on ORP and OUR control in conventional SBR technology has been successfully proven for total nitrogen and phosphorus removal from domestic wastewater (Demuynck et al., 1994). The operational strategy of conventional SBR consisting of a sequence of five phases (filling, aeration, stirring, settling and withdrawing) is in this way simplified into a four phase sequence (filling, short cycled aeration, settling and withdrawing).

However, treating high strength nitrogenous industrial wastewaters with Sequential Batch Reactor (SBR) technology has traditionally faced manifold problems and given rise to new operational strategies such as the accumulation of nitrites without much success (Abeling and Seyfried, 1992). The application of cycled aeration for total nitrogen removal in SBRs treating high strength wastewater appears to be an alternative but it has been never...
reported. The most critical aspect of the technology is the implementation of short-cycled aeration into a SBR treating wastewater fairly loaded with organic matter and nitrogen. This implementation can be done on a time basis although the application of an advanced sensor control system as a function of the oxygen concentration and ORP in the mixed liquor to control the oxygen (air) supply into the system is recommended.

This new operational strategy applied to the treatment of high strength industrial wastewater appears to allow for a more rational usage of the organic carbon and important reductions in the oxygen needs. Consequently it is expected that total nitrogen can be more efficiently removed at lower cost (less oxygen consumption and less external carbon source). In the present work the effect of the main operational parameters, aeration frequency, Hydraulic Retention Time (HRT), and Solids Retention Time (SRT), on the performance of the SBR in terms of COD, TKN and Total N removal is studied.

Materials and method
Experimental set-up
The experimental system (see Figure 1) consisting of a Plexiglas reactor of 6 litres of volume was operated during about 20 months. The reactor was seeded with 500 ml of nitrifying sludge from a sewage treatment plant sited at Valladolid, Spain. Initially the reactor was fed with synthetic wastewater containing between 1,000 mg COD/L of organic carbon, 500 mg N/L of nitrogen ammonia, and other nutrients. Ammonium salts, mostly NH₄Cl, (NH₄)₂SO₄ or a mixture of both, were used as nitrogen sources during this initial phase that lasted about eight months. Up to day 21 the synthetic wastewater contained sugar as sole carbon source, thereafter the carbon source was changed to molasses up to day 245. The solution was buffered at pH 7.5 with carbonate and phosphate, and kept refrigerated at 4°C to prevent microbial growth.

Once a stable population of nitrifiers and denitrifiers developed in the reactor, the stability and performance of the process was tested with a real wastewater. Following the synthetic wastewater feeding in a second experimental phase the effluent of an UASB reactor treating industrial wastewater (hereafter called “industrial wastewater” or IWW) was progressively introduced into the reactor, which favored the acclimation of the microorganisms to the real environment. This industrial wastewater (IWW) came from the agro-industry sector and was selected as an adequate effluent by its composition and biodegradable characteristics (Table 1).
Thus far, two different operational phases can be distinguished from the start up of the reactor, the first with synthetic wastewater and the second with IWW lasting 245 and 353 days, respectively. Throughout the experimentation several operational parameters of interest, such as the Hydraulic Retention Time (HRT), Solids Retention Time (SRT), aeration frequency (on/off cycles) and wastewater composition, were changed to determine their influence over nitrification and denitrification efficiencies. These specifications are shown in Table 2 for each operational period.

Oxygen was supplied intermittently into the reactor during the reaction phase following an on/off aeration sequence that controlled the aeration of the mixed liquor. Aeration cycles were controlled on a time basis by using an OMRON H3CR-F timer. Constant air flow rates were introduced into the system when aeration was on, this aeration provided oxygen concentrations of up to 5 mgO₂/L into the reactor at the end of the aeration. The concentration of volatile suspended solids was kept at the highest possible values reaching up to 9 gVSS/L.

Analysis
Analysis of TSS and VSS was carried out following standard methods using Millipore AP40 filters. COD and TKN analysis also followed standard procedures (APHA, 1995). Due to the high biodegradability of the wastewater, we used the soluble COD value as an accurate indicator of the organic matter content. Also Total Organic Carbon (TOC) was determined using a SHIMADZU TOC Analyzer 5050 equipped with a Shimadzu Auto Sampler ASI-5000A.

