

Characterization of absorbent polymers for the removal of volatile hydrophobic pollutants from air

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Abstract

BACKGROUND: An emerging innovation for the treatment of polluted air consists in using a liquid–solid biphasic system, in which the sequestering phase contains inert polymer beads. The different polymers tested here for this purpose were; Hytrel[®] G3548L, Hytrel[®] G4078W, styrene butadiene copolymer, 28% and 31%, silicone rubber, PEBAX[®] 2533, and rubber tires. The selection of the most effective polymer(s) first requires a determination of the uptake of the pollutants by the solid phase in terms of key polymer properties such as partition coefficient, diffusion coefficient and biodegradability.

RESULTS: A significant difference was found in the uptake levels of α -pinene from the gas phase for the different polymers tested. Based on partition coefficient measurements, relatively non-polar polymers such as Kraton[®] tend to uptake α -pinene better than polar ones, such as Hytrel[®]. A reduction in the partition coefficient of α -pinene into polymers in the presence of water has also been observed. It was also proven that the tested polymers are not biodegradable.

CONCLUSIONS: The uptake of α -pinene by the different polymers tested was determined and it was shown that such polymers could be used for air pollution control. Furthermore, their non-biodegradability justifies their use as absorbents. This paper provides a new opportunity to work with biofilters (BFs)/biotrickling filters (BTFs) using polymers as a sequestering phase.

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Keywords: α -pinene; absorption; diffusion; partition coefficient; polymer; VOCs

INTRODUCTION

α -pinene (2,6,6-trimethylbicyclo(3.1.1)-2-hept-2-ene) is an organic compound of the terpene group. It is found in the oils of many species of coniferous trees, mainly pine, and it is also found in essential oils of rosemary (*Rosmarinus officinalis*).¹ α -Pinene is readily absorbed in the gastrointestinal tract, the skin, and the respiratory tract. It is a local irritant, central nervous system depressant, and an irritant to the bladder and kidney. It may cause benign skin tumors from chronic contact. Moreover, α -pinene is one of the major volatile organic compounds (VOCs) emitted to the atmosphere by wood-related industries.² The maximum allowable limit for α -pinene in the air to which workers may be continuously exposed during an 8 h period, according to the standards established by OSHA,³ is 100 ppm (as Turpentine).

Different types of bioreactors are available for the removal of α -pinene from waste-gas streams. The oldest reactor configuration is the conventional biofilter (BF), although another popular kind of bioreactor configuration is the biotrickling filter (BTF).⁴ It has been demonstrated that continuously recirculating liquid phase bioreactors, such as the BTFs, do sometimes perform better than conventional BFs.⁵ The removal of gas phase α -pinene has been reported in previous studies using both BFs and BTFs. The highest elimination capacity (EC) in a BF under steady-state conditions was reported to be 143 g m⁻³ h⁻¹, when the fungal *Ophiostoma* species was used as the dominant microorganism.² Langolf and

Kleinheinz⁶ used a lava rock BF inoculated with a consortium of microorganisms, and reported a maximum EC of 132 g m⁻³ h⁻¹. In a fungal BTF, the highest elimination capacity reported was 232 g m⁻³ h⁻¹, under mesophilic conditions.⁷ Recent studies have also shown that the addition of an immiscible second-liquid organic phase improves the performance of bioreactors, increasing the solubility of volatile organic pollutants in the liquid phase.^{7–9} Nevertheless, BTFs that employ an organic solvent as a second phase may suffer from some drawbacks such as the formation of agglomerates of solvent and biomass in the system that generate clogging problems,¹⁰ poor mixing arising from high viscosity, and relatively high cost.

A more practical approach that is becoming increasingly popular is the use of polymers (usually in the form of polymer beads) to absorb the desired target VOC molecule in a similar way to the case of organic liquid phases, such as, for example, silicone oil.¹¹ So

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far, they have been used to replace the second liquid phase only in two-phase partitioning bioreactors (TPPBs).¹² Such polymers do sometimes present advantages over organic solvents^{13,14} in that they are biocompatible, non-biodegradable, non-volatile and inexpensive. Moreover they can be formed into a large variety of shapes and sizes, and can be tailored to a particular target molecule through monomer selection, cross-linking, and polymer processing.¹⁵

