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Xiang-Qian Wang^{a b}, Bi-Hong Lu^{a b}, Xue-Xia Zhou^b & Wei Li^a

^a Key Laboratory of Biomass Chemical Engineering of Ministry of Education, Institute of Industrial Ecology and Environment, Zhejiang University, Yuquan Campus, Hangzhou 310027, People's Republic of China

^b Institute of Environmental Engineering, Zhejiang University, Zijingang Campus, Hangzhou 310058, People's Republic of China

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Evaluation of *o*-xylene and other volatile organic compounds removal using a xylene-acclimated biotrickling filter

Xiang-Qian Wang^{a,b}, Bi-Hong Lu^{a,b}, Xue-Xia Zhou^b and Wei Li^{a*}

^aKey Laboratory of Biomass Chemical Engineering of Ministry of Education, Institute of Industrial Ecology and Environment, Zhejiang University, Yuquan Campus, Hangzhou 310027, People's Republic of China; ^bInstitute of Environmental Engineering, Zhejiang University, Zijingang Campus, Hangzhou 310058, People's Republic of China

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In this study, performance evaluation for the gas-phase *o*-xylene removal using a xylene-acclimated biotrickling filter (BTF) was conducted. Substrate interactions during aerobic biodegradation of three poorly soluble compounds, both individually and in paired mixtures (namely, *o*-xylene and ethyl acetate, *o*-xylene and dichloromethane, which are common solvents used by pharmaceutical industry), were also investigated. Experimental results indicate that a maximum elimination capacity of $99.3 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ (70% removal) was obtained at an *o*-xylene loading rate of $143.0 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, while the top packing layer (one-third height of the three packing layers) only contributed about 13% to the total elimination capacity. Kinetic constants for *o*-xylene biodegradation and the pattern of *o*-xylene removal performance along the height of the BTF were obtained through the modified Michaelis–Menten kinetics and convection–diffusion reaction model, respectively. A reduction of removal efficiency in *o*-xylene (83.2–74.5% removal at a loading rate of $40.3 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ for the total volatile organic compound (VOC) loading rate of $79 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$) in the presence of ethyl acetate (100% removal) was observed, while enhanced *o*-xylene removal efficiency (71.6–78.6% removal at a loading rate of $45.1 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ for the total VOC loading rate of $90 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$) was achieved in the presence of dichloromethane (35.6% removal). This work shows that a BTF with xylene-acclimated microbial consortia has the ability to remove several poorly soluble compounds, which would advance the knowledge on the treatment of pharmaceutical VOC emissions.

Keywords: volatile organic compound; *o*-xylene; biotrickling filter; performance evaluation; substrate interaction

Introduction

The ubiquitous presence of atmospheric volatile organic compounds (VOCs) has been a serious environmental and health concern in the recent years. VOCs are of interest in part because they participate in atmospheric photochemical reactions. These reactions contribute to global environmental effects, such as the formation of ozone and other secondary pollutants.[1] Many individual VOCs are also associated with a variety of adverse health effects. These range from acute effects, such as irritation, and headaches to more chronic effects, such as liver and kidney damage and cancer; developmental effects have also been reported.[2] According to the United States Environmental Protection Agency,[3] in 2005, approximately 16 million tons of VOCs were emitted into the atmosphere. In China, the annual VOC emissions from industrial sources were estimated at over 20 million tons.[4] In addition, the industrial emissions of toluene and xylene in the atmosphere are estimated at about 212,088 tons (155,132 and 56,956 tons, respectively) per year in Japan.[5] Atmospheric VOCs are released from a variety of sources. These include the use

of solvents, on-road vehicles, non-road equipment, other industrial processes, and so on.[3]

Among atmospheric VOCs, xylenes and dichloromethane are typically recalcitrant pollutants, which are common solvents used by chemical and process industries, especially by the pharmaceutical industry in China.[6] All of them were listed as hazardous and toxic atmospheric contaminants under the 1990 amendments to the US Clean Air Act. Gulensoy and Alvarez [7] demonstrated the most recalcitrant nature of *o*-xylene compared with two other isomers of xylene, according to a biodegradation hierarchy of the benzene, toluene, ethylbenzene, xylene (BTEX) compounds. Among xylenes, *o*-xylene is also used for making phthalic anhydride.[8] Due to the high volatility of xylenes and dichloromethane, most environmental releases partition to the atmosphere. Pharmaceutically, ethyl acetate is a flavouring aid, as inert ingredients in pesticide formulations, and used as a solvent or cosolvent,[9] which also results in its release to the atmosphere through various waste streams.

