Effects of Packing Material Type on *n*-Pentane/Biomass Partition Coefficient for Use in Fungal Biofilters

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The partition coefficient between volatile organic compounds (VOCs) and biomass is one of the most representative parameters in hydrophobic VOCs biofiltration. In this study, the *n*-pentane/dry-biomass partition coefficient ($K^{D}_{P/B}$) was determined in microcosms for the filamentous fungus *Fusarium solani*, it was grown in four packing materials (compost, peat, perlite and vermiculite) at different temperatures (15 °C, 25 °C and 35 °C). The results show that the *n*-pentane/wet-biomass partition coefficients ($K^{W}_{P/B}$) for all experiments in organic packing material were on average 160-fold lower (0.21 ± 0.09) than those in water (33.2 ± 9.4), while for inorganic packing material on average 700-fold lower (0.05 ± 0.04). On the other hand, it was observed that the $K^{W}_{P/B}$ for the fungus grown in an inorganic packing material was on average 4-fold lower than when grown in organic packing material. In conclusion, the use of inorganic packing material increases the solubility (lower $K^{W}_{P/B}$) of *n*-pentane, increasing the elimination capacity in fungal biofilter.

Key words:
Partition coefficient, biofiltration, *Fusarium solani*, *n*-pentane, hydrophobic VOCs

Introduction

The partition coefficient between volatile organic compounds (VOCs) and biomass is one of the most representative parameters in hydrophobic VOCs biofiltration. This relationship between the VOCs concentrations in the gas phase and the biomass (biofilm) is directly proportional to the bioavailability of VOCs in the biomass.[1,2]

Biofiltration is an efficient technology for application in VOCs removal because microorganisms use them as carbon and energy source.[3] Generally, hydrophobic VOCs contribute to odors in the air;[4,5] gases such as α-pinene, xylene, toluene, *n*-hexane, *n*-pentane are present in contaminated industrial environments, so they are the subject of numerous studies for removal.[6–8] *n*-Pentane is a compound used in the processing industry, including polystyrene foam production, and as a component in automotive fuels. In addition, *n*-pentane is highly hydrophobic, and thus highly toxic to human health.[9]

Research related to hydrophobic VOCs biofiltration has used various types of microorganisms such as air purifiers, contaminated streams, identifying filamentous fungi as one of the most efficient.[10–12] This is due to the enzymatic variety and physical properties of the filamentous fungi: high adhesion to the packing material and a larger surface for mass transfer (air/biomass).[13]

For the development of biomass in the VOCs biofiltration process, different packing materials have been used. Packing materials such as peat, perlite, wood chips, compost, vermiculite and modified polymers have been recommended by several authors.[2,8,14–16] However, in these studies different removal efficiencies were obtained for similar operating conditions. Guieysse *et al*.[2] suggests that the packing material affects the biological response of the microorganism in the carbon source consumption. In this sense, there is little information on the quantification of the effect of the packing material's nature and characteristics in the carbon source transport from the gas phase to the biomass, as it is expected that this will not affect the elimination capacity (EC). Research has established that the packing material generates a change in the kinetics consumption of the carbon source of fungi, since there is a biologically active relationship with the microorganism.[2,16,17]

Moreover, other factors affecting the performance of fungal biofilters include the fact that they generally grow slower and have lower metabolic activity than bacteria. Also, as a result of the mycelial growth, obstruction of air passage may lead to increased pressure drop and possibly flow obstruction, bed compaction and reduction in permeability has

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been also observed. There is an extended concern on spore emissions and possible pathogenicity of the strains used, but there are some authors maintaining that many fungi are not pathogenic at all.[18]

This paper studies the effect of the packing material type on the *n*-pentane/dry-biomass partition coefficient ($K^{D}_{P/B}$) in the biological gas treatments. For this purpose, the $K^{D}_{P/B}$ in microcosm with two inorganic packing materials (perlite and vermiculite) and two organic packing materials (peat and compost) were determined. In all the experiments, *Fusarium solani* was used as model microorganism, *n*-pentane as carbon source and three different temperature conditions.

Materials and methods

Microorganisms and microcosm preparation

Fusarium solani B1 was grown in solid media (Table 1) (Perlite, Vermiculite, Compost and Peat) imbibed with liquid mineral medium in closed environments (microcosms) with *n*-pentane as a substrate. The microcosms were inoculated with $2 \cdot 10^7$ spore's g^{-1} dry support.

