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Modelling transport and degradation of hydrophobic pollutants in biofilter biofilms

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Abstract

Treatment of air pollutants in a biofilter requires that the compound be effectively transported from the gas phase to the organisms that reside in a biofilm that forms upon a packing material. Models of biofiltration generally treat the biofilm like water by using a Henry's law constant to predict mass transfer rates into the biofilm where degradation occurs and hence, predict low rates for hydrophobic compounds. However, some compounds that are virtually insoluble in water are also treated unusually well. The objective of this research is to develop and experimentally validate a model that can explain the biofiltration rates of α-pinene. The study involved analysing transport of α-pinene through artificial biofilms in a diffusion cell along with modelling of batch and continuous kinetic experiments.

Our results support a novel mechanism of biofiltration whereby a biologically mediated transformation is taking place with α-pinene being oxidised into a more soluble compound. This model provides an explanation for relatively high removal rates of hydrophobic compounds. A simple transport and reaction model based on zero-order kinetics was developed that fit results seen in a diffusion cell using active α-pinene leachate immobilised in low melting point agarose. The proposed identity of this more soluble by-product, is *cis*-2,8-*p*-menthadien-1-ol, a menthadienol, a novel metabolite of α-pinene degradation. By extension, this model fits biofiltration data collected from Raschig ring biofilters treating α-pinene. The paper also discusses implications of the model for the treatment of hydrophobic pollutants.

Keywords: Biofilter; Biofilm; α-Pinene; Kinetic modelling

1. Introduction

1.1. Biofiltration of hydrophobic pollutants

Biofiltration is an air pollution control strategy that involves passing waste air through a column that contains a media upon which microorganisms capable of degrading pollutants live. The compound to be degraded must pass from the gas to the organisms, which reside in a biofilm that forms upon the media.

In general, biofilters achieve the highest rates of removal for compounds that are water soluble and biodegradable (e.g. ethanol and methanol). Models of biofiltration generally support this since they treat the biofilm like water by using a Henry's law constant to predict mass transfer rates into the biofilm where degradation occurs. However, some compounds that are virtually insoluble in water are also treated unusually well. For example, Mohseni and Allen [1,2] and van Groenestijn and Liu [3] show that α-pinene can be completely removed by biofiltration even with loading rates as high as 40 g/(m^3 bed h) despite the fact that the Merck Index lists it as "practically insoluble in water" [4]. Similarly, Spigno et al. [5] studied the biofiltration of hexane, another hydrophobic pollutant, and found the average removal rates to be as high as 150 g/(m^3 bed h), again despite the fact that the Merck Index lists it as "insoluble in water". Kibazohi [6] also reported hexane removal rates in a perlite biofilter to be up to 120 g/(m^3 bed h). These high removal rates for hydrophobic compounds suggest that current models do not accurately describe biofilm transport and reaction processes since we would predict poor mass transfer of these compounds and hence low removal rates.

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Nomenclature

A	the effective area of transfer on the template assembly in the diffusion cell (cm^2)
A_p	surface area of packing material (m^2/m^3)
$c_{A,high}$	concentration of the diffusing solute in air in the high side of the diffusion cell (mol/cm^3)
c_D	the concentration in the mobile or diffusing phase
D	diffusion coefficient of solute (cm^2/s)
F	flow rate in biofilter (m^3/h)
H	height of the biofilter (m)
k_{cat}	enzyme catalytic activity (1/h)
k_{0e}	enzyme zero-order rate constant ($g/(cm^3\,h)$)
$K_{A-mobile}$	air/mobile phase partition coefficient (dimensionless)
K_{AW}	air/water partition coefficient (dimensionless)
K_M	Michaelis–Menten half saturation constant
U_g	superficial velocity (m/h)
υ_{max}	the maximum enzyme conversion rate ($g/(cm^3\,h)$)
V_{biof}	the volume of the biofilter (m^3)
V_{high}	volume of high concentration air chamber in the diffusion cell (cm^3)

Previous research has shown that at steady-state, the transport rate through artificial films consisting of leachate immobilised in low melting point agar is the same as the transport rates through agar films, used as a surrogate for water [7,8]. Since this research indicates that there is no enhancement in transport rates in artificial films, work was taken further to see if a more realistic film could be formed in situ in order to study transport rates, and it was found that again transport rates remained similar as through agar films [7,9]. Hence, a new model was needed to elucidate the higher than predicted removal rates observed when treating α-pinene.