The aerobic biodegradation of the gas-phase VOCs in large volumes and low concentrations through a bioreactor

*Corresponding author. Email: w_li@zju.edu.cn

configuration is an effective and economical option in comparison with other different physico-chemical techniques, such as activated carbon adsorption, absorption, incineration, ozonation, condensation and catalytic oxidation.[10–12] This is mostly because aerobic biodegradation can achieve the complete and cost-effective elimination of VOCs into environmentally harmless end products, such as carbon dioxide, water and biomass by harnessing diverse microbial metabolic processes.[13] As one of the most extensively used bioreactors for air pollution control, the biotrickling filter (BTF) could be considered as a suitable and viable technology for controlling pharmaceutical VOC emissions, especially for these recalcitrant volatile pollutants, such as chlorinated compounds.[10] However, little data are still available on the use of the BTF system for the treatment of pharmaceutical VOC emissions containing several poorly soluble VOCs, such as the most recalcitrant dichloromethane and *o*-xylene. To date, studies that focused on substrate interactions among VOCs with similar structures and chemical properties, such as BTEX compounds, are relatively common.[14–17] Substrate interactions during aerobic biodegradation of several poorly soluble compounds, which differ in structures, chemical properties, and biodegradability are still relatively scarce.

Thus, this study was conducted to evaluate the performance of a xylene-acclimated BTF system treating *o*-xylene using convection–diffusion reaction (CDR) model and modified Michaelis–Menten kinetics. Substrate interactions during aerobic biodegradation of three poorly soluble VOCs differing in structures, chemical properties and biodegradability, both individually and in paired mixtures (namely, *o*-xylene and ethyl acetate, *o*-xylene and dichloromethane) were also studied. All the studies are essential in the application of the BTF system in treating pharmaceutical VOC emissions, which would further advance the knowledge related to this biotechnology.

Materials and methods

Chemicals and medium

o-Xylene (98.0%), ethyl acetate (99.5%) and dichloromethane (99.5%) were obtained from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All other chemicals were of analytical grade, commercially available and used without further purification.

The mineral salts medium, applied for the enrichment culture of microorganism and circulation in the BTF system, contained the following compositions in 1 L of deionized water: 2.5 g (NH₄)₂SO₄, 0.1 g MgCl₂·6H₂O, 0.01 g EDTA, 0.002 g ZnSO₄·7H₂O, 0.001 g CaCl₂·2H₂O, 0.005 g FeSO₄·7H₂O, 0.0002 g Na₂MoO₄·2H₂O, 0.0002 g CuSO₄·5H₂O, 0.0004 g CoCl₂·6H₂O, 0.001 g MnCl₂·4H₂O, 1.6 g K₂HPO₄, and 0.8 g NaH₂PO₄·2H₂O.[17] The initial pH value of the medium as trickling liquid was about 6.7.

During this study, the pH value was monitored every 1 h through a cap located on the bottom reservoir, which is also illustrated in Figure 1. About 10 mL of 1 mol/L NaOH was added into the bottom reservoir when a decrease below 6.0 was recorded, and then the pH value was adjusted to about 7.0.

Microorganism

The microorganism (the defined mixed culture) used in this study, isolated from the activated sludge of a pharmaceutical plant (Hangzhou, China), was cultured in 250 mL conical flasks containing 100 mL liquid medium at 30°C and 150 rpm on a rotary shaker with xylene as the carbon and energy source during the 7-day enrichment culture period. After enrichment, the microbial consortia were inoculated into the BTF for the rapid establishment of biofilm during the start-up period.

BTF set-up and operation

The BTF unit with three packing layers (height of 20 cm for every packing layer) used in this study is schematically illustrated in Figure 1. This unit consisted of an acrylic cylinder (120 mm diameter × 900 mm height) packed with self-made porous polyurethane (PU) balls (diameter of 15 mm). Three sampling ports were located along the column, at 30 cm intervals from the bottom (height of 20 cm for every packing layer and about 10 cm distance of the bottom from the top of every packing layer), for gas sampling and pressure drop measurements. These PU packing materials with high porosity (void space of 85.0%) has a high surface area (920 m²·m⁻³) for enhanced mass transfer of the VOCs between gas and liquid phases.[11] The void space is significantly high in BTFs packed with these PU balls, which will slow down clogging problems and pressure drop increase.[10] And the value of pressure drop during steady-state period was always about 2.5 mmH₂O. The volume of these PU packing materials in the three packing layers was about 5.9 L (bed porosity of 47%).

The BTF was operated in a counter-current mode (the upflow mode) at the temperatures of 28–30°C and an ambient pressure of 1 atm, where simulated gas-phase VOCs entered at the bottom of the unit and exited at the top after being treated. The temperature of the BTF system was always controlled at a relatively stable value (about 28–30°C) with maintenance strategy, which consisted of thermal insulation cotton for the three packing layers and a 30°C thermostatic water bath (DKS-24, Lantian, Hangzhou, China) for heating the liquid medium in the bottom reservoir. An umbrella-type impact distributor was installed on the top of the unit to ensure continuously uniform distribution of the liquid medium. The liquid medium was recycled from the top of the unit onto the PU packing material using a magnetic circulation pump at a constant liquid flow rate