To our knowledge, no attempts have been made to apply polymers in packed-bed bioreactors as BTFs. In our opinion, these organic polymers would provide new properties to a conventional BTF that could fundamentally affect its mechanism of operation. This was the motivation for the current study. As is well known, the operation of a conventional BTF is based on a contaminated air stream passing co- or counter-currently through a packed bed of inert material on which a pollutant-degrading biofilm has been established.⁵ Under optimal conditions, the presence of polymers should facilitate the uptake of α -pinene into the polymers from direct contact with the air stream. Afterwards, the pollutant should be slowly released from that solid phase into the water phase for degradation by the microorganisms. Thus, two uptake/release situations need to be considered: gas-to-polymer and polymer-to-water. This work was carried out to identify appropriate polymers for the removal of α -pinene from air in BTFs. The contribution of this study consisted in determining the parameters that are important for estimating the target molecule's environmental fate and toxicity, such as the partition coefficient of α -pinene, between the polymer and the water phase and between the polymer and the gas phase, and diffusion coefficient in order to characterize the uptake/release performance of α -pinene by polymers.

MATERIALS AND METHODS

Chemicals and polymers

Sigma Aldrich (Canada) was the supplier for α -pinene (98% purity). The polymers tested include Hytrel[®] G3548L (Dupont, Canada), Hytrel[®] G4078W (Dupont, Canada), styrene butadiene copolymer, 28% and 31% (Scientific Polymer Products Inc., Ontario, NY, USA), silicone rubber (General Electric, Waterford, NY, USA), PEBAX[®] 2533 (Arkema, Canada Inc., Burlington, ON, Canada) and rubber tires (Recovery Technologies, Cambridge, ON, Canada). The polymers were washed with water and then dried before their use. Some important characteristics of the polymers are listed in Table 1.

Biocatalyst and culture conditions

A mixed microbial consortium (derived from several soil samples) was used to study the biodegradability of the polymers.¹⁵ The consortium was grown in liquid culture which contained (per L) 10 mL of a medium solution, 10 mL of phosphate buffer solution and 2 g glucose. The medium solution contained per litre of distilled water: 1 g EDTA, 0.2 g ZnSO₄ · 7 H₂O, 0.1 g CaCl₂ · 2 H₂O, 0.5 g FeSO₄ · 7 H₂O, 0.02 g Na₂MoO₄ · 2 H₂O, 0.02 g CuSO₄ · 5 H₂O, 0.04 g CoCl₂ · 6 H₂O, 0.1 g MnCl₂ · 4 H₂O, 200 g (NH₄)₂SO₄ and 10 g MgCl₂ · 6 H₂O. The buffer solution (pH = 7) contained per L distilled water: 155 g K₂HPO₄ and 85 g NaH₂PO₄ · H₂O. Salts were added in the order described. All experiments were performed under non-sterile conditions.

Polymer partition coefficient

Different amounts of polymer, from 4 g to 20 g, were added to 164 mL serum bottles containing 80 mL distilled water and sealed

with rubber stoppers. One bottle was used as control, with no polymer. Taking into account the low solubility of α -pinene in water (~2 to 22 mg L⁻¹), equal amounts (3.8 μ L) of liquid phase α -pinene were added directly to each of the serum bottles, and these vials were placed on a shaker, maintained at 30 °C and 180 rpm.¹⁶ After reaching equilibrium, the gas phase α -pinene was analyzed by GC-FID. The amount α -pinene in the polymer phase was estimated based on mass balance calculations, while α -pinene concentration in the liquid phase was calculated using Henry's Law. The slope of the straight line of the polymer phase α -pinene concentration versus its aqueous phase concentration corresponds to the partition coefficient of that polymer towards α -pinene. Partition coefficient can be defined herein as the ratio of concentration of a mixture of two immiscible solvents at equilibrium, expressed as

$$K = \frac{[\alpha - pinene]_{polymer}}{[\alpha - pinene]_{gas,water}} \quad (1)$$

A similar procedure was followed for the determination of partitioning of α -pinene between the polymer and the gas phase, but with no distilled water.

Absorption tests

Absorption tests performed to estimate the rate of α -pinene uptake were carried out in batch experiments with different polymers and in the absence of water. The same amount of polymers and α -pinene were used, similar to the values used for partition coefficient experiments. The test bottles were maintained under constant shaking conditions (180 rpm) on an orbital shaker, at 30 °C. Gas phase sampling was stopped when equilibrium conditions were reached, that is, when a constant gas phase concentration was detected.

