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PLEASE SCROLL DOWN FOR ARTICLE

# Treatment of mixtures of toluene and *n*-propanol vapours in a compost–woodchip-based biofilter

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The present work describes the biofiltration of mixture of *n*-propanol (as a model hydrophilic volatile organic compound (VOC)) and toluene (as a model hydrophobic VOC) in a biofilter packed with a compost–woodchip mixture. Initially, the biofilter was fed with toluene vapours at loadings up to $175 \, \mathrm{g \, m^{-3} \, h^{-1}}$ and removal efficiencies of 70%–99% were observed. The biofilter performance when removing mixtures of toluene and *n*-propanol reached elimination capacities of up to $67 \, \mathrm{g_{toluene} \, m^{-3} \, h^{-1}}$ and $85 \, \mathrm{g_{\textit{n}-propanol} \, m^{-3} \, h^{-1}}$ with removal efficiencies of 70%–100% for toluene and essentially 100% for *n*-propanol. The presence of high *n*-propanol loading negatively affected the toluene removal; however, *n*-propanol removal was not affected by the presence of toluene and was effectively removed in the biofilter despite high toluene loadings. A model for toluene and *n*-propanol biofiltration could predict the cross-inhibition effect of *n*-propanol on toluene removal.

**Keywords:** biofiltration; compost–woodchip; toluene; *n*-propanol; dynamic modelling; kinetic parameter

## Nomenclature

| | |
|---|---|
| $a_s$ | Biofilm surface area per unit volume of the biofilter, $\mathrm{m^2 \, m^{-3}}$ |
| $C_t$ | Concentration of toluene in the air stream, $\mathrm{g \, m^{-3}}$ |
| $C_p$ | Concentration of propanol in the air stream, $\mathrm{g \, m^{-3}}$ |
| $C_{ti}$ | Concentration of toluene in the inlet air stream, $\mathrm{g \, m^{-3}}$ |
| $C_{pi}$ | Concentration of propanol in the inlet air stream, $\mathrm{g \, m^{-3}}$ |
| $D_{et}$ | Effective diffusivity of toluene in the biofilm, $\mathrm{m^2 \, h^{-1}}$ |
| $D_{ep}$ | Effective diffusivity of propanol in the biofilm, $\mathrm{m^2 \, h^{-1}}$ |
| $H$ | Total height of the biofilter packing, m |
| $K_t$ | Half-saturation constant of toluene in Monod kinetics, $\mathrm{g \, m^{-3}}$ |
| $K_p$ | Half-saturation constant of propanol in Monod kinetics, $\mathrm{g \, m^{-3}}$ |
| $K_i$ | Inhibition constant in Monod kinetics, $\mathrm{g \, m^{-3}}$ |
| $m_p$ | Air/biofilm partition coefficient for propanol, dimensionless |
| $m_t$ | Air/biofilm partition coefficient for toluene, dimensionless |
| $S_t$ | Concentration of toluene in the biofilm, $\mathrm{g \, m^{-3}}$ |
| $S_p$ | Concentration of propanol in the biofilm, $\mathrm{g \, m^{-3}}$ |
| $U_g$ | Superficial velocity of air through the biofilter, $\mathrm{m \, s^{-1}}$ |
| $x$ | Depth coordinate in the biofilm, m |
| $X$ | Dry cell density of the biofilm, $\mathrm{kg \, m^{-3}}$ |
| $Y_{x/s}$ | Biomass yield coefficient |
| $S_t$ | Concentration of toluene in the biofilm, $\mathrm{g \, m^{-3}}$ |
| $S_p$ | Concentration of propanol in the biofilm, $\mathrm{g \, m^{-3}}$ |

*Greek letters*

| | |
|---|---|
| $\alpha$ | Coefficient of effect of propanol on toluene removal, dimensionless |
| $\varepsilon$ | Porosity of the filter bed, dimensionless |
| $\mu_{max}$ | Maximum specific growth rate of toluene degraders, $\mathrm{h^{-1}}$ |
| $\delta$ | Biofilm thickness, m |
| $\upsilon_{max}$ | Volumetric maximum growth rate, $\mathrm{g \, m^{-3} \, h^{-1}}$ |

## 1. Introduction

Mixtures of volatile organic compounds (VOCs) are emitted from a wide range of industries, such as chemical, petrochemical, pharmaceutical, pulp paper mills, printing and paint workshops, etc. Biofiltration is an effective and relatively inexpensive technology for the control of dilute VOC vapours in waste air [1–4]. A biofilter consists of a biologically active bed through which the contaminated air stream is vented. The pollutants diffuse from the air into a moist biologically active layer (i.e. the biofilm), which develops in the filter bed and in which the pollutants are biodegraded. Treatment of pollutants in biofilters involves a series of steps consisting of absorption, diffusion, adsorption and biodegradation [1,2]. The extent of pollutant biodegradation depends largely on the nature of the pollutant and its concentration in the waste gas, the gas flow rate through the biofilter, the moisture content of

the filter bed, the microbial ecology, nutrient and oxygen availability, temperature and pH [2–5]. Aerobic biodegradation of organic pollutants results in the formation of $CO_2$, $H_2O$ and biomass growth. Initially, biofiltration was developed to treat mostly dilute odorous compounds, but recently biofiltration technology has made great progress and its application has been extended to the treatment of various VOCs [4–8].

The effectiveness of biofilters depends to a large extent on the partition of the compounds undergoing treatment in the liquid layer of the biofilm [9,10]. In petrochemical industries, *n*-propanol and toluene are among the key compounds frequently present in air emissions. Propanol is hydrophilic and easily biodegradable and thus is expected to be readily removed in a biofilter, although very few biofiltration studies report on propanol removal. Toluene, on other hand, is more hydrophobic and will partition less favourably into biofilms; therefore, it should be more difficult to remove in biofilters. Indeed, elimination capacities ranging from 120 to 150 g m$^{-3}$ h$^{-1}$ were observed for propanol in biofilters [10], while elimination capacities reported for toluene usually range from 10 to 40 g m$^{-3}$ h$^{-1}$ [10–12]. However, no study has looked at the biofiltration of mixtures of propanol and toluene, and only a few researchers have investigated the treatment of mixtures of hydrophobic and hydrophilic VOCs, despite the fact that this situation is frequently encountered in industrial emissions.

