Degradation of Isobutanal at High Loading Rates in a Compost Biofilter

Bram Sercu, Kristof Demeestere, Hans Baillieul, and Herman Van Langenhove
Environmental Organic Chemistry Research Group, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium

Willy Verstraete
LabMET, Faculty of Bioscience Engineering, Ghent University, Ghent, Belgium

ABSTRACT
Biofiltration has been increasingly used for cleaning waste gases, mostly containing low concentrations of odorous compounds. To expand the application area of this technology, the biofiltration of higher pollutant loading rates has to be investigated. This article focuses on the biodegradation of isobutanal (IBAL) in a compost biofilter (BF) at mass loading rates between 211 and 4123 g/m³/day (30–590 ppmv). At mass loading rates up to 785 g/m³/day, near 100% removal efficiencies could be obtained. However, after increasing the loading rate to 1500–1900 g/m³/day, the degradation efficiency decreased to 62–98%. In addition, a pH decrease and production of isobutanol (IBOL) and isobutyric acid (IBAC) were observed. This is the first report showing that an aldehyde can act as electron donor as well as acceptor in a BF. To study the effects of pH, compost moisture content, and electron acceptor availability on the biofiltration of IBAL, IBOL, and IBAC, additional batch and continuous experiments were performed. A pH of 5.2 reduced the IBAL degradation rate and inhibited the IBOL degradation, although adaptation of the microorganisms to low pH was observed in the BFs. IBAC was not degraded in the batch experiments. High moisture content (51%) initially had no effect on the IBOL production, although it negatively affected the IBAL elimination increasing during a 21-day time-course experiment. In batch experiments, the reduction of IBAL to IBOL did not decrease when the amount of available electron acceptors (oxygen or nitrate) was increased. The IBAL removal efficiency at higher loading rates was limited by a combination of nutrient limitation, pH decrease, and dehydration, and the importance of each limiting factor depended on the influent concentration.

INTRODUCTION
Volatile organic compounds (VOCs) are important environmental pollutants, because they contribute to tropospheric ozone formation, global warming, ozone depletion, and, more locally, odor problems. In addition, a number of VOCs are toxic and/or carcinogenic. Carbonyl compounds are common intermediates and final products of combustion processes involving liquid or gaseous fossil fuels.1 Aldehydes are known for their high potential to form urban ozone2 and, in addition, they may cause health problems, such as induction or exacerbation of asthma.3 The compounds are industrially produced for applications in the synthesis of synthetic resins, odorants or dyes, pharmaceutics, and plant protection products. Emissions originating from these industrial processes contain relatively high VOC concentrations and are traditionally treated with physical-chemical end-of-pipe technologies, such as incineration, carbon adsorption, absorption, and condensation. Other processes, however, like composting, animal rendering, and food processing, cause emissions with variable VOC concentrations. In rendering plants, for example, total VOC concentrations from 4 to 91 ppm, have been measured in the noncondensable gas streams,4 whereas during aerobic composting of biowaste, individual VOC concentrations up to 103 ppm, were observed.5 On the other hand, in the blower

IMPLICATIONS
Because biofiltration is a relatively simple, cheap, and environmentally friendly technology, there is interest in expanding its application area toward higher loading rates. It is generally assumed that high loading rates can be accommodated for readily biodegradable, nonacidifying compounds. However, in this study it is shown that at IBAL influent loading rates between 785 and 4123 g/m³/day, system upset occurred, and the removal efficiencies decreased from >98% to values between 50% and 94%. Therefore, additional research on the removal of high loading rates of other volatile organic compounds in BFs is necessary, even for compounds that are considered to be readily biodegradable.
exhaust from a composting facility processing anaerobically digested sludge, individual VOC concentrations remained <1 ppmv.\textsuperscript{6} Waste gases originating from this kind of processes often contain aldehydes, along with reduced sulfur compounds and inorganics,\textsuperscript{7} and can lead to odor nuisance in the environment. The aldehydes are formed during the degradation or processing of animal and plant materials by the breakdown of fatty acids in the Strecker degradation of amino acids.\textsuperscript{8} In such cases, biological waste gas treatment technologies like biofilters are often used, because they provide cost-effective and efficient alternatives for the more traditional treatment technologies.