Diffusion coefficients of α -pinene

The diffusion coefficients for α -pinene were tested in different polymers. These were determined experimentally by adding 4 g polymer into sealed 164 mL serum bottles. The liquid volume of α -pinene that caused saturated gas dissolution with a concentration of 52 mg L⁻¹ was injected into the gas phase, and these bottles were maintained at 30 °C and agitated in an orbital shaker at 180 rpm. Periodic gas phase measurements were made using a gas-tight syringe, through a sealed septum at the top of the bottle. The gas phase concentration was measured using gas chromatography with flame ionization detector (GC/FID). Diffusion coefficients were then determined using the method described by Amsden *et al.*¹⁷ and Daugulis *et al.*¹⁸

Biodegradability

To determine if the selected polymer beads were biodegradable, 4 g of beads were placed in 125 mL Erlenmeyer flasks containing 50 mL medium, without glucose. Each flask was inoculated with 10 mL of a mixed microbial consortium and agitated at 180 rpm and 30 °C for 4 days. A positive control without polymer was used. Samples were periodically taken to determine cell concentrations.

ANALYTICAL METHODS

Cell measurement

A cell dry weight (CDW) versus optical density (OD) calibration curve was used. Cell concentrations were measured at 600 nm with a Biocrom (Edmonton, AB, Canada) Ultraspec 3000 UV/Vis spectrophotometer.

Table 1. Sources and properties of the polymers used in this study

| Trade name | Grade | Supplier | Chemical composition | Hardness | Shore value | T_g^a (°C) | Specific gravity (g cm ⁻³) | Diameter (mm) | Weight (mg) |
|---------------------|--------|---------------------------------------|--|----------|-------------|--------------|--|---------------|-------------|
| Hytrel [®] | G3548L | DuPont, Canada | Copolymer of poly(butylene terephthalate) and polyether | Shore D | 35 | -45 | 1.18 | 3.5 | 44.6 |
| Kraton [®] | G4078W | Scientific Polymer Products Inc., USA | Styrene/butadiene triblock copolymer | Shore D | 40 | -30 | 1.15 | 4 | 34.1 |
| | D4150K | | | Shore A | 45 | -80 | 0.92 | 5 | 34.2 |
| PEBAX [®] | D1102K | Arkema, Canada | Polyether block amide | Shore A | 66 | -80 | 0.94 | 3 | 36.4 |
| | 2533 | | | Shore D | 25 | -65 | 1.01 | 2.5 | 13.6 |
| Rubber tires | N/A | Recovery Technologies, Canada | Copolymer of polyisoprene, styrene-butadiene copolymer and polybutadiene | N/A | N/A | N/A | 1.00 | 5 | 6.6 |
| Silicone rubber | N/A | GE-Mastercraft | Polymer of silicone | N/A | N/A | -127 | 0.91 | 3 | 24.8 |

^a Glass transition temperature

Gas chromatography

250 µL samples of α -pinene gas phase layer were injected into a Varian GC equipped with a FID and a VF-WAX capillary column with an internal diameter of 0.53 mm and length 30 m. The carrier gas was helium, flowing at 30 mL min⁻¹. The hydrogen and air flow rates were 30 and 300 mL min⁻¹, respectively. The following conditions were used: injector temperature 250 °C, detector temperature 270 °C, oven temperature 60 °C, hold 0.5 min, ramp to 130 °C at 50 °C min⁻¹, hold for 2.10 min. The total run time for this method was 4 min.

RESULTS AND DISCUSSION

Polymer selection

The structure of α -pinene was one of the major criteria for polymer selection. It contains a reactive four-membered ring. This four-membered ring makes it a reactive hydrocarbon. Moreover, α -pinene is a hydrophobic VOC, reflected in its high octanol:water partition coefficient value ($K_{OW} = 30\,670 \pm 260$).¹⁹ Different polymers were tested in this study, which differed in their chemical structure leading to different polarities. Polymers with different degree of softness were also tested with a presumption that polymers having high permeability would improve sorption capacity.²⁰ For the above-mentioned reasons, polymers such as Hytrel[®] and PEBAX[®] were selected, and compared with Kraton[®]. Silicone rubber was used because of the good results obtained earlier, when silicone oil was tested for the removal of α -pinene in a BTF.²¹ Rubber tire chips were used because of their easy availability and low cost: this facilitates recycling of used tires, which would otherwise be destroyed by pyrolysis.

