

Biofiltration of α -pinene and its application to the treatment of pulp and paper air emissions

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BIOFILTRATION OF GASES CONTAMINATED with volatile organic compounds (VOCs) is a relatively new application of biotechnology in waste management. In a biofilter (Fig. 1), contaminated streams are vented through biologically active materials, such as soil or compost. Microorganisms, which have the ability to degrade the pollutants, are naturally immobilized on porous support particles and form a biofilm on the surface of the solids. As the contaminated stream passes through the filter bed, pollutants are transferred from the vapor phase to the biofilm and are metabolized. The end products of the complete biodegradation of air contaminants include CO₂, water, and microbial biomass.

Biofiltration has been used for many years in Germany, the Netherlands, Japan, and to a limited extent, in the United States. Successful applications of this technology in Europe include the abatement of odorous organic and inorganic gases from a variety of industries and public places (1) (e.g., food-processing and wastewater treatment plants). Recently, biofiltration processes have expanded to include the control of VOCs emitted from a variety of contaminated sources, including wood products industries.

Air emissions from pulp, paper, and wood products industries consist of VOCs whose releases to the atmosphere are facing increasingly stringent regulations. One common component found in these emissions

are terpenes (e.g., α -pinene), which are naturally present in softwoods. The common air pollution control technologies that are currently applied include thermal incineration and chemical scrubbing. Although these techniques are suitable for treating many contaminated streams, they often become cost intensive when there are large quantities of the off-gas with low VOC concentrations. Biofiltration, on the other hand, offers an operationally and economically feasible technology for the treatment of VOCs and odors from pulp and paper air emissions because it has low capital and operating costs, especially for large volumes of dilute and moist gas streams (1). Biofiltration also has the potential to use on-site wood waste materials (e.g., wood bark) as packing media.

The inherent advantages associated with the use of biofilters have prompted a significant increase in further investigations of their operational effectiveness in controlling a variety of VOCs (2–5). However, the knowledge base associated with the fundamental mechanisms that affect biofilter performance, as well as the optimal biofilter conditions, has remained far behind existing knowledge related to conventional control technologies. Therefore, biofiltration is considered an emerging VOC control technology for which more detailed fundamental research is required.

The composition of the biofilter medium is a critical parameter that underscores the limitations and ben-

ABSTRACT

Two identical bench-scale biofilters were used to remove α -pinene, a very hydrophobic VOC discharged in pulp and paper and wood products emissions, from a contaminated air stream. The biofilter medium consisted of a mixture of wood chips and spent mushroom compost that was amended with either perlite or activated carbon. The experiment was conducted at loading rates of 5–40 g α -pinene/m³ bed medium/h. Under steady-state conditions, both biofilters, amended with perlite and GAC, performed similarly and provided removal rates of 30–35 g α -pinene/m³ bed medium/h, with gas retention times as low as 30 seconds. When the biofilters were subjected to a sudden increase in the loading rate, the performance of the biofilters decreased significantly. The reacclimation period, however, was not long, and the biofilters reached more than 99% removal within less than 48 hours of the spike load.

Application:

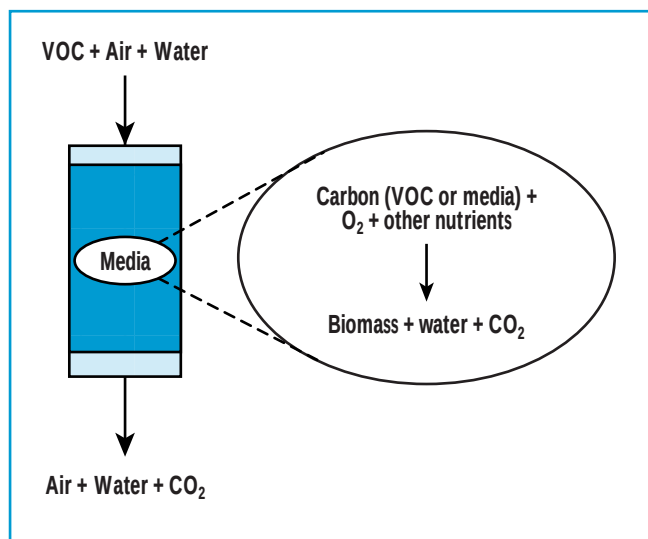
Low concentrations of volatile organic compounds (VOCs) from pulp and paper air emissions can be successfully controlled using biofiltration.

efits of biofiltration. For a biofilter to operate efficiently, the medium should have the following characteristics (1, 6, 7):

- high moisture retention capacity to prevent drying
- available nutrients for optimal microbial growth
- high porosity and/or void space to reduce head loss and to ensure even distribution of the incoming waste gas
- a diverse microbial community.

