Removal of alpha-pinene from gases using biofilters containing fungi

J.W. van Groenestijn^{a,*}, J.X. Liu^b

^a TNO Environment, Energy and Process Innovation, P.O. Box 342, 7300 AH Apeldoorn, Netherlands

^b Department of Water Pollution Control Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, P.O. Box 2871, Beijing 100085, China

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Abstract

Biofiltration is cost-effective for the treatment of gases containing low concentrations of volatile organic compounds ($<3 \text{ g m}^{-3}$). However, conventional biofilters, based on compost and bacterial activity, face problems with the elimination of hydrophobic compounds. Besides that, biofilter operational stability is often hampered by acidification and drying out of the filter bed. To overcome these problems, biofilters with fungi on inert packing material have been developed. Fungi are more resistant to acid and dry conditions than bacteria, and it is hypothesised that the aerial mycelia of fungi, which are in direct contact with the gas, can take up hydrophobic compounds faster than flat aqueous bacterial biofilm surfaces. Alpha-pinene was chosen as a model compound. It is an odorous compound emitted by the wood processing industry. In 2 l biofilter columns four different packing materials were tested: perlite, expanded clay granules, polyurethane foam cubes and compost. The filters were inoculated with forest soil and ventilated with gas containing alpha-pinene. Start up took 1–2 months and removal efficiencies of more than 90% were observed, but mostly ranged from 50% to 90% due to overloading. In the filters containing perlite, clay, polyurethane and compost volumetric removal capacities of, respectively, 24, 33, 38 and 24 g alpha-pinene m^{-3} filter bed h^{-1} were attained and the gas pressure drops in the 60 cm high filter beds measured at a superficial gas velocity of 35 m h^{-1} were 70, 550, 180 and 250 Pa. The results indicate that it is possible to develop biofilters based on the action of fungi with higher elimination capacities for alpha-pinene as reported in literature for bacterial biofilters. The use of polyurethane foam cubes is preferred because of the low gas pressure drop in combination with a high volumetric elimination capacity.

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1. Introduction

1.1. Biofilters based on the action of fungi

Biofiltration is a cost-effective treatment method for off-gases containing concentrations of volatile organic compounds lower than 3 g m^{-3} . In this concentration range adsorption and incineration are more costly (Kok,

1992). However, conventional biofilters, based on compost and bacterial activity, face problems with the elimination of hydrophobic compounds such as aromatic compounds, alkenes and alkanes. Because of the low solubility in water, the compounds are poorly absorbed by the bacterial biofilms (Devinny et al., 1999). Besides that, biofilter operational stability is often hampered by acidification and drying out of the filter bed (Kennedy and Veiga, 2001).

To overcome these problems, biofilters with fungi on inert packing material have been developed (Braun-Lüllemann et al., 1992; Cox, 1995; van Groenestijn et al.,

*Corresponding author. Fax: +31-55-5493523.

E-mail address: j.w.vangroenestijn@mep.tno.nl (J.W. van Groenestijn).

1995). Fungi are more resistant to acid and dry conditions than bacteria, which is a helpful property when operating biofilters (van Groenestijn et al., 2001). Moreover, it can be hypothesised that the aerial mycelia of fungi, which are in direct contact with the gas, can take up hydrophobic compounds faster than flat aqueous bacterial biofilm surfaces. In previous research, biofilters for the removal of styrene from gases were developed. Different biofilter packing materials to support the growth of fungi were tested. Perlite, which is an inert granular porous ceramic material, was selected as the most suitable support medium for fungal growth and it maintained a high biofilter volumetric elimination capacity. Water amended with the required nutrients had to be added at regular time intervals to support growth (van Groenestijn et al., 2001).

The biofilter for styrene has been scaled up and was demonstrated on 1.5 m³ scale at the site of two polyester factories (Kraakman et al., 1997). In addition, laboratory tests have been carried out with toluene, ethyl benzene and xylenes, and with ethene, propene, 1,3-butadiene and hexane. Fungal growth was obtained in each case when a low pH was used, except for when hexane was the substrate. Volumetric conversion capacities up to 125 g toluene m⁻³ filter bed h⁻¹ can be attained by using fungal biofilters (Woertz et al., 2002), which are high as compared to results obtained with compost-based biofilters (10–20 g m⁻³ h⁻¹) and bio-trickling filters (20–38 g m⁻³ h⁻¹) (Weber, 1995). Other research on fungal-based biofilters indicated higher capacities; Garcia et al. (2000) even attained capacities as high as 200 g toluene m⁻³ h⁻¹.