Closed flasks were used to evaluate the $K^{D}_{P/B}$ and kinetic parameters (maximum specific growth rate and affinity constant). The experiments were performed in triplicate in 125 mL serum bottles sealed with Mininert Teflon Valves (VICI; Precision Sampling, Baton Rouge, LA).

Carbon source and mineral medium

The model compound used as contaminant was liquid *n*-pentane (Merck, 99 %). The mineral medium was prepared in a buffered phosphate solution (pH 4) and contained (g L^{-1}): 18 $NaNO_3$; 1.3 KH_2PO_4; 0.38 $MgSO_4 \cdot 7H_2O$; 0.25 $CaSO_4 \cdot 2H_2O$; 0.055 $CaCl_2$; 0.015 $FeSO_4 \cdot 7H_2O$; 0.012 $MnSO_4 \cdot H_2O$; 0.013 $ZnSO_4 \cdot 7H_2O$; 0.0023 $CuSO_4 \cdot 7H_2O$; 0.0015 $CoCl_2 \cdot 6H_2O$; 0.0015 H_3BO_3. In order to prevent bacterial growth and favor the fungal population, the mineral medium was supplemented with gentamicin (40 mg L^{-1}) and chloramphenicol (50 mg L^{-1})[19] in all experiments.

Partition coefficient determination

Pentane/biomass partition coefficient experiments were performed with biomass grown in perlite, vermiculite, compost and peat. To evaluate the $K^{D}_{P/B}$, the fungal mycelium was first dried at room temperature in a closed chamber with silica. Then, 5 g of packing material with inactivated biomass were placed in closed bottles. Finally, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.5 μL *n*-pentane was added in the headspace and the samples were maintained for 48 h at 15, 25 and 35 °C.

The *n*-pentane headspace concentration ($\gamma_{headspace}$, g m^{-3}) was determined by direct gas chromatography injection. The *n*-pentane concentration in the biomass ($\gamma_{biomass}$, g m^{-3}) was obtained through mass balance. Control experiments showed negligible sorption of *n*-pentane on all support. The *n*-pentane/dry-biomass partition coefficient ($K^{D}_{P/B}$, adimensional) can be expressed as:

$$K^{D}_{P/B} = \frac{\gamma_{headspace}}{\gamma_{biomass}} \quad (1)$$

The partition coefficient for the biomass on a wet basis can be calculated by eq. (2) that includes the water fraction and the *n*-pentane/water partition coefficient ($K_{P/W}$).

$$\frac{1}{K^{W}_{P/B}} = \frac{x^{D}_{B}}{K^{D}_{P/B}} + \frac{x_W}{K_{P/W}} \quad (2)$$

where: x_W and x^{D}_{B} are the mass fractions of water or dry biomass, respectively, $K^{W}_{P/B}$ is the *n*-pentane partition coefficients in wet biomass (adimensional).

Water content of *F. solani* was obtained from Vergara-Fernández *et al.*[17]

Kinetic parameters

These were determined using the Monod model for *n*-pentane:[20]

$$\mu = \mu_{max}\left[\frac{\gamma_{headspace}}{K_S + \gamma_{headspace}}\right] \quad (3)$$

Table 1 – *Comparison of four different packing materials used in the microcosms*

Packing material	Particle size (mm)	Water retention (%)	Initial pH microcosms	Packing density (dry) (g L^{-1})	Bed porosity (%)
Perlite	4.8–3.4	79(±4)	4.92(±1.2)	110(±12)	53(±7)
Vermiculite	4.2–3.4	68(±5)	4.29(±1.1)	130(±9)	60(±5)
Compost	1.2–1.9	52(±2)	4.98(±0.9)	128(±8)	48(±3)
Peat	Variable	75(±3)	4.5 (±0.98)	85(±6)	68(±9)

where: μ_{max} is the maximum specific growth rate (h^{-1}), K_S is the affinity constant (g m^{-3}), and $\gamma_{headspace}$ is *n*-pentane concentration in the gas ($g_{pentane}$ $m^{-3}_{headspace}$).

