Short communication

Biological removal of nitrogen species from metal-processing wastewater#

Justin M Kasia, John R Duncan and Joanna E Burgess*

Department of Biochemistry, Microbiology and Biotechnology, Rhodes University, Grahamstown 6140, South Africa

Abstract

Although several nitrification/denitrification processes are established for the removal of ammonia and nitrate from municipal and industrial wastewaters, there are few reported results on the removal of these ions from metal-processing and finishing wastewaters. Unlike municipal wastewater, there is very little organic content in metal-processing wastewaters. Sources of ammonia and nitrate in the wastewater include the use of ammonium-nitrate-fuel oil as a blasting agent, and the use of other nitrogen-containing reagents during processing. The objective of this work was to investigate a biological process for the removal of nitrogenous compounds from real metal-processing wastewater. The system comprised an aerobic continuously stirred tank reactor (CSTR) followed by an anaerobic packed column and was run using real wastewater from a metal-processing operation. The system was inoculated using humus sludge from a municipal trickling filter and a period of approximately four weeks was required for a denitrifying biofilm to develop. Results showed that ammonia removal occurred readily in the CSTR while nitrite oxidation was slower to develop. The CSTR was found to be suitable for ammonia oxidation; up to 89% ammonia removal was achieved. By employing an integrated process comprising nitrification and denitrification, high ammonia removal efficiencies can be obtained. An effluent that is low in ammonia can be obtained with this system with additional carbon introduced after the CSTR. The gravel-packed column reactor was found to be unsuitable for the removal of nitrate in the configuration used (maximum 15% removal efficiency). The critical parameters for denitrification are nitrate concentration, temperature, influent flow rate and mean cell retention time. Nitrate removal did not meet the expectations projected by previous authors' work using synthetic wastewater.

Keywords: metal industry wastewater; ammonia; nitrate; nitrification

Introduction

Typical metal industry wastewater contains high levels of various toxic compounds which interfere with aquatic and terrestrial life when released into land and water ecosystems. The ratio of ammonia concentration (toxic form) to ammonium ions (relatively non-toxic) increases with rising temperature and pH (Koren et al., 2000). All nitrogenous compounds are of interest, especially nitrate, which is a strong metal ligand. This also makes it difficult to remove trace metal pollutants still contained within the wastewater. Mine and mill effluents usually contain high amounts of ammonia and/or nitrate ions owing to the use of ammonium nitrate based blasting agents and ammonium sulphate as eluent for metal extraction ion exchangers (Koren et al., 2000). In some metal-processing industries, the nitrate concentration in the wastewater can reach up to 1 000 mg/ℓ NO_3-N (Glass and Silverstein, 1999). Various non-biological methods are available for the removal of these compounds from wastewaters but these are expensive, and disposal of the end product becomes problematic, e.g. with reverse osmosis the end product is a concentrated waste brine which becomes difficult to dispose of. Biological methods are easier to operate and maintain and are consequently cheaper. Often the end products are harmless and disposal is easy.

Biological removal of ammonia and nitrate from municipal wastewaters is a well-established practice with a number of widely used process designs, from the earliest oxidation ditches to the more recent discoveries of the Anammox (Mulder et al., 1995), CANON (Schmidt et al., 2003) and SHARON (Hellinga et al., 1998) processes. Apart from Anammox, biological removal of ammonia, nitrification, is traditionally defined as the aerobic oxidation of NH_3^+ to NO_3^- via nitrite (NO_2^-). This is mainly carried out by two groups of autotrophic bacteria; ammonia oxidisers ($NH_3 \rightarrow NO_2^-$), exemplified by *Nitrosococcus* and *Nitrosomonas* spp., and nitrite oxidisers ($NO_2^- \rightarrow NO_3^-$), such as *Nitrobacter* and *Nitrospira* spp. Denitrification, the biological reduction of nitrogen oxides to dinitrogen gas, is effected by a number of bacteria, among them are *Pseudomonas*, *Flavobacterium*, and *Bacillus* spp. The nitrate ion is reduced to dinitrogen gas by the pathway:

$$2NO_3^- \rightarrow 2\ NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2$$

Although the denitrifying bacteria are aerobic microorganisms, they can utilise oxidised nitrogen compounds as terminal electron acceptors in place of oxygen, hence low oxygen concentrations or the absence of oxygen are required for denitrification to occur.