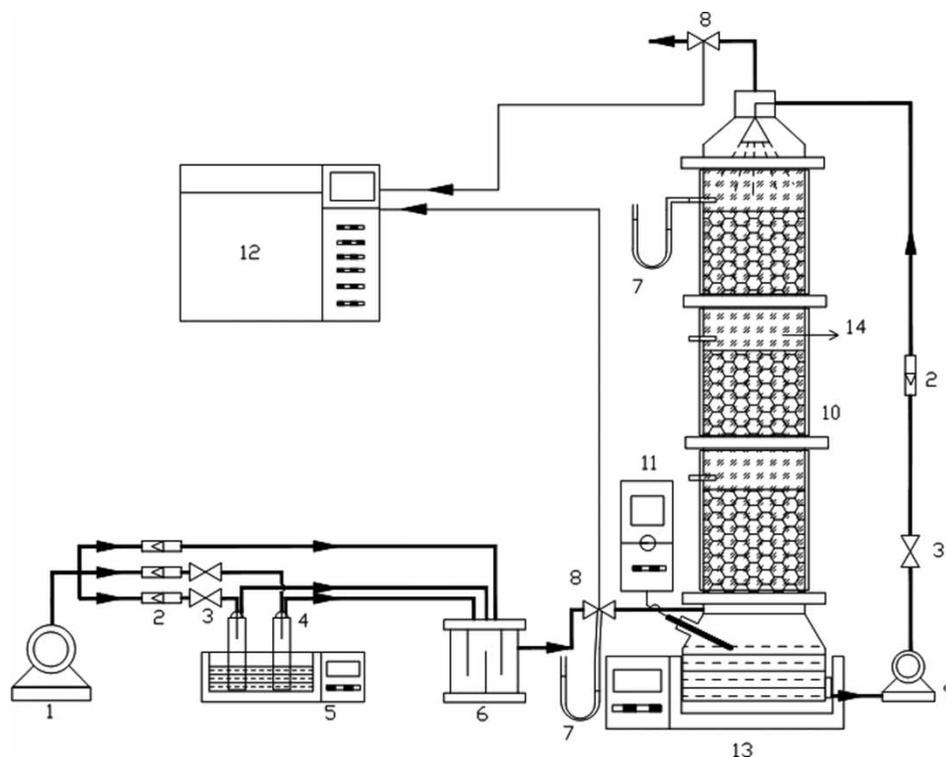


Figure 1. Schematic diagram of the BTF system for simulated gas-phase VOCs removal. 1. Air compressor, 2. Rotameter, 3. air/water valves, 4. VOC vaporization chamber, 5. thermostatic water bath for VOC vaporization, 6. mixing chamber, 7. differential manometer, 8. inlet/outlet sampling ports, 9. magnet circulating pump, 10. BTF, 11. pH meter, 12. gas chromatograph, 13. thermostatic water bath for heating the liquid medium and 14. thermal insulation cotton.

of $30 \text{ L}\cdot\text{h}^{-1}$. Three litres of the liquid medium in the bottom reservoir was completely changed with newly made mineral salts medium every 7 days. Gas-phase VOCs were generated by flowing air from a compressor into the vaporization chambers containing liquid-phase VOCs, whose temperatures were also controlled at 30°C by a thermostatic water bath (HHS-11-2, Boxun, Shanghai, China). Afterwards, the gas-phase VOCs were diluted to the appropriate concentration in the mixing chamber with a secondary air stream by varying the ratio of gas flow rates between the two air streams. Excess biomass produced during the steady-state period was partially removed by circulating the deionized water at a liquid flow rate of $80 \text{ L}\cdot\text{h}^{-1}$ for 8 h before the liquid medium was refreshed. The values of pH and pressure drop were determined at an interval of 1 h to ensure the optimal conditions for microorganism growth and VOC removal.

Experimental procedure of performance evaluation and substrate interaction

During the start-up operation, xylene-acclimated microbial consortia obtained from previous enrichment culture were added to the BTF system to establish a more stable and efficient biofilm, and then operated continuously with the inlet concentration of the most recalcitrant *o*-xylene varying between 580 and $755 \text{ mg}\cdot\text{m}^{-3}$. The BTF was acclimated

with only *o*-xylene to achieve high removal efficiency of about 90% at an empty bed retention time (EBRT) of 60 s, and a short start-up period (about 2 weeks) was attained, which are shown in Figure 2(a). The effects of EBRT on *o*-xylene removal efficiency were also investigated by varying EBRTs from 100 to 20 s (namely, 100, 80, 40, 20 s, respectively).

During the steady-state period for *o*-xylene removal, this xylene-acclimated BTF system was re-acclimated 2 days using only ethyl acetate to steady state (nearly 100% removal). During steady state for both *o*-xylene and ethyl acetate removal, *o*-xylene and ethyl acetate were simultaneously treated using the xylene-acclimated microbial consortia. And then, this xylene-acclimated BTF system was re-acclimated 8 days using only dichloromethane for its steady-state operation (only about 40% removal). During steady state for both *o*-xylene and dichloromethane removal, *o*-xylene and dichloromethane were simultaneously treated using the xylene-acclimated microbial consortia. All studies shown in Figure 2(b) were conducted to investigate substrate interactions of these three typical pharmaceutical VOCs.