Partition coefficients

Initial efforts were made to find a polymer that had a high partition coefficient towards α -pinene in the gas phase and at the same time a low partitioning of α -pinene between the polymer and the water phase. The rationale for this was that a high uptake of α -pinene from the waste gas stream would be a desirable property as this would result in good VOC removal from the contaminated

gas phase, but a lower α -pinene sequestration by the polymer relative to the aqueous phase (i.e. retention and non-release) could provide for rapid release to the microbes in the aqueous phase. As has recently been shown,²² high partition coefficients of polymers (relative to water) for target molecules can hinder their release to the cells in an aqueous phase and are a rate limiting feature to be avoided. Thus, in our BTF scenario α -pinene should be absorbed into the polymer, and gradually, but readily, transferred to the microorganisms in the water phase where it would be biodegraded.

The affinity of the selected polymers for α -pinene was quantified through the determination of partition coefficients of α -pinene in the gas phase as well as the liquid phase, taking into account its independence of surface area. The α -pinene mass balance in the batch partition coefficient tests can be expressed by

$$M_o = C_l V_l + C_g V_g + C_p V_p \quad (2)$$

where M_o is the initial mass of α -pinene at time 0, C_l , C_g , C_p are the concentrations in the liquid, gas and polymer phase, respectively, when the equilibrium is reached and V_l , V_g , V_p are the liquid, gas and polymer volumes, respectively. The aqueous phase α -pinene concentration was calculated based on the Henry's Law relationship between air and the aqueous phase (dimensionless constant 4.4) as reported by Miller and Allen.¹⁶ The equilibrium time was estimated by performing measurements for 72 h, but based on the profile, equilibrium was reached in 24 h. Linear partitioning isotherms were found for all polymers over the observed range of concentrations.

Partitioning of α -pinene between the polymer and water

During the uptake process, the gas phase concentration of α -pinene progressively decreases and is transferred to the water phase and finally to the polymer. At the same time, the absorbed amount also increases with time. It can be seen from the partitioning coefficients shown in Fig. 1 that Kraton[®] D4150K has the highest affinity for α -pinene, followed by silicone rubber. On the other hand Hytrel[®] G4078W, PEBAX[®] 2533 and Hytrel[®] G3548L are polymers with less affinity for α -pinene in the presence of a water phase.

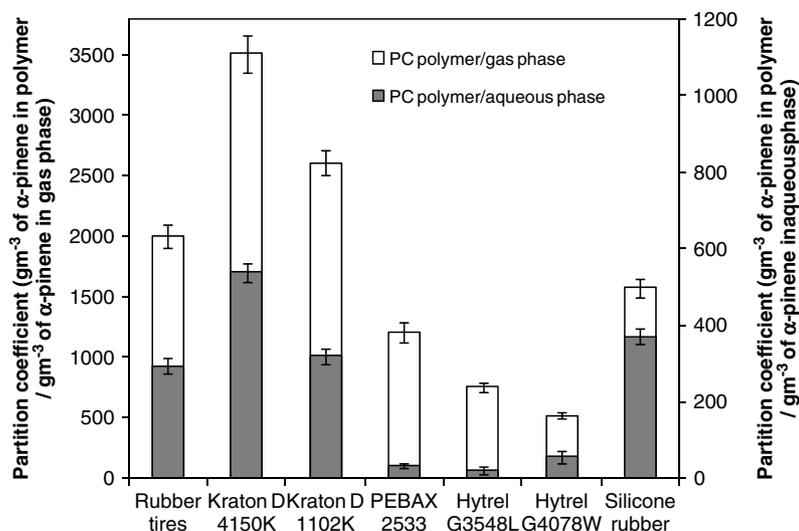


Figure 1. Partition coefficient of α -pinene between all polymers tested and aqueous or gas phase. The value was obtained based on the linear relationship (slope) between the aqueous or gas phase α -pinene concentration and polymer phase α -pinene concentration.

Partitioning of α -pinene between the polymer and gas phase

As was observed in the partitioning assays between the polymer and the water phase, Kraton[®] D4150K has the highest affinity for α -pinene, followed by Kraton[®] D1102K (Figure 1). As before, Hytrell[®] G4078W, PEBAX[®] 2533 and Hytrell[®] G3548L are polymers with less affinity for α -pinene in the absence of a water phase. The results from this study can be partly compared with the results reported by Muñoz *et al.*²³ It can be seen that only F-40 shows a similar partitioning coefficient (C_g/C_L), with a value of 0.001370, while other organic phases show higher values. From a process viewpoint, solid polymers present operational advantages due to facilitated separation and recycling and due to their lower cost.²⁴