Municipal wastewaters contain sufficient carbon and phosphorus to act as a nutrient supply for biological processing, but mineral processing wastewaters often do not. The recommended pH range for nitrification is 7.5 to 8.6 and for denitrification 7.0 to 8.0 (Metcalf and Eddy, 1991). The ratio at which nutrients should be supplied is contentious, with chemical oxygen

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* To whom all correspondence should be addressed.
☎ +2746 603-8629; fax: +2746 622-3984;
e-mail: j.burgess@ru.ac.za

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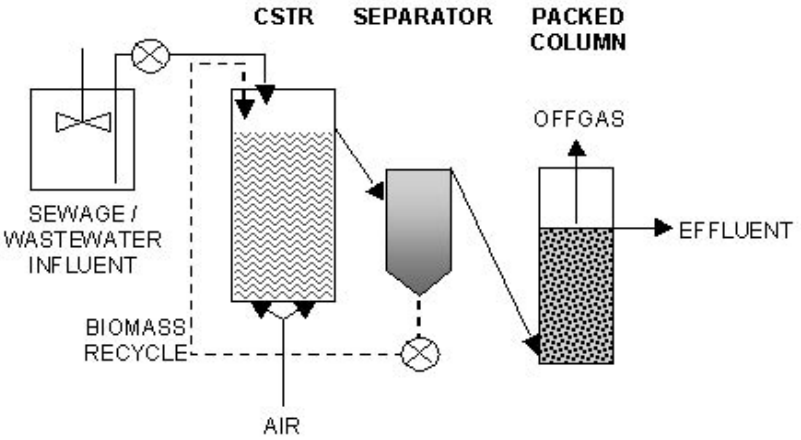

Figure 1
Schematic of the bioreactor design for the removal of nitrogenous compounds from metal-processing wastewater

demand (COD): N: P ratios of 100:20:1 (Metcalf and Eddy, 2002), 100:10:1 (Beardsley and Coffey, 1985) and 250:7:1 (Franta et al., 1994) quoted in the literature. Whichever ratio is used, wastewater streams from industries including chemical and petrochemical manufacturing, metal mining and refining, sugar refining and paper and cellulose production are regarded as too low in nutrients for biological processing. The aim of this research was to investigate the technical feasibility a biological process for the removal of nitrogenous compounds from metal industry wastewater. The process design was developed from encouraging results obtained using simulated mine wastewater (Koren et al., 2000) and comprised an aerobic continuously stirred tank reactor (CSTR) for nitrification followed by an upflow gravel packed column for denitrification.

Materials and methods

Analyses of industrial wastewater samples indicated that the wastewater to be treated was similar to those surveyed by Koren et al. (2000). The COD: N: P ratio of the wastewater was approximately 265:5:1, indicating the lack of organic nutrients available for biological treatment. It was evident that nutrient supplementation over and above simple carbon addition would be required, so a bench-scale process based on combining the industrial wastewater with domestic sewage was designed.

The biological process designed is shown in Fig. 1. A 10 ℓ flask contained the influent, which consisted of industrial wastewater and settled sewage at a ratio of 1:1. The mixture was constantly stirred to keep the contents homogeneous. The sewage served as a source of nitrogen, phosphorus and readily available carbon. The influent was pumped into the CSTR at a rate of 6 mℓ/min, which gave a 27 h hydraulic retention time (HRT) over the whole system. A long HRT is more important for nitrification than carbonaceous matter oxidation, because nitrification is a slower process. The CSTR ran as a constant aerobic environment with air being continuously bubbled into it. The operating volume of the tank was 7.9 ℓ. A consortium of bacteria collected from the humus tanks of a nitrifying trickling filter (Grahamstown Municipal Wastewater Treatment Works) was used as the inoculum in the CSTR and packed gravel column. The mean cell retention time (MCRT) in the CSTR was 30 d; 263 mℓ of sludge was wasted from the CSTR daily. The mixed liquor suspended solids (MLSS) concentration in the CSTR was monitored. The CSTR was aerated through packed sand diffusers connected to glass tubes bringing compressed air into the bottom of the tank, providing complete mixing as well as aeration.

Samples of the influent, mixed liquor and clarifier effluent were taken three times each week. Total dissolved solids (TDS), total suspended solids (TSS) and CSTR MLSS were measured according to *Standard Methods* (1999). Ammonia, nitrate, nitrite, phosphate, COD, sulphide and sulphate concentrations in the influent and effluent were measured using test kits based on standard method principles. The kits used were Merck Spectroquant kits 14752 (ammonia), 14773 (nitrate), 14776 (nitrite), 14842 (phosphate), 14539 (COD) and 14537 (sulphide) (Merck Chemicals Pty Ltd) and Sulfaver 4 Powder Pillows (sulphate) (Hach International). All analyses were carried out in duplicate and the arithmetic means reported.