Analytical methods

Gas-phase VOC samples in this study were analysed using a gas chromatograph (Model 9790, Fuli, Zhejiang,

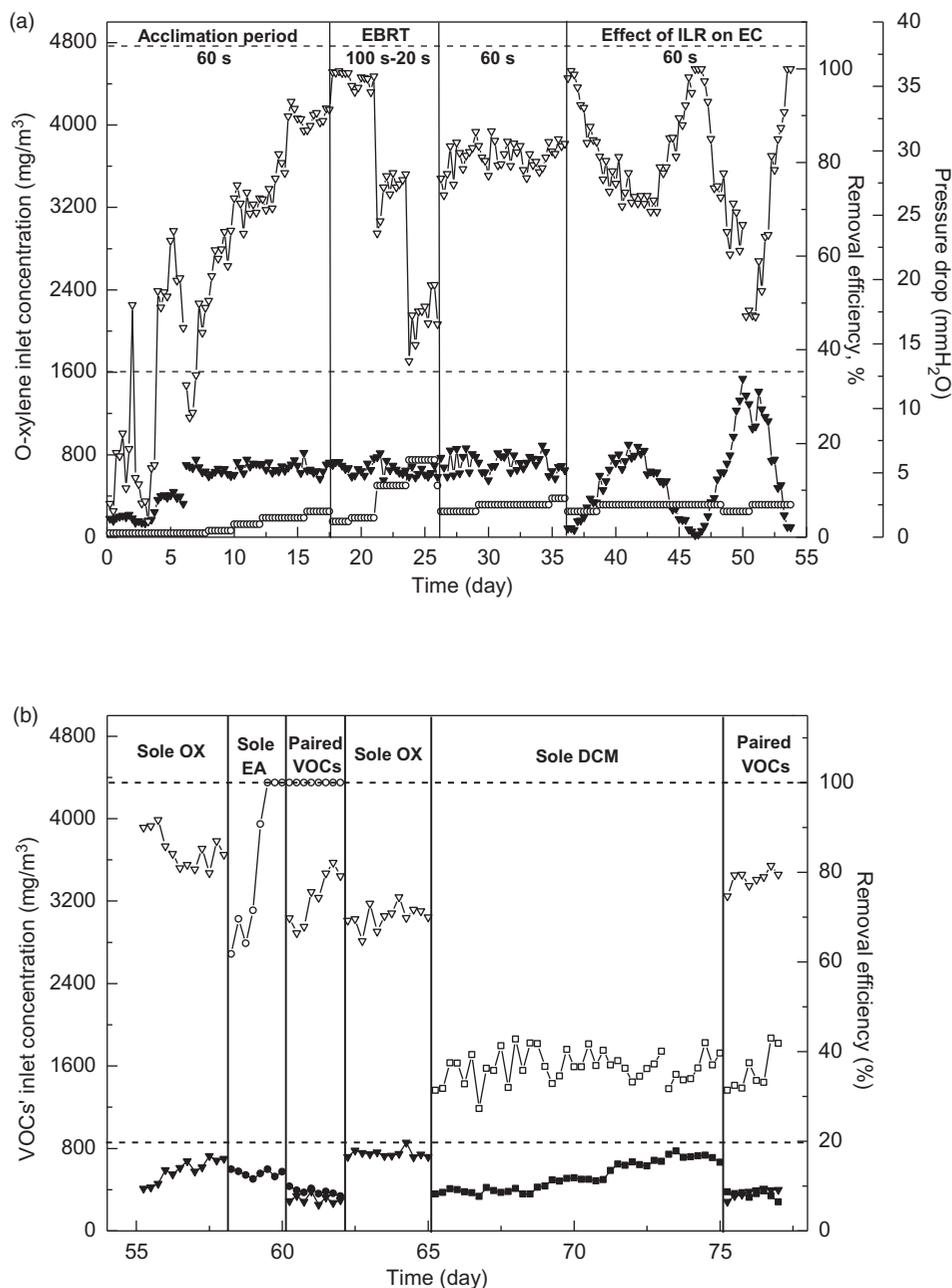


Figure 2. (a) Inlet concentration and removal efficiency profiles of *o*-xylene under different conditions during long-term operation. (▼) Inlet concentration of *o*-xylene; (▽) removal efficiency of *o*-xylene; (○) pressure drop. (b) Inlet concentration and removal efficiency profiles of *o*-xylene, ethyl acetate, and dichloromethane during the investigation of substrate interactions. (▼) Inlet concentration of *o*-xylene; (▽) removal efficiency of *o*-xylene; (●) inlet concentration of ethyl acetate; (○) removal efficiency of ethyl acetate; (■) inlet concentration of dichloromethane and (□) removal efficiency of dichloromethane.

China) with a fused silica capillary column (30 m length, 0.32 mm ID, 0.33 μm phase thickness) and a flame ionization detector. Nitrogen was used as the carrier gas at a flow rate of 30 mL min^{-1} . The temperatures of the injection port, oven, and detection port were set at 180°C , 150°C and 200°C , respectively. For quantitative analysis of the gas-phase VOCs, gas samples were withdrawn at an interval of 1 h from inlet

and outlet sampling ports using 50 mL glass syringes. These samples were then injected into the gas chromatograph.

The pH value of the circulating liquid medium was determined using a pH meter (PHS-3CW, Bante, Shanghai, China). The pressure drop across the BTF unit was determined using a differential U-tube water manometer (0–1000 Pa, Hongxing, Hebei, China).