Kinetic parameters were obtained by *n*-pentane consumption. For the test, 1.5 g of packing material was mixed with 10 mL mineral medium and inoculated with a spore suspension. The *n*-pentane consumption rates were obtained from the evolved *n*-pentane at 15 °C, 25 °C and 35 °C in microcosms using headspace initial *n*-pentane concentrations between 0.5 and 30 g m^{-3} for a period of 6 days. Microcosms consisted of 125 mL closed flasks similar to those used in the $K^{D}_{P/B}$ experiments. The relation between *n*-pentane consumption and specific growth rate was obtained according to eq. (4):

$$\mu = -\frac{Y_{X/S}}{X}\frac{d\gamma_{headspace}}{dt} \quad (4)$$

where: $\gamma_{headspace}$ is *n*-pentane concentration in the gas ($g_{pentane}$ $m^{-3}_{headspace}$), $Y_{X/S}$ is the biomass yield ($g_{biomass}$ $g^{-1}_{pentane}$), X is biomass (g m^{-3}) and t is time (h).

The μ_{max} and K_S values were calculated based on three independent measurements by plotting the *n*-pentane consumption rate against the headspace *n*-pentane concentration. The *n*-pentane headspace concentration was determined by direct gas chromatography injection.

Analytical methods

Gaseous *n*-pentane concentration was measured in triplicate by FID-GC, Shimadzu 2014 (detection temperature 220 °C, injection temperature 80 °C and column temperature 200 °C), equipped with a capillary column, model Rtx-5 Restex UE (30 m × 0.32 mm × 0.25 μm), using nitrogen as a gas carrier.

The biomass was measured as volatile solids with a thermogravimetric analyzer according to Arriaga and Revah.[21] This analysis allowed quantifying the mass losses and associated them with the processes of water and carbon combustions. These measurements were carried out in duplicate.

Results and discussions

Partition coefficients

Table 2 shows the $K^{D}_{P/B}$, $K^{W}_{P/B}$ and K_W using different packing material and growth temperature. Pentane/water partition coefficients (E13-E15) were determined as experimental control, and found to be within the reported values (Dupasquier *et al.*[22] and Höhener *et al.*[23]). It was also used to determine $K^{W}_{P/B}$.

Table 2 – *Effects of packing material type on VOCs/biomass partition coefficient at different operating temperatures*

N° of exp.	Temperature	Biomass ($mg_{biomass}$ $g^{-1}_{support}$)	$K^{D}_{P/B}$ (a) (experimental)	$K^{W}_{P/B}$ (b,c)
		n-Pentane/Perlite		
E1	15 °C	29.6(±2.5)	0.0027(±0.00075)	0.015(±0.0042)
E2	25 °C	31.3(±3.2)	0.0042(±0.00032)	0.023(±0.0018)
E3	35 °C	19.8(±1.5)	0.0058(±0.00073)	0.032(±0.0041)
		n-Pentane/Vermiculite		
E4	15 °C	34.5(±5.1)	0.0037(±0.00077)	0.021(±0.0043)
E5	25 °C	40.5(±6.2)	0.016(±0.0014)	0.088(±0.0079)
E6	35 °C	39.2(±2.1)	0.019(±0.002)	0.11(±0.011)
		n-Pentane/Compost		
E7	15 °C	25.6(±3.1)	0.022(±0.0018)	0.12(±0.0099)
E8	25 °C	35.9(±2.9)	0.037(±0.0089)	0.20(±0.049)
E9	35 °C	42.8(±4.8)	0.062(±0.0086)	0.34(±0.047)
		n-Pentane/Peat		
E10	15 °C	34.5(±2.5)	0.019(±0.0068)	0.11(±0.037)
E11	25 °C	39.8(±1.9)	0.03(±0.0048)	0.17(±0.026)
E12	35 °C	44.8(±3.6)	0.054(±0.0047)	0.30(±0.026)
		n-Pentane/Water		
E13	15 °C	---	26(±1.2)	---
E14	25 °C	---	29.9(±2.5)	---
E15	35 °C	---	43.8(±3.0)	---

(a) *n*-pentane/biomass partition coefficient in dried biomass, (b) *n*-pentane partition coefficients in wet biomass, (c) obtained from eq. 2 with w = 82 % water (Vergara-Fernández *et al.*[17]).

