Technical note

Biological treatment of industrial wastewater containing formaldehyde and formic acid

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Abstract

The biological treatment of wastewater from an aminoplastic resin-producing industry was studied in a pre-denitrification system. This study reports results on the removal of organic matter and nitrogen compounds from wastewater which contained high levels of formaldehyde and formic acid. The formaldehyde concentration in the feed varied between 2 087.0 and 2 200.0 mg/ℓ, the mean removal being 99.9%. The mean efficiency of formic acid removal was 99.7%, and its concentration in the feed ranged between 1 384.6 and 1 513.9 mg/ℓ. The total organic carbon (TOC) values in the feed varied from 1 423.0 to 1 599.5 mg/ℓ, corresponding to an organic loading rate of about 0.20 kg TOC/m^3·d. High TOC removal was achieved, around 92.0%. With regard to nitrogen compounds, the total Kjeldahl nitrogen (TKN) concentration in the feed ranged between 467.8 and 492.3 mg/ℓ. The applied nitrogen loading rate was around 0.06 kg TKN/m^3·d, and the mean percentage of TKN removal was 76.7%.

Keywords: formaldehyde, formic acid, industrial wastewater, nitrogen removal, organic matter removal

Introduction

Wastewaters from aminoplastic resin-producing industries are characterised by high levels of organic matter and nitrogen compounds. In general, the organic matter is mainly present as formaldehyde and the nitrogen compounds as urea. Consequently, the biological treatment of these wastewaters requires a combined process of carbon and nitrogen removal. This biological treatment could be carried out in a pre-denitrification system, which is usually used to treat wastewaters with a high content of organic matter that can be used as carbon source for denitrification. The pre-denitrification system avoids or decreases the need for adding an external carbon source, which is interesting from an environmental and economic point of view. Organic matter removal, hydrolysis of nitrogen compounds and denitrification of nitrate recirculated from the aerobic unit would take place in the anoxic reactor. Nitrification of ammonium provided by the anoxic unit and biodegradation of the organic matter that would not have been removed in the anoxic reactor would take place in the aerobic reactor.

Cheng et al. (1996) studied the treatment of wastewaters from a resin-producing industry using a pre-denitrification system (anoxic-aerobic-aerobic) at laboratory scale. They achieved removal efficiencies of COD and TKN around, respectively, 95.3 and 83.8%; at organic loading rates of between 0.27 and 0.72 kg COD/m^3·d and nitrogen loading rates of between 0.04 and 0.12 kg TKN/m^3·d. Garrido et al. (2000) also studied the treatment of wastewaters from a resin-producing industry using a pre-denitrification system (anoxic-aerobic) at laboratory scale. They achieved COD removal efficiencies between 70 and 85%, at organic loading rates of between 0.7 and 1.9 kg COD/m^3·d.

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Received 5 July 2004; accepted in revised form November 2005.

The purpose of this research was to study the biological treatment of wastewater from an aminoplastic resin-producing industry in a pre-denitrification system. The removal of organic matter and nitrogen compounds was analysed in a wastewater with high formaldehyde and formic acid concentrations.

Material and methods

Analytical methods

Formaldehyde was analysed spectrophotometrically according to the Hantzch reaction (Nash, 1953), using a Perkin Elmer Lambda 11 UV/Vis spectrophotometer. Formic acid and phenol were determined using a Hewlett Packard 1100 liquid chromatograph equipped with a C-18 ODS column (25 cm x 4 mm ID) and a UV diode-array detector. The mobile phases were methanol: water (60:40) and acetonitrile: phosphoric acid (80:20), respectively. Detection was performed at 210 nm for formic acid and 280 nm for phenol. Methanol was measured using a Hewlett Packard 5890-II gas chromatograph equipped with a Nukol column (30 m x 0.25 mm ID) and a flame ionisation detector. Nitrogen (1.5 mℓ/min) was utilised as carrier gas. Injector and detector temperatures were 250 and 270ºC, respectively. TOC was determined according to *Standard Methods* (1998), using a TOC-5050A Shimadzu.

Nitrite and nitrate were analysed by capillary electrophoresis using a Hewlett Packard ^{3D}CE system with a micro-capillary tube of fused silica (40 cm x 50 µm ID). UV detection was undertaken at a wavelength of 214 nm and 450 nm as reference. The biogas composition (N_2, CH_4, CO_2 and N_2O) was analysed on a Hewlett Packard 5890-II gas chromatograph equipped with a Porapack Q W80/100 column (2 m x 3.2 mm ID) and a thermal conductivity detector. Helium (15 mℓ/min) was utilised as carrier gas. Injector, oven and detector temperatures were 90, 25 and 100ºC, respectively. Ammonium, pH, TKN and VSS were evaluated according to *Standard Methods* (1998).