A typical problem connected to high-load biofilters is clogging with biomass, whether it consists of bacteria or fungi. Using packing material with larger pores or introduction of higher organisms (fungi predators) can prevent this (van Groenestijn et al., 2001). The use of polyurethane foam cubes results in high volumetric capacities (125 g toluene m⁻³ filter bed h⁻¹) and low gas pressure drops of 80 Pa m⁻¹ filter bed at gas loading rates of 150–200 m³ gas m⁻³ filter bed h⁻¹. The use of co-cultures of fungi and mites in biofilters led to a controlled but active population of fungi in the pores of biofilter packings such as perlite. Similar capacities and gas pressure drops can be attained as polyurethane foam filled biofilters (Woertz et al., 2002).

1.2. *Alpha-pinene as a model compound*

In our study, fungal-based biofilters were used for the removal of alpha-pinene from air streams. Alpha-pinene is hydrophobic and the degradation is considered as complex (Kleinheinz et al., 1999). Alpha-pinene is emitted by wood processing industries, in particular, saw mills and composite board mills. It is the major VOC emitted atmospherically by the industry sector

mentioned. Although forests emit terpenes naturally, the anthropogenic contribution of monoterpene emission may be larger (Kleinheinz et al., 1999). Since the compound is emitted in low concentrations (less than 300 ppm), treatment of the waste gases by biofiltration may be cost-effective. Several studies have been carried out using biofilters based on the action of bacteria. Kleinheinz et al. (1999) used laboratory-scale biofilters packed with aspen wood chips inoculated with bacteria. The study took 3 months in which the loading rate was slowly increased from 0 to 35 g m⁻³ filter bed h⁻¹. A removal efficiency of about 90% was attained, corresponding with a maximum volumetric removal capacity of 32 g m⁻³ h⁻¹. Dirk-Faitakis and Grant Allen (1998) also used laboratory-scale biofilters with a woodchip/compost packing and found a volumetric removal capacity ranging between 10 and 12 g m⁻³ h⁻¹. Pond (1999) concluded that biofiltration is the most cost-effective technology for air pollution in the board and laminating industry. However, Pond's biofilter studies mainly focussed on formaldehyde, phenol and methanol. Monoterpenes got more attention in the biofilter studies of Diehl et al. (2000), in which fungi were also introduced. The experimental runs gave promising results but only took 5 days. There is a need for more prolonged experimental runs with biofilters containing fungi able to degrade monoterpenes, in particular alpha-pinene.

In the current research, work it was tested if biofilters based on the action of fungi are able to develop higher volumetric elimination capacities over a prolonged time of operation. In addition, various packing materials were tested.

2. Materials and methods

Four laboratory-scale glass columns were used as biofilters. They had a filter bed height and volume of 60 and 2 litres respectively, with exception of column number 4, which had a volume of 0.75 l. The columns were filled with different packing material:

Filter 1: perlite, a granular porous ceramic material, expanded volcanic rock (AGRA 4 from Pull BV, Rhenen, The Netherlands; 4 mm diameter granules).

Filter 2: expanded clay granules with a diameter of 1 cm.

Filter 3: polyurethane foam cubes (1.3 cm, Betapol BV, Beesd, The Netherlands), pore size 0.3 mm, weight 28 g cm⁻³.

Filter 4: compost produced from household vegetable, fruit and garden waste.

Forest soil was used as an inoculant, because of the expected alpha-pinene degrading microorganisms. Before packing, the packing material was soaked in a phosphate buffered mineral medium (pH 5) and mixed