Table 2 shows that the $K^{W}_{P/B}$ for biomass grown on inorganic packing material (E1 to E6) at 15 °C, 25 °C and 35 °C are on average 1400, 530 and 620 times lower than those obtained in water at the same temperature, respectively. In addition, the $K^{W}_{P/B}$ for biomass grown on organic packing material (E7 to E12) at 15 °C, 25 °C and 35 °C are on average 230, 160 and 140 times lower than those obtained in water at the same temperature, respectively. Vergara-Fernández *et al.*[17] observed similar situations for the *n*-hexane/biomass partition coefficients. This confirms the change created by the presence of biomass in the $K^{W}_{P/B}$, increasing the solubility of *n*-pentane according to that previously reported by Davison *et al.*[24] which indicate that the presence of biomass decreases the hydrophobic VOCs/biomass partition coefficients. On the other hand, to simulate operating conditions in a fungal biofilter, the partition coefficient was determined

for wet biomass ($K^{W}_{P/B}$) (eq. 2), obtaining for all experiments an increase of six times average compared to $K^{D}_{P/B}$, a similar result to that observed by Vergara-Fernández *et al.*[17] for *F. solani* grown in *n*-hexane. The increase in the $K^{W}_{P/B}$ is an effect of the resistance caused by the presence of water on the fungus surface (hydrophilic barrier).[6,16] However, even under these conditions the *n*-pentane solubility is approximately 250 times higher than that observed in biofilters using bacterial or microbial consortia.[25]

Table 2 shows that for each set of experiments with perlite (E1 to E3) and vermiculite (E4 to E6), the $K^{W}_{P/B}$ was on average ten times lower than in the case of experiments using organic packing material (compost E7 to E9 and peat E10 to E12), for all temperatures used. This indicates a higher solubility of *n*-pentane gas in the biofilm, when the fungus is grown in an inorganic packing material compared to an organic packing material. For example, for a concentration of *n*-pentane in the gas phase of 5 g m^{-3}, at a temperature of 25 °C, it is possible to obtain a concentration in the biofilm, for the fungus grown in perlite (E2) and peat (E11) of 217 and 29 g m^{-3}, respectively. The lower $K^{W}_{P/B}$ when the fungus was grown in inorganic packing material is related to the fungus adaptation to the use of a hydrophobic carbon source in the gas phase, becoming a more hydrophobic surface caused by the production of hydrophobic proteins (hydrophobins).[26,27] However, when the fungus was grown in an organic packing material a lower hydrophobicity of the fungus, and therefore greater $K^{W}_{P/B}$ (lower adaptation to the use of *n*-pentane)[27] was observed. This could be related to the presence of another carbon source due to the nature of the packing material. Vergara-Fernández *et al.*[17] reported a similar result when the fungus was grown under hydrophobic and hydrophilic carbon sources, obtaining a lower *n*-hexane/biomass partition coefficient (higher solubility) when the fungus was grown in a hydrophobic carbon source (200-fold). These results indicate that the use of filamentous fungi in the *n*-pentane biofiltration increases the mass transfer of the contaminant increasing its EC, assuming the system is not limited by microbial biodegradation. In addition, this EC is increased when the fungus is grown in an inorganic packing material (perlite, vermiculite), due to decrease $K^{W}_{P/B}$ compared to growth in organic packing material. This higher partition coefficient, in organic packing materials, could be caused by increased water retention capacity of the packing material. Ortiz *et al.*[8] indicate that the water retention capacity for perlite and peat is 68 % and 78 %, respectively. The same authors suggest that when using an inorganic packing material (perlite), the EC of hydrophobic VOCs (*n*-hexane and *n*-pentane) was increased compared with peat, due to better control of pH and moisture.

On the other hand, experiments with inorganic packing material (E1 to E6) showed a similar $K^{W}_{P/B}$ when the fungus was grown in perlite and vermiculite (Table 2). This may be related to the similar structure and characteristics of the packing material used.[28,29] Likewise, when the fungus was grown on an organic packing material (E7 to E12) a similar $K^{W}_{P/B}$ was observed for all temperatures used. This can be related to the similar structure and characteristics of the compost and peat, water retention capacity (between 70 and 78 %),[8,30] packing densities (between 660 and 750 g L^{-1}), bed porosity (between 0.43 and 0.51), percentage of carbon (% dry mass) (between 29 and 31 %), and material density (between 1.79 and 1.46 g mL^{-1}).[31]

Finally, although the use of inorganic packing material in biofiltration systems increases the partition coefficient of *n*-pentane with regard to the use of organic packing material, Vergara-Fernández *et al.*[32] indicate that the start-up time is greater when using inorganic packing material, while the maximum EC obtained is less when using organic packing material.

