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SIMULTANEOUS NITRIFICATION AND DENITRIFICATION USING SIPORAX™ PACKING

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ABSTRACT

In this paper, we examine a biofilm process for simultaneous removal of ammonia and NO_X (nitrite and nitrate). Siporax™, a porous Raschig-ring type filter specifically designed and manufactured for fast colonisation by micro-organisms, was used to demonstrate the feasibility of simultaneous nitrification (usually an aerobic process) and denitrification (usually an anaerobic or anoxic process) inside a single reactor. Clear evidence was found that denitrification occurred inside the internal pore structure of Siporax™ rather than in an anoxic zone near the outlet of the reactor. The reactor was operated continuously and maximum nitrification and denitrification capacities of 0.61 and 0.83 g N/(l.day), respectively were observed in this study. © 1999 Published by Elsevier Science Ltd on behalf of the IAWQ. All rights reserved

KEYWORDS

Immobilised medium; simultaneous nitrification and denitrification; Siporax™; synthetic wastewater.

INTRODUCTION

Modern biological wastewater treatment processes need to be able to perform nitrification as well as denitrification. In conventional sewage treatment plants, the two reactions are carried out in different tanks or at different times (eg. in a sequencing batch reactor). This is because nitrification occurs in an aerobic environment while denitrification prevails in the absence of oxygen. However, the two reactions are complementary in many ways, i.e. nitrification produces nitrite/nitrate which are the reactants in denitrification, while denitrification generates alkalinity that is required in nitrification. There are thus obvious advantages to having both reactions happening at the same time.

In biofilm and bio-floc processes, the basic concept of simultaneous nitrification and denitrification is to create an oxygen concentration gradient across the micro-organism based agglomerates, so that both aerobic and anaerobic conditions can be established inside a single reactor. Under these conditions, both the nitrifiers and denitrifiers can prevail in performing their associated biological transformations. Kokufuta *et al.* (1988) and Santos *et al.* (1993) proposed immobilization of pure cultures of nitrifiers and denitrifiers in gels, but this is expensive and it suffers from the great fragility of such gels. Schott (Germany) have produced sintered glass Raschig rings, under the trademark of Siporax™. This porous glass matrix is robust and has a very high internal surface area, as well as being specifically designed for fast colonization by micro-organisms.

Given the specified desirable features of Siporax™, the goal of this project is to develop a Siporax ™based biofilm process to achieve simultaneous nitrification and denitrification. The basic concept of simultaneous nitrification and denitrification with Siporax™ is to create an oxygen concentration gradient across the ring, so that both aerobic and anoxic conditions can be established within the Siporax™ ring. Aerobic nitrifiers growing outside the Siporax™ consume oxygen and provide a shield (preventing against mass transfer of oxygen) for the anoxic denitrifers to grow inside the internal pore structure.

Early work on Siporax ™(Dawes, 1989; Göbel and Untergasser, 1995) focused on aquarium applications, which usually have a relatively low nutrient concentration. The work presented in this paper, however, was aimed at demonstrating the application of Siporax™ for treatment of municipal wastewater. Experimental studies were carried out with synthetic wastewater of pre-defined ammonium and nitrate concentrations. The wastewater was fed into a Siporax ™packed column and the concentrations of ammonium, nitrite and nitrate at the outlet of the column were regularly monitored. The column was subjected to step loadings of nitrate and ammonium to test the robustness of the system. The results of these studies are summarised in this paper.

METHODS

Experimental set-up

Two sets of experimental work were carried out. In the first set of experiments, the feed solution was not cooled. The feed was fed in an upward direction to the 700 mm long column while air was introduced in the feed tank. However, this set-up was found to promote biological activity in the feed tank. As a result, regular changes of the feed solution were required. To avoid the need for frequent changing of the feed solution, the experimental set-up was modified in the second experimental campaign such that there was an air gap between the feed and the Siporax™. The modified set-up is shown in Figure 1.