Thus the objective of the present study was to investigate the treatability of mixtures of toluene and propanol vapours in a biofilter packed with a compost–woodchip media. A model for the biofiltration of mixtures of hydrophilic and hydrophobic VOCs was also presented and validated using *n*-propanol and toluene as model compounds.

## 2. Materials and methods

### 2.1. Experimental setup

#### 2.1.1. Biofilter bench-scale unit

A schematic representation of the bench-scale biofilter system used in this study is shown in Figure 1. The biofilter was fabricated using a cylindrical acrylic pipe of 94 cm in total height and 19.4 cm in internal diameter. The unit had three sampling ports, one each at the top, middle and bottom for taking the samples of bed medium for analysis. Gas sampling ports were located at the bottom and top of the column. The total packed height was 42.5 cm, corresponding to a filter media volume of 12.6 l. The air stream was humidified in a counter current humidifier. The total air flow rate of air was maintained in the range of 5–10 L min$^{-1}$ depending on the experiment, corresponding to empty bed gas retention times (EBRTs) of 94–157 s. These are relatively high EBRTs compared to other studies, but conditions were selected to allow treatment of medium-to-high toluene and *n*-propanol concentrations, which would emphasize possible biokinetic effects. Initially, the biofilter
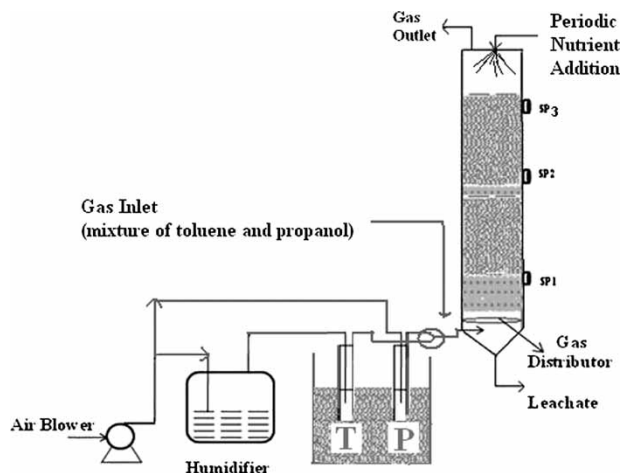


Figure 1. Schematic of the experimental setup (SP$_1$, SP$_2$, SP$_3$: Sampling ports; T: Toluene; P: Propanol); *n*-propanol was only used in experiments involving mixtures of toluene and *n*-propanol.

was fed with toluene vapours generated by vaporization of liquid toluene with a small air stream in an impinger maintained in a constant temperature of 38°C. Later, the biofilter was fed a mixture of toluene and *n*-propanol vapours in air (using two impingers) at a constant flow. Details of the concentrations are provided in Table 1.

#### 2.1.2. Biofilter packing material

Cow-dung compost, having a maturity of five months and C/N ratio of 0.37, was obtained from a dairy plant in Nagpur, India. Woodchips (1–1.5 cm × 1–1.5 cm × 0.1–0.2 mm) collected from a local furniture shop were used as bulking agent with compost in equal volumetric proportion. The bottom 6 mm of the biofilter were packed with woodchips to minimize clogging of the inlet port and ensure proper air distribution. Above this, a mixture of compost and woodchips mixture (1:1 v/v) was packed as the medium for biofiltration. The bed included a 2 cm layer of woodchips in the middle to allow for sampling at half height. Initially, 100 ml mineral medium was added to the packing material, and the damp packing was placed into the biofilter. The mineral medium contained (in g l$^{-1}$ in distilled water) $K_2HPO_4$ − 0.615, $KH_2PO_4$ − 0.385, $MgSO_4$ − $6H_2O$ 0.25, $NH_4NO_3$ − 1, NaCl − 1 and $CaCl_2$ − 0.026; the pH of the medium was adjusted to 7.0 ± 0.1 using dilute HCl (0.1 N). Subsequently, mineral medium (100–300 ml) was added weekly from the top of the biofilter, which allowed one to maintain the moisture content of the packing medium in the range of 60%–70% (wet basis) and provided some nutrient to the process. As in most biofilters, nutrient could have been partially limiting pollutant removal, although this was not investigated. Ample nutrient supply has been linked to excess biomass growth and process instabilities [13]. The initial porosity of the packing material (determined by water logging of a known packing volume) was 60%.

Table 1. Operating conditions of the biofilter during the different experimental phases.

| Phase/days | | | Inlet VOC concentration ($g\,m^{-3}$) | | EBRT (sec) |
|---|---|---|---|---|---|
| | | | Toluene | Propanol | |
| I | Startup period | 0–22 | 0.03–1.87 | – | 148 |
| II | High toluene conc. | 23–33 | 0.44–0.83 | – | 107 |
| III | Reduced EBRT | 34–62 | 0.41–1.61 | – | 75 |
| IV | Steady state condition | 63–127 | 0.24–4.59 | – | 94 |
| V | EBRT increased | 128–134 | 0.24–0.54 | – | 157 |
| VI | Steady state at high toluene conc. | 135–165 | 0.22–4.59 | – | 94 |
| VII | Propanol and toluene co-treatment | 166–200 | 0.03–2.64 | 0.05–3.19 | 94 |

### 2.1.3. Biofilter operation

The biofiltration of toluene with and without *n*-propanol was investigated for a period of more than six months (Table 1). Experiments were carried out to study the effect of toluene concentration, loading and its effect on the behaviour of the biofilter. The toluene loading rate was increased by varying the velocity of the gas entering the biofilter and the toluene inlet concentration. Samples of the packing were periodically withdrawn for analysis and the amount withdrawn was compensated by the addition of fresh packing material. After full characterization of the biofilter with toluene as a single pollutant, *n*-propanol was introduced to the biofilter and the behaviour of the system was studied for 34 days.

