Elimination of toluene vapors from air in a peat-based biofilter

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Abstract

Air biofiltration has been shown as a low-cost, competitive alternative to the physico-chemical treatment technologies to remove volatile organic compounds (VOCs) from industrial air emissions. In order to investigate the performance of this growing technology, two biofiltration pilot units were operated for a continuous period of 3 months. Commercial peat was used as the support material. At start-up, the biofilters were inoculated with a two-months conditioned culture seeded with activated sludge from an industrial wastewater treatment plant. The moisture content of the filter material was adjusted to approximately 80% (wet basis). Nutrients were added periodically to the medium. Temperature was kept on 24-28 ºC. Influences of toluene inlet concentration and gas flow rate were studied. The toluene inlet concentration was raised stepwise to 3.5 g m⁻³, using a different constant flow rate for each biofilter: 0.5 m³ h⁻¹ and 1.0 m³ h⁻¹. Maximum removal efficiencies, with a near complete removal of toluene, were reached for toluene inlet loads up to 90 g m⁻³h⁻¹. Toluene inlet concentrations greater than 2.5 g m⁻³ caused the bioprocess inhibition. Inlet gas flow rate was varied from 0.5 m³ h⁻¹ to 2.9 m³ h⁻¹ showing that empty bed residence times < 90 s lowered the removal efficiency.

Keywords: biofiltration, volatile organic compounds, toluene, peat biofilter, elimination capacity.

1 Introduction

New environmental regulations in European Union as are Directives 1999/13/CE and 2001/81/CE establish restrictive limits for the emission of organic volatile compounds (VOCs), some toxic and carcinogenic substances, from industrial
stationary sources. Emission sources of toluene come from petroleum industry, printing and coating facilities, and paint manufacturing. Substances such as toluene could enter the body by skin contact or breathing, being toxic to liver, kidneys and the central nervous system [1].

Physical and chemical treatment processes such as thermal incineration, activated carbon adsorption or absorption present some disadvantages: are expensive, require complex equipment or generate hazardous residues. Bioremediation is shown as a low-cost, competitive alternative, especially in small industrial plants with low concentrations in the waste gas. Besides, bioremediation degrades VOCs to innocuous compounds such as carbon dioxide and water [2].

Initially, biofiltration was used to remove odorous compounds and inorganic substances such as ammonia, mercaptans and hydrogen sulfide from air [3]. In last years, this technology has been extended to the removal of VOCs. VOCs such as toluene can be effectively removed at influent loads up to 100 g m⁻³ h⁻¹ [4], unless, Jorio et al. [5] indicated that for concentrations of aromatics higher than 0.5 g m⁻³, biofilter performance needs further improvement in order to meet environmental requirements.

The performance of two laboratory-plants using peat material has been investigated to treat air polluted with high concentrations of toluene over a total period of three months. A spontaneous toluene-degrading microbial population originating from sludge of municipal wastewater treatment plant was used as inoculum. In this work, the effects of operating conditions such as toluene influent concentration and empty bed residence time have been studied in order to evaluate the maximum elimination capacity and the optimal operating conditions.

2 Material and methods

2.1 Inoculum preparation and medium

The inoculum was obtained from the secondary clarifier of the Carraixet wastewater treatment plant located in Alboraya. Carraixet plant receives urban sewage from Alboraya town and pollutants from the Alboraya industrial complex. The seed culture was previously adapted to the substrate to be used. Two litres of the concentrated sludge were placed in an aerated batch reactor and diluted with 1 litre of nutrient solution containing N and P. Vitamins and trace minerals were added by diluting 3 g of Supradyn® (Roche). The reactor was continuously fed with toluene at a rate of 1 mL/h for a period of 8 weeks. Suspended solids concentration and oxygen uptake rate were controlled twice a week. By mixing 1 litre of this conditioned sludge with the filter material the seeds were performed.

Peat (ProEco Medioambiente, Spain) was used as filter material. The peat was acidic, so pH adjustment until neutral pH was made by using dilute sodium hydroxide solution. As peat is naturally rather nutrient-poor material for bacterial growth, 500 mL of nutrient solution and pH buffer (3.84 g/L K₂HPO₄, 1.94 g/L
KH₂PO₄, 3 g/L NH₄Cl, pH = 6.97) were added to the biofilters about every four days.