To determine which properties had a more significant effect on partition coefficients, data from Fig. 1 were analyzed with the polymer property data from Table 1. It clearly appears that only Hytrell[®] G4078W, Hytrell[®] G3548L and PEBAX[®] 2533 demonstrated a low affinity for α -pinene, while the other polymers tested showed the highest sorption. As summarized in Table 1, Hytrell[®] thermoplastic elastomers are block copolymers, consisting of a hard (crystalline) segment of polybutylene terephthalate and a soft (amorphous) segment based on long-chain polyether glycols. Hytrell[®] G4078W and Hytrell[®] G3548L are polymers with lower grades of hardness and present low crystallinity. Previously,²⁵ it was observed that the trend seen in the Hytrell[®] family is a function of polymer softness, as was also observed in this study when there is direct contact between the gas phase and the polymer. Both Hytrell[®] and PEBAX[®] 2533 do not possess high affinity for α -pinene. PEBAX[®] 2533 is a thermoplastic polymer of polyether block amides (Table 1), and as was the case with the Hytrell[®] polymer, the degree of crystallinity is very low, i.e. only 5%. In the case of the Kraton[®] family, corresponding to polymers with only aromatic functionality, it was observed that the polymer with a higher percentage of polystyrene (Kraton[®] D4150K, 31%) showed the highest affinity for α -pinene. Taking into account the information shown in Table 2, it can also be observed that in general the most polar polymers present the lowest sorption for α -pinene while the less polar compounds present the highest sorption.

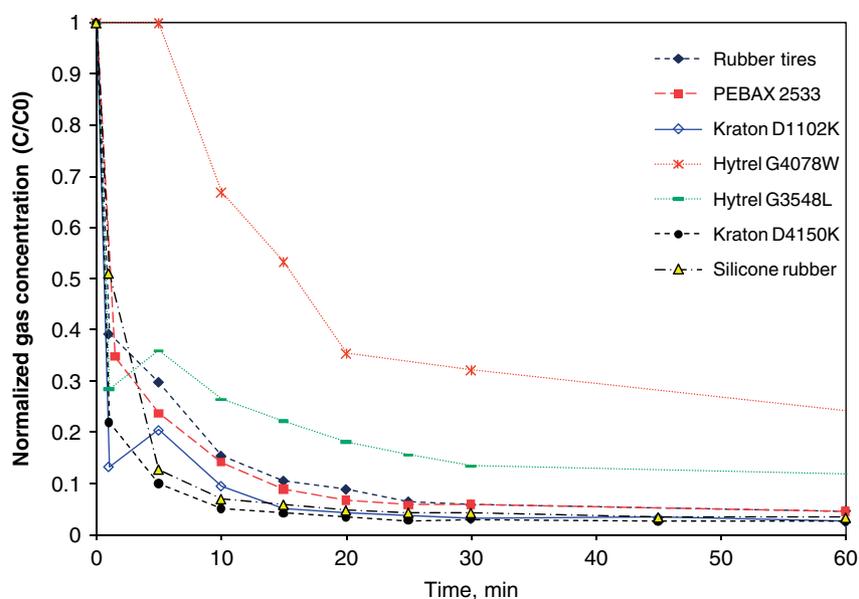
PEBAX[®] and Hytrell[®] showed less affinity to adsorb α -pinene, in both aqueous and gaseous phases, while this was not the case with silicone rubber, rubber tires and Kraton[®]. The absorption mechanism can be related to the differences in chemical structure of these compounds, polar/non-polar in nature, and their surface energy properties relative to a hydrophobic compound such as α -pinene. As evident from their chemical structure shown in Table 2, and as reported previously by Prpich and Daugulis,¹⁴ PEBAX[®] and Hytrell[®] polymers have both ester and ether linkages that open the possibility for hydrogen bonding between the polymer and the hydroxyl group of the VOC, i.e. α -pinene. However, with α -pinene, this was not the case due to the absence of a terminal -OH group in its chemical structure that weakens the intermolecular force. On the other hand, the high affinity of Kraton[®] and silicone rubber for α -pinene, in both phases, can be attributed to the surface energy properties and the hydrophobicity transfer of α -pinene. For instance, the hydrophobicity transfer onto silicone rubber can be explained here, by the mechanism reported by Shaowu.^{26,27} Silicone rubber has a well-stabilized cross-linked structure, and small quantities of highly mobile low-molecular weight chains are found on its surface. The hydrophobic α -pinene molecules once deposited on the surface of silicone rubber would gradually obtain more hydrophobicity, i.e. higher surface energy, to a different extent resulting in hydrophobicity transfer. This mechanism is also related to the inherent surface energy properties that play a major role in the adsorption process. A large difference in surface energy, the driving force of absorption, is created due to the presence of the low-molecular weight chain compounds on the surface of the silicone rubber, which then tends to absorb on the higher energy α -pinene.

