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AUTOTROPHIC DENITRIFICATION OF LANDFILL LEACHATE USING ELEMENTAL SULPHUR

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ABSTRACT

One of the most economical means of nitrogen removal from leachate is biological treatment by nitrification, followed by heterotrophic denitrification. An alternative biological denitrification process is autotrophic denitrification using *Thiobacillus denitrificans*. This autotrophic bacteria oxidizes elemental sulphur to sulphate while reducing nitrate to elemental nitrogen gas, thereby eliminating the need for addition of organic carbon compounds. For this study, pilot-scale elemental sulphur packed bed columns with fixed-film denitrification have been selected as the most suitable treatment process. The effect of hydraulic retention time as well as the effect of concentration and loading rate of nitrate on nitrate removal efficiency as a function of sulphur particle size were determined. The results indicate that (i) autotrophic denitrification can effectively remove nitrate from synthetic and actual nitrified leachate at concentrations much higher than hitherto reported; (ii) the minimum hydraulic retention time necessary for complete denitrification depends on sulphur particle size; (iii) the maximum area loading rate, in g NO_3^--N/m^2·d, appears to be the process limiting factor and is practically independent of sulphur particle size; and (iv) the observed stoichiometric relationships compare well with those previously reported. Copyright © 1996 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Autotrophic denitrification; biofilm; elemental sulphur; landfill; leachate treatment; nitrate removal; *Thiobacillus denitrificans*.

INTRODUCTION

Leachate from Hong Kong landfill sites is particularly high in total nitrogen, predominantly in the form of ammonia nitrogen, with values reported as high as 5000 mg/l (Robinson and Luo, 1991; Esnault, 1996). Removal of nitrogen is therefore required prior to discharge to foul sewers or directly to coastal waters. One of the most economical means of nitrogen removal from leachate is biological treatment by nitrification, followed by heterotrophic denitrification. However, as the C:N ratio in nitrified leachate is very low (Robinson and Luo, 1991), organic compounds such as methanol must be added for the denitrification process. An alternative biological denitrification process is autotrophic denitrification using *Thiobacillus denitrificans*. This autotrophic bacteria oxidises elemental sulphur to sulphate while reducing nitrate to elemental nitrogen gas, thereby eliminating the need for organic compounds. The stoichiometric reaction can be represented by the following equation (Batchelor and Lawrence, 1978):

$$NO_3^- + 1.10\,S + 0.40\,CO_2 + 0.76\,H_2 + 0.08\,NH_4^+ \xrightarrow{\textit{Thiobacillus denitrificans}} 0.5\,N_2 + 1.10\,SO_4^{2-} + 1.28\,H^+ + 0.08\,C_5H_7O_2N \qquad (1)$$

Autotrophic denitrification has been extensively investigated to remove nitrate from polluted groundwater (Kruithof *et al.*, 1988; Gayle *et al.*, 1989; Hiscock *et al.*, 1991), but nitrate nitrogen concentrations studied were less than 50 mg/l. However, autotrophic denitrification of leachates has not been investigated previously although the low C:N ratio would favor this process. Of further interest is the fact, that the resulting high sulphate concentration in the treated leachate does not pose an undue problem in Hong Kong where it can be discharged directly to the sea. Sulphate is a natural constituent of seawater with a mean concentration of 2700 mg/l. For this study, elemental sulphur packed bed columns with fixed-film denitrification have been selected as the most suitable treatment process as widely reported in the literature (Driscoll and Bisogni, 1978; Hiscock *et al.*, 1991; Kruithof *et al.*, 1988; Gayle *et al.*, 1989; Liu, 1992).

OBJECTIVES

The purpose of this study was thus (i) to experimentally test the feasibility of autotrophic denitrification for nitrified landfill leachate in pilot-scale elemental sulphur packed bed reactors; and (ii) to determine the effect of hydraulic retention time as well as the effect of concentration and loading rate of nitrate on nitrate removal efficiency as a function of sulphur particle size.