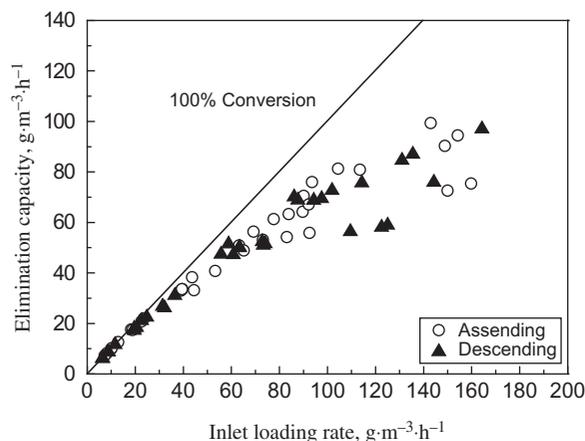


Figure 3. Effect of inlet loading rate ($0\text{--}170\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$) on elimination capacity. (\circ) Inlet loading rate in ascending order, (\blacktriangle) inlet loading rate in descending order {inlet concentration: $20\text{--}1540\text{ mg}\cdot\text{m}^{-3}$, EBRT: 60 s (gas flow rate of $0.69\text{ m}^3\cdot\text{h}^{-1}$), liquid flow rate: $30\text{ L}\cdot\text{h}^{-1}$, pH: $6\text{--}7$ }.

Results and discussion

Performance evaluation for individual *o*-xylene biodegradation

Effect of the inlet loading rate on elimination capacity

The elimination capacity of the steady-state period was assessed at different loading rates ($0\text{--}170\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, $1\text{--}2\text{ h}$ for steady state at each new loading rate) by increasing and decreasing the loading rate of *o*-xylene (in both ascending and descending modes, to assess the stability of this BTF system).

It is shown in Figure 3 that the elimination capacity increased steadily and linearly with the increased loading rate, and gradually deviated from the 100% removal line when the loading rate was raised to about $100\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$. However, past this loading rate, there was a slight decrease in the slope of this increasing trend. For inlet loading rates beyond $100\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ and up to $170\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, the elimination capacities mostly varied between 70 and $100\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$. The removal efficiency still reached about 70% at a loading rate of $143.0\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, corresponding to a maximum elimination capacity of $99.3\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$. Other studies for xylenes removal using the laboratory-scale biofilter had also been reported, with maximum elimination capacities between $22\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ and $160\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ at inlet loading rates of $100\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ – $220\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$. [18–21] Note that both ascending and descending loading rates had no significant adverse effect on the elimination capacity due to the great stability of this BTF system.

Figure 3 also shows two different operating regimes, as previously described in the literature. [19,21] First, when the loading rates varied between 0 and $80\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, the elimination capacities increased linearly with the increasing loading rates and gradually deviated from the 100% removal line. This was mainly due to the complete mineralization of *o*-xylene. The mass transfer rate between

gas-phase and liquid-phase/biofilm would be the limiting step for higher performance. Second, when the loading rates varied between $100\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ and $170\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, the elimination capacities almost remained constant. At these loading rates, the biofilm would be fully saturated and the metabolic activity of the microorganisms in the biofilm would be the limiting step. The variations of elimination capacity to different loading rates indicated the response of active microorganisms present in the BTF to sudden shock loading rates and the stability of the BTF system to effectively handle such operations.

However, a decline in the performance for *o*-xylene removal was observed after about 1 month's continuous operation, which was shown by the decreased removal efficiency from 90% to 80% at a loading rate of $80\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ (EBRT of 60 s , Figure 2(a)). The continuous accumulation of excess biomass in the biofilm is one possible reason for the decline in the performance. [22] In other words, the decrease in specific surface area due to biomass accumulation lowered the mass transfer flux of *o*-xylene from the gas-phase to the liquid-phase/biofilm. This, in turn, led to the decreased removal efficiency. Along with the effects of excess biomass accumulation, an intrinsic decline in pollutant-degrading activity may also contribute to the deteriorating performance of the BTF system. [23]

Kinetic analysis for *o*-xylene biodegradation

The kinetic parameters were calculated in order to understand kinetic behaviour of the BTF system for *o*-xylene biodegradation using modified Michaelis–Menten kinetics. [19,24–27]

$$\frac{1}{\text{EC}} = \frac{K_s}{V_{\max}} \cdot \frac{1}{C_{\text{in}}} + \frac{1}{V_{\max}}, \quad (1)$$

where $C_{\text{in}} = (C_{\text{in}} - C_{\text{out}}) / \ln(C_{\text{in}}/C_{\text{out}})$, V_{\max} is the maximum elimination rate ($\text{g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$) and K_s is the saturation constant or the Michaelis–Menten constant ($\text{g}\cdot\text{m}^{-3}$).

The kinetic constants were determined by using Equation (1), as shown in Figure 4. The values of V_{\max} and K_s for *o*-xylene biodegradation were $123.5\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ and $0.319\text{ g}\cdot\text{m}^{-3}$, respectively. The value of V_{\max} is lightly higher than the experimentally observed value of the maximum elimination capacity ($99.3\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$, as shown in Figure 3). Mathur and Majumder [24] also reported V_{\max} and K_s values for *o*-xylene biodegradation in a coal-based BTF as $86.4\text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$ and $0.679\text{ g}\cdot\text{m}^{-3}$, respectively.