2.2 Experimental setup and monitoring of biofilters

The toluene biodegradation was carried out in two identical laboratory-scale biofilters operated in parallel (fig. 1). Each biofilter was made of methacritlate, with a total length of 97 cm and an internal diameter of 13.6 cm. A 10 cm head space was used for the waste gas inlet and for nutrient feed, while a 10 cm bottom space was for the treated air outlet and leachate. Each biofilter was equipped with five sampling ports to measure VOC concentrations, located at 0 (inlet port), 25, 50, 75, and 95 (outlet port) cm of column length. Additional ports located at 20, 40, 60 and 80 cm were used for temperature measurement and to recover bed particles for humidity analyses.

Compressed, filtered and dried air was passed through the humidifier to assure a relative humidity value of at least 90%. Then, air was contaminated with toluene by using a syringe pump (New Era, infusion/withdraw NE 1800 model) with an idle through a port. The toluene line was equipped with two check valves (Swagelok) to obtain continuous feed. The contaminated air was flowed downwards into the bed. The empty bed residence time (EBRT) was adjusted by using mass flow controllers (Bronkhorst Hi-Tec, F-201ACFA33V model).

Figure 1: The schematic diagram of the biofilter system.
Temperature, pH of the leachates and pressure drop were monitored daily for both biofilters. Temperature was kept between 24 and 28 °C for the duration of the study. A differential manometer was used to measure the pressure drop along the biofilter that never exceeded 0.5 kPa. The initial pH of the biofilters was adjusted to 6.2 and was down to 5.5 with the operation. The water content of the filter material was measured weekly, and the peat was kept at constant humidity of about 80% (wet basis) by periodically pouring on top of the biofilters the nutrient solution.

2.3 Analyses of toluene

The concentration of toluene in the air stream was measured by using a gas chromatograph (CE Instruments, GC 8000 model) equipped with a 2.5 mL automated gas valve injection system and a flame ionization detector. Monitoring of the five ports of each biofilter was carried out every four hours by using a time-controlled sequencer. The response of the chromatograph was calibrated weekly by using a synthetic standard mixture of 1920 ppmv toluene and 640 ppmv of ethylbenzene in nitrogen gas (Carburos Metálicos, Spain).

3 Results and discussion

3.1 Operation of the biofilters

Biofiltration of air contaminated by toluene was carried out in two laboratory-scale biofilters operated in parallel for a total period of almost 3 months. The effect of the toluene inlet load, the toluene inlet concentration and the gas flow rate were studied. Operation parameters in biofilters 1 and 2 are summarized on table 1. Biofilter 1 was operated at constant flow rate of 0.46 m³ h⁻¹ (empty gas residence time, EBRT = 100 s). Experiments were performed in three phases as shown in fig. 2. In phase (I) the concentration was increased from 0.14 g m⁻³ to 3.5 g m⁻³ (inlet load, defined as mass of toluene fed per unit time and unit volume of the biofilter = 5 – 130 g m⁻³ h⁻¹). From the beginning of the operation, removal efficiency remained on 94-98% up to an inlet concentration of approximately 2.5 g m⁻³. These high efficiencies from the first day of operation are evidence for the right development of the inoculum. Greater inlet concentrations dropped removal efficiency to 70%. In phase (II), biofilter was operated on 2.5-3.5 g m⁻³ inlet concentration range. For concentrations below 2.8 g m⁻³, 85-95% removal efficiencies were achieved, but greater concentrations led to removal efficiencies of 60-70%. In phase (III), with concentrations lower than 2.0 g m⁻³, removal efficiency was similar to those obtained in phase (I), showing the restoration of the performance when adequate conditions were used.

The operating period of biofilter 2 was divided into three successive phases during which: (I) the flow rate was fixed to those of biofilter 1 for two weeks, 0.46 m³ h⁻¹, operating in parallel at inlet organic loads comprised between 20-50 g m⁻³ h⁻¹. Removal efficiencies reached 95%, showing the reproducibility of the results. In phase (II), the flow rate was fixed at 0.99 m³ h⁻¹ (EBRT = 48 s)
and the inlet concentration increased from 0.5 to 1.5 gm⁻³ (inlet loads = 40–120 gm⁻³h⁻¹). In the range of the inlet load tested, removal efficiency decreased from 95% to 70%. In phase (III), air flow rate varied between 0.46 m³h⁻¹ to 2.92 m³h⁻¹ and inlet load was kept constant on 56 gm⁻³h⁻¹. The effect of air flow rate studied on biofilter 2 is discussed below.

Table 1: Operating conditions of biofilters 1 and 2.