The objective of this research is to take our previous research one step further by developing and experimentally validating a mathematical model that can explain the biofiltration rates of α-pinene. The study involved modelling the transport and reaction of α-pinene through artificial biofilms in a diffusion cell along with modelling performance results of biofilters treating α-pinene. The conceptual development of the model is described elsewhere [7,9].

2. Materials and methods

2.1. Diffusion cell experiments

Two diffusion cells (volume 1.3 L each) were designed and constructed out of Teflon® in order to measure the transport and reaction rates of α-pinene in samples of biomass immobilised in agarose (Fig. 1). The diffusion cells consisted of two air chambers separated by a template assembly that contained the biofilm sample.

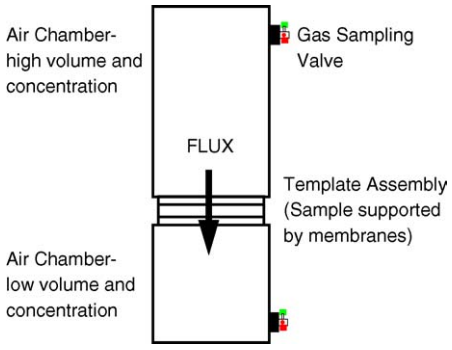

Fig. 1. Schematic diagram of the diffusion cell.

2.1.1. Transport and reaction diffusion cell experiments with artificial biofilms

The samples used in the diffusion cell were made using mixtures of biomass in leachate (from biofilters packed with ceramic Raschig rings treating α-pinene), water and low melting point agarose. The samples (ratio of 75% active leachate in 0.75% low melting point agarose) were made by boiling 0.75 g low melting point agarose (ultraPURE™ low melting point agarose, Life Technologies, Grand Island, NY, USA) in deionised (nanopure) water and then adding it to the leachate after it had cooled enough to allow the temperature after mixing to remain just above the gelling temperature. The mixture was then poured into a plastic petri dish, which contained a steel sample plate (with hole of 1.5 mm thickness and 30 mm diameter). One membrane (polyethersulfone, Supor-450, 47 mm diameter, 6 mil thick) was submerged on the top of the steel sample plate. The sample was allowed to gel overnight. The sample and plate were cut out from the agarose and another membrane was placed on the now exposed agarose film. The sample plate was sandwiched between two steel washers and then placed in the diffusion cell.

The "high" side of the diffusion cell was spiked with α-pinene and the concentrations were measured as a function of time with a gas chromatograph, a Varian GC Star 3600-CX (Varian Chromatography Systems, Walnut Creek, CA). The conditions of the GC were as follows: 30 mL/min each of H_2 and He (as the carrier gas), 300 mL/min of air, column temperature of 120 °C, injection temperature of 150 °C, and detection temperature of 250 °C (using an FID, flame ionisation detector). The GC was equipped with a 15 m, 0.53 mm i.d. megabore (5% phenyl)-methylpolysiloxane capillary column (J&W Scientific DB-5). A 250 μL Hamilton Gastight® #1825 syringe (Hamilton Company, Reno, NV) was used to obtain the air samples. In these experiments, investigating transport and reaction, the α-pinene was reacted before it reached the "low" side of the diffusion cell, which was measured to be less than 2 ppmv. Further experimental details are described elsewhere [7–9].

2.2. Biofilter experiments

The packing material used in the biofilters was ceramic Raschig rings: 1/2 in. size rings in one of the biofilters, 1 in. size rings in the second, while the third was packed with a mix of 1/2 and 1 in. size rings (larger ones in section one and smaller ones in sections two and three). All three biofilters were fed methanol (Sigma–Aldrich, >99.8% purity) for 325 days and then the first two biofilters were switched over to operate on α-pinene (Sigma–Aldrich, 98% purity) for 545 days [7,8]. Several of the operational parameters are given in Table 2 in the context of the model that was developed.