METHODS

The study was divided into three stages: (i) preparation and enrichment of a microbial culture of predominantly *Thiobacillus denitrificans* from synthetic feed solution; (ii) introduction of enriched cultures to pilot-scale elemental sulphur packed bed reactors followed by autotrophic denitrification tests using synthetic leachate; and, (iii) gradual adaptation of functioning pilot-scale elemental sulphur packed bed reactors to actual nitrified leachate and determination of relevant operating parameters.

Enrichment of microbial cultures. In the first stage of the study, cultures of *Thiobacillus denitrificans* were prepared from sludge obtained from tidal flats of the Mai Po marshes in Hong Kong. The cultures were fed synthetic media and incubated at 28 ^{0}C. The media consisted of tapwater containing 5 g/l $Na_2S_2O_3{\cdot}5H_2O$, 2 g/l K_2HPO_4, 2 g/l KNO_3, 1 g/l $NaHCO_3$, 0.5 g/l NH_4Cl, 0.5 g/l $MgCl_2{\cdot}6H_2O$ and 0.01 g/l $FeSO_4{\cdot}7H_2O$ (Liu, 1992).

Pilot-scale reactors. Three pilot-scale reactors were used for the second and third stage of this study. They had an inside diameter of 84 mm and were packed with elemental sulphur particles to a height of 1650 mm. Three sulphur particle size ranges were used, namely 2.8 to 5.6 mm, 5.6 to 11.2 mm, and 11.2 to 16 mm. Sampling ports were provided at heights of 40, 80, 120, and 155 cm, respectively. The reactors were fed continuously in the upflow mode by means of adjustable peristaltic pumps. Gas was periodically collected and measured volumetrically. All experiments were conducted at 20 ^{0}C. A schematic diagram of the continuous flow packed bed reactors is shown on Figure 1.

Experimental program. In the second stage of the study, each of the three packed bed reactors contained different size elemental sulphur particles. The enriched cultures were introduced into the packed bed reactors. After a period of incubation, the bacteria attached to the sulphur particles and formed a biofilm. Synthetic nitrified leachate containing 60 mg/l NO_3^--N was then fed to the reactors at an initial hydraulic retention time of approximately 7.5 hours. Hydraulic retention time was expressed as bed pore volume/influent feed flow rate

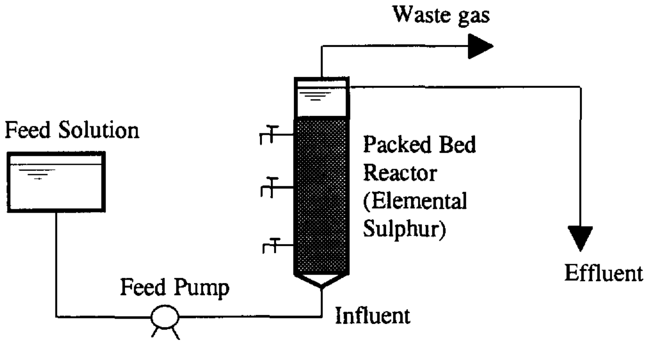

Figure 1. Schematic diagram of continuous flow packed bed reactor system

(Driscoll and Bisogni, 1978). After reaching steady-state conditions, the hydraulic retention time was step-wise reduced until the reactors became overloaded, resulting in a drastic decrease of nitrate removal efficiency. In view of the high significance of the results of the autotrophic denitrification as a function of hydraulic retention time, it was decided to conduct a second test series at a given hydraulic retention time with synthetic nitrified leachate, whereby the nitrate concentration was gradually increased until overloading of the reactors occurred. In the third stage of the study, nitrified leachate from a recently commissioned landfill was introduced into the packed bed reactors. Special attention was given to pH and alkalinity control as well as toxicity effects.

Wastewater characteristics. The synthetic nitrified leachate used was a solution of tapwater containing 60 mg/l KNO_3 (as N), 1000 mg/l $NaHCO_3$, 2 mg/l K_2HPO_4 (as P), 1 mg/l NH_4Cl (as N), 1 mg/l $MgCl_2 \cdot 6H_2O$ and 1mg/l $FeSO_4 \cdot 7H_2O$. For higher concentration of NO_3^--N, the concentrations of KNO_3 and $NaHCO_3$ were also increased, correspondingly. Nitrified leachate was obtained from the recently commissioned leachate treatment works at the Hong Kong NENT Strategic Landfill. Its composition is shown in Table 1. The values for the metal concentrations were not determined specifically for this study, but are based on average values reported by the NENT Landfill Leachate Treament Works. For purposes of this study, the nitrified leachate was diluted with tap water to the desired NO_3^--N concentration, then 1000mg/l $NaHCO_3$ and 2mg/l K_2HPO_4 (as P) were added.