Results and discussion

The major difference between this work and that already available in the literature (e.g. Koren et al., 2000) was the use of a real wastewater generated by metal refining, as opposed to the use of a synthetic wastewater whose composition was controlled. The performance of the biological process was monitored in terms of removal of COD, nitrate and ammonia. The stability of the process was indicated by the MLSS concentration in the aeration tank and the pH profile across the steps of the process unit. A summary of the results (Table 1) shows that the removal efficiencies ranged from 7.3% for COD to 88.7% for ammonia.

Process stability

The optimum pH range for a nitrification/denitrification process is 7.0 to 8.5. The industrial wastewater caused drastic changes in the pH range and consequently disrupted the nitrification process. It can be seen from Fig. 2 that although the effluent pH followed influent pH closely, the two began to diverge after 40 d, with the peaks and troughs in influent pH being less extreme in the effluent pH. It is possible to speculate that the process may have developed better buffering capacity over time. The target range of MLSS in aerobic biological processes such as activated sludge is 2 000 to 3 500 mg/ℓ (Metcalf and Eddy, 2002). It can be seen in Fig. 3 that the supply of the influent mixture promoted growth rather than retarding it, so perhaps a shorter MCRT could have been used. Excess MLSS is an unusual problem in industrial wastewater treatment, where inhibitory components of the influent often suppress bacterial growth, but the constant supply of nutrients in the sewage accounts for these results.

Process performance

The ammonia levels were high in the industrial wastewater for the first 16 d and gradually started falling until day 25 when the ammonia was at very low levels in the influent and effluent.