3. Results and discussion

3.1. Proposed conceptual model—biologically mediated transformation of α-pinene

3.1.1. Conceptual development

A simple model was developed that described results seen in the diffusion cell using active α-pinene leachate immobilised in low melting point agarose (Fig. 2) [7,9]. The model was developed based on an enzyme catalysing the initial partial oxidation of α-pinene into a more soluble and less volatile compound. The model assumes that the film is thick enough that the compound is then further degraded by microorganisms present deeper in the film.

The soluble compound denoted in the above model is given as "α-soluble" rather than *cis*-2,8-*p*-menthadien-1-ol, the compound previously identified to be building up in filtered samples [7,9]. It is possible that if different microorganisms were present in the sample, they could produce different enzymes that could oxidise α-pinene into different oxygenated terpenoids. Several terpenoids have higher solubility than that of α-pinene. Thus, depending on the metabolic pathway of the microorganisms, different soluble compounds could be formed. In addition, the concept of having a more soluble by-product formed can be generalised to other hydrophobic pollutants.

3.1.2. Solution and form of the model applied to the diffusion cell

The model is based on a mass balance of α-pinene within the diffusion cell. The rate of α-pinene loss from the high volume side of the diffusion cell is equal to the amount diffusing into the film and reacting. This is given by the following equation:

$$V_{\text{high}} \cdot \frac{\mathrm{d}c_{\text{A,high}}}{\mathrm{d}t} = A \cdot D \cdot \left.\frac{\mathrm{d}c_{\text{D}}}{\mathrm{d}z}\right|_{z=0} \quad (1)$$

The concentration gradient within the sample, assuming a steady-state concentration profile develops within the film, can be found using the steady-state continuity equation for the solute within the biofilm.

The degradation rate by an enzyme using the Michaelis–Menten expression for kinetics is as follows:

$$r = \upsilon_{\max} \cdot \frac{C}{K_{\text{M}} + C} \quad (2)$$

To simplify the above expression and allow for an analytical solution, the zero-order rate expression was used based on the assumption that the concentration of pollutant is much larger than the half-saturation constant, i.e.:

$$r_0 = \upsilon_{\max} = k_{\text{cat}} \cdot [E] = k_{0\text{e}} \quad (3)$$

There are two limiting cases of zero-order kinetics within a biofilm: the shallow biofilm (fully penetrated, reaction-limited) and the deep biofilm (incompletely penetrated, diffusion-limited). In this case, we consider a deep biofilm where all the α-pinene is converted to another compound in the first portion of the film. The differential of this profile

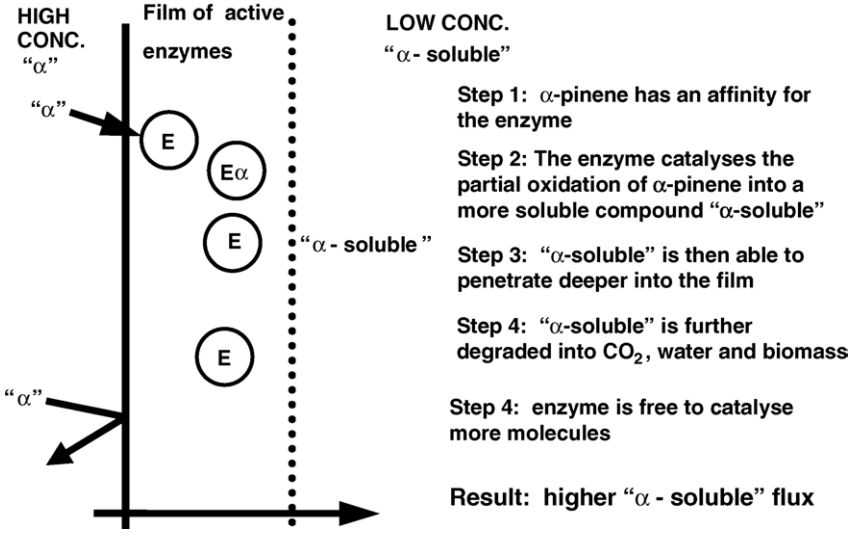

Fig. 2. Conceptual model of biologically mediated transformation [7,9].