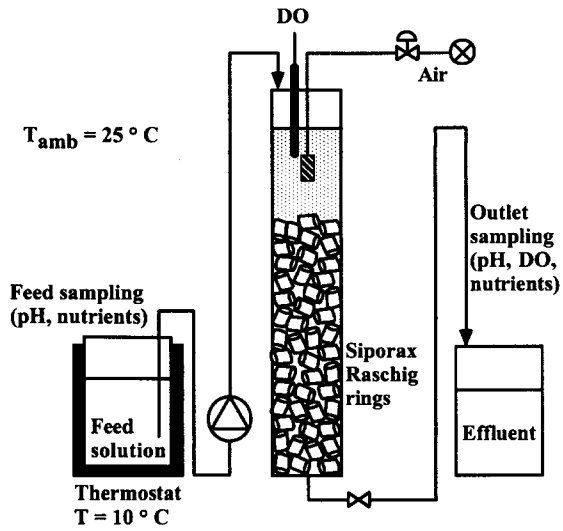

Figure 1. Set-up for the experiments with Siporax™

As shown in Figure 1, a feed solution, kept at 10°C in a glass flask, was pumped using a peristaltic pump to the top of a 53 mm inside diameter column. The laboratory was temperature controlled at 25°C. The column was packed with Siporax™ Raschig rings to give a total packing height of 200 mm. See Table 1 for the specification of Siporax™. Before the Siporax™ rings were packed inside the column, they were pre-inoculated by soaking overnight in nitrifying-denitrifying activated sludge obtained from a local sewage treatment plant. The level of liquid in the column (270 mm in this case) was adjusted by the level of the

outlet tubing and the effluent was collected in a container. Air from the laboratory supply was introduced to the liquid at the top of the column through a gas sparger. This was done to minimize any biological activity in the feed tank. The ammonium concentration in the feed tank was also monitored from time to time to ensure that there was no biological contamination in the feed tank.

Table 1. Specifications of Siporax™ Raschig rings

Manufacturer:	Schott Glaswerke, Mainz, Germany
Material:	Sintered glass
Dimensions:	15 mm diameter, 15 mm length
Open pore volume:	up to 70%
Pores sizes:	60-300 μm
Inner surface area:	1 m^2/g
Distributed weight:	286 g/l
Material density:	Approximately 0.7 g/cm^3

Medium

A synthetic wastewater with a pre-defined composition was used in this study. Two different media were used for the two different sets of experiments, their compositions are shown in Table 2.

Table 2. Per litre compositions of the two media

Chemical	Campaign 1	Campaign 2
Glucose	1001 mg (1067 COD mg)	282 mg (300.8 COD mg)
NH_4Cl		107 mg (28 mg NH_4^+-N)
NH_4NO_3	80 mg (14 mg NH_4^+-N and 14 mg $NO3^-$-N)	80 mg (14 mg NH_4^+-N and 14 mg NO_3^--N)
KH_2PO_4	30 mg (6.8 mg PO_4^{3-}-P)	44 mg (10 mg PO_4^{3-}-P)
K_2HPO_4	15 mg (2.7 mg PO_4^{3-}-P)	-
$NaHCO_3$	-	504 mg (366 mg HCO_3^-)
Nutrient solution	1 ml	1 ml

Glucose, which is known to be readily biodegradable, was used as the carbon source. Nitrate was added to promote initial denitrification, otherwise the denitrifiers would be without an electron acceptor until full nitrification was achieved. Sodium bicarbonate was added to promote nitrification as well as providing a pH buffer.

The nutrient solution contains per litre: 90g $MgSO_4 \cdot 7H_2O$, 6g $CaCl_2 \cdot 2H_2O$, 1.5g $FeCl_3 \cdot 6H_2O$, 6.5g $MnCl_2 \cdot 4H_2O$, 1.7g $ZnSO_4 \cdot 7H_2O$, 0.1g $CuCl_2 \cdot 2H_2O$, 1.9g $CoCl_2 \cdot 6H_2O$, 6.5g $NiSO_4 \cdot 6H_2O$, 0.1g H_3BO_3, 0.6g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, 1g yeast extract.

Sampling and analytical methods

Intermittent sampling was performed by withdrawing a 5 ml aliquot from the feed and effluent solutions. The effluent aliquot was filtered with a 0.22 μm Millipore™ filter unit to remove particulates and give a sterile sample. The samples were analysed immediately on a Merck Spectroquant© spectrophotometer for the ammonium, nitrate and (occasionally) nitrite concentrations. The Spectroquant© methods used were 14752, 14773 and 14776 for ammonium, nitrate and nitrite, respectively. Ammonium analysis utilises Berthelot's reaction to form a blue indophenol dye that absorbs at 690 nm. Nitrate analysis utilises a reaction involving nitrate in acidic conditions where a deep red nitro-compound that absorbs at 515 nm is formed. The nitrite determination follows Griess' reaction in which nitrite is transformed into a violet-red azo dye that can be measured at 525 nm. Standard deviations for the three methods are 2%, 7% and 1%, respectively.