Also, compaction of the medium over time needs to be minimized to

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1. Schematic of a downflow-operating biofilter

prevent increases in system pressure drop and/or channeling of untreated polluted air through the filter (1). It is also desirable for the filter medium to have a significant pH buffering capacity to prevent acidification due to the buildup of acid-laden waste gas streams (1).

Several researchers have attempted to optimize biofilter performance using different types of packing materials (3–5). They proposed that adsorbing materials, such as granular activated carbon (GAC), have characteristics that may promote higher elimination capacities for a given volume of filter bed, especially for compounds with low water solubility that are emitted in variable loads. However, the mechanism for the removal enhancement had not been clearly understood, and further development in this area was required for improved process design and performance.

The overall objective of this work was to investigate the treatability of VOCs discharged from pulp and paper industries in biofilters with activated carbon and wood waste/compost media. We expect the results from this study will also be applicable to the work that we are currently conducting on the simultaneous control of odor and VOC emissions. In particular, the focus of this

paper is on the biofiltration of off-gases contaminated with α -pinene using activated carbon and wood chip/compost media. This was accomplished in the first 4.5 months of a 9-month experimental run in two parallel bench-scale biofilters.

EXPERIMENTAL APPROACH

Biofilter setup

Two identical bench-scale biofilters were used to remove α -pinene from air streams (Fig. 2). The biofilter bed consisted of four equal segments connected in series. Each segment has a diameter of 28 cm and a height of 30 cm. Perforated stainless steel plates (mesh diam. = 7 mm) were placed between each two segments as support for the packing material and as a redistribution system for the air stream. There are six ports on each segment; these ports permit sampling the air stream axially along the column and monitoring the temperature and pressure. There is also a media access port on each segment.

Each biofilter was equipped with a control panel for controlling the flow rate of the inlet air stream and monitoring the temperature and pressure. The VOC was supplied to the biofilters by sparging air through a stainless steel vessel containing liquid α -pinene (Sigma-Aldrich, 98% pure). The concentration of α -pinene delivered to the biofilters was controlled by directing a small and controlled flow of the air stream through the sparging vessel and then mixing it with a larger air stream that was passed through a humidification system to humidify the air stream

and control its temperature. The humidification system consisted of a 15 cm diam., 155 cm high packed column (ceramic Intalox saddles, 2 cm) and a water bath. Water was continuously circulated using a pump (Model 3E-12N, Little Giant Pump Co., Oklahoma City, OK); the water temperature was controlled using a heater (Model 1112, VWR Scientific, Poly Science, Niles, IL). The temperature of the inlet air stream was accordingly controlled by the humidifier's water temperature. After humidification, the main air stream was mixed with the stream carrying the α -pinene vapor to create the contaminated air stream. The experiments were conducted in a downflow mode of operation, and the contaminated stream entered the biofilter from the top.

Media preparation

The medium for each of the two biofilters consisted of a mixture of wood chips (3.2–32 mm, mixture of oak and maple, TMP mill, Domtar Packaging, Trenton, ON) and spent mushroom compost (50/50 vol.%) that was then further amended with perlite, for the first biofilter, and activated carbon (4 mm pellets, Calgon Carbon Canada, Inc., Mississauga, ON), for the second biofilter. The wood chip/compost mixture was added to the activated carbon or perlite in a ratio of 75/25 vol.%. Perlite pellets, with similar nominal size as GAC, were added to the first biofilter to provide a similar surface area as that in the GAC biofilter (i.e., the second biofilter) so that the effect of GAC on the removal of α -pinene was examined independent of its influence on surface area. Nutricote controlled-release fertilizer pellets (Plant Products Co. Ltd., Brampton, ON) and CaCO_3 (as pH buffer) were also added to the bed media at 10 and 15 kg/m^3 of bed medium, respectively.