Comparison of removal performance among three packing layers

In order to evaluate the removal performance of different heights within the BTF system, the elimination capacities and removal efficiencies for gas-phase *o*-xylene removal among three packing layers were compared. The profiles

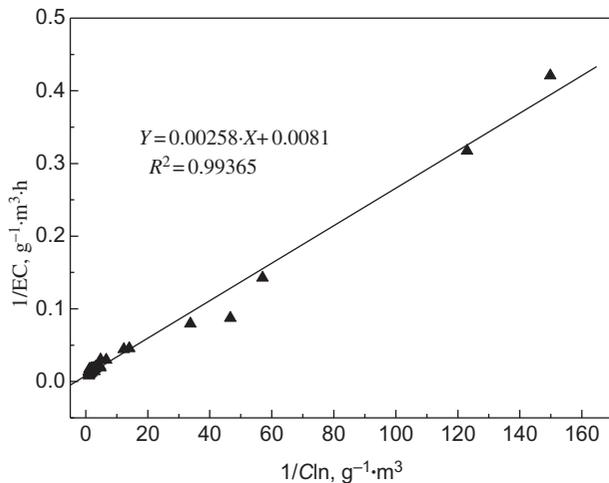


Figure 4. (Macro-) kinetic determination of Michaelis-Menten kinetic constants for *o*-xylene biodegradation.

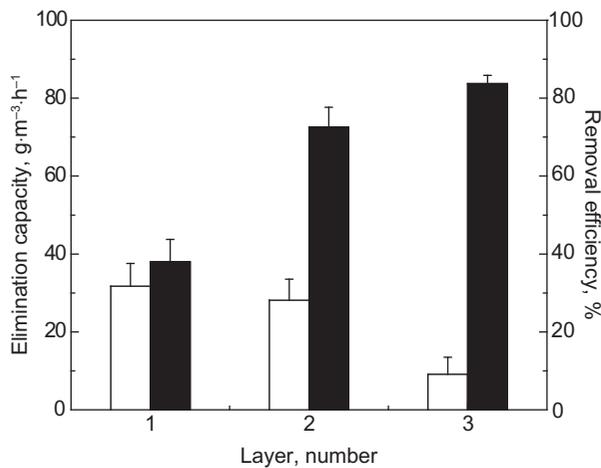


Figure 5. Comparison of elimination capacity and removal efficiency among three packing layers. (□) Elimination capacity of the packing layer, (■) removal efficiency after the packing layer {inlet concentration: 628–782 mg m⁻³ (mean value of 709.3 mg m⁻³, relative standard deviation of 8.49%), EBRT: 60 s (gas flow rate of 0.69 m³·h⁻¹), liquid flow rate: 30 L h⁻¹, pH: 6–7}.

were plotted as a function of the packing layer, as shown in Figure 5.

The elimination capacities of the first (bottom) and second (middle) packing layers were much higher than that of the third (top) packing layer. The average elimination capacities of the three packing layers (in ascending order) were 31.7 ± 5.9 g m⁻³·h⁻¹, 28.1 ± 5.4 g m⁻³·h⁻¹ and 9.1 ± 4.4 g m⁻³·h⁻¹, respectively (at the average loading rate of 82.4 g m⁻³·h⁻¹). Correspondingly, the first and second packing layers of the BTF showed higher removal efficiencies, which accounted for 72.5 ± 5.7% of the *o*-xylene removed, and the third packing layer contributed only about 11% to the total removal of 83.7 ± 2.1% (Figure 5). Assuming that the biodegradation follows Michaelis-Menten kinetics, the lower *o*-xylene inlet concentration in

Table 1. Parameters used for solving the CDR model.

Parameters	Values	Source
H_c (Pa·m ³ ·mol ⁻¹)	626	[24]
D (m ² ·s ⁻¹)	1 × 10 ⁻⁹	[24]
a_s (m ² ·m ⁻³)	920	Present work
δ (average value) (m)	1 × 10 ⁻⁴	Present work
U_0 (for gas flow rate 0.685 m ³ ·h ⁻¹) (m·s ⁻¹)	0.0168	Present work
R (Pa·m ³ ·mol ⁻¹ ·K ⁻¹)	8.314472	—
T (K)	303	Present work
k (s ⁻¹)	0.153	Present work

the top packing layer would result in a lower elimination capacity. Hence, it can be concluded in this study that as the BTF height increased, the corresponding elimination capacity would gradually decrease.

The pattern of *o*-xylene removal performance along the height of the BTF was also studied. A first order kinetic mathematical model based on CDR was used. This method has also been successfully applied by Mathur and Majumder for *o*-xylene biodegradation in a coal-based BTF,[24] by Morgan-Sagastume et al. [28] for hydrogen sulphide biodegradation in a BTF.