Monitoring of dissolved oxygen, pH and flow rate

The dissolved oxygen concentration (DO) was measured at both the top and the outlet of the column. A Ox20 meter and a O21B probe (Bacto Laboratories) were used to perform the DO measurement. Samples from the feed and effluent solutions were taken and the pH values of the samples were determined with a pH330 meter and a Sentix 21 electrode (Merck). Effluent flow rate was determined with a stop watch and a measuring cylinder.

RESULTS AND DISCUSSION

Experimental campaigns

Two experimental campaigns were carried out. Table 3 summarises the different periods of the experimental studies, while Figure 2 and Figure 3 show the results for both experiments.

Table 3. Description of the two experimental campaigns

	Description	Duration
Campaign 1		
Run 1.0	Stabilisation (2.9 l/d)	Day 0-17
Run 1.1	Nitrate step increase from 14 to 70 mg NO_3^--N/l	Day 17-32
Run 1.2	Flow rate step increase from 2.9 to 9.0 l/d	Day 32-35
Campaign 2		
Run 2.0	Stabilisation (1.7 l/d)	Day 0-28
Run 2.1	Flow rate step change	
	from 1.7 to 3.4 l/d	Day 28-37
	from 3.4 to 6.6 l/d	Day 37
	from 6.6 to 3.4 l/d	Day 37-42
Run 2.2	After clogging	Day 43-56

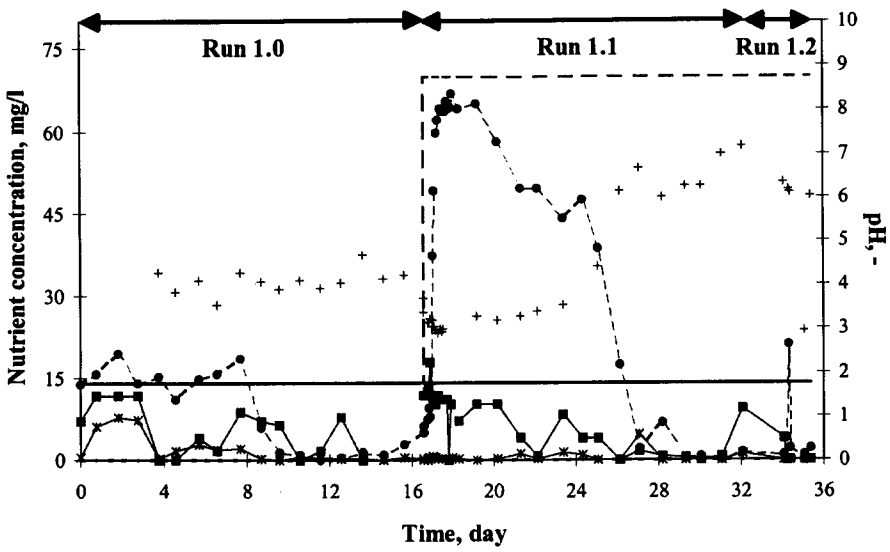

Figure 2. Experimental campaign 1: Height of the Siporax™packed bed is 700 mm. Average pH and DO concentration in the feed are 6.8 and 8.0 mg/l, respectively. Average DO concentration in the effluent is 3.6 mg/l. ——— inlet NH_4^+-N, — — inlet NO_3^--N, —■— outlet NH_4^+-N, —✳— outlet NO_2^--N, —●— outlet NO_3^--N, + outlet pH.

