Biological treatment of mixtures of toluene and n-hexane vapours in a hollow fibre membrane bioreactor

Kang Zhao, Guangli Xiu*, Lihang Xu, Danian Zhang, Xiaofeng Zhang and Marc A. Deshusses*

*State Environmental Protection Key Lab of Environmental Risk Assessment and Control of Chemical Processes, East China University of Science and Technology, Shanghai 200237, P.R. China; †Department of Civil and Environmental Engineering, Duke University, Durham, North Carolina 27708, USA

(Received 11 February 2010; Accepted 7 July 2010)

Membrane bioreactors are gaining interest for the control of contaminated air streams. In this study, the removal of toluene and n-hexane vapours in a hollow fibre membrane bioreactor (HFMB) was investigated. The focus was on quantifying the possible interactions occurring during the simultaneous biotreatment of the two volatile pollutants. Two lab-scale units fitted with microporous polypropylene hollow fibre membranes were connected in series and inoculated with activated sludge. Contaminated air was passed through the lumen at gas residence times ranging from 2.3 to 9.4 s while a pollutant-degrading biofilm developed on the shell side of the fibres. When toluene was treated alone, very high elimination capacities (up to 750 g m$^{-3}$ h$^{-1}$ based on lumen volume, or 1.25 g m$^{-2}$ h$^{-1}$ when normalized by the hollow fibre membrane area) were reached. When toluene and hexane were treated simultaneously, toluene biodegradation was partially inhibited by n-hexane, resulting in lower toluene removal rates. On the other hand, hexane removal was only marginally affected by the presence of toluene and was degraded at very high rates (upwards of 440 g m$^{-3}$ h$^{-1}$ or 0.73 g m$^{-2}$ h$^{-1}$ without breakthrough). Overall, this study demonstrates that mixtures of toluene and n-hexane vapours can be effectively removed in hollow fibre membrane bioreactors and that complex biological interactions may affect one or more of the pollutants undergoing treatment in gas-phase membrane bioreactors.

Keywords: membrane bioreactor; biofilter; air pollution control; toluene; n-hexane; VOC mixtures

Introduction

Volatile organic compounds (VOCs) are common contaminants widely found in point-source and fugitive air emissions of wastewater treatment plants, processing facilities, paint shops and a wide range of industries. The impacts of VOCs on human health range from odour nuisance to chronic and acute toxic effects. Emissions of VOCs also contribute to local and global air pollution. These factors and widespread environmental regulations motivated engineers to develop a range of techniques for air pollution control. Control methods for VOCs include thermal or catalytic oxidation, condensation, adsorption and biological treatment. Because of simple designs, low capital and operating cost, low energy requirement and the absence of secondary pollution, biological treatment methods are more and more popular for the control of VOCs and odours [1,2]. Indeed, biofilters and biotrickling filters are increasingly deployed in full-scale systems.

A newer development in air biotreatment is the use of membrane bioreactors, which remains experimental at this time [3–5]. In these bioreactors, the air undergoing treatment and the pollutant-degrading culture are separated by a gas-permeable membrane. The pollutant diffuses through, or is transferred across, the membrane and is degraded by microorganisms, generally forming a biofilm on the other side of the membrane. The membrane material can be dense, microporous, porous or composite, and in the form of hollow fibre modules or flat sheets [6–9]. For membranes made of dense material, solute diffusion through the membrane material is required, which can add significant mass transfer resistance, depending on the membrane material and its thickness [6–9]. Microporous hydrophobic membranes are the most frequently used membranes in gas separation applications because they provide high gas permeability, while preventing transport of water across the membrane [5]. Porous membranes generally have a well-defined pore structure, with either highly connected, non-connected or straight pores depending on the membrane material and membrane synthesis method. Composite membranes are made of a porous support layer such as polyvinylidene fluoride (PVDF) or...
polyacrylonitrile (PAN) and coated with a thin layer (usually between 0.5 µm and 20 µm thick) of a dense material such as polydimethylsiloxane (PDMS). They combine the best characteristics of porous materials (better mass transfer) and a dense layer (better selectivity) [5–9]. In membrane bioreactors fitted with composite membranes, biofilm grows at the surface of the dense layer which prevents microbial growth through, and plugging of, the membrane [5]. Both flat sheets and hollow fibre bundle geometries have been used.