Table 1. Composition of nitrified leachate from the Hong Kong NENT Strategic Landfill (units in mg/l, except pH)

NO_3^--N	1665.0	COD	1153.0	pH	8.4	Ni	0.19
NO_2^--N	1.1	BOD_5	12.0	Mn	0.76	Cu	<0.05
SO_4^{2-}	99.0	PO_4^{3-} (as P)	1.9	Fe	1.6	Cd	<0.05
NH_3-N	5.1	Alkalinity($CaCO_3$)	1058.0	Zn	0.22	Pb	<0.05

Sampling and analysis. All reactors were sampled daily and analysed for nitrate, nitrite, pH, alkalinity and sulphate according to "Standard Methods for the Examination of Water and Wastewater" (APHA, 1989).

RESULTS AND DISCUSSION

Effect of hydraulic retention time. For a given influent concentration of synthetic leachate, the steady-state data for the effluent concentrations as a function of hydraulic retention time for the packed bed reactor with elemental sulphur particle size of 2.8 to 5.6 mm are summarized in Table 2. The effect of hydraulic retention time on nitrate nitrogen NO_3^--N removal efficiency as a function of different sulphur particle size is depicted in Figure 2. It appears that there exists for each mean sulfur particle size a different minimum retention time below which nitrate removal would deteriorate. These minimum retention times are approximately 1.2, 2.3 and 4.2 hours for mean sulphur particles sizes of 4.4, 8.4 and 13.6 mm, respectively.

Table 2. Steady-state experimental results of elemental sulphur packed bed reactor (sulphur particle size 2.8--5.6mm)

Hydraulic retention time (hrs)	Influent NO3-N mg/l	Influent SO_4^{2-} mg/l	Influent pH	Influent Alkalinity mg/l	Effluent NO3-N mg/l	Effluent SO_4^{2-} mg/l	Effluent pH	Effluent Alkalinity mg/l
6.72	60.3	9.8	8.65	674.9	n.d.	475.2	6.84	435.6
4.46	61.2	10.8	8.67	677.2	0.08	492.3	6.92	444.4
2.44	61.8	12.1	8.63	667.4	0.14	495.8	6.85	410.5
1.83	60.7	14.3	8.69	682.5	0.11	505.2	6.82	405.3
1.46	59.7	9.6	8.44	669.8	0.02	482.3	6.87	401.3
1.2	62.3	12.4	8.71	682.1	0.52	471.4	6.9	414.2
0.89	59.5	10.6	8.53	668.7	8.95	381.5	7.14	469.3

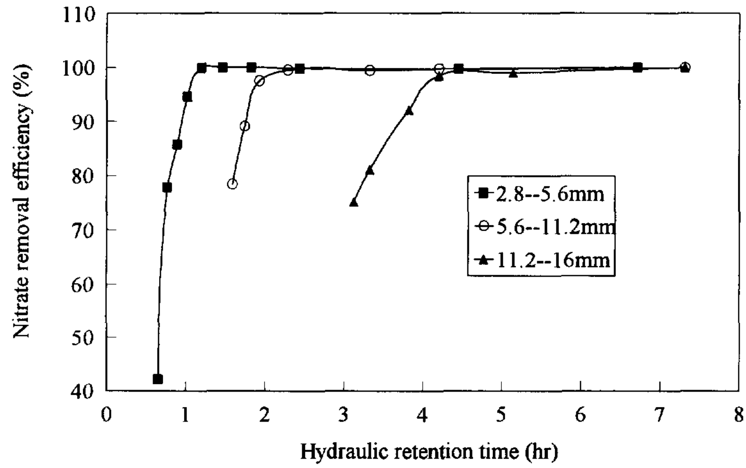

Figure 2. Nitrate removal efficiency as a function of hydraulic retention time for different sulfur particle size