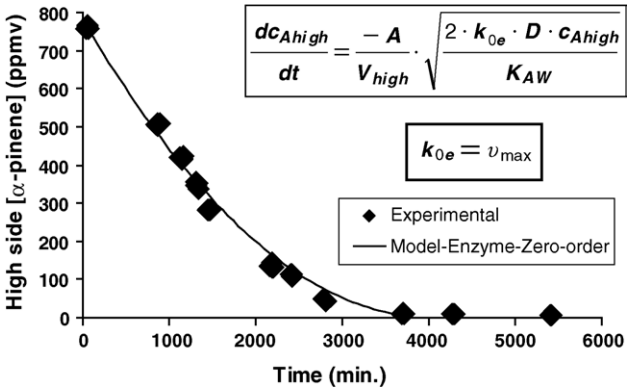

Fig. 3. Mathematical model of biologically mediated transformation (line) compared to typical experimental results in the diffusion cell (data points [7]).

at the interface is then given by the following equation for a zero-order reaction:

$$\left.\frac{dc_D}{dz}\right|_{z=0} = -\sqrt{\frac{2 \cdot k_{0e} \cdot c_{A,high}}{D \cdot K_{A-mobile}}} \quad (4)$$

The α-pinene air/water partition coefficient can be used as the air/mobile phase partition coefficient based on transport experiments in the diffusion cell, which show that the mobile phase in the film has the properties of water. The above equation is then substituted into the mass balance equation of the diffusion cell:

$$\frac{dc_{A,high}}{dt} = \frac{-A}{V_{high}} \cdot \sqrt{\frac{2 \cdot k_{0e} \cdot D \cdot c_{A,high}}{K_{AW}}} \quad (5)$$

Table 1 shows the values used in the above model to calculate the concentration in the high side as a function of time.

The model predictions using the parameters given above fit the experimental results from the diffusion cell experiments, as clearly evident in Fig. 3, which shows the concentration in the high side of the diffusion cell as a function of time for a typical spike in one diffusion cell. The model concentrations were generated using E-Z Solve™ Version 1.0 (John Wiley & Sons Inc.).

The only parameter in the above model that was not measured or based on the transport experiments with agarose and biomass was the zero-order rate constant which was chosen to fit the experimental data. The next section describes determining whether the zero-order rate constant chosen was reasonable for an enzyme, in order to provide some support as to whether or not the model is reasonable.

3.1.3. Model parameter evaluation—zero-order rate constant and penetration depth

Literature pertaining to relevant enzymes was sought in order to determine whether the value chosen for the zero-order rate constant was reasonable. The literature did not report zero-order rate constants, but rather, the specific catalytic activity of the enzyme systems studied, k_{cat}, which when multiplied by the concentration of enzyme gives the zero-order rate constant. This enzyme catalytic activity could be used with the model value of the rate constant to calculate a hypothetical enzyme concentration, which could then be compared with other literature values. Bell et al. [10] studied the oxidation of α-pinene using mutants of the cytochrome $P450_{cam}$ enzyme system, which has been widely studied for the oxidation of camphor into 5-exo-hydroxycamphor. One of the highest rates of α-pinene oxidation reported for one of the mutants was 270 nmol product/(nmol P_{450} min), which is 70% of the rate of camphor oxidation by the wild type enzyme. Using this rate, the enzyme molecular weight and the model zero-order rate constant yields an enzyme concentration of 400 mg/L. Griffiths et al. [11] reported a rate of 312 μmol product/(mg min) for α-pinene oxide lyase, an enzyme which cleaves both rings of α-pinene oxide. Using this rate and the model zero-order rate constant gives an enzyme concentration of 8 mg/L. Colocousi and Leak [12] reported a rate of 206 μmol product/(mg min) for α-pinene monooxygenase, which catalyses the NADH-linked oxygenation of α-pinene to α-pinene epoxide. Using this rate and the model zero-order rate constant gives an enzyme concentration of 12 mg/L. Therefore, theoretical enzyme concentrations of between 8 and 400 mg/L have been calculated using the model zero-order rate constant and literature values of enzyme catalytic activities that could then be compared to literature values of enzyme concentrations to see if they are in turn reasonable.

