Biological denitrification of fertiliser wastewater at high chloride concentration

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Abstract

Wastewater from the fertiliser industry is characterised by high chloride concentration, normally varying between 60 and 76 g/ℓ. Experiments with biological denitrification were performed in laboratory-scale 'fill and draw' reactors with synthetic fertiliser wastewater, with chloride concentrations up to 96.7 g Cl/ℓ at 37°C; the pH was controlled in the range 6.8 to 7.2. Potassium acetate was added as carbon source for the suspended cultures. The results of the experiments showed that biological denitrification was feasible at the extreme environmental conditions prevailing in undiluted fertiliser wastewater. However, the extreme conditions affected the denitrification rates. The volumetric rates were reduced by a factor of ten between chloride levels of 4.8 to 96.7 g/ℓ. The results from the performed tests can also be applied to other wastewaters with similar characteristics as that of the fertiliser industry, i.e. with high salinity. As an example, the pharmaceutical and aquacultural industries can be mentioned.

Keywords: biological denitrification; fertiliser wastewater; inhibition; high chloride concentration; high salinity.

Introduction

The fertiliser industry produces wastewater with an elevated level of salinity mainly due to the calcium chloride content. Depending on the location of the fertiliser treatment plant, the chloride concentration varies between 60 and 76 g/ℓ. In addition to this significant chloride concentration, the high concentration of nitrate-nitrogen is also an important pollutant in the wastewater.
The traditional treatment of wastewater originating from the fertiliser industry is the dilution method. The wastewater is diluted either by other industrial wastewater or municipal wastewater before being treated in wastewater treatment plants. However, the brine, such as calcium chloride in the wastewater is wasted. To enable commercial re-use of the calcium chloride, the possibility of removing the nitrate in the wastewater is investigated. Moreover, if nitrate is reduced, the environmental impact of brine would be significantly minimized and alternative disposal methods, such as open sea disposal could be developed, since only calcium and potassium chloride would remain.

Although direct electrochemical processes using a catalyst for the process can remove nitrate-nitrogen, the most attractive process for the removal of nitrate is biological denitrification. However, the information on this biological process under extreme conditions, such as high chloride concentration, is limited and it is believed that high salt content in wastewater significantly decreases treatment efficiency of conventional activated sludge, attached growth, anaerobic, nitrification and denitrification processes (Dan et al., 2003).
Few studies have considered denitrification under very high concentration and as a result there is no consensus on the effect of salinity on denitrification. Vredenbregt and his colleagues (1997) studied both biological nitrification and denitrification in high salinity wastewater by using a fluid-bed reactor, and concluded that biological denitrification was effective up to 45 g Cl/ℓ where both nitrate and nitrite were removed effectively. Kristensen and Jepsen (1991) studied biological denitrification in the presence of sodium ions at high temperatures of 40 to 50 ºC and achieved successful denitrification at 30 g/ℓ NaCl. The pilot plant studies for the flue gas scrubbing liquors at 20 g Cl/ℓ reported in Dahl et al., 1997, showed satisfactory denitrification rates. The maximum denitrification rate was 3 mg N/ g VSS•h. Van der Hoek and his colleagues (1987) showed that the combined ion exchange/biological denitrification process was a feasible technique for nitrate removal from groundwater, and denitrification was possible in the presence of 10 to 30 g/ℓ sodium chloride or sodium bicarbonate. Panswad and Anan (1999b) also achieved biological denitrification at the same salinity, 30 g/ℓ NaCl, where the specific nitrate uptake rate was reduced from 2.54 to 1.82 mg N/g MLSS•h. Finally, Glass and Silverstein (1999) managed to achieve denitrification of a wastewater containing 8.2 g/ℓ NO_3-N with ionic strength of 3.0 (total dissolved solids: 180g/ℓ) by using activated sludge in bench-scale sequencing batch reactors. The synthetic wastewater in their study contained 12.23 g KCl/ℓ and 71.24 g NaCl/ℓ and the pH of the wastewater was 9. A similar attempt to acclimate activated sludge to denitrify the high total dissolved solids; high-nitrate wastewater at pH 7.5 was unsuccessful. The other studies in the literature mainly focus on COD removal at high salinity levels.

The main objective of this study, therefore, is to investigate whether biological denitrification is possible at chloride levels of 60 to 76 g/ℓ and, if so, to evaluate the performance of the biological denitrification process.