Ammonia nitrogen was measured using an electrode selective ORION (Model 95) connected to a meter ORION (Model 290A). Measures of pH values were done using a CRI-SON meter. Concentrations of anions (NO₂⁻, NO₃⁻, and PO₄³⁻) were determined using a HPLC Cromatograph equipped with a column Waters IC-Pack™ Anion 4.6x50 mm, Waters Oven and Temperature Controller, Waters Sample Injector (Model 231), Waters Pump (Model 510), Gilson Dilutor 401, and a Waters Conductivity Detector (Model 430).
Activity tests

Sludge samples were withdrawn from the reactor throughout the experimentation and the specific activities of heterotrophic aerobes, nitrifiers and denitrifiers were determined. Aerobic micro-organisms’ activity was determined by closed respirometry. The respirometer consists of a gas tight thermostatic cell of 544 ml of volume providing three inlets. The first inlet is used to introduce the sludge sample and the aeration. Through the second an oxymeter ORION 870 is introduced and connected to a computer for recording oxygen concentration data. The third inlet is a sampling port to inject liquid substrates and withdraw liquid samples (Figure 2).

Activity, in terms of specific Oxygen Uptake Rate (OUR), was measured for three types of aerobic microorganisms: ammonia and nitrite oxidizers and organic matter oxidizers. For the same initial oxygen concentrations, different solutions without micronutrients were successively introduced into the respirometer. The final substrate concentrations were 30 mg/L of acetic acid, 5 mg/L of nitrite, and 10 mg/L of ammonia for zero order reaction rate conditions with respect to the substrate (Cech et al., 1984). The ratio between initial substrate and microorganisms concentrations was smaller than 3 to minimise biomass growth during the experiments (Chudoba et al., 1992). Endogenous oxygen uptake was constant during the whole experiment, which lasted 40 minutes.

The results are expressed as mg O₂ consumed per gram of volatile suspended solids (VSS) and per hour (mg O₂/g VSS · h). Due to the difficulties experienced for determination of nitrifiers’ activities by respirometry, Substrate Uptake Rate (SUR) experiments were also performed. Substrate Uptake Rates (SUR) of denitrifiers were also determined. These activity tests are based on measuring maximum rates of substrate utilization per biomass unit (µmax/Y) for nitrifiers and denitrifiers for different mixed liquor samples. The assembly used for determination of nitrifiers’ activity was a New Brunswick Scientific shaker table with 16 closed 250 ml-capacity Erlenmeyer flasks wherein a known concentration of substrate was introduced together with the centrifuged sample of mixed liquor. Initial concentrations of 50 mgN/L were introduced for ammonia and nitrite. The conditions under which these tests were carried out are described elsewhere (Villaverde et al., 1997). For determination of the activity of denitrifiers an experimental set-up similar to that used for respirometry assays was employed. Prior to the assay oxygen was stripped off the liquid sample with nitrogen gas. Oxygen concentration in the sample was always under 0.05 mg/L. Final

![Figure 2 Set-up for closed-respirometry assays](image-url)
concentrations of 50 mgN/L of nitrite and nitrate was introduced into the respirometer at the beginning of the experiments. The $\mu_{\text{max}}/Y$ values were expressed as mgNH$_4^{+}$–N oxid. /gVSS·h and mgNO$_2^–$–N oxid. /gVSS·h for ammonia and nitrite oxidizers respectively, and as mgNO$_2^–$–N red. /gVSS·h and mgNO$_3^–$–N red. /gVSS·h for nitrite and nitrate reducers respectively. These values were obtained from the slope of the straight lines referring to substrate consumption over time.

Results and discussion
Reactor performance
The reactor performance was followed throughout the experimentation phases evaluating the removal percentages of organic matter, ammonia and total nitrogen from the wastewater. Throughout the experimental period several operational parameters of interest, such as the Hydraulic Retention Time (HRT), Solids Retention Time (SRT), aeration frequency (on/off cycles) in the reaction phase, and wastewater composition, were changed to determine their influence over nitrification and denitrification efficiencies. These different operational strategies followed are shown in Table 3 with the removal percentages observed for soluble COD, TKN and total nitrogen.