TABLE 1 Composition of wastewater from the aminoplastic resin-producing industry (all parameters are in mg/ℓ, except pH)		
Parameter	**Range**	**Average**
CH_2O	2087.0 - 2200.0	2144.4
HCOOH	1384.6 - 1513.9	1436.2
CH_3OH	240.0 - 264.1	249.4
C_6H_6O	0.9 - 2.0	1.6
TOC	1423.0 - 1599.5	1552.6
TKN	467.8 - 492.3	477.8
$N\text{-}NH_4^+$	11.3 - 19.2	14.9
$N\text{-}NO_3^-$	0.4 - 1.1	0.6
pH	6.3 - 7.0	6.7

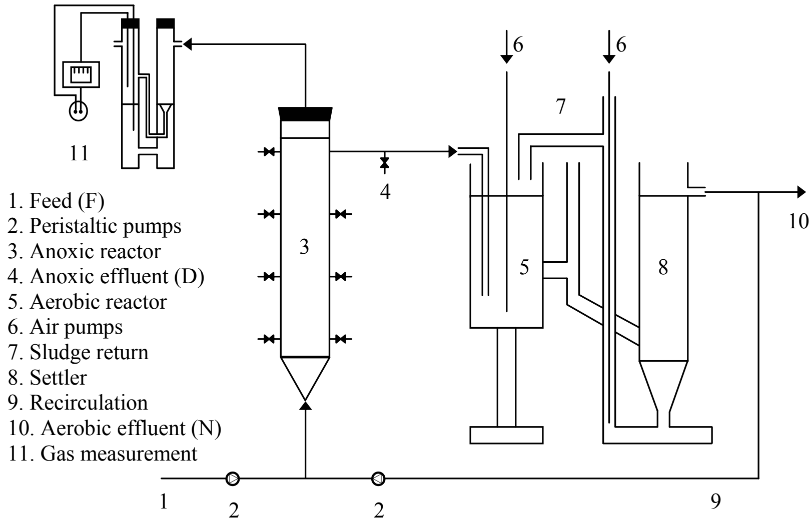

Figure 1
Scheme of the pre-denitrification system

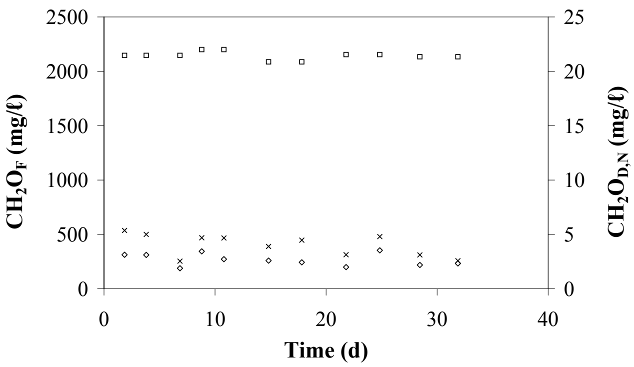

Figure 2
FFormaldehyde concentration in the feed (□) and in the effluent of the anoxic (x) and aerobic (◊) reactors

Laboratory-scale reactor

The pre-denitrification system consisted of an anoxic upflow sludge blanket reactor (0.8 ℓ) and an aerobic activated sludge reactor (1.8 ℓ) (Fig. 1). The system was provided with a liquid displacement biogas measurement device (Veiga et al., 1990). The feed to the anoxic reactor was supplied by a peristaltic pump and the effluent of this reactor was continuously fed to the aerobic reactor. Diffusers, located at the bottom of the aerobic reactor, supplied air from an air pump and maintained complete mixing. The water was separated from the sludge in the settler and the sludge was recycled intermittently to the aeration basin. Part of the effluent of the aerobic unit was recirculated to the anoxic reactor by another peristaltic pump. The reactors were inoculated with sludge from the full-scale wastewater treatment plant of an aminoplastic resin-producing factory. Assays were performed in a thermostatic chamber at 20ºC.

The concentrations of the different parameters in the feed (F) and in the effluent of the anoxic (D) and aerobic reactors (N) are presented in the figures. Mass balances with regard to the feed were performed in order to calculate the removal percentages of the different compounds in the global system and in each individual unit.

Results and discussion

The removal of organic matter and nitrogen compounds was determined in the biological treatment of wastewater with high formaldehyde and formic acid concentrations. For this study, the system was fed with wastewater obtained from the industry mentioned above, the composition of which is shown in Table 1. The feed was supplied by a peristaltic pump at a flow rate of 0.33 ℓ/d, with a recirculation from the aerobic to the anoxic unit at a rate of 3.6 ℓ/d. The total hydraulic retention time was 7.9 d, corresponding to 2.4 d in the anoxic reactor and 5.5 d in the aerobic unit. The anoxic and aerobic reactors were inoculated with 7.5 and 2.7 g VSS/ℓ, respectively.