### 2.1.4. Growth kinetics and biodegradation experiments

Flask experiments were conducted to study the growth kinetics of the mixed microbial population of the biofilter and determine its VOC degradation parameters. The single substrate degradation kinetics were evaluated at seven different initial concentrations of toluene (20, 40, 60, 80, 100, 150, 200 mg l$^{-1}$) and four different concentrations for *n*-propanol (25, 50, 75, 100 mg l$^{-1}$) prepared in 250 ml Erlenmeyer flasks containing 100 ml mineral medium (see composition above); 10 ml of well-acclimatized and enriched mixed microbial culture was used as inoculum. This mixed microbial consortium was prepared by taking 10 g (wet basis) sample from the biofilter bed and inoculating it in a mineral medium containing toluene or toluene *n*-propanol mixtures as a sole source of carbon. For the kinetic experiments, the culture flasks were incubated at 37°C. The dissolved oxygen (DO) content in these flasks was also measured at regular interval so as to ensure the presence of sufficient oxygen for microbial growth. Samples were withdrawn for analysis at regular time intervals.

### 2.2. Analytical methods

A side gas stream (0.5 l min$^{-1}$ for 10 min) from the inlet and outlet of the biofilter was periodically absorbed in 20 ml methanol, and 5 μl of methanol was injected into a gas chromatograph (GC) for analysis. It was found that this method adequately averaged short-term variations in

the inlet and outlet concentrations and resulted in greater accuracy over direct injection of grab gaseous samples. The GC (Perkin Elmer Clarus-5000, USA) was equipped with a flame ionization detector (FID) and a DB-5 capillary column (0.025 mm × 30 m, fused silica). A temperature program was used to separate toluene and *n*-propanol, and possible metabolites.

Leachate samples were first filtered using 0.2 μm filter and their soluble total organic carbon (TOC) concentrations were measured by a TOC analyser (Thermo Electron Corporation's, Model: TOC 1200). A Shimadzu QP2010 (Tokyo, Japan) gas chromatograph mass spectrometer (GC-MS) model equipped with an AOC 20i auto sampler was also used for analysis of leachate to detect the presence of dissolved VOCs along with possible intermediate products formed during biodegradation. The separation was performed on a 30 m, BP-20 capillary column (SGE, International, and Ringwood, Australia) with 0.25 mm inner diameter (i.d.) and 0.25 μm film thickness. A temperature program (70–220°C) was used to separate the analytes. A simple extraction step (1:1 vol. dichloromethane) was used prior to injection into the GC-MS.

The pressure drop across the biofilter bed was monitored using a water manometer. A bench-top pH meter was used for monitoring the pH of liquid samples. The $CO_2$ concentration in the outlet gas stream of the biofilter was measured using the infrared $CO_2$ sensor MI 70 (Vaisala, Finland).

Plating was used to enumerate total and specific VOC degrading bacterial population as per the standard methods [14]. For specific VOC degrading counts, plates were incubated in a propanol or toluene atmosphere. Bacterial strain identification was carried out by profiling the fatty acid content of culture using the FAME (fatty acid methyl ester) analysis method of bacterial identification and comparing with standard microbial databases available at the Sherlock libraries [15].

### 2.3. Mathematical model

A mathematical model was used to describe the performance of the biofilter treating mixtures of toluene and *n*-propanol. The model is a slight variation of the one developed by Deshusses et al. [16], which considers the

most relevant phenomena occurring during the biofiltration process, that is, convection, absorption, diffusion and biodegradation. Monod-type kinetics with inclusion of cross-inhibition effects of the substrate–pollutant mixture was used. The assumptions made in deriving the governing equation were as follows.

1. The gas–biofilm interface equilibrium is represented by the air/biofilm partition coefficient.
2. The biofilm grows on the exterior surface of the support particles only; hence, no biodegradation occurs in the interior pores of the particles.
3. Planar biofilm geometry is used to derive model equations, since the solid support size is significantly greater than the biofilm thickness.
4. There is no gas-phase boundary layer at the air/biofilm interface and, hence, the gas-phase mass transfer resistance can be neglected.
5. Biomass properties, such as specific surface area, thickness and kinetic coefficients, are uniform along the bed and there is no excess accumulation of biomass in the filter bed.
6. Toluene and *n*-propanol are the only substrates affecting the biodegradation rate. Oxygen was assumed to be not limiting, consistent with the original model assumptions. No evidence of oxygen limitation (e.g. acid or metabolite production) was ever observed during these studies.

### 2.3.1. Governing equations

Under dynamic condition the model equations describing the removal of toluene and mixture of toluene and *n*-propanol in the biofilm are

$$\frac{\partial S_t}{\partial t} = D_{et}\frac{\partial^2 S_t}{\partial x^2} - \mu_{\max(t)}\frac{X}{Y_{x/s}}\frac{S_t}{K_s + S_t + \alpha} \qquad (1)$$

$$\frac{\partial S_p}{\partial t} = D_{ep}\frac{\partial^2 S_p}{\partial x^2} - \mu_{\max(p)}\frac{X}{Y_{x/s}}\frac{S_p}{K_s + S_p} \qquad (2)$$