A comparison of estimates of typical enzyme concentrations in other systems suggests that the model parameter estimate is reasonable. Colocousi and Leak [12] reported that the α-pinene monooxygenase enzyme made up an estimated 0.5% of the total cytoplasmic cell protein. Using these data and estimates of the composition of cells [13] and a biofilm

Table 1
Parameter values for zero-order enzyme model

Parameter	Variable	Value	Units	Source
Initial α-pinene concentration	$c_{A,high,0}$	760	ppmv	Measured
Surface area	A	7.068	cm^2	Measured
Volume of high side	V_{high}	1130	cm^3	Measured
Diffusion coefficient	D	3.4×10^{-6}	cm^2/s	From experiments with agar[a]
Air/water partition coefficient	K_{AW}	6	–	From experiments with agar[a]
Zero-order rate constant	k_{0e}	0.02	$g/(cm^3\ h)$	Chosen to fit experimental data

[a] Ratio of D/K, which is proportional to the transport rate through the film, was also found to be the same for artificial films made of biomass immobilised in agarose after an initial lag phase where sorption occurred and hence the diffusion coefficient is the same as the agar value [7,8].

density of 100 g dry cell/L yields an enzyme concentration of 250 mg/L. If one assumes a cell density of 10 g dry cell/L, this gives 25 mg/L. These enzyme concentrations are similar in magnitude to the values calculated using the zero-order rate constant in the model, resulting in the value chosen to fit the data falling within the range of values for other enzyme systems (8–400 mg/L compared to 25–250 mg/L).

In order to test to see if the model is reasonable, the penetration depth, δ^*, of α-pinene can also be calculated using the following equation:

$$\delta^* = \sqrt{\frac{2 \cdot D \cdot c_{A,high}}{k_{0e} \cdot K_{AW}}} \quad (6)$$

Using the values given in Table 1 gives a penetration depth of 10 μm at the beginning of the experiment using the initial high side concentration. As the concentration becomes lower with time, this penetration depth also becomes smaller. This would mean that there would be a thin film of active enzymes and that the product would be further degraded by microorganisms deeper in the film. This penetration depth is reasonable for a thin film of enzymes effecting a small change of α-pinene into a more soluble compound. Conversely, if this rate constant were for bacteria or fungi converting α-pinene all the way to carbon dioxide, water and more biomass, as is the case in conventional biofilter models, the calculated penetration depth of 10 μm would be unreasonably small compared to typical values in biofilms (∼100 μm [14–16]). Therefore, the magnitude of the calculated penetration depth for an enzyme catalysed reaction makes logical sense and supports the proposed model of diffusion and reaction within biofilms.

In summary, the model fits the experimental data observed in the diffusion cell. This model has advantages over other models because it suggests the potential underlying mechanism of transport and reaction while using physically realistic parameters. By extension, this model can be applied to fit biofiltration data as seen in the next section.

3.1.4. Modelling of biofilters treating α-pinene

The model developed to describe the diffusion cell results was extended to model the Raschig ring biofiltration results for α-pinene. The model developed for the diffusion cell was applied to the biofilter equations. An equation describing the removal rate as a function of loading rate to the biofilter was developed, again based on zero-order kinetics of an enzyme catalysed reaction and an incomplete penetration of α-pinene in the biofilm. The loading rate to the biofilter is given as:

$$\text{Loading} = \frac{F \cdot c_{Air,in}}{V_{biof}} = \frac{U_g}{h} \cdot \varepsilon \cdot c_{Air,in} \quad (7)$$

The removal rate is given as:

$$\text{Removal rate} = \frac{F \cdot (c_{Air,in} - c_{Air,out})}{V_{biof}} \quad (8)$$

The zero-order biofilter equation for a deep biofilm, incomplete penetration or mass transfer limitation can be integrated along the height of the biofilter.