Biological removal of organic matter

The wastewater used in this study had a high formaldehyde concentration. The evolution of this compound in the feed and in the effluent of the anoxic and aerobic reactors is shown in Fig. 2. The formaldehyde concentration in the feed varied between 2 087.0 and 2 200.0 mg/ℓ, being the organic loading rate around 0.11 kg C/m^3·d. During the operation period its concentration in the effluent was always lower than 3.5 mg/ℓ, corresponding to a mean formaldehyde removal of 99.9%. In spite of the presence of other carbon sources in the wastewater (Table 1), formaldehyde was removed efficiently. This compound was almost completely removed in the anoxic reactor (99.1%). Therefore, the anoxic removal of high formaldehyde concentrations is possible in the presence of other organic compounds. This corroborates the results obtained by our group in studies on formaldehyde biodegradation in an anoxic reactor in the presence of urea (Eiroa et al., 2004a) or phenol (Eiroa et al., 2005) and found in the literature (Campos et al., 2003).

One of the other organic compounds present in the wastewater at high concentrations was formic acid. Its concentration in the feed ranged between 1 384.6 and 1 513.9 mg/ℓ (Fig. 3), corresponding to an organic loading rate of around 0.05 kg C/m^3·d. The average concentration in the effluent was 3.6 mg/ℓ, being the mean formic acid removal of 99.7%. Formic acid removal also took place mainly in the anoxic reactor (98.8%).

The TOC in the feed and in the effluent of the anoxic and aerobic reactors is shown in Fig. 4. The TOC values in the feed were between 1 423.0 and 1 599.5 mg/ℓ, corresponding to an organic loading rate of about 0.20 kg TOC/m^3·d. The efficiency of organic matter removal was high, around 92.0%, obtaining TOC values in the effluent between 94.0 and 141.4 mg/ℓ. The

Available on website **http://www.wrc.org.za**
ISSN 0378-4738 = Water SA Vol. 32 No. 1 January 2006
ISSN 1816-7950 = Water SA (on-line)

organic matter was almost completely removed in the anoxic reactor, although a small amount was eliminated in the aerobic reactor. Consequently, competition between nitrifying and heterotrophic bacteria could exist in the aerobic unit since the presence of organic matter stimulates the growth of heterotrophic bacteria, which compete with nitrifying bacteria for their basic substrates, ammonium and oxygen (Hanaki et al., 1990; Eiroa et al., 2004b).

Since the sum of formaldehyde and formic acid concentrations did not correspond to the amount of organic matter measured, it was concluded that the wastewater contained other organic compounds in a lower proportion. Therefore, the potential presence of methanol and phenol was investigated. The presence of methanol was confirmed and its concentration in the feed varied between 240.0 and 264.1 mg/ℓ. It was completely removed during the operational period. Phenol was also detected in the wastewater but at very low concentrations (between 0.9 and 2.0 mg/ℓ). It was also completely removed.

Biological removal of nitrogen compounds

The removal of nitrogen compounds was also studied in the wastewater with high formaldehyde and formic acid concentrations. The TKN concentration in the feed ranged between 467.8 and 492.3 mg/ℓ, reaching values in the effluent between 82.6 and 137.6 mg/ℓ (Fig. 5). The applied nitrogen loading rate was around 0.06 kg TKN/m^3·d, being the percentage of TKN removal of 76.7%. Most of the TKN was present in the wastewater as organic nitrogen since the ammonium concentration was between 11.3 and 19.2 mg N/ℓ (Fig. 5). As a result, the TKN removal depended on the efficiency of the hydrolysis of organic nitrogen.

The ammonium and nitrate concentrations in the feed were very low, with a mean value of 14.9 and 0.6 mg N/ℓ, respectively. In the aerobic reactor, the ammonium from the anoxic reactor was nitrified and assimilated by micro-organisms, being the ammonium removal around 99.8%. Meanwhile, the denitrification of the nitrate recirculated from the aerobic unit took place in the anoxic reactor, obtaining removal efficiencies above 99.9%.

In pre-denitrification systems an important parameter to take into account is the recirculation ratio. In these systems high recirculation ratios are generally used to achieve high nitrogen removal percentages. The maximum removal efficiency for each ratio can be calculated theoretically assuming 100% removal in the anoxic and aerobic reactors. In this study the recirculation ratio was 10.9 which is higher than that generally found in the literature (Morgan-Sagastume et al., 1994; Cheng et al., 1996). For this ratio the maximum removal efficiency would be 91.6%; however the TKN removal was 76.7%. The limiting step of the TKN removal was organic nitrogen hydrolysis.

