Nitrate Removal of Flue Gas Desulfurization Wastewater by Autotrophic Denitrification

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ABSTRACT: As flue gas desulfurization (FGD) wastewater contains high concentrations of nitrate and is very low in organic carbon, the feasibility of nitrate removal by autotrophic denitrification using *Thiobacillus denitrificans* was studied. This autotrophic bacteria oxidizes elemental sulfur to sulfate while reducing nitrate to elemental nitrogen gas, thereby eliminating the need for addition of organic compounds such as methanol. Owing to the unusually high concentrations of dissolved salts (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, B^{+}, SO_4^{2-}, Cl^{-}, F^{-},) in the FGD wastewater, extensive laboratory-scale and pilot-scale tests were carried out in sulfur-limestone reactors (1) to determine the effect of salinity on autotrophic denitrification, (2) to evaluate the use of limestone for pH control and as source of inorganic carbon for microbial growth, and, (3) to find the optimum environmental and operational conditions for autotrophic denitrification of FGD wastewater. The experimental results demonstrated that (1) autotrophic denitrification is not inhibited up to 1.8 mol total dissolved salt content; (2) inorganic carbon and inorganic phosphorus must be present in sufficiently high concentrations; (3) limestone can supply effective buffering capacity and inorganic carbon; (4) the high calcium concentration may interfere with pH control, phosphorus solubility and limestone dissolution, hence requiring pretreatment of the FGD wastewater; and, 5) under optimum conditions, complete autotrophic denitrification of FGD wastewater was obtained in a sulfur-limestone packed bed reactor with a sulfur:limestone volume ratio of 2:1 for volumetric loading rates up to 400g NO_3-N/m^3.d. The interesting interactions between autotrophic denitrification, pH, alkalinity, and the unusually high calcium and boron content of the FGD wastewater are highlighted. The engineering significance of the results is discussed.

KEYWORDS: autotrophic denitrification, boron, flue gas desulfurization (FGD) wastewater, pH control, sulfur-limestone reactor

1 INTRODUCTION

To reduce sulfur dioxide emission in coal fired power plants, flue gas desulfurization (FGD) systems are installed. A common FGD system is the wet limestone process, whereby the flue gas is injected with a limestone suspension ($CaCO_3$), which reacts with the sulfur dioxide present to produce gypsum slurry ($CaSO_4$). The gypsum slurry is then dewatered and as a result gypsum in cake form is obtained. The remaining filtrate or FGD wastewater is characterized by high salinity (20-40 g/L $CaCl_2$ or NaCl), high nitrate content (300-800 mg/L as N), high temperature (30° to 50°C) and many volatisable trace elements from coal such as heavy metals, boron, and fluoride. Conventional treatment of FGD wastewater consists of suspended solids and heavy metals removal by lime addition, sedimentation and pH adjustment; however, nitrate is generally not removed.

One of the most economical and effective means of nitrate removal from wastewater is biological treatment by heterotrophic denitrification, which requires organic substances as electron donor. Since FGD wastewater contains little organic matter (TOC < 15 mg/L), it is necessary to add organic compounds such as methanol or acetate for successful heterotrophic denitrification. An alternative biological denitrification process is autotrophic denitrification with *Thiobacillus denitrificans*, which can reduce nitrate to elemental nitrogen gas while utilizing elemental sulfur as electron donor, thereby eliminating the need for addition of organic compounds. Autotrophic denitrification using elemental sulfur has been shown to be a promising method to remove nitrate from wastewaters with low COD:N ratios (Koenig and Liu, 1996, 2001a; Zhang and Lampe, 1999). The stoichiometric reaction can be represented by the following equation (Koenig and Liu, 2001a):

$$1.06\ NO_3^- + 1.11\ S + 0.30\ CO_2 + 0.785\ H_2O \xrightarrow{\textit{Thiobacillus denitrificans}} 0.5\ N_2 + 1.11\ SO_4^{2-} + 1.16\ H^+ + 0.06\ C_5H_7O_2N \qquad (1)$$

While only limited information is available on heterotrophic biological denitrification of FGD wastewater (Kristensen and Jepsen, 1991; von Bettenworth *et al.*, 1995; Weinig, 1996), no research has been reported on autotrophic denitrification of FGD wastewater. Owing to the unusual chemical characteristics of the FGD wastewater, extensive laboratory-scale and pilot-scale tests were carried out to determine the feasibility of autotrophic denitrification using sulfur-limestone reactors. Initial results from the laboratory-scale tests on microbial aspects of autotrophic denitrification and the use of limestone for pH control were reported previously (Koenig and Liu, 2001a; Liu and Koenig, in press). In this paper, some interesting interactions between autotrophic denitrification, salinity, pH, alkalinity, limestone, and the unusually high calcium and boron content of FGD wastewater are reported, with special emphasis on the engineering significance of the results. Specific issues addressed were: (1) determination of the effect of salinity on autotrophic denitrification, (2) evaluation of the use of limestone for pH control and as a source of inorganic carbon for microbial growth, and, (3) the optimum environmental and operational conditions for autotrophic denitrification of FGD wastewater.