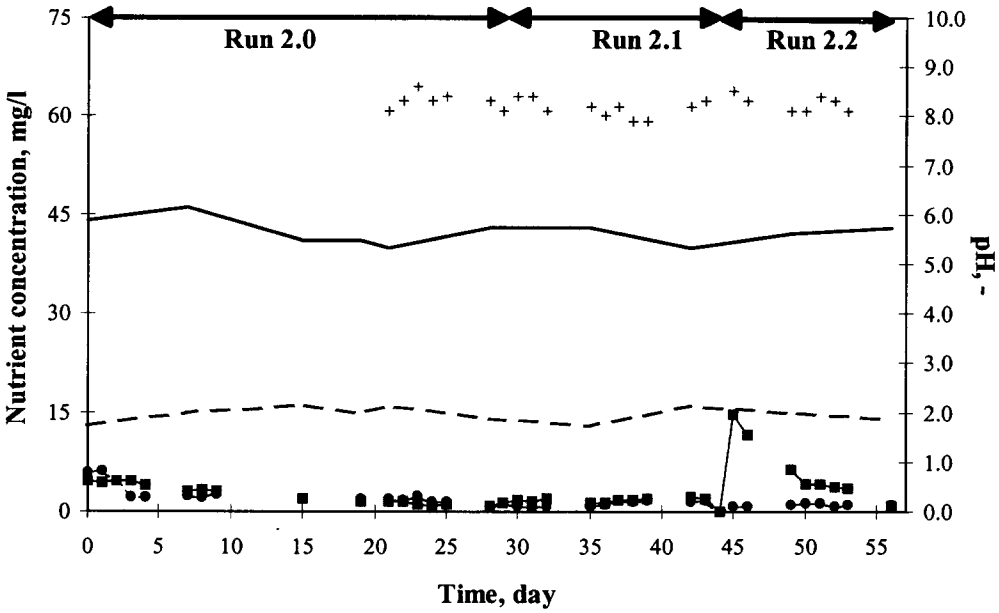

Figure 3. Experimental campaign 2: Height of the Siporax ™packed bed is 200 mm. Average pH and DO concentration in the feed are 7.7 and 6.5 mg/l, respectively. Average DO concentration in the effluent is 2.0 mg/l. ——— inlet NH_4^+-N, — — inlet NO_3^--N, —■— outlet NH_4^+-N, —•— outlet NO_3^--N, + outlet pH.

Stabilisation

In both sets of experiments, it can be seen that the micro-organisms in the column took approximately 1-2 weeks to acclimatise to the new environment, as shown in Figure 2 and Figure 3. This is a relatively short time compared to the acclimatisation period usually observed for other biofilm processes such as a trickling filter. In the first set of experiments, the initial nitrate-nitrogen concentration in the effluent was found to exceed the influent concentration. This shows the contribution of nitrate-nitrogen from nitrification (NH4 → NO3), in addition it also suggests that the success of denitrification is controlled or delayed by the establishment of nitrifier colonies outside the Siporax™ring, so that an anaerobic environment is available inside the Siporax ™ring. In the second set of experiments, no such delay was observed. This is attributed to the fast colonization of the nitrifiers, which is enhanced by the addition of bicarbonate in the feed since autotrophic nitrifiers use inorganic carbon as their cell carbon source.

Once adapted to the new conditions, both nitrifiers and denitrifiers were found to be capable of removing both ammonia and nitrate to low concentrations in the range of 0-5 mg N l^{-1}.

Location of the denitrifiers

The primary goal of this project was to demonstrate the feasibility of simultaneous nitrification and denitrification with Siporax™. Specifically, the aim was to demonstrate that denitrification was occurring inside the pore structure of Siporax™ instead of along the length of the column, ie. an aerobic zone followed by an anoxic zone. To show this, the dissolved oxygen concentration was measured at both the inlet and the outlet of the column. In general, a DO concentration higher than about 0.5 mg/l is known to inhibit denitrification (Rittmann and Langeland, 1985). Although the inhibition mechanism is not clear, it is well accepted that at a high DO concentration, denitrifiers can switch their electron acceptor from nitrate to oxygen, thereby ceasing to denitrify.

In our experimental systems, simultaneous nitrification and denitrification was consistently observed for an effluent DO concentration in excess of 2.0 mg/l. Average effluent DO concentrations for experimental

campaigns 1 and 2 were 3.5 mg/l and 2.0 mg/l, respectively. This demonstrates that denitrification was occurring inside the pores of the Siporax™ rings rather than in an anoxic zone near the outlet of the column.

Step increase in nitrate concentration

A five-fold step increase in the inlet nitrate-nitrogen concentration was used to disturb the column performance, see Figure 2. However, both nitrifiers and denitrifiers were found to adapt to the new conditions in less than two weeks, providing effluent essentially free of both ammonia and nitrate.

Although nitrite was not introduced in the influent, nitrite at low concentrations was detected throughout the experiment. This confirms nitrite as the intermediate for a two-step nitrification scheme, and the low concentration of nitrite suggests that the first step is the rate-limiting step.

$$NH_4^+ + {}^3/_2O_2 \rightarrow HNO_2 + H^+ + H_2O \qquad \text{(Step 1)}$$
$$HNO_2 + {}^1/_2O_2 + H_2O \rightarrow HNO_3 + H_2O \qquad \text{(Step 2)}$$

Step changes in feed flow rate

Numerous changes in the feed flow rate were carried out (see Table 3). The process was found to be very robust when subjected to changes in feed flow rate, as seen in Figure 2 and Figure 3. No noticeable changes in the effluent ammonium and nitrate concentrations were observed when the flowrate was increased. The micro-organisms were found to adapt to the new flow rate almost instantaneously.

