Biological treatment of mixtures of toxic compounds emitted from formaldehyde resin-producing industries

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ABSTRACT. A series of single- and multi-stage bioreactors were used for the removal of hazardous compounds commonly emitted from formaldehyde production in synthetic resin-producing factories, namely formaldehyde, methanol, dimethylether and carbon monoxide. An aerobic sludge obtained from the wastewater treatment facilities of one of these industries was used as biocatalyst, with good results. Also, carbon monoxide removal could be effectively performed by means of an *Oligotropha carboxidovorans* OM5 culture both in batch studies and in a biotrickling filter. A single-stage biotrickling filter was able to remove high concentrations of formaldehyde and methanol, and moderate concentrations of dimethylether. A three-stage system composed of three single bioreactors (BTF-BF-BTF) linked in series could carry on the removal of all four compounds, with elimination efficiencies around 100 % for both formaldehyde and methanol.

1 INTRODUCTION

The production of formaldehyde-based resins has increased widely over the past decades, as their uses in industrial processes keep on expanding. Formaldehyde used as raw material in the production of resins is formed by chemical reaction between methanol and air in a catalytic reactor (Eiroa *et al*., 2004). This process leads to the release of harmful chemicals emitted to the atmosphere. Such waste gases from formaldehyde resin-production industries are composed mainly of methanol, formaldehyde, dimethylether and carbon monoxide. All of them are known to cause different negative effects both on human health and on the environment. Hence, the application of treatment technologies is necessary in most cases.

Some previous works have shown that the removal of both formaldehyde and methanol from waste air can be effectively performed by means of bioreactors (Tautz and Rutenfranz, 1992; Doronina *et al*., 1996; Prado *et al*., 2005). However, hardly any information is available on the biofiltration of compounds as dimethylether and carbon monoxide. Also, the elimination of the complex mixture of the four pollutants has not been studied yet. The present work is aimed first at optimizing the elimination of both

formaldehyde and methanol. The elimination of the other compounds in mixture with them was studied afterwards.

2 MATERIALS AND METHODS

The two different bioreactor-systems shown in Figure 1 were employed during the present work.

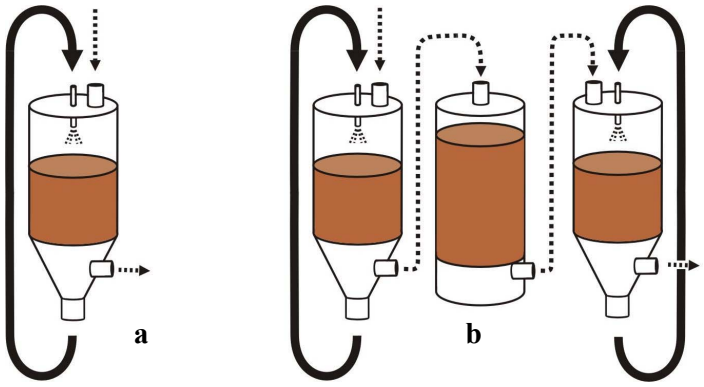

Figure 1. Schemes of the two bioreactor-systems used in the study. (a): biotrickling filter. (b): three-stage bioreactors (BTF-BF-BTF). Solid lines represent the liquid flow. Dotted lines represent the gas flow.

Gas-phase pollutant concentrations were determined by means of a HP-6890 gas chromatograph equipped with both a flame ionization (FID) and a thermal conductivity (TCD) detector. Two GC-columns were connected in series. A 30 m x 0.53 mm HP-PLOT Q column was used to detect formaldehyde, methanol and dimethylether with a FID, and a 15 m x 0.53 mm HP-PLOT Molecular Sieve 5A was used for carbon monoxide determination with a TCD. The conditions used for formaldehyde, methanol and dimethylether detection were described elsewhere (Prado *et al*., 2004a). For carbon monoxide determination, an initial oven temperature of 50 ºC was maintained for 5 minutes, followed by a 20 ºC/min increase during 2 minutes, and a final period of constant temperature at 90 ºC. In both methods, the temperature of the injector and the detector was 150 ºC.