$$\int_{c_{Air,in}}^{c_{Air,out}} \frac{dc_{Air}}{\sqrt{c_{Air}}} = -\frac{A_p}{U_g} \cdot \sqrt{\frac{2 \cdot k_{0e} \cdot D}{K_{A-mobile}}} \cdot \int_0^{h=H} dh \quad (9)$$

Integrating, solving, and rearranging for the outlet concentration, $c_{Air,out}$, gives:

$$c_{Air,out} = \left[\sqrt{c_{Air,in}} - \frac{A_p}{2 \cdot U_g} \cdot \sqrt{\frac{2 \cdot k_{0e} \cdot D}{K_{A-mobile}}} \cdot H\right]^2 \quad (10)$$

Table 2
Parameter values for zero-order enzyme model—biofiltration data

Parameter	Variable	Value	Units	Source
Inlet α-pinene concentration	$c_{Air,in}$	Varied to change loading		Based on experimental values to enable comparison to loading rates
Surface area packing material	A_p	370 (1/2 in.)	m^2/m^3	Known for packing material – 1/2 and 1 in. Raschig rings – assumes complete coverage
		190 (1 in.)		
Volume of biofilter	V_{biof}	0.006185	m^3	Measured
Height of biofilter	H	0.35	m	Measured
Flow rate	F	0.288	m^3/h	Known from biofilter operation
Superficial velocity	U_g	25.5 (1/2 in.)	m/h	Known from flow rate and measured cross-sectional area and void fraction of packing material
		22.0 (1 in.)		
Diffusion coefficient	D	3.4×10^{-6}	cm^2/s	From experiments with agar[a]
Air/water partition coefficient	K_{AW}	6	–	From experiments with agar[a]
Zero-order rate constant	k_{0e}	0.055	$g/(cm^3\,h)$	From results with diffusion cell (rate constant from spike with higher rate using visual best fit)

[a] Ratio of D/K, which is proportional to the transport rate through the film, was also found to be the same for artificial films made of biomass immobilised in agarose after an initial lag phase where sorption occurred and hence the diffusion coefficient is the same as the agar value.

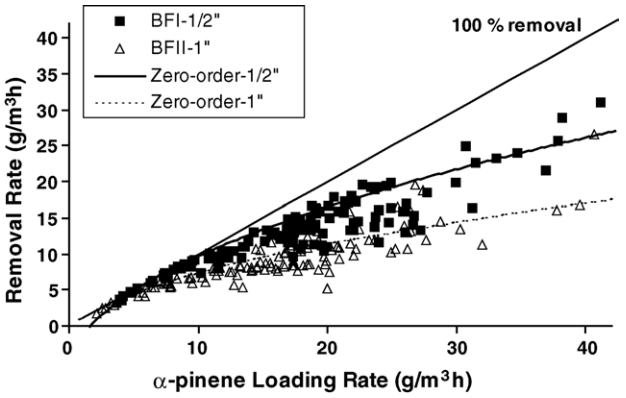

Fig. 4. Mathematical model of biologically mediated transformation compared to experimental results in the 1/2 and 1 in. Raschig ring biofilters—100% removal line shown for reference.

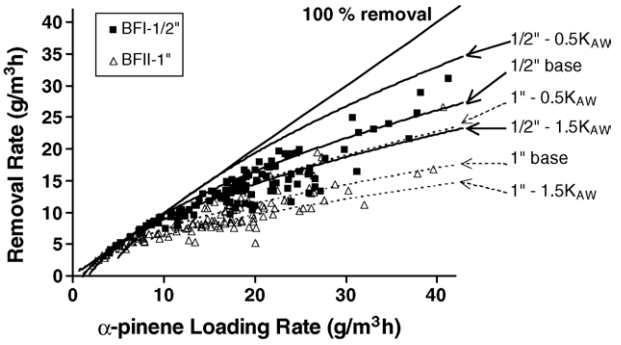

Fig. 6. Sensitivity of mathematical model of biologically mediated transformation to 50% changes in the air/water partition coefficient compared to experimental results in the 1/2 in. (solid lines and symbols) and 1 in. (dashed lines and open symbols) Raschig ring biofilters—100% removal line shown for reference.