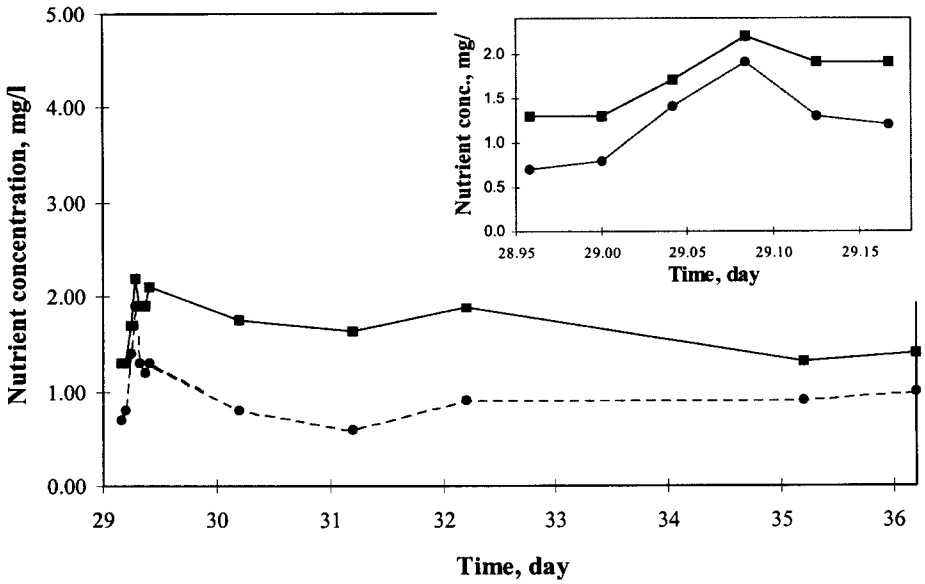

Figure 4. Enlargement of the experimental results shown in Figure 3. The experimental conditions are as listed under Figure 3.

Figure 4 shows an enlargement of the flow rate increase from 1.7 to 3.4 l/d in experimental campaign 2. Within 3 hours, most of the shock was "absorbed" and the effluent ammonium and nitrate concentrations returned to their previous levels (ie. before the flow rate increase) in about 3 to 7 days. Note the relatively low level of the nutrient concentration (0-2 mg/l).

Clogging and unclogging of the column

In both columns, clogging occurred after a period of 40-45 days. In the second set of experiments, the column was washed out. Two litres of water, introduced from the outlet of the reactor, were found necessary to unclog the 0.4 litre reactor. After washing, the column was found to return to its previous performance level within six days.

Loading capacity for simultaneous nitrification and denitrification

In Table 4, we compare nitrification and denitrification capacities found in this study with those in the literature. Most systems found in the literature focus on either nitrification or denitrification, therefore, only a limited comparison can be drawn. As shown in Table 4, the nitrification and denitrification capacities of the current system are in the same order of magnitude as those found in the literature, and it is obvious that there is still room for improvement in the Siporax™ system.

Table 4. Comparison of nitrification and denitrification capacities of the Siporax™ system with those reported in the literature

	Nitrification, kgN / (m^2.day)	Denitrification, kgN / (m^3.day)
Run 1.1-1.2	0.03-0.08	0.16-0.49
Run 2.1	0.16-0.61	0.21-0.83
Garrido *et al.* (1997)	5.00	-
Koch and Siegrist (1997)	-	1.00
Lazarova *et al.* (1997)	1.00-1.50	-
Pochana and Keller (1997)	0.19-0.46	0.19-0.34
Semon *et al.* (1997)	-	1.90

CONCLUSIONS

Overall, this study demonstrates the feasibility of simultaneous nitrification and denitrification with Siporax ™. It was clearly demonstrated that denitrification occurred inside the pores of the Siporax rings, as the outlet DO concentration was consistently higher than 1 mg/l, a concentration level known to inhibit denitrification. The system is fairly robust, as it shows a quick response when subjected to major perturbations such as changes in feed flow rate. A maximum simultaneous nitrification/denitrification capacity of 0.61/0.83 gN/(litre.day) is estimated in this study. Further work is being undertaken to optimise the nitrification and denitrification capacities of the system.

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