2 MATERIAL AND METHODS

2.1 Experimental apparatus

The experiments were carried out with a continuous flow packed bed reactor in the upflow mode, which was filled with a mixture of sulfur and limestone particles of 2.8—5.6 mm diameter. The volumetric ratio of sulfur to limestone was 2:1, based on previous experimental results. A schematic diagram of the experimental equipment is shown in Figure 1. The internal diameter of the reactor was 86mm. Packing height was 1600mm. At the heights of 200mm, 400mm, 600mm, 800mm, 1200mm and 1600mm, the reactors were equipped with sample ports to measure concentration profiles over the bed height. The preparation and enrichment of *Thiobacillus denitrificans* cultures as well as the formation of active biofilm in the packed bed reactor has been described previously (Koenig and Liu, 1996).

2.2 Experimental Program

In the first test series, the effect of salinity on autotrophic denitrification was investigated using synthetic wastewater with the following composition: 100mg/L NO_3-N, 100mg/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 1 mg/L $FeSO_4 \cdot 7H_2O$. Increased amounts of sodium chloride were then gradually added to the synthetic wastewater until nitrate removal efficiency decreased. A similar test was carried out with sodium sulfate. This test series was designed to obtain comparative baseline data and to adapt the sulfur-limestone reactor to high salinity, independent of any possible interference due to the unusual characteristics of the FGD wastewater. In the second test series, highly saline FGD wastewater was used. Two sub-series of tests were carried out, one with FGD wastewater from which calcium had been removed, and another with FGD wastewater without prior removal of calcium. In all tests, the reactor was operated at a constant flow rate of 0.5L/h.

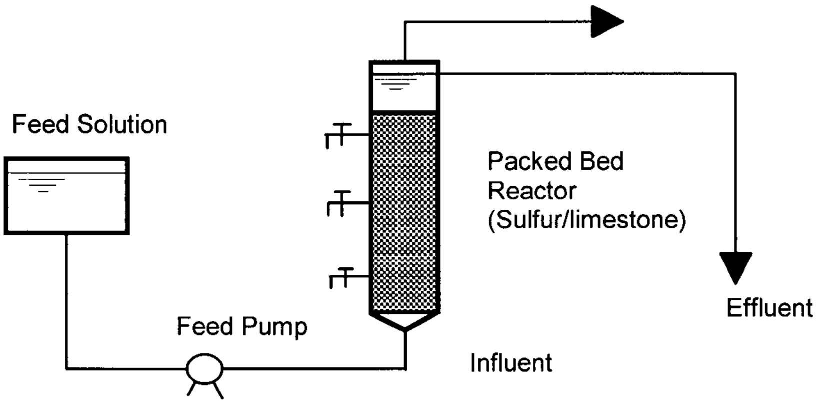


Fig. Schematic diagram of continuous flow packed bed reactor system

2.3 Source and Characteristics of FGD Wastewater

The FGD wastewater was obtained from the outlet of the physical-chemical FGD wastewater treatment plant of a local coal fired power plant. The composition of the effluent FGD wastewater is shown in Table 1.

2.4 Sampling and Analysis

Samples were taken from different heights of the reactor at steady state conditions. Samples were analyzed according to Standard Methods (APHA, 1995) for NO_3^--N, pH, alkalinity, chloride, sulfate and hardness. The FGD wastewater was analyzed for inorganic constituents by the laboratory of the Hong Kong Chemical Waste Treatment Centre, operated by Enviropace Limited, using specialized equipment such as ICP and AAS.