with the soil (50 g l^{-1} packing). The filters were placed in a temperature controlled room (25°C) and connected to a gas supply system. A large stream of compressed air was humidified up to 97% relative humidity (RH) by passing it through vials with water (placed in a 37°C water bath). A small stream of air was bubbled through a vial containing pure alpha-pinene and was mixed with the larger humidified gas stream, resulting in an inlet gas with a concentration of about $400 \text{ mg alpha-pinene m}^{-3}$. The gas loading rates applied varied between 60 and $120 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$ and the flow direction was downward. The biofilter gas inlet and outlet were connected (by a tube) to a flame ionisation detector (Total Hydrocarbon Analyzer Model 51, Thermo Environmental Instruments Inc., USA, supplied by THIS, Breda, The Netherlands) with automatic sampling (each channel once every 2 h) and to a carbon dioxide analyser with automatic sampling (ADC 7000 Gas Analyser, Analytical Development Co., Ltd., UK). The concentrations were measured 12 times a day. Gas loading rates were calculated from the gas flow rates as measured daily from calibrated flow meters (rotameter-type, Model 1355/D2D3A1B5B000, Brooks Instruments BV, Veenendaal, The Netherlands). The pressure drop over the filterbed was measured each month by connecting a water filled U-shaped manometer to sample ports in the top and bottom section of the biofilter.

During the first few weeks of operation, the filters were completely filled with fresh medium weekly to add depleted nutrients and drained to remove accumulated compounds. The pH of the drained water was measured. After 2 weeks, the wetting frequency depended on the

activity in the filter. After a decline in activity, new medium was added, which usually resulted in an increased activity.

The medium contained per litre demineralised water: $4.5 \text{ g KH}_2\text{PO}_4$, $0.5 \text{ K}_2\text{HPO}_4$, $2.0 \text{ g NH}_4\text{Cl}$, $1.0 \text{ g MgSO}_4 \cdot 7\text{H}_2\text{O}$, 2 ml of a solution of minerals and 2 ml of a vitamin solution. The pH was adjusted to 5 using HCl. The solution of minerals contained per litre demineralised water: 120 mg FeCl_3 , $50 \text{ mg H}_3\text{BO}_3$, $10 \text{ mg CuSO}_4 \cdot 5\text{H}_2\text{O}$, 10 mg KI , $45 \text{ mg MnSO}_4 \cdot \text{H}_2\text{O}$, $20 \text{ mg Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $75 \text{ mg ZnSO}_4 \cdot 7\text{H}_2\text{O}$, $50 \text{ mg CoCl}_2 \cdot 6\text{H}_2\text{O}$, $20 \text{ mg AlK(SO}_4)_3 \cdot 12\text{H}_2\text{O}$, $13.25 \text{ g CaCl}_2 \cdot 2\text{H}_2\text{O}$ and 10.0 g NaCl . The vitamin solution contained per litre demineralised water: 100 mg nicotinic acid, 200 mg calcium pantothenate, 25 mg cyanocobalamin, 100 mg inositol, 20 mg *p*-aminobenzoate, 50 mg thiamin $\cdot \text{HCl}$, 25 mg pyridoxin $\cdot \text{HCl}$, 10 mg biotin, 10 mg riboflavin, 10 mg folic acid and 10 mg thiocetic acid.

3. Results and discussion

3.1. Performance

The gas flow rate in the filters is given in Fig. 1. The influent gas and effluent gas concentrations of alpha-pinene for four biofilters are shown in Figs. 2–5. Since the biofilters were not inoculated with pure cultures of fungi but with forest soil, a long start-up period could be expected. From the figures it is clear that start up takes 1 or 2 months, compost filled biofilters showing the fastest

Fig. 1. Gas flow rate in filter 1 (◆), filter 2 (□), filter 3 (△) and filter 4 (×).

Fig. 2. Influent gas concentration of alpha-pinene (thin line) and effluent gas concentration (bold line) of biofilter 1 (perlite).

Fig. 3. Influent gas concentration of alpha-pinene (thin line) and effluent gas concentration (bold line) of biofilter 2 (expanded clay).

Fig. 4. Influent gas concentration of alpha-pinene (thin line) and effluent gas concentration (bold line) of biofilter 3 (polyurethane foam cubes).

development of activity. Fungal growth was observed in filters 1, 2 and 3, whereas in the compost biofilter fungal growth was less pronounced. The packing material in

filters 1, 2 and 3 were completely covered with a dense aerial mycelium. By visual observation a mycelium thickness of 1 mm in filters 1 and 3 and 2 mm in filter 2

Fig. 5. Influent gas concentration of alpha-pinene (thin line) and effluent gas concentration (bold line) of biofilter 4 (compost).