The coefficient $\alpha$ in Equation (1) is to account for the effect of *n*-propanol (*p*) on toluene (*t*) biodegradation and can be represented as in Equation (3). No such term is included in Equation (2), since experiments in flasks (see Section 3.2.1) indicated that *n*-propanol had an inhibitory effect on toluene biodegradation, but toluene had no such effect on *n*-propanol biodegradation:

$$\alpha = \frac{S_p^2}{K_i} \qquad (3)$$

The boundary conditions for above equation are as follows. At the air/biofilm interface, or $x = 0$,

$$S_t = \frac{C_t}{m_t} \text{ and } S_p = \frac{C_p}{m_p} \qquad (4)$$

At $x = \delta$,

$$\frac{\partial S_t}{\partial x} = 0 \text{ and } \frac{\partial S_p}{\partial x} = 0 \qquad (5)$$

The concentrations of toluene and *n*-propanol in the air, along the biofilter column, are described by

$$\varepsilon\frac{\partial C_t}{\partial t} = U_g\frac{\partial C_t}{\partial h} - a_s D_{et}\left[\frac{\partial S_t}{\partial x}\right]_{x=0} \qquad (6)$$

$$\varepsilon\frac{\partial C_p}{\partial t} = U_g\frac{\partial C_p}{\partial h} - a_s D_{ep}\left[\frac{\partial S_p}{\partial x}\right]_{x=0} \qquad (7)$$

The corresponding boundary conditions are

$$C_t = C_{ti} \text{ and } C_p = C_{pi} \text{ at } h = 0 \qquad (8)$$

where subscript '*i*' represents the concentration of the respective VOCs at the inlet of the biofilter.

### 2.3.2. Mathematical solutions

The set of partial differential equations were discretized along the height of the biofilter and along the biofilm thickness and a computer code was developed using MATLAB 7.0 software. The equations were solved using the method of lines, which is a general technique used for the solution of partial differential equation. This method utilizes ordinary differential equations for time derivative and finite differences on spatial derivatives [17].

The model parameter optimization was achieved by minimizing the value of the sum of the squared residuals between experimental and simulated values in a way that the errors were randomly distributed [18].

## 3. Results

### 3.1. Overall biofilter performance

#### 3.1.1. Biofiltration of toluene

Figure 2 shows the overall biofilter performance for toluene with and without *n*-propanol. The removal efficiency observed when the biofilter was fed toluene alone was generally in the range of 60%–99%, with significant variations depending on the inlet concentration and the EBRT. On several occasions the removal fell below 50%, usually as a result of system failure or temporary bed drying. Generally, the biofilter recovered from such upsets within days of re-establishing proper operating conditions. The toluene elimination capacities during Phases I–VI were in the mid-to-high range of what is observed for compost-based biofilters [9–11]. The compost-based packing displayed a good water retention capacity, neutral pH and nutrients throughout the study. The pressure drop (3–4 cm water column per meter of bed) is in the range normally seen for compost biofilters [2]. The pH of the biofilter bed and leachate was found to be in the range of 6.5–7.3 during the study. The pH, pressure drop and overall performance indicate that the process was stable and that treatment could be sustained over the long term.
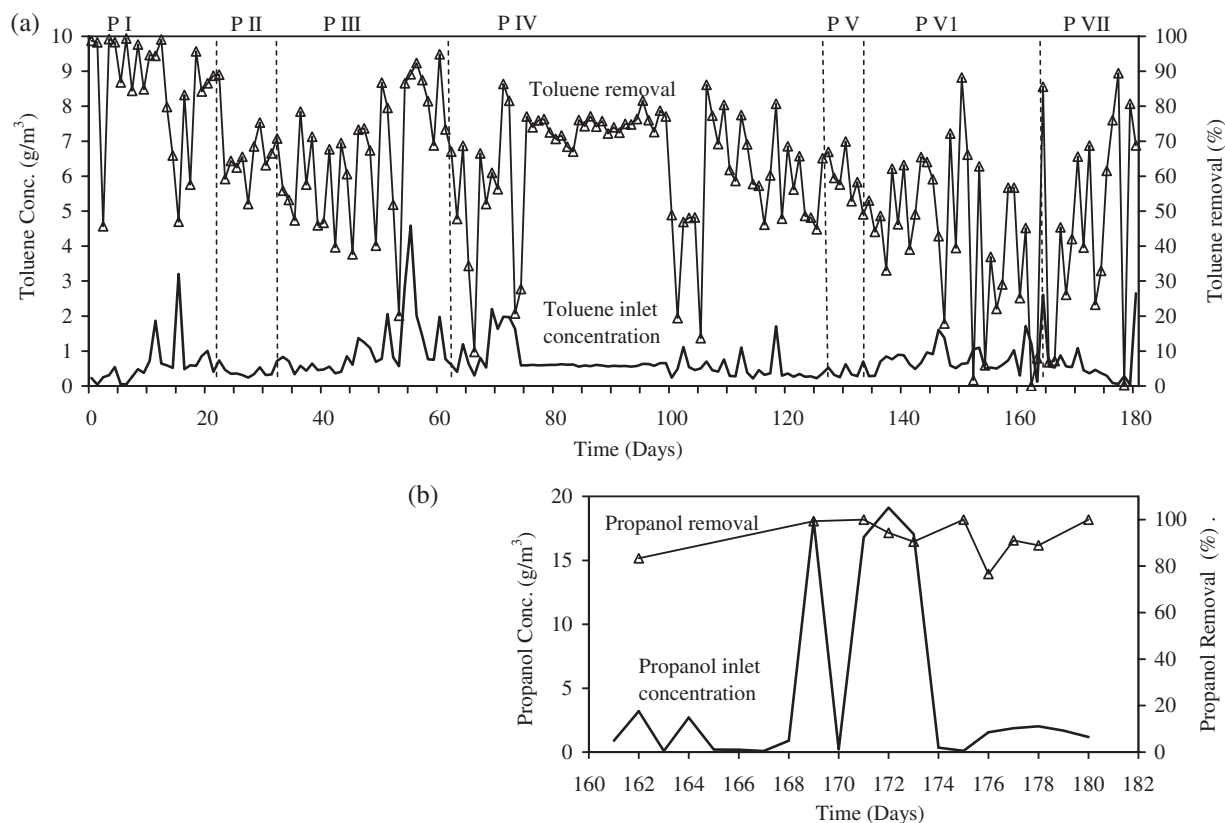
Figure 2. Overall performance of the biofilter during the experiment. The different phases of operation denoted by P I–P VII are described in Table 1: (a) toluene; (b) *n*-propanol (introduced in Phase VII only).