During the first experimentation phase, i.e. synthetic wastewater feeding, the main goal was to achieve co-current nitrification/denitrification in the SBR. The coexistence of a stable population of nitrifiers and denitrifiers in the reactor is mainly controlled by the availability of their electron acceptor, i.e. oxygen and nitrite/nitrate, respectively, considering no carbon limitation. In this sense we focussed on selecting the aeration frequency which the most adequate for such purpose. Three short aeration frequencies were tested during the first phase: 15/15, 9/6 and 6/9 minutes of on/off aeration. The best removal percentages of ammonia and total nitrogen corresponded to a frequency of 15/15 minutes of on/off aeration (Table 3). However the activity of nitrifiers and denitrifiers within the sludge flocs was more similar operating with a frequency of 6/9 minutes (data not shown). Consequently since no significant differences in the removal percentages of ammonia and total nitrogen were obtained between the two aeration frequencies, the last frequency (i.e. 6/9 minutes of on/off aeration) was selected to proceed with the second experimentation phase. At this point total nitrogen was removed from the system at rates of 0.2 kg m$^{-3}$ d$^{-1}$.

The reactor operated with HRT ranging between 20 and 60 hours. At the beginning of the IWW feeding we increased the HRT from 20 to 40 hours to favor the acclimation of the sludge to the feed. As was expected in this second phase higher values of HRT allowed for

<table>
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<th>Phase</th>
<th>On/off aeration frequency</th>
<th>SRT (d)</th>
<th>HRT (h)</th>
<th>CODs</th>
<th>TKN</th>
<th>Total N</th>
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<td>83</td>
<td>-</td>
<td>23</td>
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<tr>
<td></td>
<td>9/6</td>
<td>20</td>
<td>20</td>
<td>95</td>
<td>-</td>
<td>36</td>
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<td></td>
<td>15/15</td>
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<td>20</td>
<td>84</td>
<td>44</td>
<td>33</td>
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<td></td>
<td>6/9</td>
<td>20</td>
<td>20</td>
<td>84</td>
<td>37</td>
<td>29</td>
</tr>
<tr>
<td>II Industrial wastewater</td>
<td>6/9</td>
<td>20</td>
<td>40</td>
<td>70</td>
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<td>60</td>
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<td>69</td>
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<td>6/12</td>
<td>17</td>
<td>40</td>
<td>90</td>
<td>98</td>
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higher nitrification efficiency in terms of ammonia removal percentages. This behavior can be better observed in Figure 3 wherein influent and effluent TKN concentrations and its percentage removal are presented versus time during the second experimental phase. It can be observed that the removal percentage of TKN increased up to values of 80% as a consequence of increasing the HRT from 40 to 60 hours on day 306. Thereafter until the end of the experimentation the nitrification efficiency was maintained over averaged removal percentages of 95%. According to the values of Table 3 an increase of the removal percentage of TKN in the second experimentation phase can only be due to the increase of the HRT. This is true assuming no significant effect of the changes in the feeding composition (see Table 2) and taking into account that the changes in SRT (decreasing from 20 to 17 days) and aeration frequency (changing from 6/9 to 6/12 minutes of on/off aeration) have an opposite effect on the nitrification.

Another parameter of great significance, the SRT, was maintained between 17 and 20 days. In this sense it has been reported that for treating high nitrogen loads it is necessary to maintain SRT over the typical values for conventional systems (Gupta and Sharma, 1996). Lower SRT allows for better denitrification and higher SRT values being more adequate for the growth and retention of nitrifiers within the sludge flocs.
These criteria can be checked in Figure 4 where the concentration values of ammonia (influent and effluent), nitrite and nitrate in the effluent, and total nitrogen removal percentage versus time during the second experimentation phase are presented. It can be clearly observed that the removal percentage of total N started to increase on day 419 as the SRT decreased from 20 to 17 days. Removal percentages over 70% were reported a few weeks later. This can be explained as a consequence of a greater denitrification within the reactor, which is in accordance with the criteria of Gupta and Sharma (1996). On the other hand it can be observed in Figure 3 that this reduction of the SRT on day 419 did not affect significantly the nitrification process.

Regarding the removal of organic matter the aim was to preserve the highest amount of carbon for denitrification and minimize its consumption in aerobic conditions. Figure 5 presents the concentration values of soluble COD in the influent and effluent with its removal percentage versus time during the second experimentation phase. Overall the removal of soluble COD was high and the above mentioned changes of HRT (from 40 to 60 hours) on day 306 and of SRT (from 20 to 17 days) on day 419 caused a positive effect on the removal of soluble organic matter.