This equation for the outlet concentration can then be combined with Equation (8) to calculate the predicted removal rate at various concentrations or loading rates.

Table 2 shows the values used in the above model to calculate loading rates and predicted removal rates. The biofilter parameters given in the table such as the flow rate and superficial gas velocity were chosen to enable comparison to all the experimental data collected between operating days 64 and 436. During this period, the empty bed retention time was 85 s and the inlet loading rate was varied by changing the inlet α-pinene concentration. The surface area was based on complete coverage of the packing material. The surface area assumed could be less if the biofilm does not grow on all exposed areas of the packing material or it could be greater if the biofilm is rough and uneven. All of the other parameters in the model are either measured or derived from experiments. The model incorporates the data from the transport and transport-reaction diffusion cell experiments using leachate and agarose and applying it to model the data collected in the Raschig ring biofilters.

Fig. 4 shows the removal rate as a function of loading rate and the model predictions for both biofilters. As shown in Fig. 4, the model predicts the removal rate of α-pinene in the 1/2 and 1 in. Raschig ring biofilters within the experimental error of the data. The model predicts almost complete removal at low loading rates with the removal efficiency decreasing with loading rate, which agrees with the experimental results within the associated error. Also, as expected, the model for the 1 in. Raschig ring biofilter predicts poorer removal rates than the 1/2 in. Raschig ring biofilter due to the lower surface area per volume packing material.

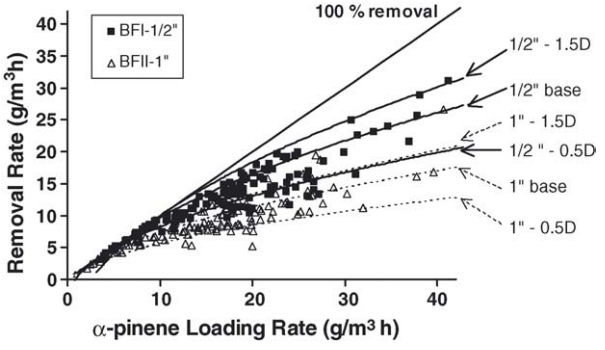

Fig. 5. Sensitivity of mathematical model of biologically mediated transformation to 50% changes in diffusion coefficient compared to experimental results in the 1/2 in. (solid lines and symbols) and 1 in. (dashed lines and open symbols) Raschig ring biofilters—100% removal line shown for reference.

The sensitivity of the model to the diffusion coefficient or rate constant and the air/water partition coefficient was also examined. The model was found to be sensitive to 50% changes in the diffusion coefficient (or rate constant) and the air/water partition coefficient (Figs. 5 and 6).

These results demonstrate that the model is sensitive to the following factor in the model:

$$\frac{2 \cdot k_{0e} \cdot D}{K_{A-mobile}} \tag{11}$$

As expected, a 50% increase in the rate constant or diffusion coefficient or a 50% decrease in the air/mobile partition coefficient increases the predicted removal rates for both biofilters. A 50% increase or decrease in the factor also brackets the experimental data.

The penetration depth of α-pinene in the biofilm can be calculated as it was in the diffusion cell model according to Equation (6) to see if the depth is reasonable for a thin film of enzymes in contrast with bacteria. In the biofiltration model, the penetration depth is smaller than in the diffusion cell, and ranges between 0.5 and 2.6 μm for the range of loading rates examined which would be unreasonably thin for a film of bacteria. The smaller magnitude of the penetration depth compared with the diffusion cell value is due to the lower inlet α-pinene concentrations to the biofilters, which range between 5 and 160 ppmv, whereas the beginning concentration in the diffusion cell was 760 ppmv. Of course, as the concentration in the diffusion cell drops, the penetration depth would also drop and reach values comparable to those in the biofilters.