### 3.1.2. *Biofiltration of mixtures of toluene and n-propanol: effect of propanol on toluene removal*

During Phase VII, mixtures of various concentrations of toluene and propanol were treated at a constant EBRT, and cross-inhibition effects of propanol on toluene were monitored. Propanol was immediately well removed (Figure 2), even though the biofilter had never been exposed to *n*-propanol. High toluene concentrations did not have a significant impact on the removal of *n*-propanol, suggesting that the presence of toluene in the air stream did not affect the activity of the *n*-propanol degrading organisms. On the contrary, *n*-propanol had both positive and negative effects on toluene removal, depending on the *n*-propanol concentration (Figure 3). At low concentrations of *n*-propanol, the removal of toluene in the biofilter increased compared to when the biofilter was operated without *n*-propanol. The mechanisms for this enhancement are unclear. They could range from a general enhancement of biomass growth and activity to cometabolism. At high concentrations of *n*-propanol, a negative effect was observed on the toluene removal, possibly due to some sort of competitive inhibition by *n*-propanol, which appeared to be the preferred substrate. Competition between substrates has been observed in a number of gas-phase bioreactor studies [16,19–21], but enhancement of performance is rare. Improvement of dimethyl sulfide (DMS)

removal in a biofilter was observed when methanol was added as a co-substrate [21]. It was hypothesized that methanol increased DMS removal by enhancing biomass growth in the biofilter. Although the overall effect was positive, the prolonged exposure to the methanol was reported to decrease in DMS removal due to competition with DMS.

### 3.1.3. *Fate of toluene and n-propanol during biofiltration*

Biodegradation of toluene can lead to the formation of various intermediates, such as hydroxylated toluene, benzyl alcohol, benzaldehyde, benzoate, catechols and final mineralization products ($CO_2$ and $H_2O$). Propanol, being an easily biodegradable VOC, usually biodegrades to $CO_2$ and $H_2O$ without the formation of intermediates, unless there is an oxygen limitation or severe overloading of the bioreactor. Thus, to determine the presence of dissolved toluene and propanol and possible intermediate products, the biofilter leachate was analysed for TOC and subjected to GC-MS analysis. The TOC of the sample was found to be $368\,mg\,C\,l^{-1}$, that is, a low value when considering partition of the gaseous species in the leachate or considering the total amount of VOCs fed to the bioreactor. GC-MS analysis of the leachate sample showed the absence of any of
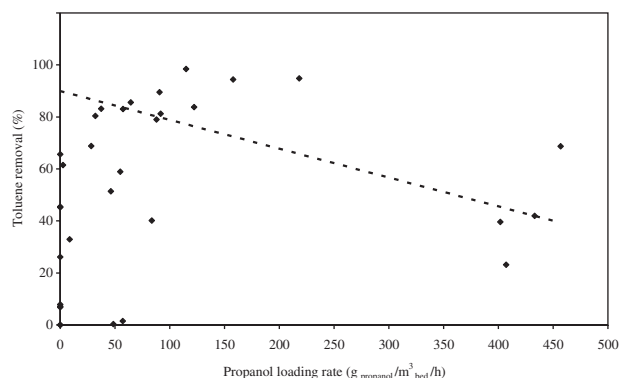
Figure 3. Effect of propanol loading on toluene removal during Phase VII (EBRT = 94 s). The dashed line shows the rough trend (linear) for toluene removal as affected by high loadings of propanol $>50\,\mathrm{g\,m^{-3}\,h^{-1}}$.

the above-mentioned intermediates, but the presence of low levels ($<100\,\mathrm{mg\,l^{-1}}$) of toluene and *n*-propanol. Overall, this shows that the vast majority of toluene and *n*-propanol was mineralized. The $CO_2$ concentration increase in the outlet gas on that same day was found to be 91% of that expected from the complete mineralization of the pollutant degraded, consistent with the results of the analysis of the leachate.

### 3.1.4. Microbiological status of the biofilter

The biofilm growth on the compost–woodchip-based packing was analysed for total microbial counts and for specific microbial counts of toluene and propanol degraders. Over time, total bacterial counts increased to a density of over $10^8\,\mathrm{CFU\,g_{compost}^{-1}}$ (wet basis); the counts for toluene degraders increased progressively to $4.2 \times 10^8$ and $8.2 \times 10^9\,\mathrm{CFU\,g_{compost}^{-1}}$ after the long-term biofilter operation, due
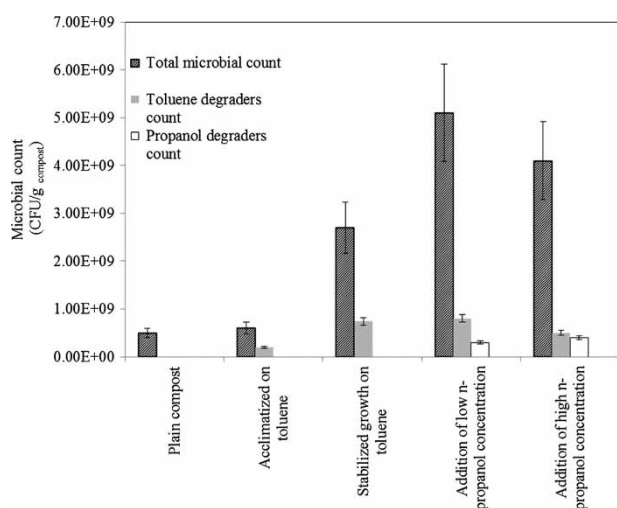