Effect of influent nitrate concentration. For a given hydraulic retention time, the effect of influent nitrate concentration on nitrate nitrogen (NO_3^--N) removal efficiency for the packed bed reactor with sulphur particle size of 11.2-16mm is shown in Figure 3. It is clearly demonstrated that higher influent nitrate concentrations lead to incomplete denitrification. The critical influent nitrate concentration for complete denitrification of nitrified leachate is very near that of synthetic leachate at about 100mg/l nitrate nitrogen (NO_3^--N) for a hydraulic retention time of 6.09 hours. No significant performance difference was observed between synthetic and actual leachate, indicating the absence of inhibitory or toxic characteristics for actual leachate.

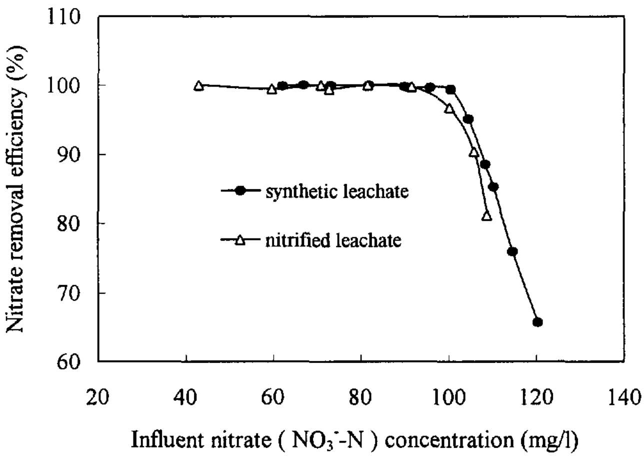

Figure 3. Nitrate removal efficiency as a function of influent nitrate concentration in the packed bed reactor with sulfur particle size of 11.2--16mm at hydraulic retention time 6.09 hours

Effect of loading rates. Table 3 summarizes the estimated maximum volumetric and area nitrate nitrogen NO_3^--N loading rates of synthetic leachate at the minimum hydraulic retention times for the three packed bed reactors. The data indicate clearly that area loading rate is the limiting factor of operation, practically independent of sulphur particle size, while the volumetric loading rate appears to be a function of sulphur particle size. The maximum loading rates found appear to be much higher than previously reported.

Table 3. Volumetric and area loading rates of nitrate nitrogen NO_3^--N at minimum hydraulic retention times for different mean sulphur particle size

Mean particle size (mm)	Specific surface area (m^2/m^3)	Minimum hydraulic retention time (hours)	Volumetric loading rate (g NO_3^--N/m^3·d)	Area loading rate (gNO_3^--N/m^2·d)
4.4	1363.6	1.2	501.1	0.61
8.4	714.3	2.3	254.5	0.59
13.6	441.2	4.2	153.5	0.58

Total area = specific surface area * volume * (1 - ε), with ε = 0.4 where ε is porosity
Volume = 0.0091 m^3

Concentration profiles in reactors. Figure 4 shows an example of steady-state concentration profiles of NO_3^--N, NO_2^--N, and SO_4^{2-} in the packed bed reactor (sulfur particle size 2.8-5.6mm) operated with synthetic leachate. Figure 5 shows a NO_3^--N concentration profile as a function of different sulphur particle size. The concentration profiles point to a half order reaction, as would be expected for a biofilm process with partial pore diffusion only (Harremoes, 1976). When nitrate removal is incomplete, nitrite nitrogen NO_2^- -N does appear in the effluent indicating that nitrite reduction is the rate limiting step in the denitrification process.