Biofilter experiments

The removal of α -pinene under continuous flow conditions was investi-

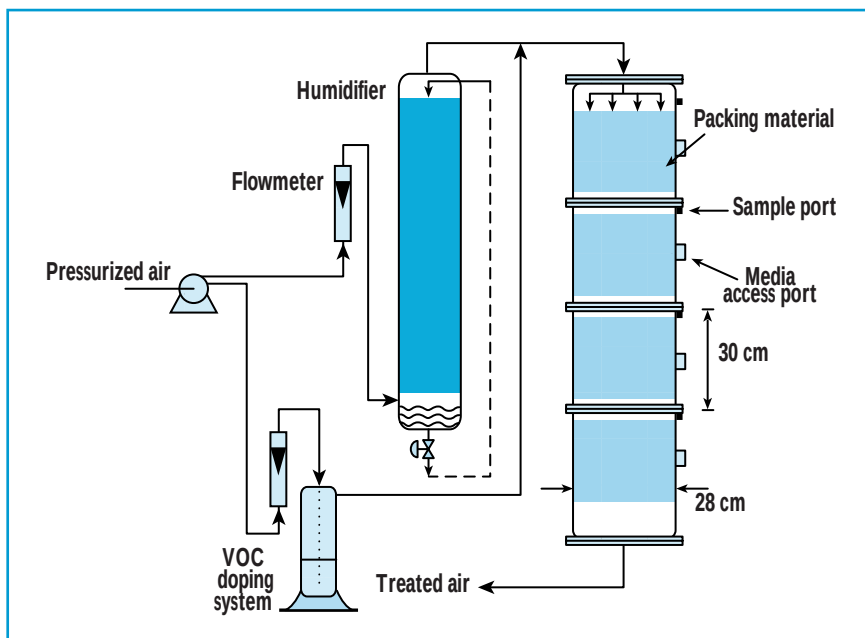
gated during bench-scale biofiltration experiments at various loading rates of α -pinene (g α -pinene/m³ of bed medium/h). Samples were taken from the inlet and outlet streams as well as axially along the biofilter through the sampling ports.

The operating temperature was constant at 38–40°C; this corresponds to the upper limit for the activity of mesophilic microorganisms. The moisture content and pH of the bed materials were also nearly constant at 60–70% and 7.5–7.8, respectively. Other parameters that were monitored during the biofiltration experiments were pressure drops of the biofilters and the humidity of the incoming air stream.

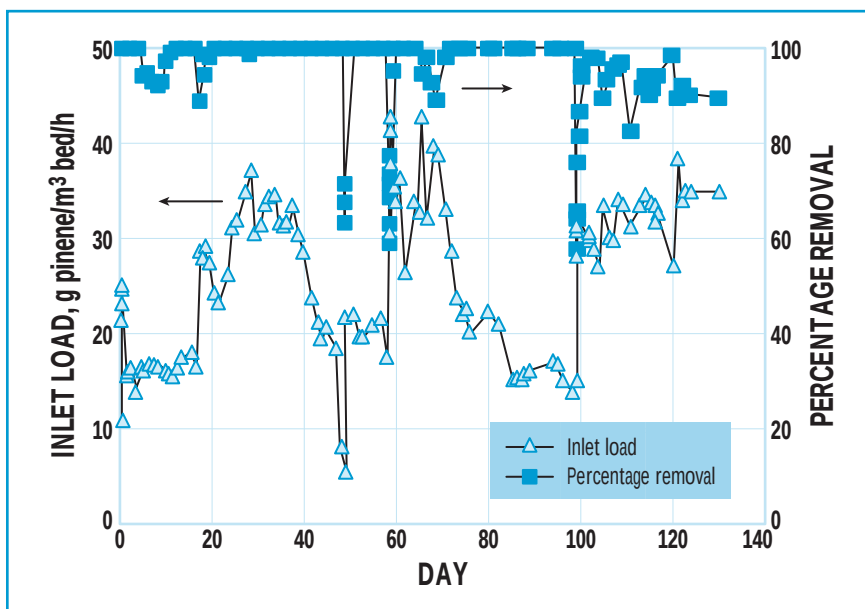
Analytical methods

The concentration of α -pinene in the gas phase was determined via gas chromatographic analysis using a Hewlett-Packard 5700A gas chromatograph (GC). Samples were taken from the inlet and outlet streams, as well as from between the biofilter sections, on a daily basis. The sampling/injection apparatus consisted of a 16 position stream selector valve (Valco Instruments Co., Inc., Houston, TX) connected to a six position switching valve (Valco Instruments Co., Inc.) on the GC. Both valves were mounted in a heating enclosure so that the temperature could be controlled. The GC was equipped with a Porapak Q stainless steel packed column (1.83 m high, 3.2 mm diam., Porapak Q containing 6% SSAP 80/100, Supelco, Mississauga, ON), and helium was used as the carrier gas. The pinene concentration was determined at an oven temperature of 200°C and using a flame ionization detector (FID) at 250°C.