Finally, after observing the effects of HRT and SRT on the nitrification and denitrification processes in our system, the final tuning of the system was done on day 530 at the end of the experimentation. With the aim of reducing the operation costs and keeping the removal percentages of TKN and total nitrogen at maximal values we reduced the HRT from 60 to 40 hours and increased the non-aeration time from 9 to 12 minutes, i.e. a frequency of 6/12 minutes of on/off aeration instead of 6/9 minutes. These changes allowed for a higher availability of organic matter for denitrification and oxygen for nitrification thus causing the removal percentages of COD, TKN and total nitrogen to reach maximal values of 90, 98 and 79%, respectively (Table 3). At this point total nitrogen was removed from the system at rates of 0.65 kg m$^{-3}$ d$^{-1}$.

![Figure 5: Concentration values of soluble organic matter in the influent and effluent (as COD), and its removal percentage versus time during the second experimentation phase](image)

<table>
<thead>
<tr>
<th>Microorganisms</th>
<th>OUR and SUR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heterotrophic aerobes</td>
<td>19.87 mg O$_2$/g VSS d</td>
</tr>
<tr>
<td>Ammonia oxidizers</td>
<td>12.52 mg NH$<em>4^+$-N$</em>{oxidized}$/g VSS d</td>
</tr>
<tr>
<td>Nitrite oxidizers</td>
<td>Non detected</td>
</tr>
<tr>
<td>Nitrite reducers</td>
<td>6.69 NO$<em>2^-$-N$</em>{reduced}$/g VSS d</td>
</tr>
<tr>
<td>Nitrate reducers</td>
<td>10.14 NO$<em>3^-$-N$</em>{reduced}$/g VSS d</td>
</tr>
</tbody>
</table>

Table 4: Specific activity values obtained from the oxygen uptake rate and substrate uptake rate assays at the end of the experimentation.
Specific activity of microorganisms

The existence of co-current nitrification and denitrification processes was experimentally confirmed and followed by performing activity assays. Sludge samples were withdrawn from the reactor and OUR and SUR assays were performed to evaluate the activity of microorganisms. Table 4 shows the averaged values of specific activity of heterotrophic aerobes, nitrifiers and denitrifiers at the end of the experimentation when the SBR showed the highest removal percentages of soluble COD, TKN and total nitrogen.

The results of Table 4 confirmed the existence of a significant population of nitrifiers and denitrifiers within the sludge. However, it must be pointed out that no activity of nitrite oxidizers was detected at that point in any sludge sampled from the reactor. This indicates that growth of nitrite oxidizers was severely limited under the operating conditions of 40 hours of HRT, 17 days of SRT and 6/12 minutes of on/off aeration. The authors postulate two possible explanations. The first is a phenomenon of selective inhibition of nitrite oxidizers by free ammonia, as has been previously reported (Fdz-Polanco et al., 1996, Villaverde et al., 1997), since the reactor has been operated with free ammonia concentrations of up to 30 mg NH₃–N/L. The second is a possible amensalism interaction between ammonia oxidizers and nitrite reducers, i.e. most of the nitrite generated by the formers is immediately reduced to molecular nitrogen by nitrite oxidizers (Brock and Madigan, 1991). Taking into consideration the information available it is not possible to come to any conclusion but it must be emphasized that in our operating conditions nitrite oxidizers were out-competed from the reactor.

Conclusions

The main conclusions that can be drawn from the experimental observations here reported are as follows:

1. Organic matter and total nitrogen were 90 and 80 percent removed from an industrial wastewater fairly loaded with up to 2,000 mg COD/L and 700 mg TKN/L, in a single SBR reactor operated with short cycled aeration.

2. Treating high strength wastewater, the implementation of short aeration cycles in a Sequential Batch Reactor allowed for the merging of the conventional phases of aeration and stirring (anoxic) in a single aerobic/anoxic phase of cycled aeration wherein co-current nitrification and denitrification occurred.

3. The operational parameters that controlled the removal process of organic matter and total nitrogen were Hydraulic Retention Time (HRT), Solids Retention Time (SRT) and aeration frequency. Optimal values of these parameters reporting the highest removal percentage of COD, TKN and total N were 40 hours, 17 days and 6/12 minutes of on/off aeration, respectively.

4. Specific activity values collected through Oxygen and Substrate Uptake Rates (OUR and SUR) assays showed that under the optimal operation conditions no nitrite oxidizing activity was detected which indicates that nitrite oxidizers were out-competed from the reactor.

Acknowledgements

This research was supported by the Spanish Government Projects AMB98-0833 and 1FD97-2175. The authors also thank the Commission for Cultural Education and Scientific Exchange between USA and Spain for its support (Reference 99036/1999).

References