Table 1. Composition of flue gas desulphurization (FGD) wastewater (Units: mg/L except pH otherwise stated)

Constituent	Concentration	Constituent	Concentration
Total solids	36244	Cr	0.057
NO_3^--N	300	Cu	<0.05
Cl^-	13372	Fe	<0.1
SO_4^{2-}	5108.5	Pb	<0.1
Ca^{2+}	2545	Mn	<0.02
Mg^{2+}	665	Hg	<0.05
Na^+	8880	Ni	<0.1
K^+	160	Ag	<0.4
PO_4	<1	Sn	<1.0
B^-	650	Zn	<0.1
F^-	33.63	Alkalinity(as $CaCO_3$)	1091
Br^-	74.02	TIC	8.28
As	<0.1	Conductivity, in mS/m	3120
Ba	0.45	pH	8.22
Cd	<0.1	TOC	13.84

3 RESULTS AND DISCUSSION

3.1 Effect of salinity using synthetic wastewater

Previous laboratory scale studies demonstrated that the effect of salinity on autotrophic denitrification is a function of the total molarity of dissolved salts in the wastewater, with successful autotrophic denitrification up to a concentration of 0.85 mol/L (Koenig and Liu, 2001a). For the pilot-scale reactor, the relationship of relative nitrate removal efficiency with total mol of all dissolved salts is shown in Figure 2, indicating the validity of this approach. Autotrophic denitrification rates started to decrease when total molarity of salt ions exceeded 1.8 mol/L, which was much higher than in the laboratory scale study. The probable reason is that in the continuous flow packed bed reactor the biofilm was acclimated by a step-wise increase in influent salt concentration over the duration of many weeks, while the laboratory scale tests lasted only a few days. The observed salinity tolerance of 1.8 mol/L greatly exceeds the salinity of seawater of 1.1 mol/L. In a literature survey on heterotrophic denitrification under highly saline conditions, no consensus on the effect of salinity was reported (Glass and Silverstein, 1999).

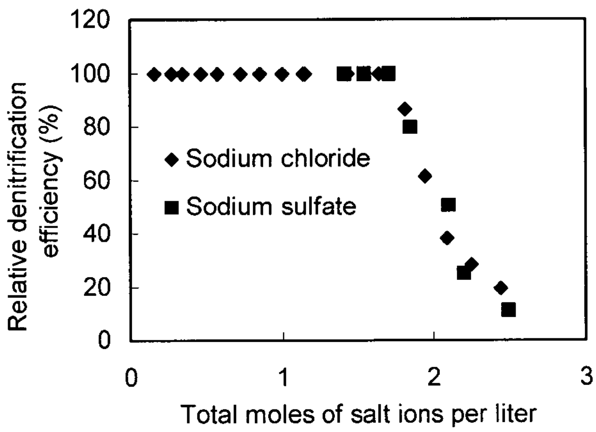


Fig. 2 Relationship of relative nitrate removal efficiency versus total molarity of salt ions

3.2 Autotrophic denitrification of FGD wastewater after removal of calcium

After the completion of treatment tests with synthetic wastewater, FGD wastewater was gradually introduced into the reactor. As alkalinity, inorganic carbon and phosphorus content were not present in stoichiometrically sufficient amounts for complete denitrification (see Table 1), bicarbonate and phosphate had to be added. However, they could not be added successfully since the high calcium concentration of FGD wastewater led to immediate precipitation of calcium carbonate and phosphate. Hence, the calcium was first removed from the FGD wastewater by precipitation with sodium carbonate.

3.3 Addition of sodium bicarbonate as alkalinity and inorganic carbon supply

After the removal of calcium, the FGD wastewater was initially diluted to 100mg/L NO_3^--N, the same concentration as in the synthetic wastewater experiments, in order to prevent shock loading of nitrate. The concentration of FGD wastewater was then gradually increased to 100%. Sodium chloride was added to the diluted FGD wastewater to keep the total moles of all salt ions of the influent at about 1.12 mol/L, which was equal to the total moles of all salt ions in the FGD wastewater. To provide inorganic carbon, alkalinity and phosphorus, sodium bicarbonate ($NaHCO_3$) and polyphosphate were added in sufficient amounts. To prevent precipitation of calcium phosphate, polyphosphate $(NaPO_3)_x$ was used instead of orthophosphate, as previous studies showed no difference in autotrophic denitrification rates (Koenig and Liu, 2001a). Figure 3a shows the nitrate profiles for influents with different dilution percentages of FGD wastewater. The profiles corresponded to the half-order kinetic model (Koenig and Liu, 2001b) and it was found that the half-order kinetic constant for the influents with 40%, 50%, 60% and 70% of FGD wastewater was nearly the same as that of synthetic wastewater. For influents with more than 80% FGD wastewater, the nitrate profiles were different from that of synthetic wastewater as shown in Figure 3b. The half-order kinetic constants were hence lower, indicating that inhibiting factors existed in FGD wastewater.