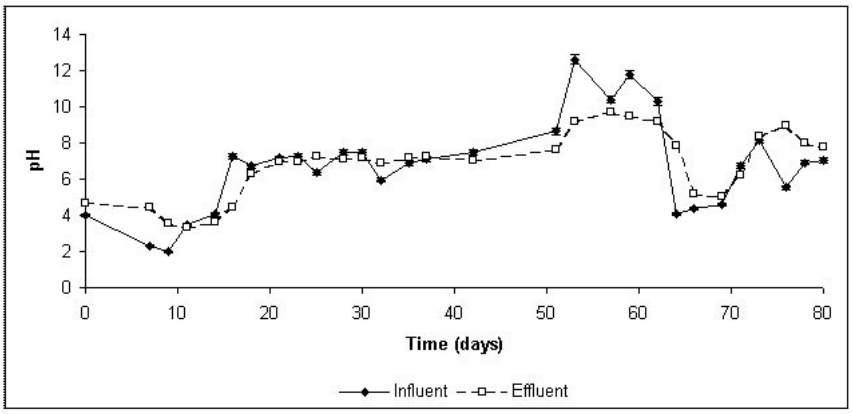

Figure 2
Influent and effluent pH

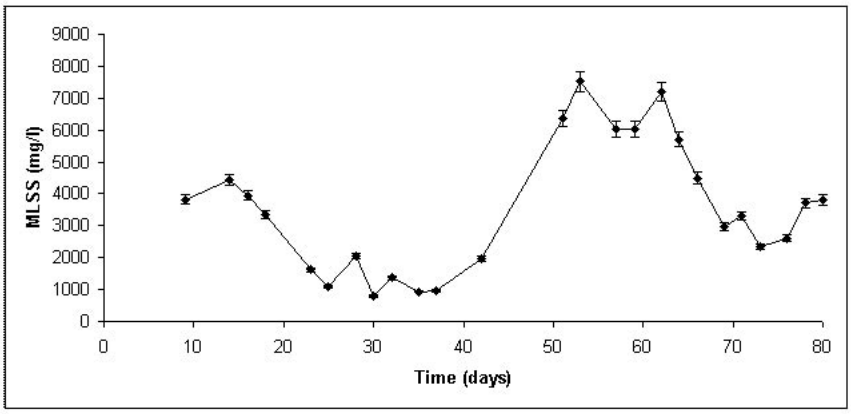

Figure 3
Mixed liquor suspended solids concentrations in the CSTR

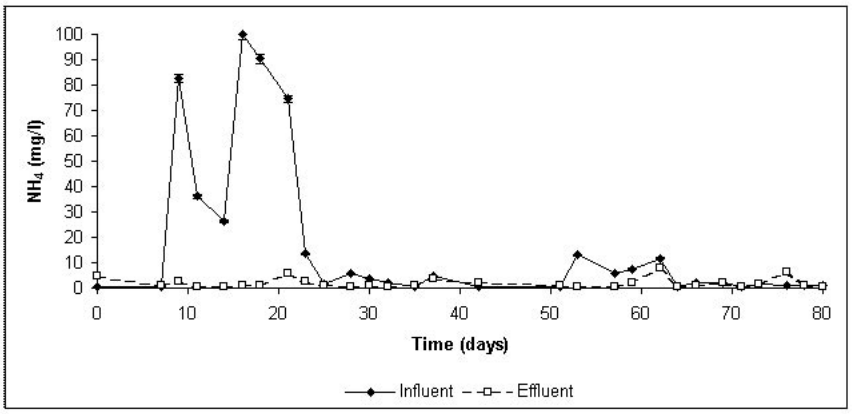

Figure 4
Influent and effluent ammonia concentrations

TABLE 1
Process performance indicators over 80 days

		Ammonia (mg/ℓ)	Nitrate (mg/ℓ)	COD (mg/ℓ)	pH	Phosphate (mg/ℓ)	Sulphate (mg/ℓ)	Sulphide (mg/ℓ)	TDS (mg/ℓ)	TSS (mg/ℓ)
Maximum	Influent:	101.00	272.0	9440	12.60	169.0	5130	-	-	-
	Effluent:	7.80	321.0	8570	9.70	70.0	5375	1.42	1000	1990
Mean	Influent:	16.96	71.6	5254	6.69	29.9	1750.2	-	-	-
	Effluent:	1.92	61.1	4869	6.79	20.8	1692.2	0.37	191.4	496.7
Minimum	Influent:	0.33	0.3	943	1.99	10.0	173.0	-	-	-
	Effluent:	0.27	0.3	390	3.34	2.0	150.6	0.13	0.40	10.00
Std. Deviation	Influent:	29.93	75.4	2652	-	28.9	1397.9	-	-	-
	Effluent:	1.98	81.6	2903	-	13.4	1304.8	0.27	280.8	457.8
Mean removal efficiency (%)		88.7	14.7	7.3	N/A	9.2	58.0	-	-	-

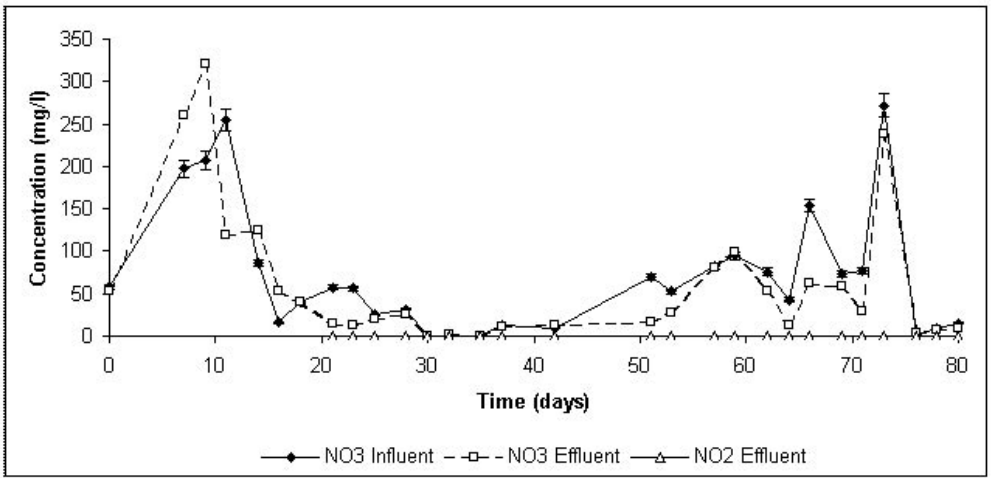

Figure 5
Nitrate concentrations in the process influent and effluent and nitrite concentration in the effluent