Effect of temperature over partition coefficients

Table 2 shows the effect of temperature on $K^{W}_{P/B}$. In all experiments, an increase in $K^{W}_{P/B}$ (twice between 15 °C and 35 °C) with temperature was observed, indicating a decrease in the solubility of *n*-pentane on the fungal biomass. These results were also observed by Fischer *et al.*[33] for methyl *tert*-butyl ether (MTBE). This implies a lower *n*-pentane biodegradation, however, at higher temperature it increases the biological activity (see Table 3), which partially offsets the lower solubility, increasing the concentration gradient and thus the mass transfer from the gas phase to the biomass.

Kinetic parameters

Table 3 shows the results of the kinetic parameters obtained for *F. solani* grown in gaseous *n*-pentane using perlite and compost, at three temperatures (15 °C, 25 °C and 35 °C). Table 3 shows that for both packing material types, when the temperature is increased, μ_{max} increases, clearly indicating that temperature has an effect on the growth of *F. solani*. On the other hand, it was observed that there are differences between the values of K_S obtained for the temperatures tested. However, there are no definite trends concerning the temperature when using different packing materials. Overall, when using compost, the value of K_S increases by an average of 2.5 times more than when using

Table 3 – *Kinetic parameters of F. solani grown with gaseous n-pentane, using compost and perlite as packing material at three temperatures*

Parameters		Temperature		
		15 °C	25 °C	35 °C
Perlite growth				
μ_{max}	h^{-1}	0.15(±0.012)	0.20(±0.009)	0.23(±0.012)
K_S	g m^{-3}	9.57(±1.94)	5.03(±0.76)	8.76(±3.0)
R^2	---	0.973	0.984	0.910
Compost growth				
μ_{max}	h^{-1}	0.02(±0.007)	0.08(±0.012)	0.14(±0.014)
K_S	g m^{-3}	11.32(±8.08)	27.05(±7.5)	24.45(±4.5)
R^2	–	0.810	0.981	0.985

R^2 is the correlation coefficient.

perlite, i.e. the organism's affinity for the substrate decreases in the presence of compost.

The results of μ_{max} (Table 3) when the fungus was grown in compost shows that this was on average ten times lower than when grown in perlite. This indicates a lower solubility of the *n*-pentane in the biomass when the fungus is grown in an organic packing material.

The $Y_{X/S}$ average obtained for all temperatures, in both packing materials used was 0.98 (± 0.10) g g^{-1}.

Conclusion

The type and characteristics of the packing material used in a biofiltration system has an effect on the $K^{W}_{P/B}$ of *Fusarium solani*. When the fungus is grown in an inorganic packing material the $K^{W}_{P/B}$ decreases, which causes an increase in solubility of *n*-pentane, compared with that grown in an organic packing material. The effect generated by the packing material type used is the result of physical-chemical characteristics such as water retention capacity, porosity, hydrophobicity and packing density. The increase in temperature decreases the solubility of *n*-pentane in the biomass (higher partition coefficient), however, it increases the biological activity partially counteracting the lower solubility.

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List of symbols

$\gamma_{headspace}$ – *n*-pentane headspace concentration, $g_{pentane}\ m^{-3}{}_{headspace}$
$\gamma_{biomass}$ – *n*-pentane concentration in biomass, g m^{-3}
K_S – affinity constant, g m^{-3}
$K_{P/W}$ – *n*-pentane/water partition coefficient, –
$K^{W}_{P/B}$ – *n*-pentane/wet-biomass partition coefficient, –
$K^{D}_{P/B}$ – *n*-pentane/dry-biomass partition coefficient, –
μ – specific growth rate, h^{-1}
μ_{max} – maximum specific growth rate, h^{-1}
R^2 – correlation coefficient, –
t – time, h
w – mass fraction, %
X – biomass concentration, g m^{-3}
x_W – water-mass fraction, –
x^{D}_{B} – dry-biomass mass fraction, –
$Y_{X/S}$ – biomass yield, $g_{biomass}\ g^{-1}{}_{pentane}$

List of abbreviations

VOCs – volatile organic compounds
EC – elimination capacity, $g_{pentane}\ m^{-3}\ h^{-1}$
MTBE – methyl *tert*-butyl ether

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