Material and methods

To accomplish this objective, 'fill and draw' reactors were operated for ten months with increasing salinity levels in order to compare the experimental results.

The system was first operated for a month to establish steady-state conditions at a chloride concentration of 4.83 g/ℓ, after which the calcium chloride concentration in the influent was increased gradually up to 96.7 g/ℓ (total dissolved solids: 210 g/ℓ) during the

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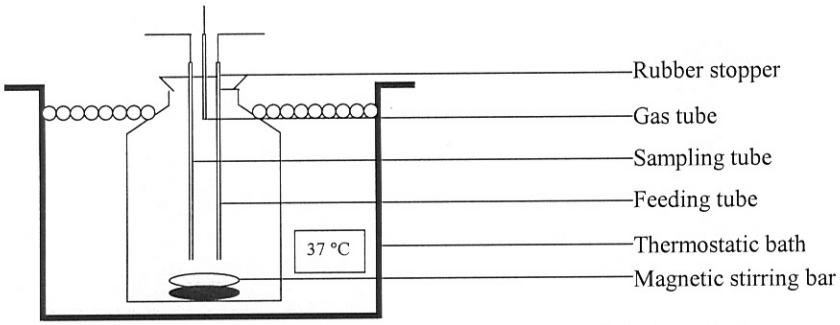

Figure 1
Experimental set-up for the biological denitrification process

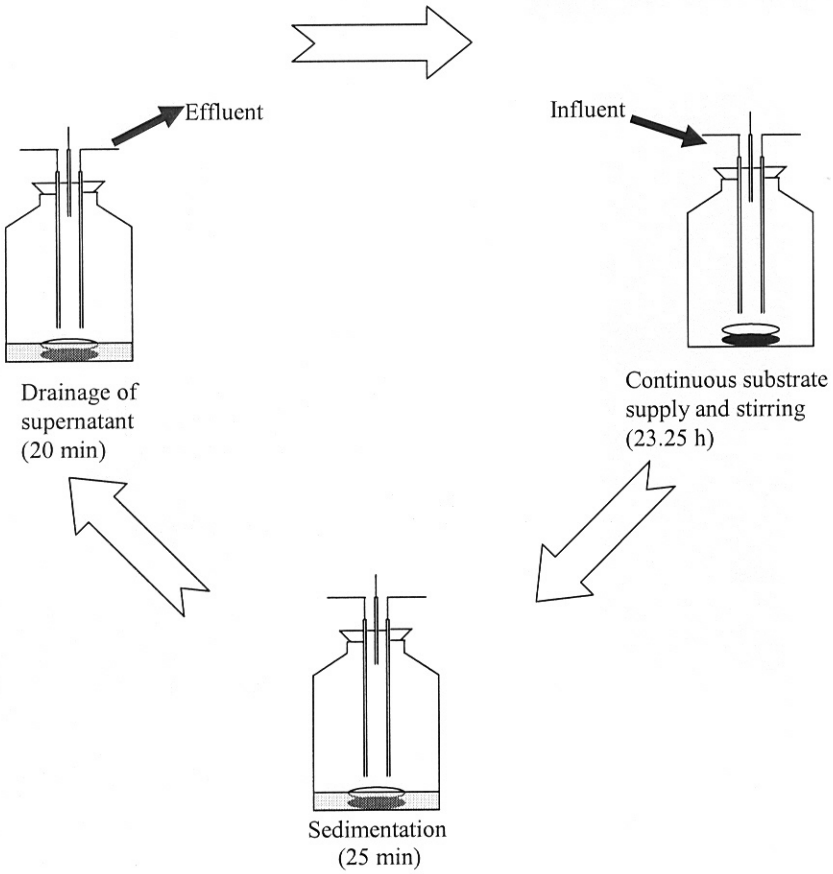

Figure 2
Operational cycle for biological reactors

following nine months. The chloride concentration was increased gradually, since rapid shifts in salt concentration typically cause more problems (Woolard and Irvine, 1995; Kargi and Dincer, 1996).