Figure 4. Microbial counts (in CFU $\mathrm{g_{compost}^{-1}}$) in the biofilter packing during the experiment.

to adaptation of the culture to toluene (Figure 4). After stable counts were observed, pure cultures of toluene degraders were isolated from the biofilter. Three morphologically different cultures were observed to grow on specific agar plate. These cultures were studied for their fatty acid content. The fatty acid composition is highly conserved genetically, and FAME composition has been shown to be a powerful tool for bacterial strain analysis [15]. The FAME analysis of the three cultures isolated from the biofilter revealed the presence of *Microbacterium schleiferi*, *Bacillus coagulans* and *Stenotrophomonas maltophilia* [15]. Greater functional analysis would be needed to identify their role in degrading the model pollutants. The addition of *n*-propanol to the biofilter coincided with a marked increase of total heterotrophs and a significant build up of propanol degraders. As in other studies, primary pollutant degraders accounted for only about 10%–30% of the total bacterial counts [1,2].

### 3.2. Model simulation and comparison with experimental results

#### 3.2.1. Model parameters and calibration

The operating temperature of the biofilter bed was in the range of 26–28°C; hence, diffusion coefficients reported at 25°C in the literature were used for the modelling studies [22,23]. Diffusion coefficients in biofilms ($D_e$) are reported to be affected by the density of the cells in the biofilm [24–26] and are significantly lower than those in water ($D_w$). In those studies, the ratio $D_e/D_w$ for organic compounds ranges from 68%–81% in the top biofilm layer to 38%–45% in the bottom layer where cell density is the highest. Considering the relatively high density of the biofilm due to the low water content of the biofilter, a single value of $D_e/D_w$ of 40% was chosen for the effective diffusivities of toluene and *n*-propanol. Values used in the model are reported in Table 2.

Many biofilter models treat the biofilm similar to water and ignore the effect of the presence of microorganisms and organic matter in the biofilm on pollutant partition. Thus, the air/water partition coefficient is used instead of the air/biofilm coefficient. This may be a reasonable assumption for hydrophilic compounds, such as *n*-propanol, but may need to be changed for hydrophobic compounds, such as toluene, since the presence of microorganisms and organic matter in the biofilm is expected to change the partition coefficient [27]. The air/biofilm partition coefficient for toluene was estimated using the method proposed by Mackay [28] and further adjusted through simulation; values are reported in Table 2.

The biokinetic parameters for the microbial consortium were determined in flask experiments. The biodegradation kinetic parameters obtained using a Monod model for toluene were found to be $\mu_{\max}$ of $0.95\,\mathrm{h^{-1}}$ and $K_s$ of $1.91\,\mathrm{mg\,l^{-1}}$. The *n*-propanol inhibitory effect on toluene

Table 2. Summary of model parameters values

| Symbol | Parameter | Value | Source |
|--------|-----------|-------|--------|
| $a_s$ | Biofilm surface area | $460\,\mathrm{m^2\,m^{-3}}$ | Adapted from [30] and adjusted by simulation |
| $H$ | Biofilter bed height | $0.425\,\mathrm{m}$ | Experiment |
| $\delta$ | Biofilm thickness | $0.0001\,\mathrm{m}$ | Adapted from [22] and adjusted by simulation |
| $D_{et}$ | Effective diffusivity of toluene in the biofilm | $1.396 \times 10^{-6}\,\mathrm{m^2\,h^{-1}}$ | Adapted from [22] |
| $D_{ep}$ | Effective diffusivity of $n$-propanol in the biofilm | $0.792 \times 10^{-6}\,\mathrm{m^2\,h^{-1}}$ | Adapted from [23] |
| $D_e/D_w$ | Tortuosity factor | 0.4 | Adapted from [20] |
| $\varepsilon$ | Bed porosity | 0.6 | Experimentally determined |
| $m_t$ | Air/biofilm partition coefficient of toluene (at 25°C) | 0.44 | Adapted from [31] and adjusted by simulation |
| $m_p$ | Air/biofilm partition coefficient of propanol (at 25°C) | 0.000295 | Adapted from [32] and adjusted by simulation |
| $\mu_{\max,t}$ | Maximum growth rate during toluene biodegradation | $0.95\,\mathrm{h^{-1}}$ | Experimentally determined (in flasks) |
| $\mu_{\max,p}$ | Maximum growth rate during propanol biodegradation | $0.84\,\mathrm{h^{-1}}$ | Experimentally determined (in flasks) |
| $Ks(t)$ | Half-saturation constant for toluene | $1.91\,\mathrm{g\,m^{-3}}$ | Experimentally determined (in flasks) |
| $Ks(p)$ | Half-saturation constant for $n$-propanol | $4.36\,\mathrm{g\,m^{-3}}$ | Experimentally determined (in flasks) |
| $Ki$ | Inhibition constant | $9.19\,\mathrm{g\,m^{-3}}$ | Experimentally determined (in flasks) |
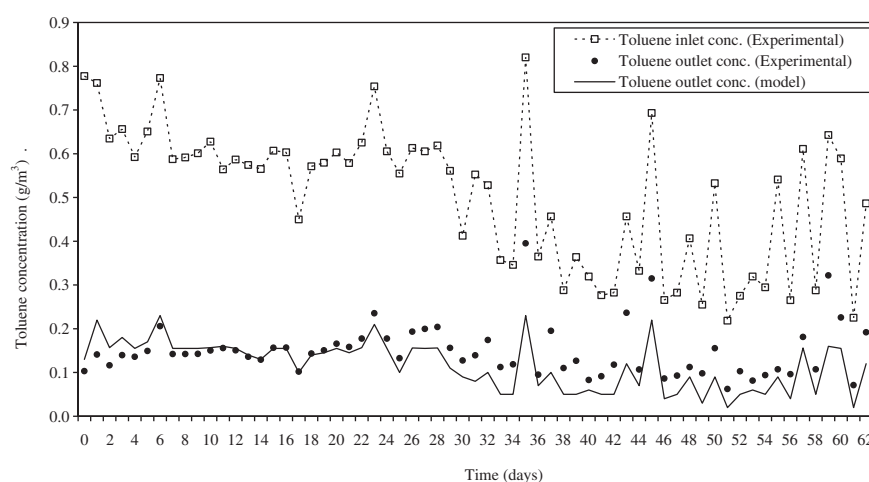