The interest in membrane bioreactors for air pollution control lies in the fact that the pollutant-degrading culture can be isolated from the gas undergoing treatment. This provides opportunities for optimum control of the culture conditions, allows maintenance of a pure culture if needed, and is beneficial in applications where direct contact of the air being treated with microorganisms is undesirable [5]. The configuration of membrane bioreactors also allows a better control of excess biomass growth and can potentially be used to alleviate plugging issues observed in highly loaded biofiltration filters [10]. Membrane bioreactors can be configured as hollow fibre membrane bioreactors (HFMBs) with very large membrane specific areas (500–20,000 m² m⁻³) and can be built with membranes that favour the transport of hydrophobic compounds. For example, dichloroethane (DCE) vapours were removed in a membrane bioreactor made of a spiral-wound silicone rubber module coupled with a stirred tank bioreactor [11]. At a gas flow rate of 770 mL min⁻¹, corresponding to a gas residence time of 80–160 s, in the membrane module and at an inlet DCE concentration of 0.65 g m⁻³, 91% of the influent DCE was removed and biodegraded. This corresponds to a volumetric mass transfer flux almost three times higher than in conventional biofiltration.

Much of the research in this field has been conducted with toluene as a model pollutant and is a good benchmark for comparison. A hydrophobic polyethylene microfiltration hollow fibre membrane bioreactor was operated for over 150 days with sustained removal of 86–97% of the toluene influent loadings of 35–180 g m⁻³ h⁻¹ (calculated based on the lumen volume) [12]. A very high specific activity of the toluene-degrading culture was observed, although oxygen limitation was detected when the toluene inlet concentration was high. The ability to work with a monoculture was exploited by Kumar et al. [13]. They deployed Burkholderia vietnamiensis G4 in a membrane bioreactor fitted with a composite membrane of porous PAN, used as a support, and a very thin (0.3 µm thick), dense layer of PDMS. Toluene removal efficiencies ranged from 78% to 99% and elimination capacities (ECs), based on lumen volume, of 175–600 g m⁻³ h⁻¹ were observed [13]. Maintaining a pure culture over time proved to be a challenge, but did not seem to affect the performance of the bioreactor. Other research focused on the removal of dimethyl sulphide from waste air using a composite membrane bioreactor [14]. The gas residence time was varied from 8 to 24 s. The bioreactor was able to rapidly adapt to changing conditions, and very high ECs were observed (200 g m⁻³ h⁻¹ based on the lumen volume at a removal of 74%). Several studies also addressed the fate and transport of pollutants in HFMBs and conceptual models were developed, see for example [15,16]. Despite much progress accomplished in gas-phase membrane bioreactors over the past decade, the removal of mixtures of pollutants has not been greatly investigated in these bioreactors. A few reports on the treatment of pollutant mixtures using gas-phase membrane bioreactors were concerned with the treatment of benzene, toluene, ethylbenzene and xylene (BTEX) vapours [17,18], or dimethyl sulphide and toluene [19]. Even so, these studies did not focus on specific issues, such as cross-inhibition during biodegradation [20,21], that can arise when mixtures of pollutants are treated.

Thus, the objective of this study was to investigate the biodegradation of mixtures of toluene and n-hexane vapours in a hollow fibre membrane bioreactor (HFMB) and to quantify possible interactions occurring during the treatment of these binary mixtures.

**Materials and methods**

**Hollow fibre membrane bioreactor**

The bioreactor used in this study consisted of two HFMBs made of glass vessels (each 23 cm long by 5.0 cm internal diameter) fitted each with 75 hydrophobic, microporous polypropylene membrane fibres potted into epoxy resin fittings at both ends. The hollow fibres were synthesized via thermally induced phase separation following methods reported earlier [22,23]. The fibres had an inner diameter of 1.0 mm, an outer diameter of 1.5 mm, and the effective length of the fibres was 20 cm, resulting in a total lumen volume of 11.8 cm³ and a total outer surface area of 707 cm². The specific surface area of the membrane was 6000 m² m⁻³. The membrane pore size was about 0.2 µm (determined by liquid permeation [24]). Two membrane modules were connected in series (see setup in Figure 1).