Experimental set-up

Four 'fill and draw' reactors were operated at identical conditions in the laboratories of Environment & Resources DTU, Technical University of Denmark. Each reactor had a volume of 5ℓ of which 4.4ℓ were used for the denitrification process. The reactors had rubber stoppers to create anoxic conditions for the denitrification process. Three tubes to provide sampling and feeding as well as to prevent overpressure in the reactor (by purging the build-up of nitrogen gas bubbles) penetrated the rubber stoppers. By placing the reactors in a thermostatic water bath the temperature was held at 37°C for all the reactors. Satisfactory agitation was achieved with magnetic stirring. The experimental set-up for each denitrification reactor is shown in Fig. 1.

The operational cycle is illustrated in Fig. 2. The duration of each cycle was 24 h. One litre of synthetic wastewater was pumped to the reactors continuously throughout a period of 23.25 h. During this period, magnetic stirrers kept the micro-organisms in the reactors in suspension. After the filling period the micro-organisms were allowed to settle for 25 min before the supernatant was drained off. The hydraulic retention time (HRT) of the system was regulated to 5 d.

Synthetic wastewater

The initial wastewater was identical for all the reactors. The composition of this water for each chloride level is given in Table 1. Both potassium nitrate and potassium acetate concentrations in the feedstock were changed gradually according to the biomass activity in the reactors. When the total effluent oxidised nitrogen (sum of nitrite and nitrate) concentration measured equal or higher than 3 mg N/ℓ, the concentrations of nitrate and carbon sources in the feed were reduced to the initial levels for potassium nitrate and potassium acetate - 242 mg/ℓ and 918 mg/ℓ, respectively (Table 1). After a 1 d feeding period, chloride concentration was increased to the next level.

Denitrification increases alkalinity. To avoid influence on reaction rates the pH was thus regulated in the range of 6.8 to 7.2 by adding concentrated acid solution to the synthetic wastewater, since the chosen pH-range provided the highest denitrification rates according to the literature (Grady and Lim, 1980; Henze et al., 2001). Potassium nitrate and potassium acetate concentrations were used in the synthetic wastewater; potassium being the best antagonist for reducing the inhibitory concentration of a cation such as calcium in the wastewater (McCarty, 1964 and acetate being the best carbon source for the denitrification process (Gerber 1987; Henze, 1990; Moser-Engeler, 1998).

Biomass

The reactors were inoculated with activated sludge from the Fredericia Municipal Wastewater Treatment Plant, in which the biomass had already adapted to a chloride concentration of 4.83 g/ℓ due to the addition of industrial wastewater from the Kemira Agro Fertilizer Plant. After a month, the steady-state conditions at the new process temperature (37°C) were established and the biomass was ready for further increase in chloride concentration. The experiments were all performed at 37°C, which was the

temperature of the fertiliser wastewater in question and the expected reactor temperature for a denitrification process.

Experimental procedure

The experiments comprised the chloride concentration range from 4.83 to 96.7 g/ℓ as illustrated in Fig. 3. After start-up and stabilisation of denitrification in the reactors the chloride concentration was gradually increased to the final levels. At each chloride concentration level samples were taken from the reactors to determine the corresponding denitrification rates. At each chloride concentration the micro-organisms were allowed to acclimatise for 4 to 5 d to the new chloride level. Daily effluent supernatant samples were filtered and analysed for total oxidized nitrogen (sum of nitrate and nitrite nitrogen) during the experimental period. Moreover, suspended (SS) and volatile suspended solids (VSS) were also measured for the first two months in terms of *Standard Methods* (1992). Total oxidized nitrogen and nitrate and nitrite nitrogen were analysed on a Technicon Autoanalyzer.

TABLE 1
Variations in the composition of synthetic wastewater

Constituent	Concentration (mg/ℓ)
Potassium nitrate	242 – 3 056
Potassium acetate	918 – 12 779
Calcium chloride dihydrate ($CaCl_2.2H_2O$)	10 000 – 200 000

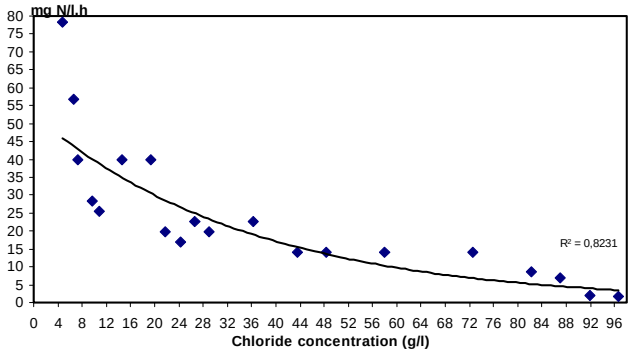

Figure 3
Maximum volumetric denitrification rates at different chloride concentrations

Results and discussion

Variations in total suspended solids (TSS) and volatile suspended solids (VSS)

The change in the properties of biomass was followed by measurements of TSS and VSS. The variations in the concentrations of TSS and VSS are given in Table 2. The high TSS level in the first period of the experiments is due to the seed sludge from the municipal wastewater treatment plant.