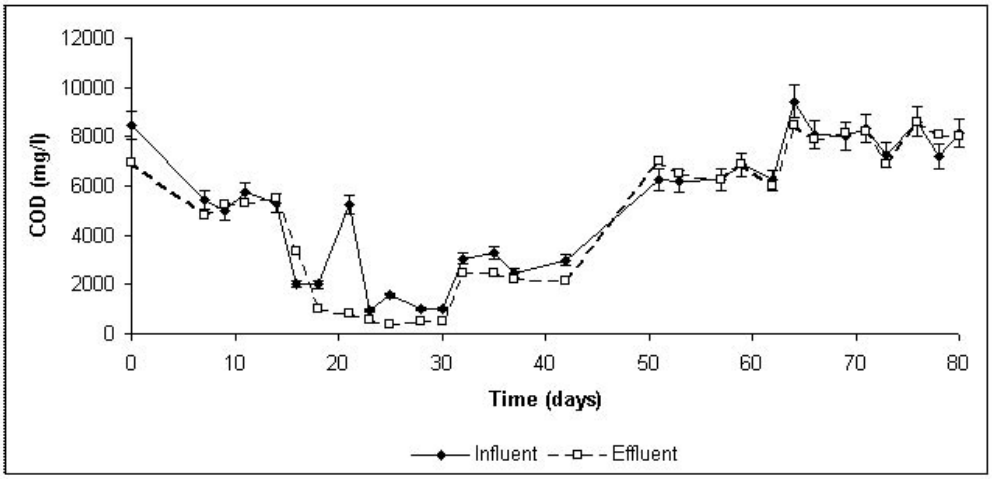

Figure 6
Influent and effluent COD concentrations

During the first 16 days the process showed very good ammonia removal, with the effluent ammonia concentration remaining below 1.02 mg/ℓ (Fig. 4). A new batch of industrial wastewater used to make up the influent after day 16 contained much less ammonia, so the removal efficiency fell in percentage terms, although the effluent quality remained stable, with the concentration of ammonia leaving the process being always less than 6.37 mg/ℓ.

It is difficult to assess the capacity of the process to remove ammonia because it was not challenged with a high ammonia load for much of the trial period. However, over the 16 d in which the influent ammonia was high, the process appeared very robust. The mean ammonia removal efficiency of the process during this high loading period was 95.8%. These results compare well with the standard figures given for acceptable ammonia removal in biological treatment of industrial wastewaters, which are 70 to 85% (Metcalf and Eddy, 1991).

Koren et al. (2000) reported a 97.2% removal of ammonia from wastewater using a similar bench-scale process. However, the HRT in their process was 38 h compared to this experiment in which the HRT was 27 h. Koren et al. (2000) also used synthetic wastewater including methanol as a carbon source for their nitrifying bacteria population. In contrast, sewage was used in this experiment for nutrients and also as a carbon source.

The nitrite levels were very low, as can be seen in Fig. 5. This is because the formation of nitrite is transient; it does not persist in the water because it is constantly being converted to nitrate by bacteria such as *Nitrobacter* which occur in a higher population than *Nitrosomonas*.

Nitrate levels between day 16 and 51 were low due to the absence of ammonia and nitrate in the influent (Fig. 5). Nitrate removal varied, with effluent nitrate concentrations following the same trend as influent concentrations. Although the ammonia removal was good, the high effluent nitrate suggests that the denitrification process was not being completed. The low nitrite concentrations in the effluent (maximum nitrite was only 0.247 mg/ℓ) indicate that the aerated nitrification sludge was providing full ammonia oxidation, but that the denitrification step was not working as well. The mean nitrate removal (14.8%) could have been improved if an alternative carbon source was used for the bioprocess, e.g. methanol or lactate. Sewage contains a variety of unknown substances including surfactants which could have inhibited nitrification. The nitrite levels were low in the denitrified effluent and the aim of measuring them was to find out whether the denitrified effluent could be recycled. Although the use of a clean carbon source in place of sewage has cost implications, the benefits may outweigh them. Another possible improvement could be the addition of further carbon immediately before the denitrification column. A similar process using synthetic wastewater developed and tested by Koren et al. (2000) included the addition of methanol prior to anaerobic denitrification and achieved 100% nitrate removal.

Chemical oxygen demand is defined as the amount of a specified oxidant that reacts with the sample under control-

led conditions (*Standard Methods*, 1999) and is often used as a measurement of pollutants in wastewater and natural water. Wastewaters have high COD values, as can be seen in Fig. 6, showing measurements of industrial wastewater COD concentration. Values from day 16 to 51 are low compared to the rest of the days because different batches of wastewater were collected and used during the study. During the rest of the time, the average influent COD was 5 254 mg/ℓ.