<table>
<thead>
<tr>
<th>Phases</th>
<th>Days</th>
<th>Inlet concentration (g m⁻³)</th>
<th>Inlet load (g m⁻³h⁻¹)</th>
<th>Flow rate (m³ h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biofilter 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1-53</td>
<td>0.14 - 3.5</td>
<td>5 - 130</td>
<td>0.46</td>
</tr>
<tr>
<td>II</td>
<td>54-65</td>
<td>2.5 – 3.5</td>
<td>94 - 130</td>
<td>0.46</td>
</tr>
<tr>
<td>III</td>
<td>66-80</td>
<td>&lt; 2.0</td>
<td>&lt; 75</td>
<td>0.46</td>
</tr>
<tr>
<td>Biofilter 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1-14</td>
<td>0.6 – 1.6</td>
<td>20 -57</td>
<td>0.46</td>
</tr>
<tr>
<td>II</td>
<td>15-60</td>
<td>0.5 – 1.5</td>
<td>40 - 120</td>
<td>0.99</td>
</tr>
<tr>
<td>III</td>
<td>61-80</td>
<td>0.22 – 1.4</td>
<td>56</td>
<td>0.46 – 2.90</td>
</tr>
</tbody>
</table>

Figure 2: Performance of Biofilter 1: inlet (●) and outlet (○) concentrations.

3.2 Influence of toluene inlet load

The influence of the toluene inlet load on the elimination capacity is show in fig. 3, which presents data for operating phases I-III of biofilter 1 (constant flow rate = 0.46 m³h⁻¹, EBRT = 100 s) and operating phase II of biofilter 2 (constant flow rate = 0.99 m³h⁻¹, EBRT = 48 s). The elimination capacity (EC, in g m⁻³h⁻¹) was defined as the amount of toluene removed per unit time and unit volume of the biofilter. At an EBRT of 100 s, two zones can be defined, the toluene elimination capacity increased linearly in proportion to toluene inlet load up to 90 g m⁻³h⁻¹, following the line of 100% removal, showing that the microbial
population can completely degrade toluene in this operating range. For toluene
inlet loads higher than 90 g m$^{-3}$ h$^{-1}$, elimination capacity was lower than 100% removal. The elimination capacity reached a maximum of 100 g m$^{-3}$ h$^{-1}$, remaining in the 80-100 g m$^{-3}$ h$^{-1}$ range for the 22 days of operation at toluene inlet loads higher than 90 g m$^{-3}$ h$^{-1}$. At these operating conditions the process is limited by the bioreaction, the mass of effective microorganisms is insufficient to degrade the toluene transferred to the biofilm. The oscillations of the elimination capacity between 80 and 100 g m$^{-3}$ h$^{-1}$ can be explained on the basis of the possible toxic behaviour of toluene at concentrations higher than 2.5 g m$^{-3}$, leading to the inhibition of the biodegradation reaction. Data corresponding to biofilter 1 phase III shown that 100 % of biofilter removal capacity can be achieved after a long period of stress related to higher inlet loads (> 100 g m$^{-3}$ h$^{-1}$) and concentrations (> 2.5 g m$^{-3}$) of phase II. Maximum elimination capacity obtained is similar to data reported in the literature for toluene biodegradation on peat biofilter by Kiared et al. [6] (90-100 g m$^{-3}$ h$^{-1}$), being higher than other published results as are 70 g m$^{-3}$ h$^{-1}$ [7] or 72.9 g m$^{-3}$ h$^{-1}$ [8]. Thus showing that the protocol implemented for control of moisture, pH and nutrients was adequate for the biofilter performance. At a shorter EBRT of 48 s and toluene inlet loads lower than 90 g m$^{-3}$ h$^{-1}$, biofilter may be operated with almost good elimination capacity, although a slight decrease on the efficiency removal was obtained: 85-95% at 48 s of EBRT in comparison with 94-98% obtained at 100 s of EBRT. At greater inlet loads, elimination capacity reached a constant value between 80-95 g m$^{-3}$ h$^{-1}$, similar to those obtained at 100 s of EBRT.

![Figure 3: Elimination capacity versus toluene inlet load](image-url)

- EBRT = 100 s
- EBRT = 100 s
- EBRT = 48 s

Figure 3: Elimination capacity versus toluene inlet load: (●) Biofilter 1, phases I-II; (★) Biofilter 1, phase III; (○) Biofilter 2, phase II.
Results are also presented in fig. 4 as the evolution of removal efficiency versus the toluene inlet concentration. Up to an inlet concentration of 2.5 g m\(^{-3}\) for 100 s of EBRT, removal efficiency could be kept on over 90%, demonstrating that biofilter is a competitive technology over this operating condition range. Higher concentrations caused a linear decrease on the removal efficiency, due to the limitation of the biodegradation reactions. For short contact times, the decrease on the removal efficiency appeared at lower inlet loads: concentrations greater to 1.1 g m\(^{-3}\) (equivalent to 2.3 g m\(^{-3}\) for 100 s of EBRT) lowered from 90% the removal efficiency, indicating the influence of the EBRT on the biofilter performance.