The determinations of TSS and VSS were terminated after six weeks because of highly varying results. The reason why extremely low TSS and VSS were obtained might be the high calcium concentration in the wastewater, since calcium promotes both attachment and precipitation (Henze and Harremoes, 1983). During the experiment a major part of the solids was attached as calcium components at the bottom of the reactors.

The same phenomenon was also detected by Vredenbregt and his group (1997), where the level of scaling due to calcium carbonate formation in the reactor was so high that the reactor had to be shut down. In the pilot plant study (Dahl et al., 1997), the adapted municipal activated sludge loaded with artificial wastewater showed a typical VSS/SS ratio of 60% VSS at first. However, the VSS/SS ratio decreased due to the precipitation of gypsum onto the activated sludge at high chloride concentration, and at the end of the study it was concluded that the VSS/SS ratio of 25% could be expected if the modified flue gas scrubbing liquor was continuously added. The samples taken from the reactors, therefore, would not give the correct concentration of suspended and volatile solids due to the high amount of attached solids.

Nitrate removal at different chloride concentrations

During the experimental run, a series of experiments were performed for determination of the maximum denitrification rates corresponding to the different chloride levels. In Fig. 3, the maximum volumetric denitrification rates at each chloride concentration are shown. At 96.7g/ℓ chloride, the maximum rate was found to be 1.70 mgN/ℓ·h. In the experiments, the maximum denitrification rates, based on the effluent limits for the fertiliser treatment plant were determined, 5 mg NO_3-N/ℓ. The presented denitrification rates provided total oxidised nitrogen effluent concentration of 3 to 5 mg N/ℓ, that is less than the effluent limits.

The rates presented in Fig. 3 show that biological denitrification can function at all the chloride levels in fertiliser wastewater and even up to 96.7 g Cl/ℓ. However, extreme conditions affected the denitrification rates. The volumetric rates were reduced by a factor of ten between chloride levels of 4.8 and 96.7 g/ℓ.

Both nitrate and nitrite were removed efficiently during the experimental period. No nitrite accumulation was detected during the experiment. Since the effluent contained negligible amounts of nitrite, the decrease on the maximum denitrification rate was due only to the increase in salinity, and not to nitrite inhibition. It is interesting that the decrease in the maximum volumetric denitrification rates shows an exponential trend with the increase in salinity.

TABLE 2
The experimental data for TSS and VSS

Date of experiment	Chloride (g/ℓ)	VSS (g/ℓ)	TSS (g/ℓ)	VSS/TSS	Reference
10/07	4.83	7.37 (± 0.30)	9.79 (± 0.51)	0.76 (± 0.01)	All of the four reactors
22/07	4.83	4.93 (± 1.66)	6.58 (± 2.64)	0.77 (± 0.05)	All of the four reactors
31/07	4.83	1.18 (± 0.46)	2.22 (± 0.85)	0.53 (± 0.01)	All of the four reactors
06/08	4.83	1.62 (± 0.57)	1.97 (± 0.77)	0.83 (± 0.04)	Reactor A and B
06/08	6.53	1.89 (± 0.21)	2.52 (± 0.76)	0.78 (± 0.15)	Reactor C and D
16/08	7.26	0.23 (± 0.03)	1.30 (± 0.54)	0.02 (± 0.06)	All of the four reactors