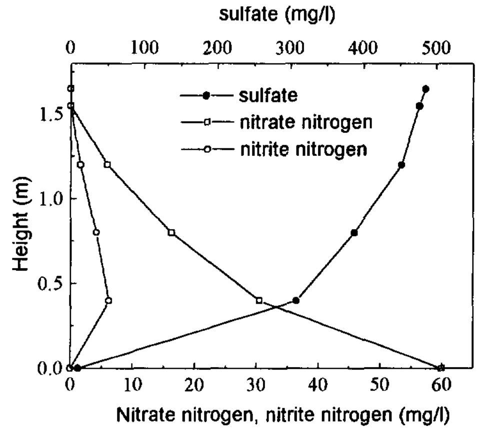

Figure 4. Profile of nitrate, nitrite and sulfate in a sulfur packed reactor at hydraulic retention time 1.7 hours (particle size 2.8-5.6mm)

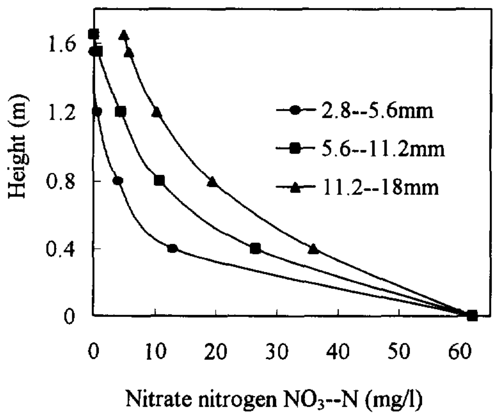

Figure 5. NO_3^--N profile in sulfur packed reactors for different sulfur particle size reactor media (hydraulic retention time 3.16hrs)

Figure 6 shows NO_3^--N profiles for different influent nitrate concentrations, when nitrified leachate dilutions were treated in the packed bed reactor in which the sulfur particle size is 11.2--16mm. The results obtained with nitrified leachate are very similar to those obtained with the synthetic leachate, with no inhibitory or toxic effects observed.

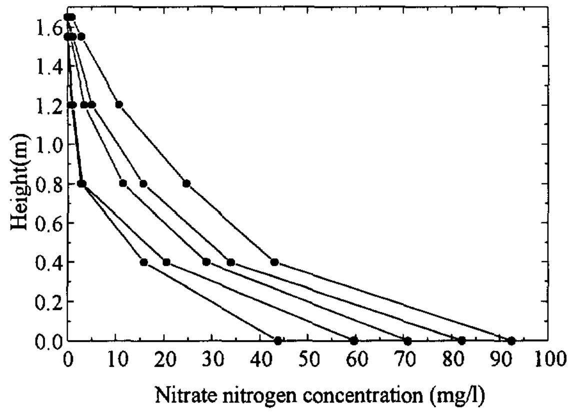

Figure 6. NO_3^--N profile in sulfur packed bed reactor at hydraulic retention time 6.09hrs (sulfur particle size 11.2--16mm)

Stoichiometric relationships. Table 4 compares the observed stoichiometric relationships of this study with the relationships expected from Equation (1). The results obtained compare well with the findings of Batchelor and Lawrence (1978) although they used a suspended growth system instead of packed bed reactors. The high consumption of alkalinity in the wastewater could result in a dramatic pH drop if buffer capacity is insufficient. The typical decrease in effluent alkalinity as a result of nitrate removal is also indicated in Table 2.

Table 4. Theoretical and observed stoichiometric relationships for the removal of 1mg nitrate nitrogen (NO_3^--N) by autotrophic denitrification(sulphur particle size 2.8-5.6mm)

		Theoretical	Observed
mg S	consumed	2.51	2.64
mg SO_4^{2-}	generated	7.54	7.89
mg alkalinity	consumed	4.57	4.19
ml N_2	generated	0.86	0.79

CONCLUSIONS

Based on the experiments carried out, the following conclusions are made:

1. Nitrate removal from nitrified leachate with *Thiobacillus denitrificans* using elemental sulfur is feasible.
2. Autotrophic denitrification in elemental sulphur packed bed reactors can effectively remove nitrate from nitrified leachate at concentrations much higher than hitherto reported for other wastewaters.
3. For a given influent nitrate concentration, the minimum hydraulic retention time necessary for complete denitrification depends on sulphur particle size. However, the maximum area loading rate, in gNO_3-$N/m^2{\cdot}d$, appears to be the process limiting factor and is practically independent of sulphur particle size.
4. The observed stoichiometric relationships compare well with those previously reported.

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