Aldehydes are usually considered to be easily biodegradable in biofilters (BFs)\textsuperscript{9–11} and, consequently, not much literature is available about the biofiltration of these compounds.\textsuperscript{12} In wood-bark BFs, for example, a hexanal removal efficiency of 85% was observed in short-term (<360 hr) experiments,\textsuperscript{13} whereas for butanal, a mean removal efficiency of 97% was obtained for 84 days with supplementation of a nutrient solution,\textsuperscript{14} both at influent concentrations of 10 ppmv. For the latter BF, a maximum butanal elimination capacity of 2160 g/m²/day was observed (75% removal efficiency). Other authors observed >90% removal of formaldehyde for a period of almost 5 months, although pH control was needed because of acidification of the medium.\textsuperscript{15} However, no research was done on the causes of the observed pH decrease. In none of the studies investigating the biofiltration of aldehydes was attention paid to the mechanisms contributing to the formation of byproducts. Also, little knowledge is available about the degradation potential of BFs for waste gases containing high (e.g., >50 ppmv) aldehyde concentrations. Yet, industrial users and vendors of BFs have been attracted by the concept of treating higher concentrations and operating at higher loading rates of VOCs in BFs.\textsuperscript{16} In this way, the application area of biofiltration could be expanded from odor removal to the sanitation of specific, more-concentrated air streams originating from a variety of industries. In Europe, the recently issued European Solvent Emissions Directive (1999/13/EC) will be an additional motivation for an increased implementation of the more economical biotechnologies for cleaning polluted waste gases. Therefore, the aim of this study was to investigate the compost biofiltration of isobutanal (IBAL) at medium to high loading rates (211–4123 g/m²/day). In addition, experiments were performed to study critical factors in intermediate formation and degradation.

**MATERIALS AND METHODS**

**Laboratory-Scale BFs and Batch Degradation Tests**

Three continuous biofiltration experiments were conducted. In biofiltration experiment 1 (110 days), the effect of mass loading rate (LR) on the removal of IBAL was investigated. In biofiltration experiment 2 (21 days), the effects of pH and moisture content on the biofiltration of IBAL and on the formation and/or degradation of its intermediates were investigated. A third short biofiltration experiment (7 days) was performed to investigate the effect of increased oxygen concentrations on the formation of isobutanol (IBOL).

The BF used in experiment 1 (Figure 1a) consisted of a Plexiglas column (i.d. 0.195 m and overall height 1 m) divided in three detachable parts for sampling purposes (section 1, inlet; section 2, middle; section 3, outlet). Gas sampling points were provided at the influent (port A) and effluent (port D), between section 1 and 2 (port B), and between section 2 and 3 (port C). Each BF section was filled with 6.7 L of compost material, supported by a perforated plate. The compost was produced from source separated municipal organic waste (the garden, fruit and vegetable fraction) by the DRANCO process, in other words, anaerobic digestion followed by aerobic treatment.\textsuperscript{17} Compost samples for microbiological and physical-chemical analyses were taken by opening the BFs during short interruptions of the airflow (maximum 30 min). Laboratory air was supplied at 33 L/min by a diaphragm pump (KNF Neuberger) and was humidified up to >97% relative humidity (21 °C) in a scrubber before entering the BFs in downflow mode (empty bed residence time [EBRT] 36 sec). The gas flow rate was kept constant during the entire experiment. Until day 17, IBAL was dosed by bubbling a calibrated airstream through an impinger containing the pure liquid compound (99+%, Acros Organics) kept at a constant temperature (25 °C). However, this resulted in oxidation of the IBAL and the presence of partially oxidized compounds in the influent stream between days 5 and 17. Thereafter, IBAL was dosed by bubbling a calibrated nitrogen stream through the impinger. The setup of the three BFs used in biofiltration experiment 2 (Figure 1b) was similar to biofiltration experiment 1, but only one section filled with 6.7 L of compost was used for each BF. All three of the BFs were subject to the same EBRT (33 sec) and influent concentration by dividing one influent stream of 36 L/min equally to the three BFs in an upflow direction. Gas sampling ports were provided before and after the BFs. BF 1 acted as the reference BF, with initial moisture content (weight/weight [w/w]) and pH value of 36% and 8.4, respectively, whereas BF 2 and BF 3 had moisture contents of 51% and 36% and pH values of 8 and 5.2, respectively. The initial pH value of 5.2 was obtained by adding diluted HCl to the compost. The third biofiltration experiment was performed by using only one of the BFs of biofiltration experiment 2 (EBRT = 33 sec).