Samples were injected into the GC via the six-position valve with a 1 mL sample loop. Samples were drawn via negative pressure through the heated valves and sample loop/line using 3.2 mm (0.125 in.) diam. stainless steel tubing. A vacuum



2. Experimental setup for each of the two biofilters used in the biofiltration of α -pinene

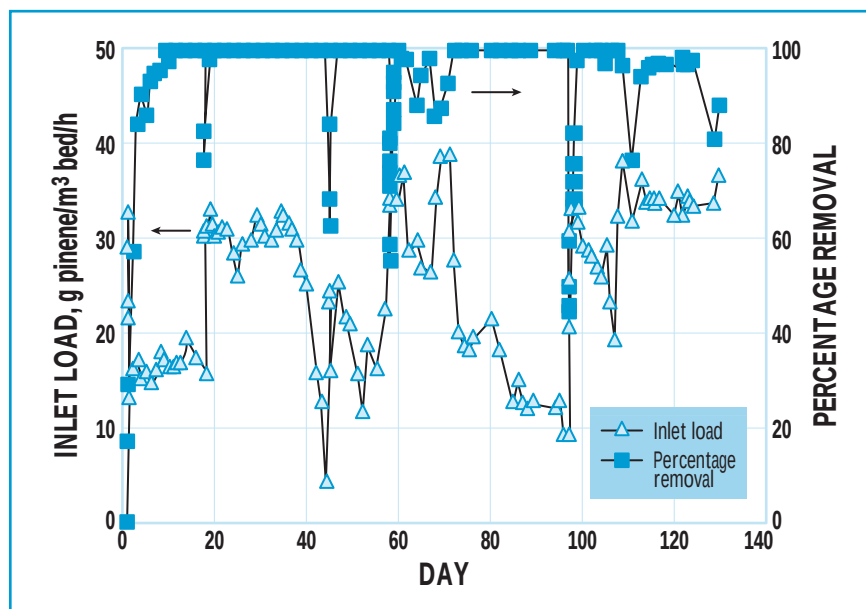


3. Performance of the GAC biofilter in removing α -pinene

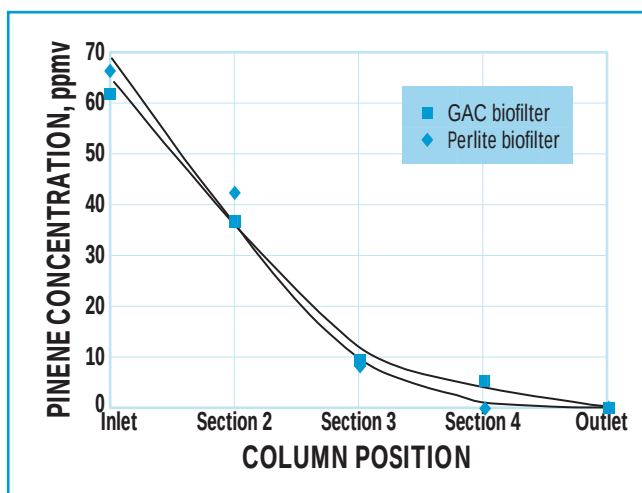
pump (0211 series, Gast Manufacturing Co., Benton Harbor, MI) was used to create negative pressure in the line.

The relative humidity of the air streams entering the biofilters was monitored using a temperature–humidity probe (Tri-Sence Meter, Cole-Parmer, Inc.). The moisture content of the biofilter bed materials was measured using a gravimetric method. A mea-

sured quantity of bed medium was dried in an oven for about 24 hours at 105°C, and the mass reduction was considered as the water content of the sample. The final values were then calculated as the percentage of water on a wet basis (i.e., water content to the original wet sample). The void space of the biofilter packing medium was determined by measuring the volume displaced by water.