For the generation of the synthetic waste air, a metered stream of oil-free compressed air was passed through a flask in which n-hexane and toluene were allowed to evaporate as needed. This concentrated hexane and toluene vapour was diluted to the desired concentration with oil-free compressed air. The synthetic waste air stream was delivered to the lumen of first HFMB, and the exhaust of the first bioreactor was
fed to the second HFMB. The air flow rates tested were 0.15, 0.30, 0.45 and 0.60 L min\(^{-1}\), corresponding to a total gas residence time (for the two units in series) of 9.4, 4.7, 3.1 and 2.3 s, respectively. The inlet VOC concentration ranged from 30 to 1100 mg m\(^{-3}\). Selected experiments consisted of fixing the toluene inlet concentration and varying the n-hexane concentration, and vice versa. A nutrient solution (NH\(_4\)Cl 25 mg L\(^{-1}\), KH\(_2\)PO\(_4\) 8.5 mg L\(^{-1}\), K\(_2\)HPO\(_4\) 217.5 mg L\(^{-1}\), CaCl\(_2\) 27.5 mg L\(^{-1}\), MgSO\(_4\)·7H\(_2\)O 22.5 mg L\(^{-1}\), FeCl\(_2\) 0.25 mg L\(^{-1}\), trace elements 1 mL L\(^{-1}\)) \([25]\) was recirculated from a 20 L tank at a rate of 1 L min\(^{-1}\) (each HFMB) to the shell side of the fibres, and fresh nutrient was added at a rate of 2 L d\(^{-1}\). There was no need to aerate the liquid, as oxygen was supplied by the contaminated air; throughout the experiments the dissolved oxygen was measured by a dissolved oxygen analyser (JPBJ-608, Shanghai Rex Instrument Factory, China) and remained at 7.0–7.5 mg L\(^{-1}\). The pH was maintained at 7.0 by adding a NaHCO\(_3\) solution to the nutrient tanks as needed.

The two HFMBs were initially inoculated with an enrichment culture derived from activated sludge from a wastewater treatment plant in Shanghai, China. Pollutant-degrading organisms were enriched in mineral medium (see above for the composition) and supplied with toluene and n-hexane as sole carbon and energy source. Several transfers were made over a period of three weeks. At start-up, about 1 L of enrichment culture (4 g dry biomass L\(^{-1}\)) was added to the liquid tank of the HFMBs. The start-up lasted about 35 days after which the treatment performance reached a pseudo-steady state. In this study, steady state was defined as a condition in which various measured parameters did not vary over two days. All experiments were conducted at room temperature (20–24 °C).

**Analytical methods**

Hexane and toluene were sampled by taking 100 µL air samples from the inlet or outlet port of the HFMBs using a gas-tight syringe followed by manual injection into a gas chromatograph (Tianmei 7890II, Shanghai, China) equipped with a 2 m PEG-20M packed column and a flame ionization detector. The column temperature was 60 °C, injector temperature was 110 °C and detector temperature was 150 °C. The flow rate of carrier gas was 15 mL min\(^{-1}\), the flow rate of hydrogen was 33 mL min\(^{-1}\) and that of the make-up air was 150 mL min\(^{-1}\). Toluene in liquid samples were quantified using a gas chromatograph (Agilent 6890, Wilmington, DE, US) fitted with a 30 m HP-5 capillary column, an auto sampler and a flame ionization detector. Injector temperature was 180 °C, detector temperature was 250 °C, and column temperature was ramped from 40 °C to 130 °C at 60 °C min\(^{-1}\). The flow rate of carrier gas was 5.6 mL min\(^{-1}\), the flow rate of hydrogen was 40 mL min\(^{-1}\) and the flow rate of air was 400 mL min\(^{-1}\). The liquid sample (10 mL) was placed in a 20 mL vial fitted with a gas-tight cap, and gas/liquid was allowed to equilibrate for 20 min at 40 °C. One millilitre was taken from the headspace of the sample and injected into the gas chromatograph. Liquid and gas standards were used for calibration. An optical microscope (Eclipse 80i Nikon, Tokyo, Japan) was used for bacterial observation.
Results and discussion

Start-up of the reactor

Before start-up of the HFMB, adsorption tests were carried out on pristine hollow fibres, and abiotic losses for the HFMB were determined. These experiments (not shown) demonstrated that abiotic losses were negligible compared with the loading imposed on the HFMB. After inoculating the enrichment culture into the HFMB, only toluene was fed to the bioreactor at an inlet concentration of about 400 mg m$^{-3}$, for three weeks. A noticeable removal of toluene was observed on the sixth day (Figure 2). Over the 37 days of start-up, the toluene removal efficiency increased progressively to nearly 70%. At the same time, a brown biofilm became visible on the outer surface of the hollow fibre membrane. Dissolved oxygen in the recycled liquid was 7.4 mg L$^{-1}$ in the effluent of the first module and 7.6 mg L$^{-1}$ in the effluent of the second module. This indicated that there was no oxygen limitation. Observation of the culture in the first three weeks revealed enrichment of a mixture of cocci and bacilli, which evolved over time to become a majority of bacilli. No further microbiological investigations were conducted.