Absorption tests

As mentioned before, when used in packed-bed bioreactors such as BTFs, it is very important that the polymer shows high and rapid affinity for α -pinene relative to the gas phase, so that the microorganisms are not exposed to high, inhibitory, pollutant concentrations. In the absence of water, and using 4 g of polymers, it was confirmed that only about 20 min was needed to reach

Table 2. Structures of the polymers used in this study

| Trade name | Structure |
|-----------------|--|
| Hytrel® | |
| Kraton® | |
| PEBAX® | <p>PA: Polyamide PE: Polyether</p> |
| Silicone rubber | |

**Figure 2.** α -pinene normalized concentration profile in an absorption test with polymers tested (polymer 4 g).

more than 90% absorption, except for Hytrel® G3548L and Hytrel® G4078W, which needed more than 3 h to achieve 90% absorption of α -pinene into the polymers (Fig. 2). However, gas phase sampling was stopped after equilibrium conditions were reached (24 h).

Diffusivity

The reason for using a polymer as a second phase is to ensure that the pollutant is sequestered at a rate high enough to minimize high VOC exposure to microbes. It is well known that the structure of polymers can affect the diffusion of small molecules²⁸. The following Crank equation was used to model α -pinene absorption

Table 3. Gas diffusivities of α -pinene in polymer beads

| Polymer | D_e (30 °C) ($\times 10^8$ cm ² s ⁻¹) |
|-----------------|---|
| Kraton® D4150K | 21.8 |
| Rubber tires | 19.9 |
| Silicone rubber | 12.6 |
| Kraton® D1102K | 8.19 |
| Hytrel® G4078W | 4.17 |
| Hytrel® G3548L | 3.18 |
| PEBAX | 2.25 |

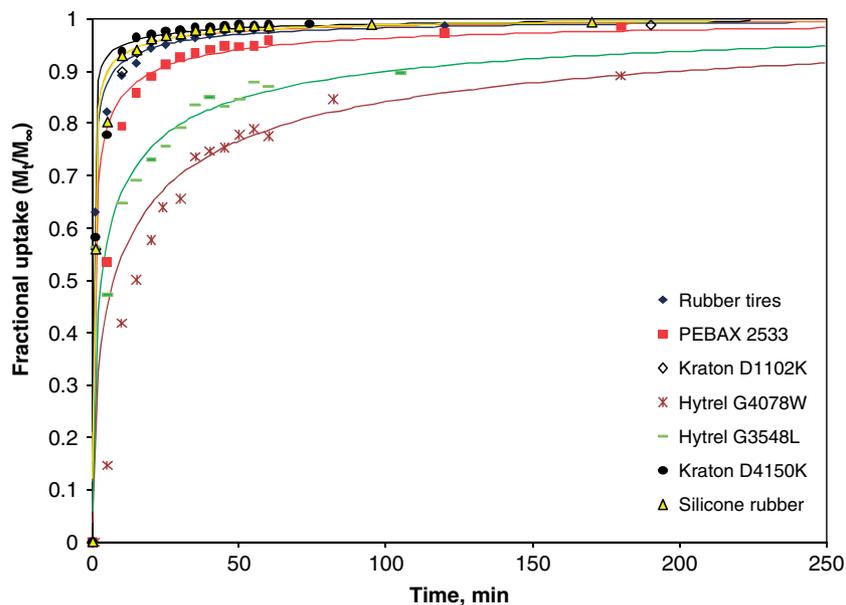


Figure 3. Sorption kinetics of α -pinene. The solid line represents the fit of the Crank equation to the data, using the method of least squares.

into polymers,^{17,18,29} assuming radial diffusion into a sphere:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6 \alpha (\alpha + 1) \exp\left(\frac{-q_n^2 D_c^t}{r^2}\right)}{9 + 9 \alpha + q_n^2 \alpha^2} \quad (3)$$

where M_t is the mass of α -pinene absorbed from a single bead at time t , M_∞ is the total mass of α -pinene absorbed by a bead, D_e is the average effective diffusivity of α -pinene within the polymer, r is the average radius of a bead. α is expressed in terms of the final fractional uptake of α -pinene by the bead by the relation

$$\frac{M_\infty}{VC_0} = \frac{1}{1 + \alpha} \quad (4)$$

and q_n are the roots of the following equation:

$$\tan(q_n) = \frac{3q_n}{3 + \alpha q_n^2} \quad (5)$$

Equation (5) was solved by the method of least squares, as implemented in the SOLVER toolbox of MS-Excel.