4. Performance of the perlite biofilter in removing α -pinene



5. Concentration of α -pinene along the column in the biofilters under steady-state operating conditions (day 24 and beyond)

RESULTS AND DISCUSSION

Overall biofilter performance

Pinene removal rates for the biofilters amended with GAC and perlite were investigated at different loading rates (Figs. 3 and 4). The experiment was initiated with a loading rate of 15–17 g α -pinene/m³ bed medium/h, corresponding to an inlet concentration of 40 ppmv α -pinene and an empty bed retention time (EBRT) of 55 seconds. The removal of α -pinene in the GAC biofilter was instantaneous, indicating the adsorption of α -

pinene on the activated carbon confirmed this observation in that the amount adsorbed by the bed materials was approximately equivalent to one week of the biofilter operation at about 20 g α -pinene/m³ bed medium/h.

Between days 18 and 97, the EBRT was relatively consistent at about 45 seconds, and the performance of the biofilters was examined at different loading rates (i.e., inlet pinene concentrations). Under steady-state conditions, both the perlite and the GAC biofilters removed 30–35 g α -pinene/m³ bed medium/h (and with a removal of more than 99%); this was significantly higher than the 2–10 g removal of α -pinene/m³ bed medium/h obtained from other experiences in the treatment of α -pinene in biofilters with different media components (4, 8).

pinene on the GAC particles (Fig. 3).

At the end of the first week after startup, the percentage of pinene removal decreased to about 90% because the bed materials were becoming saturated with α -pinene and the microorganisms were still being acclimated. By day 15, the microorganisms

became acclimated to the α -pinene, and the percentage removal increased to more than 99%. The perlite biofilter, on the other hand, had no adsorption capacity, so its initial performance was poor. However, after about 10 days, the microorganisms were able to completely remove the incoming α -pinene (Fig. 4).

The difference between the performance of the biofilters in the first few days corresponds to the distinct adsorption capacities of the carbon particles in the GAC biofilter. Sepa-

rate adsorption tests on the activated carbon confirmed this observation in that the amount adsorbed by the bed materials was approximately equivalent to one week of the biofilter operation at about 20 g α -pinene/m³ bed medium/h.

On day 97 of the experiment, the airflow rate through the biofilters increased such that the EBRT decreased to 30 seconds, and the loading rate increased to about 35 g α -pinene/m³ bed medium/h. This resulted in removals of 90–98% at steady state. Overall, the biofilters successfully removed α -pinene from the air streams under various operating conditions.

The impact of α -pinene concentration step increases on the biofilter performance was first investigated on day 18, when the loading rate to the biofilters increased from 15 to about 30 g α -pinene/m³ bed medium/h (corresponding to 70 ppmv α -pinene and 45 seconds EBRT). As shown in Figs. 3 and 4, the removal rates for the GAC and the perlite biofilters decreased to about 90% and 75%, respectively. Similar results were obtained when the biofilters were subjected to step increases throughout the course of the experiment. Nonetheless, the reacclimation periods for the microorganisms were not long, and both biofilters reached steady state

(and in most cases, more than 99% removal) within 48 hours of the step increase.

In the early stage of the experimental run (e.g., before day 20), the GAC biofilter had slightly better performance immediately after the step change; this was likely due to the adsorptive characteristics of the carbon particles. In the later stage of the run, however, the performance of both biofilters decreased similarly after each step increase. This indicates that all of the particles in the bed, including the GAC, were fully covered by the biofilm and hence were not able to adsorb the excess amount of α -pinene introduced to the system. The relatively short reacclimation time suggests that the microorganisms present in the biofilter media may require an intermediate acclimation period to adapt to moderate increases in the α -pinene loading rate.