HFMB performance removing toluene as a single pollutant

After operation for 37 days, the performance of the HFMB for the removal of toluene as a single pollutant was assessed. This experiment lasted about 60 days. Steady-state toluene removal efficiency and EC are shown for four different gas residence times in Figures 3 and 4, respectively. The EC is defined as the mass of pollutant degraded hourly per volume of bioreactor. Here, the volume basis used for the EC calculation is the lumen volume. As is usual for gas-phase bioreactors, the removal efficiency decreased and EC increased as the inlet concentration was increased. For a constant inlet concentration, the removal decreased as the residence time decreased; at a given loading, the EC was independent of the concentration, as shown in Figure 4. This indicates that biological degradation was rate limiting. Depending on the conditions, high removal (mainly at long residence times and low inlet concentrations) or high elimination capacities (mainly at high concentrations and short residence time) of toluene were observed.

During these experiments, the toluene concentration in the liquid was measured; it was found to be below 0.87 mg L$^{-1}$ (at a gas retention time of 5.5 s and an inlet gas concentration of 3 g m$^{-3}$). This indicates that only a small fraction of the toluene removed was found in the liquid and that toluene losses from recycling liquid to the air could be neglected. Also, the mass of toluene...
leaving the system via the purge was less than 0.2% of the mass of toluene fed to the system.

The toluene ECs obtained in this research ranged from 30 to 750 g m$^{-3}$ h$^{-1}$, calculated based on the lumen volume, or 0.05 to 1.25 g m$^{-2}$ h$^{-1}$ when normalized by the outer surface area of the hollow fibres. For performance comparison, using the EC calculated on the basis of the lumen volume of the fibre area is warranted as gas-to-liquid volume ratios vary greatly between various reactors. For indication, because of the low fibre volume to reactor volume, the pollutant EC was 0.0173 to 0.433 g m$^{-3}$ h$^{-1}$ when calculated on the basis of the total bioreactor volume (including the liquid recycle tank).

For studies conducted with similar conditions, the highest toluene volumetric EC was 2520 g m$^{-3}$ h$^{-1}$ obtained by Ergas et al. using a bioreactor fitted with polypropylene hollow fibre membranes inoculated with activated sludge [26]. Kumar et al. found that the toluene EC of a composite membrane bioreactor inoculated with activated sludge ranged between 75 and 609 g m$^{-3}$ h$^{-1}$ [27] depending on the conditions. The same bioreactor reached a maximum EC of 600 g m$^{-3}$ h$^{-1}$ at a loading rate of 725 g m$^{-3}$ h$^{-1}$ after inoculation with Burkholderia vietnamiensis G4 [13]. Parvatiyar et al. [4] studied biodegradation of relatively high concentrations toluene in a membrane bioreactor, at residence times ranging from 16 to 32 s, and ECs between 38 and 391 g m$^{-3}$ h$^{-1}$ were observed. Kim and Kim [28] used a hydrophobic polyethylene HFMB inoculated with Pseudomonas putida to remove toluene vapours and showed consistent toluene removal efficiencies of 86% to 97% at loadings of 35 to 180 g m$^{-3}$ h$^{-1}$ for over 150 days [12], whereas Song et al. reached toluene elimination rates of up to 415 g m$^{-3}$ h$^{-1}$. Jacobs et al. [29] used a flat composite membrane bioreactor and achieved a maximum toluene EC of 0.79 g m$^{-2}$ h$^{-1}$, which converts to 397 g m$^{-3}$ h$^{-1}$ at a gas residence time 24 s. They explained their high EC by the high capacity of Pseudomonas putida TVA8 to metabolize toluene and its good adhesion properties to the PDMS film. Finally, Van Langenhove et al. [19] reached a toluene EC$_{\text{max}}$ of 396 g m$^{-3}$ h$^{-1}$ or 0.8 g m$^{-2}$ h$^{-1}$ per unit of membrane area. Thus, the performance of the HFMB in the present research compares favourably with the prior reports of other research groups.