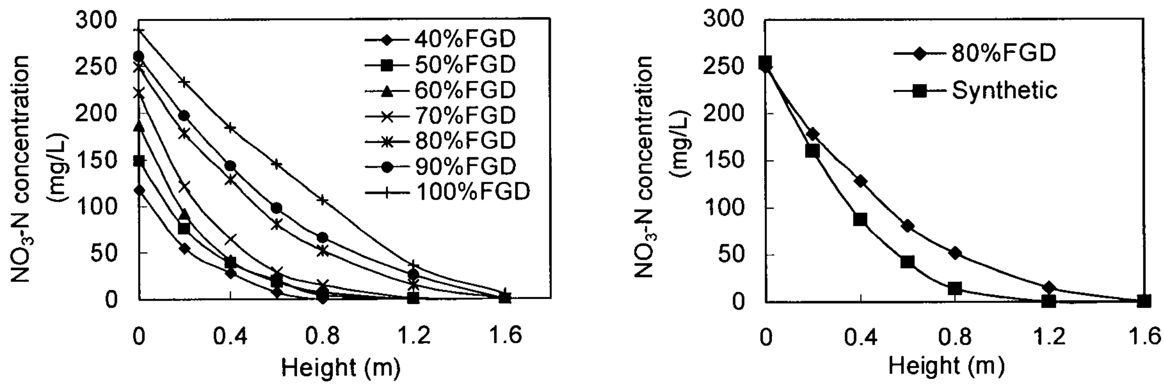


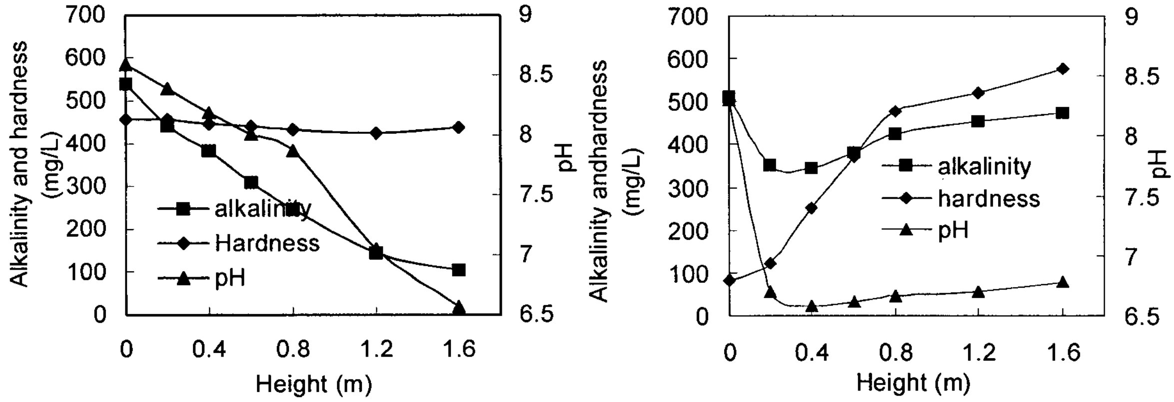
Fig.3 Nitrate profiles of influents with different dilution percent of FGD wastewater

3.4 Use of limestone as alkalinity and inorganic carbon source

In this test, the limestone in the sulfur-limestone reactor was investigated as the extra alkalinity and inorganic carbon source, and no sodium bicarbonate was added. For this purpose, two parallel tests were conducted with influents of 55% dilution of FGD wastewater, one influent with addition of 0.67g/L $NaHCO_3$, the other one without $NaHCO_3$. It was found that the nitrate removal efficiency for the FGD wastewater without addition of $NaHCO_3$ was significantly lower than for the one with addition of $NaHCO_3$ or the synthetic wastewater, similar to Figure 3. A comparison of the alkalinity, hardness and pH profiles (Figure 4) shows that, in wastewater without addition of $NaHCO_3$, alkalinity and pH decreased gradually along the entire height of the reactor. Hardness did not significantly increase, indicating no dissolution of limestone. The above results seemed to imply that FGD wastewater had a buffer system, which was different from the common carbonate buffer system.