Axial profiles

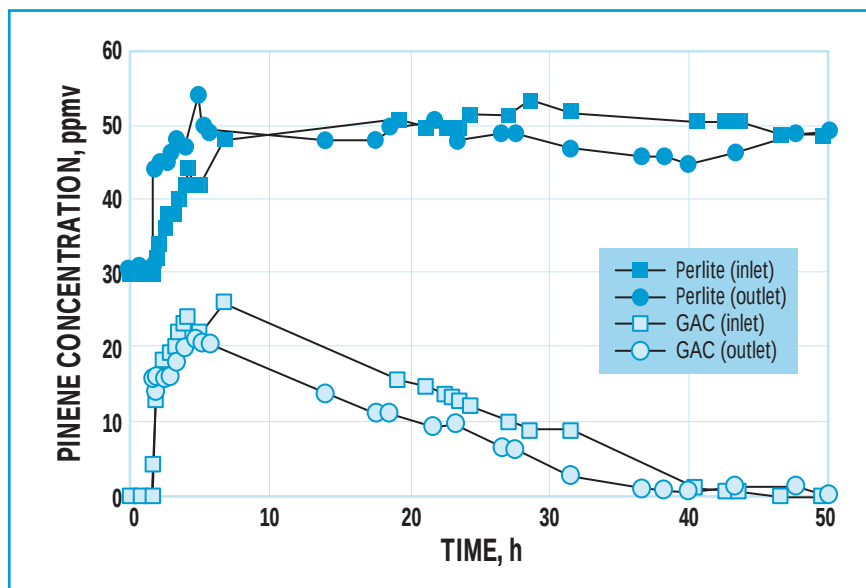
Figure 5 shows the depletion of α -pinene along the GAC and the perlite biofilters under steady-state operating conditions (e.g., day 24). Both biofilters had similar performances in removing the VOC along the column through biodegradation by an acclimated microbial community. Similar results were obtained throughout the course of the experiment, suggesting that the addition of GAC does not significantly enhance the performance of the biofilter at steady state. This result challenges the previously proposed hypothesis (2, 3, 9) that the presence of activated carbon in a biofilter medium may couple the adsorptive and high-surface-area-per-unit-volume properties of the activated carbon with biological activity to obtain a higher-capacity treatment.

Our results suggest that the higher surface area per unit volume of the activated carbon is significant and may contribute to greater VOC removal but that this effect can also be obtained without adsorbing

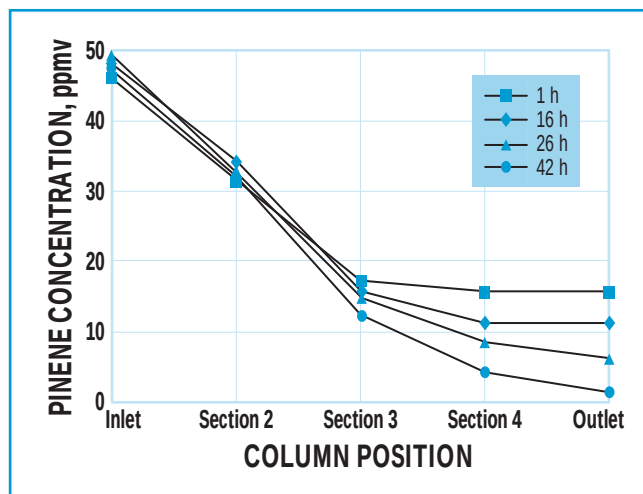
media (e.g., by using perlite). The adsorptive properties of activated carbon appear to be only significant during the startup, when there is little biofilm on the particles and the adsorptive sites are not saturated with the VOC. Therefore, considering the cost associated with activated carbon, it may not be economically feasible to add GAC in biofilters except under low loadings or where biofilm growth can be reduced.

Transient conditions

The transient response of the biofilters to the step changes in the α -pinene concentration on day 97 is illustrated in Fig. 6. The inlet α -pinene concentration was increased from about 30 ppmv to about 50 ppmv (corresponding to an increase in the loading rate from about 15 to about 30 g α -pinene/m³ bed medium/h). This increase caused an

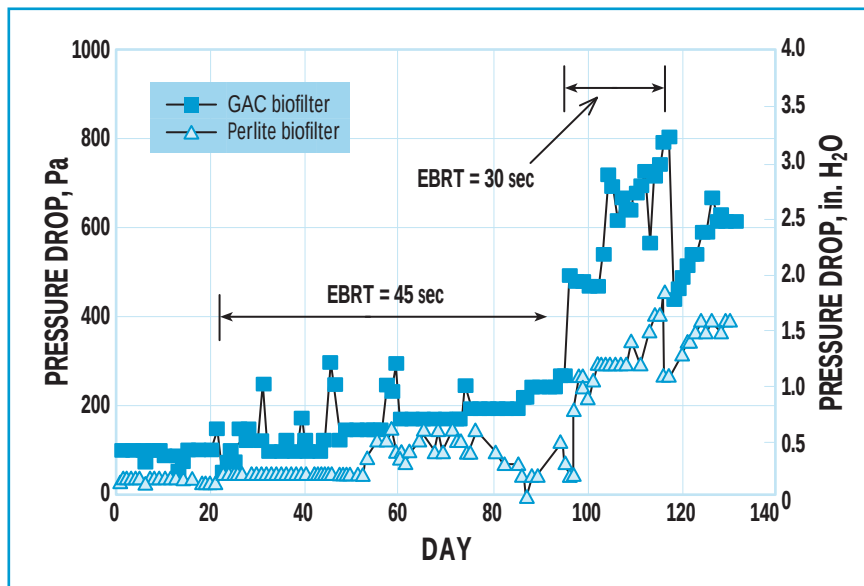


6. Performance of the perlite and GAC biofilters after α -pinene step increase



7. Concentration profiles of α -pinene along the GAC biofilter at different times after the step increase from 15 to 30 g pinene/m³ bed medium/h