The sludge used as biocatalyst to inoculate the reactors has been described elsewhere (Prado *et al*., 2004b). The nutrient solution employed during the study contained $MgSO_4 \cdot 7H_2O$ (0.12 g/L), KH_2PO_4 (0.25 g/L), $(NH_4)_2SO_4$ (1.18 g/L), NaCl (1.00 g/L), NH_4Cl (0.96 g/L). Vitamins and trace minerals solutions were added as described in Prado *et al*. (2002).

3 RESULTS AND DISCUSSION

3.1 Degradation of the pollutants in batch assays

Preliminary tests aimed at determining the ability of the sludge to eliminate the four compounds were carried out in batch assays. Each vial contained 100 mL sludge with a concentration of 3.5 g VSS/L and 50 mL medium. The vials, with a total liquid volume of 150 mL, were maintained at 30 ºC with continuous 200 rpm shaking, after setting the pH at 7.5. Also, a pure culture of *Oligotropha carboxidovorans* OM5 was tested for

carbon monoxide removal. The conditions were the same as in the studies with the sludge, although the biomass concentration was 0.35 g VSS/L. Figure 2 shows the removal patterns in the batch studies.

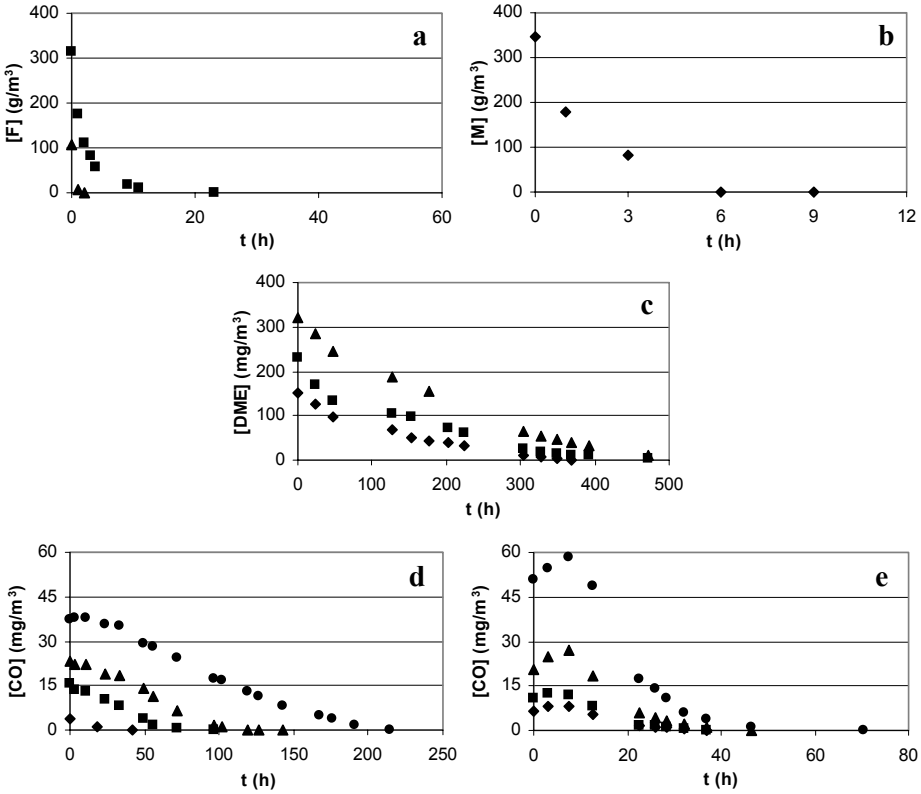

Figure 2. Pollutants removal in batch assays. (a): formaldehyde. (b): methanol. (c): dimethylether. (d): carbon monoxide, sludge. (e): carbon monoxide, *O. carboxidovorans* culture.