Figure 5. Experimental data (symbols) and dynamic model predictions (lines) for toluene removal in the biofilter.

degradation was best represented by a competitive-like inhibition and a constant $K_i$ of $9.19\,\mathrm{mg\,l^{-1}}$. Similarly, the $\mu_{\max}$ and $K_s$ values for $n$-propanol were found to be $0.84\,\mathrm{h^{-1}}$ and $4.36\,\mathrm{mg\,l^{-1}}$, respectively. Incorporating these constants into the model requires knowledge of the active cell density ($X$) in the biofilm and substrate to the biomass yield coefficient ($Y_{x/s}$), which are unknown and difficult to determine. Instead, the volumetric maximum growth rate $\upsilon_{\max}$ ($= \mu_{\max}X/Y_{x/s}$) was used to avoid further adjustments and assumptions on $X$ and $Y_{x/s}$. Thus, the ratio ($X/Y_{x/s} = 860\,\mathrm{kg\,m^{-3}}$) was adapted from Dorado et al. [29] for toluene and the experimentally determined $\mu_{\max}$ values were then used to calculate volumetric maximum growth rates.

The model calibration was done as per the procedure described in Section 3.2.2. The values of model parameters were adjusted to minimize the value of the sum of the squared residual close to zero for the calibration period. The resulting values for model parameters obtained are given in Table 2.

### 3.2.2. Model validation

For model validation, the experimental data obtained during Phases II–VII were used (Table 1). The model predictions were in good agreement with the experimental values (Figures 5–7), both in the cases when the biofilter was
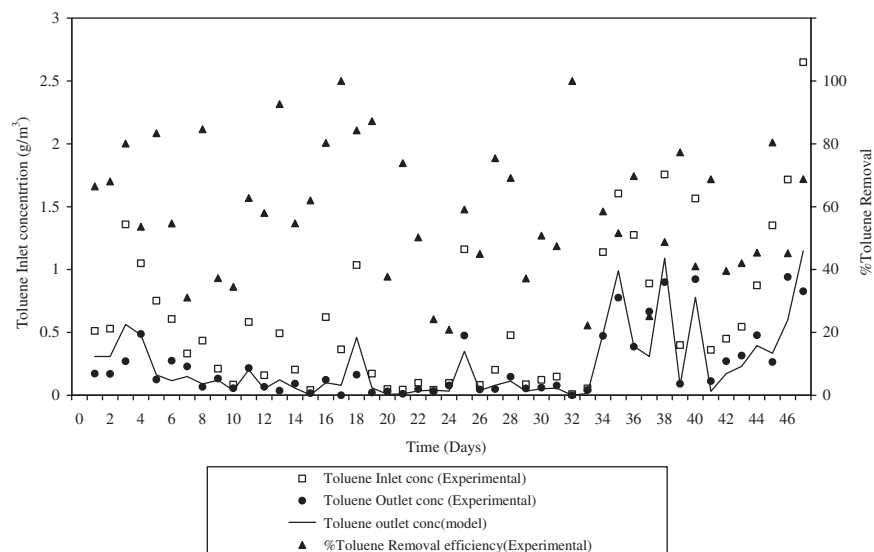
Figure 6. Experimental data (symbols) and dynamic model predictions (lines) for toluene removal in the presence of propanol (propanol load: 0.65–85 g m$^{-3}$ h$^{-1}$). Day zero is the first day of Phase VII.
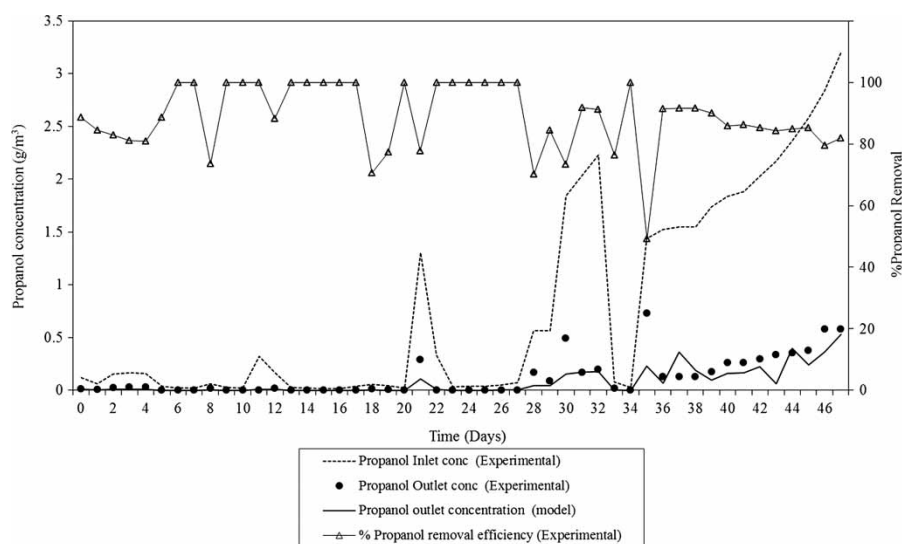


Figure 7. Experimental data (symbols) and dynamic model predictions (lines) for propanol removal in presence of toluene (toluene load: 0.34–101 g m$^{-3}$ h$^{-1}$). Day zero is the first day of Phase VII.