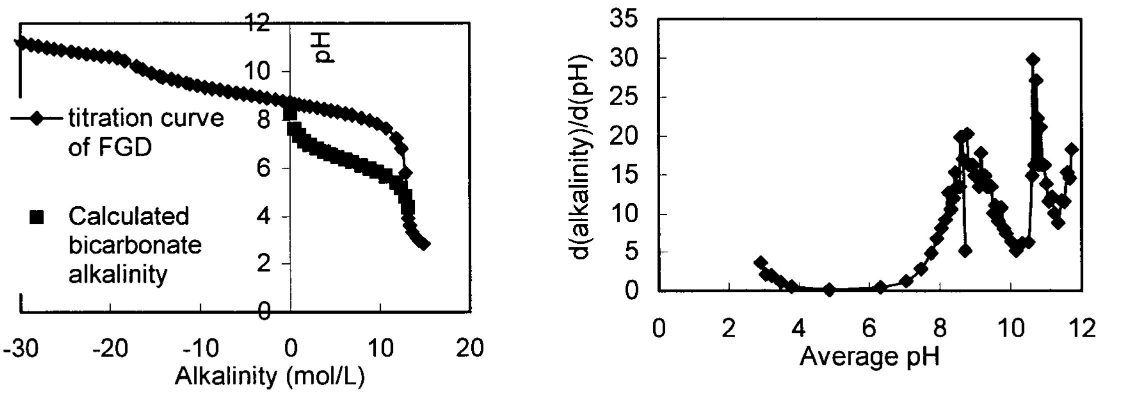
3.5 Importance of borate buffer system

Since FGD wastewater contains less than 10 mg/L inorganic carbon, but more than 1000 mg/L alkalinity (as $CaCO_3$) (Table 1), the alkalinity of FGD wastewater could not be governed by the carbonate system. The titration curve of FGD wastewater (Figure 5a) shows a different pattern than would be expected for bicarbonate. According to Figure 5b, the relevant pK_A value (–Log Acidity Constant) of FGD wastewater is about 8.7, which closely approximates the pK_A value of boric acid (H_3BO_3) in seawater (Skirrow, 1975). In addition, the alkalinity concentration of FGD wastewater agreed well with the concentration of boron. Hence the alkalinity as well as the buffer system of FGD wastewater are based on borate, a rarely encountered phenomenon in wastewater. As borate was the only pH buffer source of FGD wastewater and the pK_A value of borate in FGD wastewater is 8.7, the pH value in the reactor was maintained above 7 until almost all alkalinity was consumed by the autotrophic denitrification process. Since limestone generally does not dissolve at pH higher than 7 (Liu and Koenig, 2002), no alkalinity and inorganic carbon could be supplied to the autotrophic denitrification process. Therefore, lack of available inorganic carbon will be a limiting factor for biosynthesis of autotrophic denitrification bacteria and hence autotrophic denitrification. With a borate buffer system present in FGD wastewater, limestone cannot be used to supply alkalinity and inorganic carbon for autotrophic denitrification.



a. 55% dilution of FGD wastewater without adding $NaHCO_3$ b. Synthetic wastewater

Fig. 4 Alkalinity, hardness and pH profiles



a. Titration curve of FGD wastewater b. Buffer intensity of FGD wastewater

Fig. 5 Titration curve of FGD wastewater

3.6 Autotrophic denitrification of FGD wastewater after addition of sulfuric acid for pH control

Because of the high calcium concentration in FGD wastewater, its removal prior to autotrophic denitrification is not practical because sedimentation of large quantities of calcium carbonate sludge is required. Besides, the borate buffer system maintains a high pH in the FGD wastewater thus preventing the dissolution of limestone for supply of alkalinity and inorganic carbon. Therefore, instead of removing calcium from FGD wastewater, the FGD wastewater was pretreated with up to 1 mL/L of concentrated sulfuric acid to lower the pH to around 7 so that $NaHCO_3$ and polyphosphate could be added without being precipitated. Alternatively, $NaHCO_3$ and polyphosphate were added first to FGD wastewater, regardless of the precipitation, and then concentrated sulfuric acid was added until the precipitates dissolved. The results in terms of nitrate removal efficiency and nitrate profiles were similar to those obtained with prior removal of calcium. For $NaHCO_3$ additions as low as 50% of the recommended alkalinity requirement (corresponds to 1.6 times the theoretical alkalinity requirement), no reduction in nitrate removal efficiency was found, indicating sufficient additional alkalinity supply through dissolution of limestone. If less $NaHCO_3$ was added, the pH dropped below 6 and autotrophic denitrification rates were inhibited.