Two series of batch experiments were performed, the first one to investigate the degradation of IBAL and its intermediates (IBOL and isobutyric acid [IBAC]) and the
second one to investigate the IBAL biodegradation after adding electron acceptors. The experiments were performed at 30 °C in 250-mL Schott bottles that were provided with a septum. After adding the compost, the bottles were closed gas-tightly, and volatiles were dosed through the septum on a small filter paper to allow for rapid evaporation. Depending on the pollutant investigated, 1.65 mL of pure liquid IBAL, IBOL, or IBAC was dosed, resulting in theoretical gas phase concentrations of \( \sim 1364 \text{ ppmv} \) in the absence of compost. In the first series of batch experiments, 2 g of compost was added to the bottles. A bottle containing untreated compost and a reference bottle containing compost inactivated by drying (48 hr at 105 °C) were prepared. The moisture content of the latter was adjusted to the value of the untreated compost with sterile deionized water. The concentration decrease measured with these samples was attributed to sorption, whereas the additional concentration decrease in bottles containing regular compost was considered to be caused by biodegradation. Inactivation of the dried compost was verified by the absence of respiration during 7 days of incubation. By comparing the VOC removal in the active and in the inactive compost, it was verified that the biodegradation was high enough compared with sorption to produce reliable results in these batch tests. In the second series of batch experiments, 1 g of compost was used, and nitrate and oxygen were added to change the amount of available electron acceptors. This was done by adding 0.2 mL of 5 g NO\(_3^–\)/N/L to the compost or by adding 0.2 mL of distilled water to the compost and flushing with 100% oxygen (O\(_2\); 100% relative humidity) for 72 hr. Also, a control was prepared by adding only 0.2 mL of distilled water to 1 g of compost before putting this into the bottle. The moisture content of the compost material was set to 45% for all of the experiments. The VOC degradation rates (units, \( \text{min}^{-1} \)) in all of the experiments were calculated as the negative slope of the straight regression line obtained by plotting the logarithms of the ratio of the concentration at time \( x \) and the concentration at time zero as a function of time. The IBOL production rate in the second batch experiment was expressed as the slope of the straight regression line obtained by plotting the IBOL concentration as a function of time (units, g/m\(^3\)/hr). All of the batch experiments were performed in duplicate.

**Analysis of the Pollutants**

Concentrations of VOCs were measured with a Varian 3700 gas chromatograph (GC) equipped with a flame-ionization detector and a 30-m DB-5 capillary column (J&W Scientific; i.d. 0.53 mm; film thickness 1.5 \( \mu \text{m} \)) with He as carrier gas. Using a Pressure-Lok Precision Analytical Syringe (Alltech Ass.), 1-mL gas samples were taken. The lower limit for quantification of the different VOCs (1 ppmv) was determined by measuring decreasing standard concentrations until a reproducible signal was no longer obtained.

Identification of gaseous intermediates was performed by comparing the residence time of the unidentified peaks in the chromatogram with the retention time of some likely intermediates. In addition, 100-\( \mu \text{L} \) gas samples were injected in a GC-mass spectrometry (MS) apparatus, consisting of a Varian 2700 GC fitted with a flame-ionization detector and a MAT 112 mass spectrometer. A
60-m 100% polydimethylsiloxane (PDMS) column was used (i.d. 0.53 mm; film thickness 1.5 μm) with He as carrier gas. A temperature program was used, increasing from 25 to 100 °C at 2 °C/min and then additionally to 250 °C at 4 °C/min. Mass spectrometer conditions were as follows: source pressure, 10⁻⁶ Torr; electron energy, 70 eV; scan range, 40–250 m/e; scan speed, 2.5 sec/scan. Identification of organic acids in the compost was performed by solvent extraction. Therefore, 5 g of compost was mixed with 15 mL of H₂PO₄⁻/HPO₄²⁻ buffer (pH 7) and shaken for 20 min. The liquid fraction was then separated from the compost by means of a Büchner filter and filter papers (Qual 15; 90 mm, Ederol). Subsequently, 2 mL of diethyl ether and 0.1 g of NaCl were added per 5 mL of filtrate, which was then acidified to a pH < 2 with HCl. The ether phase was transferred to a test tube and evaporated until a volume of 0.1 mL was obtained, of which 1 μL was injected in the GC–MS apparatus as described above.

Analysis of the BF Material
For the analysis of the physical–chemical parameters of the compost, the upper part of each BF section was mixed before taking samples. The moisture content was calculated from the weight difference before and after drying 5 g of compost material at 105 °C to constant weight (typically 24 hr). The pH was measured with an electronic pH sensor (Jenway 3310) after mixing 2 g of compost with 20 mL of distilled water during 20 min. To analyze the NH₄⁺-N and (NO₂⁻+NO₃⁻)-N content of the compost, an extract was prepared by mixing 5 g of compost with 25 mL 1 M KCl. This solution was shaken for 1 hr. The compost was separated from the liquid phase by means of a Büchner filter and filter papers (Qual 15; 90 mm, Ederol). Analysis of the NH₄⁺-N and (NO₂⁻+NO₃⁻)-N contents was performed by steam distillation, as previously described.¹⁸

RESULTS
Biofiltration Experiment 1 (Long-Term IBAL Biofiltration)
In the first biofiltration experiment (110 days), the effect of LR on the removal of IBAL was investigated. In Figure 2, IBAL concentrations and mass loading rates measured at the different sampling ports are shown as a function of time. The experiment was subdivided in three periods, according to the applied IBAL influent loading rates.