Fig. 6. Volumetric alpha-pinene loading rate (◆) and elimination efficiency (x) of biofilter 3 (polyurethane foam cubes).

was estimated. Removal efficiencies of more than 90% are possible, but since the filters were challenged with very high-loading rates most of the time, the efficiency ranged between 50% and 90%. It indicates that the filters were overloaded. The volumetric loading rate and elimination efficiency can be calculated from the difference between the influent and effluent concentration, the gas flow rate and the volume of the filter. As an example both two parameters of filter number 3 are presented in Fig. 6. The difference between influent and effluent concentration was calculated in the last month of the run (despite of the presence of peaks, 80% of the 360 observations varied within $\pm 20\%$). In the last month the average gas loading rates were 69, 90, 96 and $64 \text{ m}^3 \text{ m}^{-3} \text{ h}^{-1}$ for filters 1, 2, 3 and 4, respectively, with a variation of only $\pm 10\%$. These filters attained 24, 33,

38 and $24 \text{ g alpha-pinene removal per m}^3 \text{ filter bed per hour}$. By analysis of the CO_2 concentration of the effluent, it could be concluded that about 85% of the alpha-pinene removed was converted into CO_2 . The remaining 15% may be biomass and organic compounds in the drainage water. So, sufficient conversion into CO_2 , the desired end product, was observed. Such high conversion ratios to CO_2 and as consequence low biomass yield factors are typical for microorganisms at very low growth rates (Pirt, 1985).

The pH of the water in all four biofilters started at 5.2 and by uptake of NH_3 from the medium by the microorganisms, the pH dropped to 3.5 within 1 week, except for filter 3 in which the pH decrease took some more weeks (Figs. 7–10). During the run the pH in the filters with perlite and polyurethane foam the pH

Fig. 7. Course of pH in the medium of biofilter 1 (perlite); the peaks coincide with addition of fresh medium.

Fig. 8. Course of pH in the medium of biofilter 2 (expanded clay).

Fig. 9. Course of pH in the medium of biofilter 3 (polyurethane foam cubes).

stabilised at 3 and in the other filters (expanded clay and compost) between 3 and 4.5. At the end of the experimental run at day 220, the gas pressure drops in the 60 cm high filter beds measured at a standard superficial gas velocity in the filter bed of 35 m h^{-1} were

70, 550, 180 and 250 Pa in filters 1, 2, 3, and 4, respectively.

The results indicate that it is possible to develop biofilters based on the action of fungi with higher volumetric elimination capacities for alpha-pinene than

Fig. 10. Course of pH in the medium of biofilter 4 (compost).

reported in literature for bacterial biofilters (Dirk-Faitakis and Grant Allen, 1998; Kleinheinz et al., 1999). Interestingly, the coarse packing material (expanded clay and foam cubes) yielded higher volumetric elimination capacities, which may be due to a higher microbial activity as a result of a larger intra-porous water and nutrient storage capacity per mm² extra-porous surface area, or to a more equal gas flow distribution in the filter bed. However, the abundant mycelium growth on the expanded clay granules caused a high gas flow resistance, which is an unfavourable aspect of fungal growth. Therefore, the use of polyurethane foam cubes is preferred because of the low gas pressure drop in combination with high volumetric elimination capacity.

Moreover, based on our studies on better tolerance of fungal biofilters against acidification and dry conditions, the operational stability may also be higher than that of bacterial biofilters. Recently, it has been proven that the addition of mites in fungal biofilters further improves the capacity (Woertz et al., 2002), which may be an interesting starting point for further development of the biofilter for alpha-pinene removal. The volumetric capacities found are slightly lower than those found for biofilters filled with perlite and fungi for the removal of styrene (Kraakman et al., 1997).

3.2. Secondary atmospheric emissions

Another factor that deserves consideration is the secondary atmospheric emission caused by different treatment technologies. As incineration and adsorption (including regeneration) require more energy than biofiltration, the emission of CO₂ can be higher by the use of fossil energy carriers. If in a certain case fungal-based biofilters emit 0.7 kg CO₂ per 1000 m³ gas treated,

adsorption causes the emission of 0.95 and incineration 6.5–70 kg CO₂ per 1000 m³ gas treated.

4. Conclusions

Removal of alpha-pinene from gases is possible in biofilters based on the action of fungi. Start up takes 1–2 months, the volumetric removal capacity can be 38 g alpha-pinene m⁻³ filterbed h⁻¹, which is higher than found in bacteria based biofilters. The elimination efficiency can be over 90%, but was generally between 50% and 90%.

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