immediate increase in the outlet concentration of about 20 ppmv, corresponding to a decrease in the removal efficiency to about 55% and 45% for the GAC and the perlite biofilters, respectively. The biofilters then performed at low removal rates for a few hours before the microorganisms started to reacclimate and gradually remove higher percentages of α -pinene. After less than 40 hours from the step increase, the biofilters reached steady state with more than 95% removal efficiency.



8. Pressure drops in the perlite and the GAC biofilters

The α -pinene concentration profiles along the GAC biofilter column after the step increase on day 97 are shown in Fig. 7. There was no pinene removal in the last two sections of the GAC biofilter in the first few hours after the step increase. This suggests that the GAC had no significant adsorption capacity to remove the excess amount of α -pinene entering the biofilter, likely because the carbon particles were completely covered with a thick layer of the biofilm. The reacclimation of the microorganisms in the lower sections of the biofilter eventually led to the removal of α -pinene via biodegradation. Once again, these results indicate that the adsorptive characteristics of activated carbon do not significantly affect the performance of the biofilters for long-term operation.

Pressure drop

Pressure drops in the biofilter columns were constantly monitored

throughout the experimental run. As shown in Fig. 8, the pressure drop in the perlite biofilter was very low and less than 50 Pa (0.2 in. H_2O) in the first 50 days of the experiment. The GAC biofilter, on the other hand, had a slightly higher pressure drop of 100–200 Pa (0.4–0.8 in. H_2O). Between days 50 and 97, the pressure drops in the perlite and the GAC biofilters increased to about 150 and 250 Pa (0.6 and 1.0 in. H_2O), respectively. Higher gas flow rates (i.e., a lower retention time) after day 97 resulted in much higher pressure drops in the biofilters.

The GAC biofilter had a pressure drop of 550–800 Pa (2–3 in. H_2O), and the pressure drop for the perlite biofilter was 300–400 Pa (1.2–1.6 in. H_2O). The GAC biofilter experienced a slightly higher pressure drop probably because the void space in the GAC biofilter was about 30%; this was smaller than the 34% void space in the perlite biofilter. Cylindrical activated carbon pellets had a more uniform size distribution and hence tended to fill in the void spaces in the biofilter; this, in turn, resulted in a smaller void fraction and higher pressure drop. Perlite, on the other hand, was irregular and less uniform and therefore did not occupy the void spaces in the biofilter.

The distribution of the pressure drop along the biofilters was also measured during the experiment. The first sections of the biofilters had the highest pressure drops, with 60–80% of the total pressure drops in the columns. Higher pinene concentrations, and hence higher microbial activity in the first section of the biofilters, resulted in more biofilm growth; this, in turn, reduced the void space and increased the pressure drop.

CONCLUSIONS

We drew the following conclusions from these experiments:

- Biofiltration is a promising technology for controlling selected pulp and paper emission sources that contain low concentrations of VOCs.
- The perlite and the GAC biofilters provided complete removal of α -pinene for loading rates of 30–35 g α -pinene/ m^3 bed medium/h and with gas retention times as low as 30 seconds.
- Activated carbon is most effective for the early stages of the biofiltration process (i.e., process startup).
- The adsorptive characteristics of activated carbon do not enhance the removal capacity of the biofilter. The presence of the biofilm on the GAC makes the adsorption sites inaccessible to the VOC after prolonged periods of operation.
- Pressure drop in the biofilters gradually increased with time over the course of experiment, with the perlite biofilter experiencing a lower pressure drop than the GAC biofilter. The top/first sections of the biofilters had the highest pressure drop. TJ

KEYWORDS

Acer, activated carbon, air pollution, biological treatment, chips, compost, emission, filtration, mushrooms, pinenes, quercus, separation, VOC.

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