The CDR model is represented as follows:

$$\frac{C_{out}}{C_{in}} = \exp \left[-\frac{D \cdot a_s \cdot H \cdot R \cdot T}{H_c \cdot U_0 \cdot \delta} \cdot \Phi \cdot \tanh(\Phi) \right] \quad (2)$$

and

$$\Phi = \delta \sqrt{\frac{k}{D}}, \quad (3)$$

where D is the diffusion coefficient in the liquid phase (m²·s⁻¹), a_s is the average specific surface area (m²·m⁻³), H_c is the Henry's law constant (Pa m³ mol⁻¹), H is the height of the packing layer (m), δ is the biofilm thickness (m), U_0 is the superficial velocity (m·s⁻¹), R is the ideal gases constant (Pa·m³·mol⁻¹·K⁻¹), T is the temperature (K) and k is the reaction rate constant (s⁻¹).

This experiment was conducted to determine *o*-xylene concentration along the height of the BTF. Gas samples were taken from the three sampling ports at the distances 25, 55, and 85 cm from the bottom of the packing layers (height of 20 cm for every packing layer). About 10 cm distance of the bottom from the top of every packing layer has not been considered since it is assumed that there are not any conversion taking place in these sections. In order to predict the microbial kinetics behaviour along the height of the packing layers, an attempt was made to fit a first-order kinetic mathematical model based on CDR. Parameters used for solving the CDR model are presented in Table 1.

As shown in Figure 6, a similar trend for both experimental values (at average inlet concentration of 709.3 mg·m⁻³) and model results was observed. The removal performance of *o*-xylene along the height of the BTF system is higher and slightly different from the

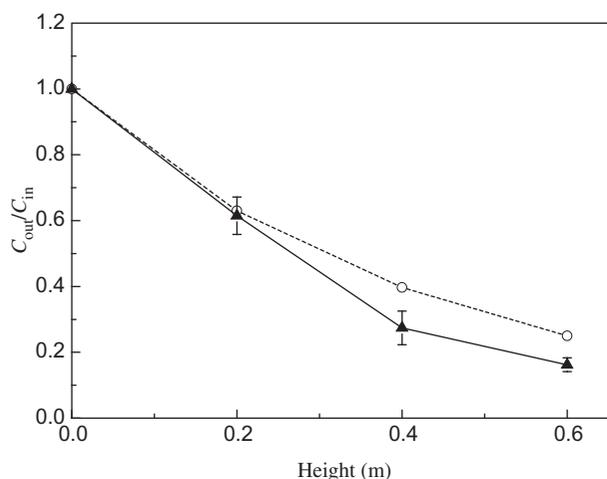


Figure 6. Experimental and model predicted concentration profiles of *o*-xylene along the height of the packing layer. (○): Model values; (▲): experimental values (standard deviation of 0.057, 0.051 and 0.021 for 8 times to the corresponding three points, respectively) {average inlet concentration of $709.3 \text{ mg}\cdot\text{m}^{-3}$, EBRT: 60 s (gas flow rate of $0.69 \text{ m}^3\cdot\text{h}^{-1}$) and liquid flow rate: $30 \text{ L}\cdot\text{h}^{-1}$, pH: 6–7}.

predicted values of the CDR model, which is in agreement with the results of Mathur and Majumder's [24] study for *o*-xylene removal in a coal-based BTF. The removal performance in the lower parts of the packing layer was higher than that in the upper parts, which can be observed from a slight decrease in the slope of this decreasing trend. The discrepancy in the model results from the experimental values can be attributed to several factors,[24,29] such as experimental errors in both performance evaluation and the estimation of the kinetic model parameters given in Table 1.

Substrate interaction during the biodegradation of paired VOC mixtures

In this study, the removal of *o*-xylene, ethyl acetate and dichloromethane (three poorly soluble compounds identified in VOC emissions, which are common solvents used by the pharmaceutical industry) was conducted in this xylene-acclimated BTF. Due to the differences in biodegradability, structures and chemical properties, substrate interactions of these three VOCs cannot definitively be anticipated when considering the use of the BTF system for the treatment of pharmaceutical VOC emissions. Thus, the aim of this study was to investigate substrate interactions of these three VOCs, both individually and in paired mixtures, and to develop a method of comparing these observed interactions.

Substrate interaction during aerobic biodegradation of ethyl acetate and *o*-xylene

Ethyl acetate and *o*-xylene were applied individually to the BTF system, and both of the removal efficiencies were monitored at the inlet loading rate of about $70 \text{ gm}^{-3}\cdot\text{h}^{-1}$.

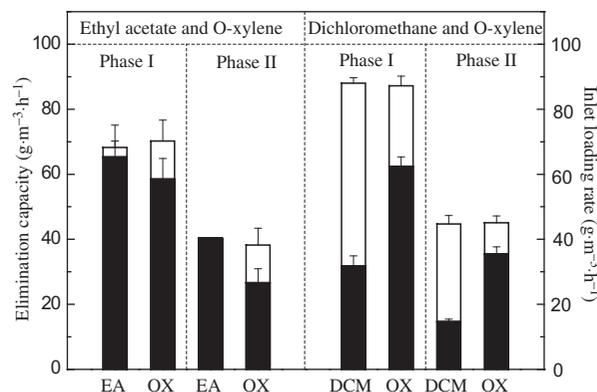


Figure 7. Comparison of inlet loading rate and elimination capacity of ethyl acetate, dichloromethane and *o*-xylene both individually and in paired mixtures. (□) Inlet loading rate, (■) elimination capacity {OX: *o*-xylene, EA: ethyl acetate and DCM: dichloromethane}.