As Figure 2 shows, total removal of the pollutants was achieved in all the assays. It is important to observe that the time-scale used in each figure is different. Formaldehyde and methanol proved to be the most easily biodegradable pollutants. This was expected, as both pollutants appear in high concentrations in the sludge, hence, allowing a more intense growth of strains capable of degrading it. Regarding carbon monoxide removal, better results were obtained when using the *O. carboxidovorans* culture as biocatalyst, even though its VSS concentration was 1/10 of the sludge concentration. Batch studies performed with mixtures of the compounds suggest that high concentrations of formaldehyde or methanol inhibit the removal of dimethylether (data not shown).

3.2 Treatment of mixtures of formaldehyde, methanol and dimethylether in a biotrickling filter

In the present experiment, the treatment of mixtures of formaldehyde, methanol and dimethylether was studied in a biotrickling filter packed with 2 L lava rock. The system shown in Figure 1a was operated for eight months, with an empty bed residence time of

72 s. 2 L nutrient solution was recirculated through the bioreactor at a rate of 3.0 L/h. This liquid solution was renewed weekly, after readjusting the pH at 7.5. The system had been employed previously for the treatment of mixtures of formaldehyde and methanol. Hence, a fast start-up was expected for these compounds. Results obtained during the study are presented in Figure 3.

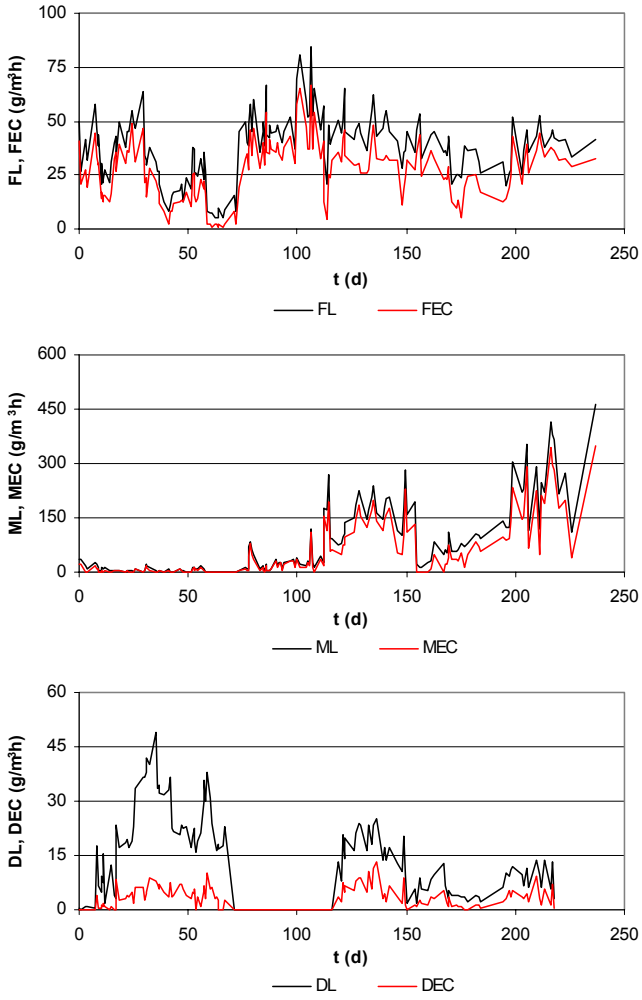

Figure 3. Long-term formaldehyde, methanol and dimethylether removal in a biotrickling filter. FL: formaldehyde load. FEC: formaldehyde elimination capacity. ML: methanol load. MEC: methanol elimination capacity. DL: dimethylether load. DEC: dimethylether elimination capacity.

Figure 3 shows that the degradation of dimethylether began already a few days after starting the study. Dimethylether elimination capacity reached stable values around 10 g/m^3h. On day 73 of operation, the supply of dimethylether was stopped for more than six weeks, in order to study the persistence of the dimethylether-degrading strains in the

bioreactor. The degradation of dimethylether started as soon as it was again supplied. Between days 157 and 178 of operation the nutrient solution recirculation was stopped, with no clear effect on performance. Also, on day 183, the system was reinoculated with 2 L of fresh, non-adapted sludge. This resulted in an immediate decrease in the dimethylether elimination capacity, which remained low for the next 10 days. The removal of formaldehyde and methanol was not affected, as the sludge was adapted to them.