exposed to toluene alone and when it was exposed to a mixture of toluene and *n*-propanol. The relative error between experimental data and model predictions when the biofilter was operated on toluene alone was in the range of 3%–27%, with the largest discrepancies being towards the lower end of the concentration range (0–0.4 g m$^{-3}$, Table 3). Table 4 compares experimental data with model predictions when the biofilter was removing mixtures of toluene and *n*-propanol. The error for toluene removal in the presence of *n*-propanol was in the range of 11%–14% with the maximum error in the concentration range of 0.2–0.5 g m$^{-3}$, while for *n*-propanol it was observed in the range of 1%–18% with the maximum error in the concentration range of

Table 3. Mean relative error between experimental data and model predictions for toluene removal in the biofilter.

| Compound | Concentration range | % removal efficiency | | |
|---|---|---|---|---|
| | | Experimental | Model | % error |
| Toluene | 0–0.4 g/m$^3$ | 58–85 | 84–92 | 7–27 |
| | 0.4–0.8 g/m$^3$ | 57–78 | 76–90 | 12–19 |
| | 0.8–1.2 g/m$^3$ | 59–86 | 75–88 | 2–16 |
| | 1.2–2.0 g/m$^3$ | 73–92 | 76–94 | 3 |

0.04–0.6 g m$^{-3}$. Thus the inhibition effect of *n*-propanol on toluene removal at higher *n*-propanol loading seemed to be reasonably well simulated by the model.

Table 4. Mean relative error between experimental data and model predictions for toluene and propanol removal in the biofilter.

| | Concentration range | | Experimental | | Model | | % error | |
|---|---|---|---|---|---|---|---|---|
| | | | % removal efficiency | | | | | |
| Compound | Toluene | Propanol | Toluene | Propanol | Toluene | Propanol | Toluene | Propanol |
| Mixture of | $0$–$0.2\,\mathrm{g\,m^{-3}}$ | $0$–$0.05\,\mathrm{g\,m^{-3}}$ | 73–98 | 64–98 | 86–98 | 99 | 13 | 1 |
| toluene and | $0.2$–$0.5\,\mathrm{g\,m^{-3}}$ | $0.04$–$0.56\,\mathrm{g\,m^{-3}}$ | 58–84 | 73–100 | 72–84 | 97–100 | 14 | 18 |
| propanol | $0.5$–$1.0\,\mathrm{g\,m^{-3}}$ | $0.06$–$0.17\,\mathrm{g\,m^{-3}}$ | 54–83 | 83–98 | 65–85 | 95–97 | 11 | 1–12 |
| | $1.0$–$2.64\,\mathrm{g\,m^{-3}}$ | $0.16$–$3.19\,\mathrm{g\,m^{-3}}$ | 43–68 | 81–100 | 54–69 | 85–97 | 11 | 3–4 |

Table 5. Sensitivity analysis for selected model parameters.

| | | | Removal efficiency (predicted) | | |
|---|---|---|---|---|---|
| Parameter | Optimum value | Removal efficiency (experimental) | Optimum value | +10%* | −10%* |
| $m_t\ (-)$ | 0.44 | 84% | 87.2% | 86.4% | 87.4% |
| $v_{\max}\ (\mathrm{g\,m^{-3}\,h^{-1}})$ | 815 | 84% | 90% | 91% | 88% |
| $K_{s(t)}\ (\mathrm{g\,m^{-3}})$ | 1.91 | 84% | 90% | 88% | 91% |
| $K_{s(p)}\ (\mathrm{g\,m^{-3}})$ | 4.36 | 84% | 90% | 89% | 91% |
| $a_s\ (\mathrm{m^2\,m^{-3}})$ | 460 | 84% | 87% | 89% | 86% |
| $\delta\ (\mu\mathrm{m})$ | 100 | 84% | 87% | 87.5% | 86.5% |

To quantify the agreement between experimental results and model predictions, a paired $t$-Student's test was conducted. A $t$ value of 0.61 with 30 degrees of freedom with a 95% confidence interval was obtained when the biofilter was operated with toluene alone; this, coupled with a $p$ value of 0.05, suggests that there was no significant difference between model predictions and experimental results. Similarly, a $t$ value of 0.79 at 25 degrees of freedom with a 95% confidence interval was obtained for $n$-propanol when the biofilter was operated on mixture of toluene and $n$-propanol with a $p$ value of 0.05, indicating again agreement between experimental and modelling results. However, for toluene during the same period, a $t$ value of 4.89 at 25 degrees of freedom with 95% confidence with a $p$ value of less than 0.05 was obtained, indicating that there was a significant difference between modelled and experimental data, despite the relatively good visual agreement between model and experimental data, as was shown in Table 4 and discussed above. This indicates that the form of competitive inhibition of $n$-propanol on toluene removal that was used did not fully capture the actual phenomena occurring during the biodegradation of toluene and $n$-propanol.

A sensitivity analysis of the model to selected parameters was conducted (Table 5). In general, the model was found to be moderately sensitive to the selected parameters, with variations of plus or minus 10% on given parameters resulting in less than 3% difference on pollutant removal. The model was sensitive to both kinetic parameters and to those affecting mass transfer, indicating that the conditions modelled were resulting in a mixed regime of kinetic and mass transfer limitation.

## 4. Conclusion

This study reported on the removal of both toluene and $n$-propanol in a compost-based biofilter. Both pollutants were well removed. When treated together, propanol had a significant effect on the removal of toluene. The presence of $n$-propanol at low concentrations had a favourable effect, enhancing the removal of toluene, likely by providing a readily degradable carbon and energy source to enhance biomass growth in the biofilter. This is supported by the finding that microbial density in the biofilter increased when $n$-propanol was fed to the bioreactor along with toluene. On the other hand, high $n$-propanol concentrations ($>1\,\mathrm{g\,m^{-3}}$) negatively affect toluene removal, possibly due to biokinetic competition. A biofilter model was proposed and could describe the removal of the mixtures of VOCs in the biofilter with reasonable accuracy.

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