The gas diffusivities resulting from these absorption tests using the experimental procedure described above were in the range 10^{-7} to 10^{-8} $\text{cm}^2 \text{s}^{-1}$, using a least-square fit. Diffusivity values for each polymer, calculated from the Crank equation, are given in Table 3. Figure 3 illustrates the absorption of α -pinene expressed as the normalized α -pinene concentration absorbed versus time. The uptake of α -pinene for most of the polymers is very rapid, and after a 15 min period more than 90% of the total amount of α -pinene added had been taken up for Kraton[®] D4150K, rubber tires, silicone rubber and Kraton[®] D1102K.

Biodegradability

Another very important factor in polymer selection is the potential biodegradability of the polymer. In the case of using such polymers

in a packed-bed bioreactor for the removal of pollutants, one does not want the polymer to become biodegraded. With polymer beads as the only source of carbon, no bacterial growth was detected over a 4 day period, suggesting that none of the polymers tested is biodegradable.

CONCLUSIONS

Based on the results presented in this investigation, polymer screening has identified an effective sequestering solid phase to remove α -pinene from a gas phase. Kraton[®] D4150K showed a high partition coefficient towards α -pinene, relative to the gas phase. Moreover the uptake of α -pinene was relatively fast with that polymer ($D_e = 21.8 \times 10^8 \text{ cm}^2 \text{ s}^{-1}$). Nevertheless, considering the anticipated mechanism of biotrickling filtration involving the use of a polymer sequestering/releasing phase, system performance may be enhanced by using a polymer exhibiting simultaneously relatively good uptake of α -pinene from the gas phase, and effective release of the pollutant to the water phase, such as would be the case for PEBAX[®] 2533 or Hytrel[®] G3548L. Research is presently being carried out to study the degradation of α -pinene by microorganisms in a trickling filter in the presence of polymers. In BTFs, the solid polymers will be continuously covered by the recirculating aqueous-phase. Taking into account the mechanism proposed for the transfer of α -pinene into the polymers, significant enhancement due to the presence of polymers is not expected, contrary to what happens when using a second organic liquid phase, although it would also depend on the mass of polymers used.³⁰ However, this paper provides a new opportunity to work in biofilters or trickling biofilters using a polymer as a sequestering phase, which is currently being studied in more depth.