Chemical oxygen demand removal efficiency was low (mean removal = 7.3%). The COD concentrations were measured in order to assess the likelihood of water recycling opportunities. The high and variable effluent COD (4 869 ± 2 903 mg/ℓ) means that wastewater with this treatment only cannot be reused on site and further treatment would be necessary.

The COD removal normally achieved by a biological process treating wastewater is 85 to 95% (Metcalf and Eddy, 2002). However, this process was designed and operated for maximum nitrogen removal. For example, the long MCRT allowed for slow growth rates of the autotrophic bacteria, but the heterotrophic species which are usually responsible for COD removal will not have been kept in the exponential phase of their growth cycle, hence their substrate utilisation rates were low.

Phosphate, sulphate and sulphide were measured mainly to determine reuse opportunities for the effluent. The measurements of phosphate showed that although nitrogen and phosphorus removal can be combined (e.g. in the UCT and Bardenpho processes), this process did not achieve phosphorus removal (Table 1). The peaks observed in the influent phosphate levels were flattened in the effluent, but not enough to claim phosphate treatment by this process. This was not unexpected, since maximum phosphate removal by an optimised system is only 10 to 25% (Metcalf and Eddy, 2002).

Sulphate levels in the metal wastewater were high, as shown in Table 1. Since this bioprocess was based on nitrifying and denitrifying bacteria, significant populations of sulphate-reducing bacteria were neither expected nor observed. Unfortunately, the effluent sulphate concentrations are conducive to the formation of sulphate-reducing biofilms in pipework if this water were to be used on site, and this would create problems with odours and corrosion due to hydrogen sulphide generation. Sulphate levels acceptable for industrial use range from 0 to 500 mg/ℓ (DWAF, 1996). The sulphide concentrations in the effluent were negligible (Table 1), apart from one peak between days 53 and 64. This peak coincided with a sharp increase in influent sulphate, and indicates that a small number of sulphate-reducing bacteria were present, probably in the anaerobic column. However, the sulphide generated was insignificant compared to the ~ 600 mg/ℓ found in the effluent of sulphidogenic anaerobic digesters operated in this laboratory. It was clear from the measurements of sulphate and sulphide in the effluent that the effluent would not be suitable for direct reuse in other on-site processes but is amenable to another treatment step to improve the quality to useable levels.

The TDS and TSS in the effluent (Table 1) were monitored to determine whether the effluent could be reused or discharged. Total dissolved solids in water used for industry usually range from 0 to 1 600 mg/ℓ (DWAF, 1996). The highest level in this study was 1 000 mg/ℓ and these are acceptable levels for recycling of the effluent for other on-site processes such as cooling water, ash quenching, dust suppression, fire fighting and rough washing. Total suspended solids are made up of settleable solids and non-settleable solids. Wastewater typically contains high levels of TSS. Recommended industrial process water TSS levels range from 0 to 25 mg/ℓ (DWAF, 1996). Levels above this cause damage and fouling of equipment and structures. The nitrified effluent in this experiment cannot be reused onsite without further treatment because the TSS levels are too high. Problems with biofilm sloughing from the gravel packed column contributed to the high effluent TSS concentrations.

Conclusions

It is justified to conclude by saying that a nitrogen removal process from municipal wastewater and industrial effluent treatment can be adapted for the extraction of nitrogenous compounds from metals industry wastewater. Some of the compounds in the wastewater were not efficiently removed and this could be due to the nature of the bioprocess. Low cost methods were used in this experiment with a view to future scale-up e.g. sewage as a free carbon source and the use of air for the CSTR containing little oxygen (approx. 21% of total air provided). It is important to note that optimisation of the reaction conditions, e.g. pH, temperature, might greatly improve the efficiency of the bioprocess. To alleviate bioprocess problems such as blocking of the gravel column and poor COD removal, the MCRT could be decreased in order to bring the MLSS down, thus reducing the amount of microbial biomass in the gravel column and encouraging faster growth and substrate utilisation rates in the aeration tank. The use of an alternative carbon source such as methanol or lactate could be subjected to a cost-benefit analysis to assess its potential as a process optimisation tool. Sewage contains various substances which inhibit nitrification (e.g. surfactants), and therefore the use of methanol or lactate would provide for a uniform and "clean" carbon source which will produce very little biomass compared to sewage. This will also be a great advantage in the maintenance of the packed column, because less build-up of biomass means less back-flushing and shorter process downtime periods.

Acknowledgements

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