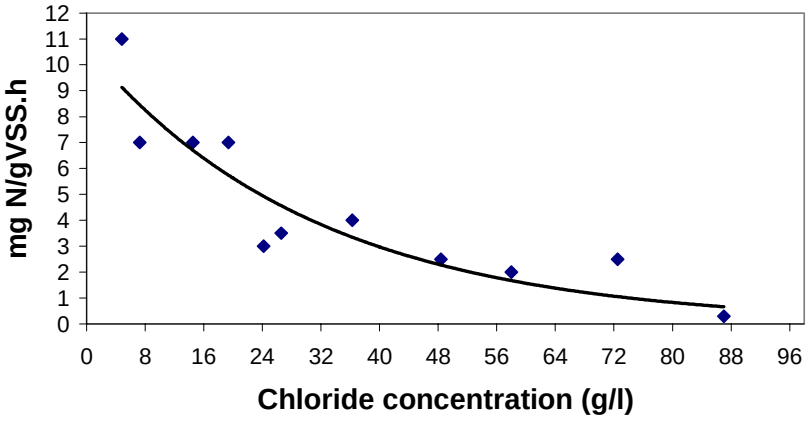

Figure 4a
Denitrification rates of the selected reactor based on 1 290 mg/ℓ VSS at different chloride concentrations

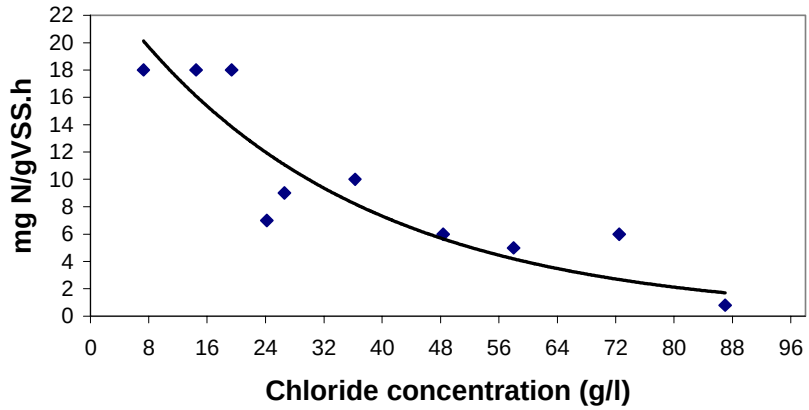

Figure 4b
Denitrification rates of the same reactor based on 500 mg/ℓ VSS at different chloride concentrations

Although the measurement of TSS and VSS was terminated after a short time period due to the precipitation and attachment of the biomass in the reactors, the denitrification rates based on VSS were estimated by the following assumptions based on the experimental data. The concentration of VSS was assumed to be 1 290 mg/ℓ at the chloride level of 4.83 g/ℓ, where there was only little attachment and the value was gradually decreased for each chloride level. Fig. 4a presents the specific removal rate of the reactor based on 1 290 mg/ℓ VSS concentration. At the last chloride concentration (96.7 g/ℓ), the concentration of VSS in the attached material was assumed to be 500 mg/ℓ, and specific removal rates were recalculated as illustrated in Fig. 4b. It can be concluded that specific removal rates at given chloride levels could vary between the values given in Figs. 4a and 4b.

Compared to rates in domestic wastewater (Henze et al., 2001), the specific removal rates were about a factor of ten lower. Thus the high chloride concentration significantly inhibited the denitrification, but the process still continued to function at the reduced rate. However, the assumptions of VSS, especially for the final chloride concentrations could be too high, which means that the VSS-specific rates given are low estimates. Thus, the maximum volumetric denitrification rate could be a better indicator to evaluate the performance of the biological denitrification process.

Conclusions

- The results of the experiments show that nitrite and nitrate could be removed by biological denitrification under the extreme environmental conditions prevailing in fertiliser wastewaters.
- Biological denitrification could function at chloride levels up to 96.7 g Cl/ℓ. However, the extreme conditions affected the denitrification rates. The volumetric rates as well as VSS-specific denitrification rates were reduced significantly between chloride levels of 4.8 to 96.7 g/ℓ. Compared to rates in domestic wastewater, the VSS-specific denitrification rates were estimated to be a factor of ten lower.
- Considerable precipitation and attachment of biomass was observed. Due to the high concentration of calcium in fertiliser wastewater, calcium carbonates (scaling) were formed easily during denitrification. The risk of scaling was more pronounced when applying high nitrate loads. The negative effect of this could be sludge washout in the fertiliser wastewater treatment plant and space occupation by inorganic precipitates. The precipitation of carbonates, however, might be reduced if the pH is kept in the low active range of the denitrifying bacteria.

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