HFMB performance removing toluene and n-hexane binary gas

Simultaneous removal of toluene and hexane vapours was investigated next. This experiment was completed in about 45 days. Good and steady removal of n-hexane was observed about one week after it was added into the system (data not shown). The gas residence time was kept constant at 9.4 s, and either the hexane or the toluene inlet concentration was kept constant while the inlet concentration of the other pollutant was varied. For all conditions tested, excellent treatment of toluene and hexane was observed demonstrating that these two compounds could be simultaneously removed in the HFMB.

Detailed results are reported in Figure 5 and 6. Examination of Figure 5a reveals that hexane has a detrimental effect on the removal of toluene. For example, for the two HFMB modules in series, breakthrough of toluene was not detected until the inlet toluene concentration exceeded 600 mg m$^{-3}$ when toluene was treated as a single pollutant, whereas it occurred at an inlet concentration of 450 mg m$^{-3}$ in the presence of 550 mg m$^{-3}$ of hexane. Overall, the toluene removal was roughly 5% to 10% lower when hexane was present.
The removal of hexane during these experiments is reported in Figure 5b. The removal rate of hexane was significant and corresponded to volumetric and surface ECs ranging from about 160 to 220 g m\(^{-3}\) h\(^{-1}\) and 0.27 to 0.37 g m\(^{-2}\) h\(^{-1}\), respectively. Although analysis of the trends is made difficult by the scattering of the data, it appears that hexane removal was only moderately affected by the increasing concentration of toluene.

The results of the symmetrical experiment, i.e. the determination of the removal of various concentrations of hexane at a fixed concentration of toluene, are reported in Figure 6. A behaviour consistent with that reported in Figures 5a and 5b was observed. First, there was a quasi-insignificant effect of the presence of toluene on hexane removal (Figure 6a). At all concentrations tested, hexane was extremely well removed. No breakthrough occurred after the second module, even at the highest concentration tested. This corresponds to an EC of 440 g m\(^{-3}\) h\(^{-1}\), or 0.73 g m\(^{-2}\) h\(^{-1}\) when normalized by the surface of the membrane. This surface-normalized EC is in the upper range of the many values reported in the review by Kumar et al. [5]. Interestingly, the removal of hexane was virtually unaffected by the presence of 450 mg m\(^{-3}\) toluene. This result corroborates the results of Figure 5b, where little effect of varying toluene inlet was observed on hexane removal. Secondly, examination of the concentrations of toluene after the first module (Figure 6b) reveals that, consistent with the results of Figure 5a, the removal of toluene was affected by the presence of hexane and the effect increased with increasing concentration of hexane. Even so, removal of toluene was complete over the entire system even at the highest hexane concentration, since the bioreactor had excess biotreatment capacity in the second HFMD module.

The observation that some competition occurred during the biodegradation of hexane and toluene differs from the results obtained by Attaway et al. [18], who treated mixtures of BTEX vapours in two membrane bioreactors. Attaway et al. found that there was no preferential removal of the individual BTEX components. The difference between the two studies may be due to the nature of the pollutants treated and the nature of the cultures that were enriched in the membrane bioreactors, or to differences in the rate-limiting step between the two systems. It is difficult to speculate why toluene removal was affected by the presence of hexane, whereas hexane removal was virtually unaffected by the presence of toluene in the present study. Some in-depth biokinetic determinations would be needed to understand the fundamental mechanisms of this complex interaction.

Conclusions

This study demonstrated that mixtures of toluene and n-hexane vapours can be effectively removed in hollow fibre membrane bioreactors. When toluene was treated alone, very high elimination capacities (up to 750 g m\(^{-3}\) h\(^{-1}\) based on lumen volume) were reached. When toluene and hexane were treated simultaneously, toluene biodegradation was partially inhibited by n-hexane resulting in lower toluene removal rates. On the other hand, hexane removal was only marginally affected by the presence of toluene. This behaviour illustrates the complex interaction that can occur during the biodegradation of mixtures of pollutant that are degraded by essentially the same bacteria. Overall, the study adds additional evidence of the promising possibilities of hollow fibre membrane bioreactors for the treatment of contaminated air streams.
References