The paired application protocol was then repeated with a 1:1 ratio of ethyl acetate paired with *o*-xylene at a total loading rate of about $79 \text{ g}\cdot\text{m}^{-3}\cdot\text{h}^{-1}$. The removal efficiency was measured for each component at an interval of 1 h during the steady-state period. The corresponding loading rates of ethyl acetate and *o*-xylene, both individually and in paired mixtures, are shown in Figure 7.

The maximum elimination capacities for ethyl acetate and *o*-xylene in phase II were about $50 \text{ gm}^{-3}\cdot\text{h}^{-1}$ (100% removal) and $35 \text{ gm}^{-3}\cdot\text{h}^{-1}$ (76.4% removal), respectively. It was clearly shown that the removal efficiency of ethyl acetate (nearly 100% removal) was higher than that of *o*-xylene whether it was in phase I or phase II. Therefore, it can be surmised that ethyl acetate was more easily degraded by the mixed microbial consortia in this BTF system. It was also shown that the removal efficiency of *o*-xylene in phase I was higher than that in phase II. Consequently, it was anticipated that the presence of ethyl acetate in paired mixtures would result in the reduced removal efficiency of *o*-xylene. This was mainly due to the competition for the more easily biodegraded ethyl acetate among the xylene-acclimated microorganisms in the biofilm. This oxygenated compound with simple chemical structure which is also a less hydrophobic pollutant (water solubility of 80 g/L at 25°C) may benefit the pollutant-degrading activity of xylene-acclimated microbial consortia. Similar behaviour was observed by Alvarez-Hornos et al. [30] in treating a 1:1 (wt) ethyl acetate and toluene mixture.

Substrate interaction during aerobic biodegradation of dichloromethane and *o*-xylene

Dichloromethane and *o*-xylene were also applied individually to the BTF, in which both of removal efficiencies were monitored at the loading rate of about $88 \text{ gm}^{-3}\cdot\text{h}^{-1}$. The paired application protocol was then repeated with a 1:1 ratio of dichloromethane paired with *o*-xylene at a total

loading rate of about $90 \text{ gm}^{-3}\text{h}^{-1}$. Additionally, the steady-state removal efficiency was measured for each component at an interval of 1 h. The corresponding loading rates of dichloromethane and *o*-xylene, both individually and in paired mixtures, are also shown in Figure 7.

The maximum elimination capacities for *o*-xylene and dichloromethane in phase II were $37.8 \text{ gm}^{-3}\text{h}^{-1}$ (79.0% removal) and $16.0 \text{ gm}^{-3}\text{h}^{-1}$ (only 33.1% removal), respectively. Additionally, the biodegradation of *o*-xylene in the presence of dichloromethane (phase II) by the xylene-acclimated microorganisms was enhanced (71.6–78.6% removal), compared with the removal efficiencies when *o*-xylene was introduced individually. A possible explanation for this phenomenon is the recalcitrant nature of dichloromethane and the formation of acid end products (hydrogen chloride), [31–33] which further led the microorganisms to choose the more easily degraded *o*-xylene as the carbon and energy source. The removal efficiencies of dichloromethane showed its poor performance both in phase I and II, which was mainly due to the poor biodegradability of dichloromethane and the decreased activity of the xylene-acclimated consortia resulted from the acid end products. Therefore, further acclimation of the BTF system with individual dichloromethane is essential to achieving high performance for this recalcitrant compound.

In conclusion, the results described above indicated that the operating conditions of the BTF system during the steady-state period was the most favourable for ethyl acetate biodegradation, followed by *o*-xylene and then dichloromethane both individually and in paired mixtures. A reduction of removal efficiency in *o*-xylene (83.2–74.5% removal) in the presence of ethyl acetate (100% removal) was observed, while enhanced *o*-xylene removal efficiency (71.6–78.6% removal) was achieved in the presence of dichloromethane (35.6% removal). Strauss et al. [34] also demonstrated that the presence of toluene in paired mixture with *o*-xylene resulted in reduced removal efficiency of *o*-xylene, while enhanced toluene removal efficiency was achieved in the presence of *o*-xylene under thermophilic conditions. Results of other studies on the removal of VOCs in mixtures also showed that the removal of one component may be affected by other components in the mixtures. This process could involve non-interaction, stimulation, competitive inhibition, non-competitive inhibition or co-metabolism. [15–17,35] Substrate interactions among VOCs in mixtures are complicated, especially for those with different chemical properties, structures and biodegradability. Hence, studies on these substrate interactions of these three VOCs in mixtures can contribute to a better understanding on the treatment of pharmaceutical VOC emissions.

Conclusion

A BTF system dominated by xylene-acclimated microbial consortia was found to have the ability to degrade

o-xylene, ethyl acetate and dichloromethane, three poorly soluble compounds differing in structures, chemical properties and biodegradability. This study was also conducted to investigate substrate interactions of three typical pharmaceutical VOCs, both individually and in paired mixtures, and a method of comparing these observed interactions was developed. Results obtained that a BTF with great performance and stability would contribute to a better understanding on the treatment of pharmaceutical VOC emissions.

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