3.7 Effect of boron concentration on autotrophic denitrification

The salinity of FGD wastewater (1.12 mol/L) was less than the upper limit of 1.8 mol/L, at which autotrophic denitrification could be carried out without inhibition. Therefore, any deviations in nitrate removal performance in comparison to synthetic wastewater, as observed in the nitrate profiles for FDG wastewater above 70% dilution rate, had to be caused by some inhibiting factor other than salinity, provided the pH remained above 6.5-6.8 (Koenig and Liu, 2001a). Since previous laboratory scale studies showed that boron concentrations above 500mg/L might inhibit autotrophic denitrification, the relative nitrate removal efficiency was plotted against the boron concentration as shown in Figure 6. Figure 6 confirms that at boron concentrations higher than 500mg/L autotrophic denitrification was inhibited, with no difference observed between laboratory scale or pilot scale experiments.

3.8 Effect of volumetric nitrate loading rate

Figure 7 illustrates the dependency of nitrate removal efficiency on the volumetric NO_3-N loading rate, in g NO_3-N/m^3.d, for synthetic and FGD wastewater, with the volumetric loading rates being calculated on the basis of empty bed volume. The Figure shows that for NO_3-N loading rates up to 400g/m^3.d the nitrate removal efficiency remains close to 100%. At higher loading rates, the nitrate removal efficiency gradually decreases, though less so for the synthetic wastewater. The faster decrease for FGD wastewater is probably due to the high boron concentration in the FGD wastewater, which inhibited denitrification.

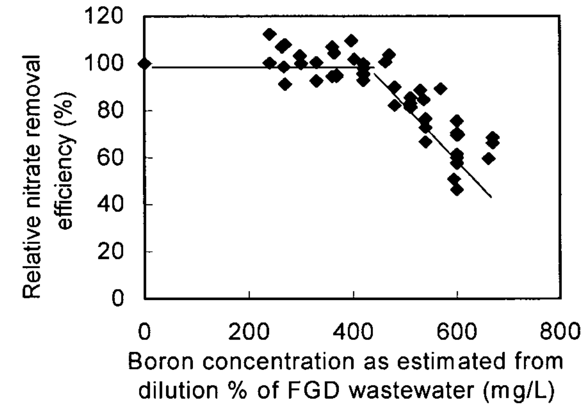


Fig. 6 Effect of boron concentration on autotrophic denitrification

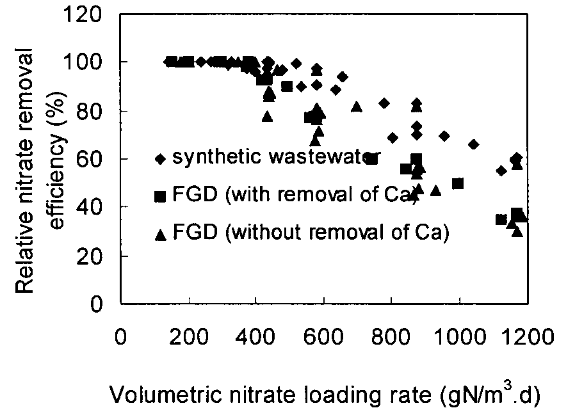


Fig. 7 Nitrate removal efficiency as a function of volumetric loading rate

4 CONCLUSION

Based on the pilot scale experiments with sulfur-limestone reactors, the following conclusions can be drawn:

1) Autotrophic denitrification is not inhibited by salinity up to a concentration of 1.8 mol/L of dissolved salt ions, which is much higher than the concentration of seawater.
2) FGD wastewater is deficient in inorganic phosphorus and inorganic carbon, but its high calcium concentration causes their immediate precipitation when added. Two pretreatment methods help to overcome this problem: 1) removal of calcium, or, 2) addition of concentrated sulfuric acid to lower the pH to about 7. Then the added bicarbonate and inorganic phosphate (added as polyphosphate) remain in solution and autotrophic denitrification of FGD wastewater will proceed. The second pretreatment method appears to be more suitable as no sedimentation and handling of calcium carbonate sludge is required.
3) The borate buffer system in FGD wastewater keeps the pH high thus preventing the dissolution of limestone to supply alkalinity and inorganic carbon autotrophic denitrification. Addition of concentrated sulfuric acid will overcome this problem.
4) The only inhibiting factor in FGD wastewater is boron, which will reduce the autotrophic denitrification rate in concentrations above 500mg/L.
5) At volumetric loading rates of up to 400g NO_3-N/m^3.d, complete autotrophic denitrification of FGD wastewater was obtained.

5 ACKNOWLEDGEMENTS

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