The elimination capacity along the peat bed is shown in fig. 5 for several days of operation of the biofilter 1. For all cases, toluene removal rates between different ports were not totally regular, thus indicating a non-homogeneous distribution of microorganisms along the filter bed. Similar results have been reported elsewhere [9]. The distribution of microorganisms strongly depends on the operating conditions of the biofilter. In all cases, nearly no removal was obtained on the last half part of the biofilter, thus showing the absence of active biomass. It could be related to the fact that more carbon source, moisture and nutrients were present in the earlier sections, causing removal efficiencies of 94-99% in the first section of the bed along 42 days of operation. This phenomenon led on the lost of inoculated microorganisms in the subsequent part of the bed. Comparison of elimination capacity reached in the first section after 42, 51 and 65 days of operation indicated that, in few days, inlet concentration of toluene higher than 2.5 g m\(^{-3}\) reached toxic levels for the degrading microflora, causing partial death. Toxic behaviour for aromatic compounds was before reported [10]. As could be deduced from data corresponding to the 79 day of operation, the loss of biomass was not be recuperated although the inlet concentration of toluene was decreased. From day 51 of operation, the elimination capacity of the second
section (18-44 cm) was spontaneous increased to compensate the first section decrease, but not re-inoculation of ports 3 to 5 was occurred.

![Figure 5: Evolution of toluene elimination capacity profiles along the peat bed for Biofilter 1 (EBRT = 100 s).](image)

**3.3 Influence of flow rate**

The influence of contact time on the removal rate is shown in fig. 6, which presents data for operating phase III of biofilter 2, corresponding to a constant inlet load of 56 g m$^{-3}$ h$^{-1}$. This value was selected due to the high removal efficiency obtained at 100 s of EBRT, related to the absence of biodegradation limitations. As can be observed, the air flow rate is a significant limiting parameter in the biodegradation process. A decrease in the EBRT from 91 to 50 s caused a decrease in the removal efficiency from 92% to 83%. But for contact times lower than 50 s, a sharp linear decrease was observed, achieving a removal efficiency of 51% at 16 s. This suggests that a minimum EBRT of about 1 minute may be needed to reach adequate removal efficiencies, and 1.5 min of EBRT could be considered as optimal to assure the absence of limitations associated to contact time. These data are consistent with the literature values [5] for biofiltration of alkylbenzene vapours.

The effect of the flow rate on the toluene removal profile in the column is presented in fig. 7. The profiles are characterised by highest removal efficiencies in the first section with gradually decreases in the subsequent sections, and low removal rates in the last section of the biofilter. The increase in the flow rate caused a decrease in the removal rate along the column, due to the shorter contact times that affected to the biological reactions. Influence being greater where microbial reactions occurred in greater extent: removal efficiency decreased from 60% at 91 s of EBRT to 20% at 16 s of EBRT at the first section.
In ports 2 to 4 (20-73 cm) a smooth decrease on the slope of the profile was observed as flow rate increased: 30% of toluene was removed for 91 s of EBRT and only 20% was removed for 16 s of EBRT. No influence was observed for the last section of the column where nearly no biodegradation occurred.

Figure 6: Removal efficiency versus empty bed residence time: toluene inlet load = 56 g m⁻³ h⁻¹.

Figure 7: Influence of the empty bed residence time on the profile of toluene along the peat bed: toluene inlet load=56 g m⁻³ h⁻¹.
4 Conclusions

Two laboratory-scale peat biofilters were operated in parallel for a continuous period of 3 months to remove toluene vapors showing an adequate performance. Operational parameters to obtain a complete removal of toluene were determined as: inlet loads < 90 g m\(^{-3}\) h\(^{-1}\), inlet concentrations < 2.5 g m\(^{-3}\) and empty bed residence times > 90 s. Inlet loads greater than 120 g m\(^{-3}\) h\(^{-1}\), inlet concentrations greater than 3.0 g m\(^{-3}\) or empty bed residence times lower than 40 s results in removal efficiencies lower than 70%.

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References