Considering a fixed film thickness of enzymes, δ, would result in a plateau in calculated removal rates at large loading rates. The situation would correspond to the case when the thickness of the enzyme film is smaller than the penetration depth of the pollutant, δ^*. The removal rates would then be calculated based on zero-order removal rates in a shallow or fully penetrated, reaction-limited film as in the following equation based on the biofilter equations:

$$\text{Removal rate} = \frac{F \cdot A \cdot k_{0e} \cdot \delta \cdot H}{V_{bed} \cdot U_g} \quad (12)$$

For a given film thickness the maximum removal rate is obtained from the expression Eq. (12). For the greatest loading rates achieved in the present study, the corresponding film of enzymes would be thinner than 2.6 μm. Based on the Raschig ring results, however, a plateau was not reached in this study. Results by Mohseni and Allen [1] for wood chip biofilters show that a plateau was reached, with their maximum removal rates averaging (45–50) g/(m^3bed h). Mohseni and Allen [1] used a film thickness of 100 μm in their model but they also used an estimate for the air/biofilm partition coefficient of 0.011, which is about 2 orders of magnitude lower than the air/water partition coefficient. Even though Mohseni and Allen's [1] model provided a good fit to the removal data they obtained, the research presented here shows that the model does not truly represent what is taking place in the biofilm. The model presented here provides a more plausible mechanism. Here we have shown that in fact, the transport into and through the biofilm is actually the same as through water and so the mass transfer is governed by the air/water partition coefficient at steady-state. The enhanced mass transfer rate in the enzyme model presented here is due to the reaction of α-pinene to a more soluble compound taking place in a thin film.

The proposed model assumes that the enzyme concentration is constant through the film thickness. A constant degradation rate throughout the film is then predicted since it is a function of enzyme activity and enzyme concentration. It could be that the reaction rate due to the enzyme is not constant throughout the depth of the film. If there is an enzyme concentration gradient across the film, with the greatest enzyme concentration at the surface of the film, enzymatic reaction rates would change throughout the depth of the film. Nevertheless, the rate as measured from the diffusion cell data fits the biofiltration data well and could represent an average reaction rate.

The proposed model also does not incorporate any convection terms or enhancement in mass transfer due to mobile enzymes. It is possible that the enzymes are able to move within the film, which would increase mass transfer. Enhanced mass transfer might result because even though the actual rate of reaction is much smaller, the enzymes are able to move. If this were the case, the zero-order rate constant from the diffusion cell experiments may actually reflect not only enzyme activity, but also enhancement due to mobile enzymes within the film.

In summary, a biofilter model was developed based on zero-order kinetics and an inferred zero-order rate constant derived based on diffusion cell experiments. The model predicts behaviour observed in the Raschig ring biofilters within the error of the experiments.

4. Significance

The present research impacts model formulations used for biofiltration, particularly of hydrophobic pollutants. Conventional models treat the transport properties of a pollutant in a biofilm the same as those in water, which has been confirmed by related research by the authors [7–9]. However, conventional models also consider that the pollutant is directly degraded to carbon dioxide, water and more biomass within the biofilm at a certain rate. While this is true in a global sense, by-products that are being formed could significantly affect the rates of degradation observed in the biofilter. If there is an initial conversion of the compound into something more soluble by a thin film of enzymes, the mass transfer rate of α-pinene into the film will be greater than predicted because of the smaller film depth and steeper concentration gradient. The present study also explains why other hydrophobic pollutants may be treated in biofilters at higher than predicted removal rates. Other compounds could have a similar mechanism of degradation within biofilters whereby they are converted into more soluble and less volatile compounds by an enzyme present within the biofilm.

5. Conclusions

A simple transport and reaction model based on zero-order kinetics was developed that fit results seen in a diffusion cell using active α-pinene leachate immobilised in low melting point agarose. The model was developed based on zero-order kinetics of an enzyme catalysing the initial partial oxidation of α-pinene into a more soluble compound. By extension, the model fit data collected from laboratory-scale biofilters packed with Raschig rings.

Our results support a novel mechanism of biofiltration whereby a biologically mediated transformation is taking place with α-pinene being oxidised into a more soluble compound. The proposed model provides an explanation of why other hydrophobic pollutants may be treated in biofilters at higher than predicted removal rates. Other compounds could have a similar mechanism of degradation within biofilters whereby they are converted into more soluble and less volatile compounds by an enzyme present within the biofilm.

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