The composition of the biogas produced in the anoxic system was periodically analysed, obtaining percentages of nitrogen, carbon dioxide and methane between 55.8 and 78.0, 3.0 and 7.2 and 12.2 and 33.0%, respectively. From these results it is clear that two processes, denitrification and methanogenesis occurred simultaneously in the same unit. Previous studies indicate that if there are enough carbon sources in the influent, both processes can occur in the same system. In such case, methanogenesis starts once denitrification has been completed and the surplus carbon source is then effectively converted to methane and subsequently a low effluent COD concentration is reached (Chen and Lin, 1993; Her and Huang, 1995). In this study the mean TOC/TKN ratio was 3.2.

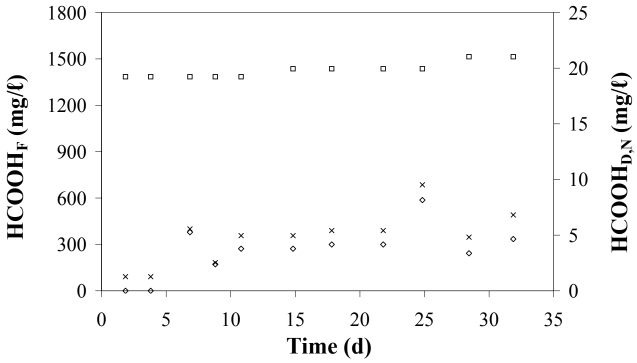

Figure 3
Formic acid concentration in the feed (□) and in the effluent of the anoxic (x) and aerobic (◊) reactors

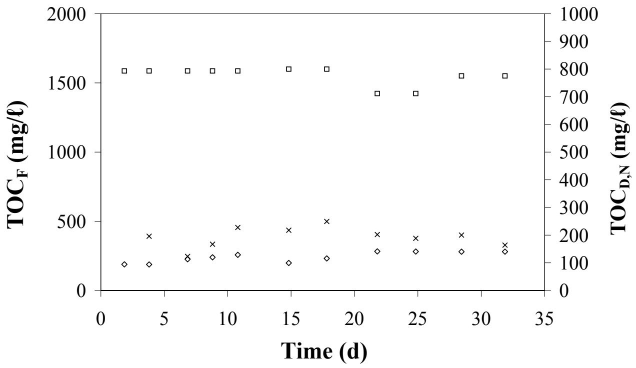

Figure 4
TOC in the feed (□) and in the effluent of the anoxic (x) and aerobic (◊) reactors

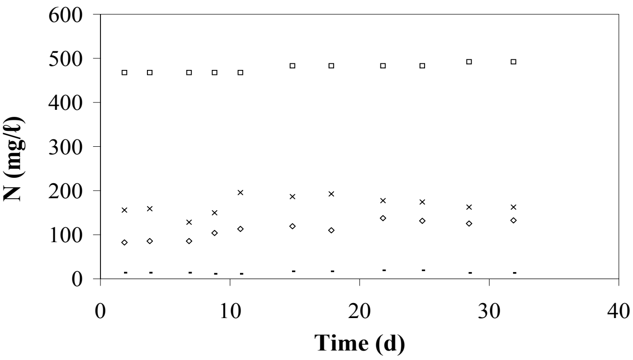

Figure 5
TKN (□) and ammonium (-) in the feed and TKN in the effluent of the anoxic (x) and aerobic (◊) reactors

During the study sludge with good settling properties and a satisfactory effluent with low concentrations of suspended solids, between 0.002 and 0.048 g VSS/ℓ, were obtained.

Conclusions

The formaldehyde concentration in the feed varied between 2 087.0 and 2 200.0 mg/ℓ, being the mean removal of 99.9%. The mean efficiency of formic acid removal was 99.7%, ranging its concentration in the feed between 1 384.6 and 1 513.9 mg/ℓ. The TOC values in the feed were between 1 423.0 and 1 599.5 mg/ℓ, corresponding to an organic loading rate of about 0.20 kg TOC/m^3·d. A high TOC removal was achieved, around 92.0%.

The organic matter was almost completely removed in the anoxic reactor. Therefore, the anoxic removal of high formaldehyde and formic acid concentrations is possible in the presence of other organic compounds.

With regard to nitrogen compounds, the TKN concentration in the feed ranged between 467.8 and 492.3 mg/ℓ. The applied nitrogen loading rate was around 0.06 kg TKN/m^3·d, being the mean percentage of TKN removal of 76.7%. Most of the TKN was present as organic nitrogen since the ammonium concentration was between 11.3 and 19.2 mg N/ℓ. As a result, the TKN removal depended on the efficiency of organic nitrogen hydrolysis.

Acknowledgements

The Spanish Ministry of Science and Technology (project PPQ2002-02882) and the Xunta de Galicia (project PGIDIT-03PXIC10304PN and PGIDIT03AM13E) funded this research.

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