3.3 Carbon monoxide elimination by Oligotropha carboxidovorans OM5 in a biotrickling filter

Preliminary studies indicated that carbon monoxide was hardly degraded in bioreactors fed a mixture of all four pollutants. Therefore, a system similar to the one used in the previous study (Figure 1a), packed with 2 L perlite, was employed for six weeks to test the removal of carbon monoxide alone. The empty bed retention time was 800 s. 2 L of a pure culture of *O. carboxidovorans* OM5, with a concentration around 0.35 g VSS/L, was continuously recirculated at a rate of 7.3 L/h. This culture was renewed weekly. No carbon monoxide elimination was observed during the first month of operation (data not shown). After this start-up phase, carbon monoxide elimination capacity started to increase gradually (Figure 4), reaching maximum values close to 0.4 g/m^{3}h. Seemingly, both the low biomass content of the filter bed and mass transfer limitation played an important role in the performance of the system. Fluctuations of the pH value were observed and did presumably also affect the reactor´s performance.

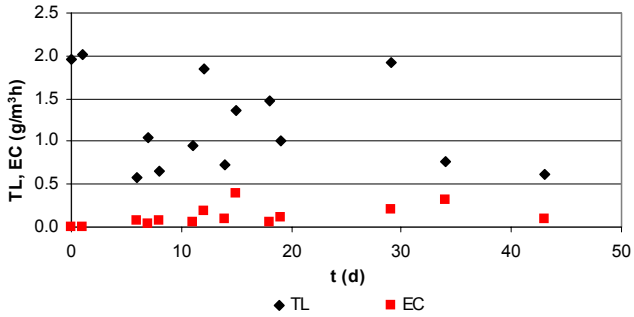

Figure 4. Carbon monoxide elimination in a biotrickling filter (start-up phase data not shown). TL: toxic load; EC: elimination capacity.

3.4 Treatment of waste gas containing mixtures of formaldehyde, methanol, dimethylether and carbon monoxide in a three-stage bioreactor

Previous experiments performed in our laboratory have shown that, for the removal of high loads of formaldehyde and methanol, biotrickling filters show a number of advantages compared to conventional biofilters. However, elimination efficiencies close to 100 % are hardly achieved, as a consequence of mass transfer limitation. Such phenomenon is less pronounced in conventional biofilters, although critical loads in these systems are commonly lower. Therefore, a two-stage bioreactor was designed and operated. It was composed of a biotrickling filter and a conventional biofilter connected in series. Each reactor was packed with 1 L lava rock. This system was employed for

the removal of mixtures of high loads of formaldehyde and methanol during eleven months with very good results. Afterwards, a third stage consisting of a biotrickling filter packed with 2 L perlite was connected to this system. This reactor had been inoculated with a culture of *O. carboxidovorans* and employed for the elimination of low loads of carbon monoxide for six weeks (see previous section). A scheme of the system is shown in Figure 1b. The total EBRT of the reactors in series was 4 min. Results, though preliminary yet, clearly show that significant quantities of dimethylether and carbon monoxide can be removed by means of this system, while formaldehyde and methanol are completely degraded.

4 CONCLUSIONS

The results presented herein show that the elimination of gas-phase pollutants emitted from formaldehyde resin-producing factories can be performed, with high efficiencies, by means of biological technologies. The sludge present in the wastewater treatment facilities of such industries usually contains measurable amounts of the main pollutants as well as microbial strains capable of biodegrading them. This sludge can be used as inoculum in biological systems, with good results. The present work shows that formaldehyde and methanol are the most easily biodegradable of the four pollutants commonly present in the mixture. Elimination efficiencies around 100 % can be achieved for high formaldehyde and methanol loads when using a multi-stage system. On the other hand, dimethylether and carbon monoxide were only moderately removed. Carbon monoxide elimination can be improved by seeding the reactor with a culture of *Oligotropha carboxidovorans*. The biodegradation of carbon monoxide is presently being studied in a biotrickling filter with constant pH in order to optimize this removal.

5 ACKNOWLEDGEMENTS

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