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REFERENCES

- Gachkar L, Yadegari D, Rezaei MB, Taghizadeh M, Astaneh SA and Rasooli I, Chemical and biological characteristics of *Cuminum cyminum* and *Rosmarinus officinalis* essential oils. *Food Chem* **102**:898–904 (2007).
- Jin Y, Veiga MC and Kennes C, Performance optimization of the fungal biodegradation of α -pinene in gas phase biofilter. *Process Biochem* **41**:1722–1728 (2006).
- Masten S, Turpentine (turpentine oil, wood turpentine, sulfate turpentine, sulfite turpentine). Review of Toxical Literature. National Institute of Environmental Health Sciences (2002).
- Kennes C, Montes M, López ME and Veiga MC, Waste gas treatment in bioreactors: environmental engineering aspects. *Can J Civil Eng* **36**:1887–1894 (2009).
- Kennes C and Veiga MC, *Bioreactors for waste gas treatment*. Kluwer Academic Publishers, Dordrecht, The Netherlands (2001).
- Langolf BM and Kleinheinz GT, A lava rock-based biofilters for the treatment of alpha-pinene. *Bioresource Technol* **97**:1951–1958 (2006).
- Montes M, Veiga MC and Kennes C, Two-liquid phase mesophilic and thermophilic biotrickling filters for the biodegradation of α -pinene. *Bioresource Technol* **101**:9493–9499 (2010).
- van Groenestijn JW and Lake ME, Elimination of alkanes from off-gases using biotrickling filters containing two liquid phases. *Environ Prog* **18**:151–155 (1999).
- Djeribi R, Dezenclous T, Pauss A and Lebeault J-M, Removal of styrene from waste gas using a biological trickling filter. *Eng Life Sci* **5**:450–457 (2005).
- Fazaelipour MH and Shojaosadati SA, The effect of silicone oil on biofiltration of hydrophobic compounds. *Environ Prog* **21**:221–224 (2002).
- Darracq G, Couvert A, Couriol C, Amrane A, Thomas D, Dumont E, *et al*, Silicone oil: An effective absorbent for the removal of hydrophobic volatile organic compounds. *J Chem Technol Biotechnol* **85**:309–313 (2010).
- Rehmann L, Sun B and Daugulis AJ, Polymer selection for biphenyl degradation in a solid-liquid two-phase partitioning bioreactor. *Biotechnol Prog* **23**:814–819 (2007).
- Gao F and Daugulis AJ, Bioproduction of the aroma compound 2-phenylethanol in a solid-liquid two-phase partitioning bioreactor system by *Kluyveromyces marxianus*. *Biotechnol Bioeng* **104**:332–339 (2009).
- Prpich GP and Daugulis AJ, Polymer development for enhanced delivery of phenol in a solid-liquid two-phase partitioning bioreactor. *Biotechnol Prog* **20**:1725–1732 (2004).
- Littlejohns JV and Daugulis AJ, Response of a solid-liquid two-phase partitioning bioreactor to transient BTEX loadings. *Chemosphere* **73**:1453–1460 (2008).
- Miller MJ and Allen DG, Biodegradation of α -pinene in model biofilms in biofilters. *Environ Sci Technol* **39**:5856–5863 (2005).
- Amsden BG, Bochanysz J and Daugulis AJ, Degradation of xenobiotics in a partitioning bioreactor in which the partitioning phase is a polymer. *Biotechnol Bioeng* **84**:399–405 (2003).
- Daugulis AJ, Amsden BG, Bochanysz J and Kayssi A, Delivery of benzene to *Alcaligenes xylosoxidans* by solid polymers in two-phase partitioning bioreactor. *Biotechnol Lett* **25**:1203–1207 (2003).
- Copolovici LO and Niinemets Ü, Temperature dependencies of Henry's law constants and octanol/water partition coefficients for key plant volatile monoterpenoids. *Chemosphere* **61**:1390–1400 (2005).
- Khan TR and Daugulis AJ, Application of solid-liquid TPPBs to the production of L-phenylacetylcarbinol from benzaldehyde using *Candida utilis*. *Biotechnol Bioeng* **107**:633–641 (2010).
- Montes M, Rene ER, Veiga MC and Kennes C, α -Pinene removal from air in one- and two- liquid phase thermophilic and mesophilic biotrickling filters, in *Biotechniques for Air Pollution Control*, ed. by Bartacek J, Kennes C and Lens PNL. CRC Press/Balkema, AK Leiden, The Netherlands, pp 34–37 (2010).
- Rehmann L and Daugulis AJ, Biodegradation of PCBs in two-phase partitioning bioreactors following solid extraction from soil. *Biotechnol Bioeng* **99**:1273–1280 (2008).
- Muñoz R, Chambaud M, Bordel S and Villaverde S, A systematic selection of the non-aqueous phase in a bacterial two liquid phase bioreactor treating α -pinene. *Appl Microbiol Biotechnol* **79**:33–41 (2008).
- Quijano G, Hernandez M, Thalasso F, Muñoz R and Villaverde S, Two-phase partitioning bioreactor in environmental biotechnology. *Appl Microbiol Biotechnol* **84**:829–843 (2009).
- Gao F and Daugulis AJ, Polymer solute interactions in solid-liquid two-phase partitioning bioreactors. *J Chem Technol Biotechnol* **85**:302–306 (2010).
- Shaowu W, Xidong L, Zhicheng G and Xun W, Hydrophobicity transfer properties of silicone rubber contaminated by different kinds of pollutants. *Electrical Insulation and Dielectric Phenomena. Annual Report and Conference* **1**:373–376 (2000).
- Shaowu W, Xidong L, Zixia C, Xun W, Zhi L, Yuanxiang Z, *et al*, Hydrophobicity changing of silicone rubber insulators in service. CIGRE, Paper 15–305, Session (2002).
- Gavara R, Catalá R, Hernández-Muñoz PM and Hernández RJ, Evaluation of permeability through permeation experiments: Isostatic and Quasisostatic methods compared. *Packaging Technol Sci* **9**:215–224 (1996).
- Crank J, *The Mathematics of Diffusion*. Oxford University Press, New York (1975).
- Boudreau NG and Daugulis AJ, Transient performance of two-phase partitioning bioreactors treating a toluene contaminated gas stream. *Biotechnol Bioeng* **94**:448–457 (2006).