During period 1 (days 0–38) the BF was subject to IBAL loading rates from 211–1026 g/m³/day. Immediately after startup, at a loading rate of 760 g/m³/day, no IBAL was detected in the effluent (>99% removal efficiency). At the end of period 1, a maximum elimination capacity (EC) of 785 g/m³/day was obtained, at a removal efficiency (η) >99%. The initial instability of the influent concentration was because of problems with the IBAL dosing until day 24. In Table 1, the physical–chemical compost parameters are shown. During period 1, a gradual decrease of the compost pH could be observed, especially in BF section 1, where a value of 5.9 was measured on day 36. The moisture content increased slightly from 47% (day 0) to 49–54% (day 36). Changes in both operational parameters did not affect the biodegradation efficiency of IBAL in the BF. On day 24, the IBAL inlet loading rate increased from 322 to 756 g/m³/day. At the same time, IBOL was detected in port B. However, an earlier increase of the LR from 364 to 1029 g/m³/day on day 11 did not
result in IBOL detection. From day 38 on, IBOL could also be detected in the effluent of the BF, as shown in Figure 3. Because the pH on day 24 was lower than on day 11, it could be a determining factor in the production of IBOL. Additional experiments were carried out to investigate the effect of pH and moisture content on the formation and/or degradation of IBOL (see below).

In period 2 (days 39–86), the inlet loading rate was additionally increased and reached 1535 ± 191 g/m²/day during days 54–86. After an initial lower removal efficiency during adaptation to these higher loading rates, a removal efficiency of 86 ± 2% was observed at a LR of 1670 ± 160 g/m³/day (days 60–82). In this period, a maximum elimination capacity (EC_{max}) of 1695 g/m³/day

---

**Table 1.** Results of the measurements of the compost parameters during experiment 1.

<table>
<thead>
<tr>
<th>Period</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td>8.2</td>
<td>8.2</td>
<td>8.2</td>
</tr>
<tr>
<td>9</td>
<td>6.6</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>18</td>
<td>6.0</td>
<td>6.9</td>
<td>7.4</td>
</tr>
<tr>
<td>36</td>
<td>5.9</td>
<td>7.7</td>
<td>8.7</td>
</tr>
<tr>
<td>43</td>
<td>5.5</td>
<td>4.9</td>
<td>7.9</td>
</tr>
<tr>
<td>58</td>
<td>4.9</td>
<td>5.0</td>
<td>5.9</td>
</tr>
<tr>
<td>71</td>
<td>4.4</td>
<td>4.7</td>
<td>5.6</td>
</tr>
<tr>
<td>86</td>
<td>36</td>
<td>43</td>
<td>53</td>
</tr>
<tr>
<td>93</td>
<td>51</td>
<td>48</td>
<td>51</td>
</tr>
<tr>
<td>96</td>
<td>43</td>
<td>48</td>
<td>51</td>
</tr>
<tr>
<td>102</td>
<td>32</td>
<td>48</td>
<td>51</td>
</tr>
<tr>
<td>103</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>103b</td>
<td>38</td>
<td>40</td>
<td>52</td>
</tr>
<tr>
<td>113</td>
<td>52</td>
<td>50</td>
<td>52</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>pH</th>
<th>8.2</th>
<th>8.2</th>
<th>8.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Section 1</td>
<td>6.6</td>
<td>6.9</td>
<td>7.4</td>
</tr>
<tr>
<td>Section 2</td>
<td>5.9</td>
<td>7.7</td>
<td>8.7</td>
</tr>
<tr>
<td>Section 3</td>
<td>5.5</td>
<td>4.9</td>
<td>8.7</td>
</tr>
</tbody>
</table>

**Note:** Moisture and N content are expressed on a wet and dry weight (DW) basis, respectively. On days 89 and 93, a mineral medium was added to the compost. The measurement on day 103b was performed after adding tap water to the compost. Measurements below the detection limit (0.01 g N/kg DW) were indicated as < dl.

---

**Figure 3.** Effluent concentrations of IBOL (IBOL out) and IBAC (IBAC out) measured during biofiltration experiment 1. The periods with different loading rates are separated by the dashed lines and indicated with I, II, and III.
was obtained ($\eta = 90\%$). IBOL was formed in section 1 and measured in the effluent all through period 2. By comparing Figures 2 and 3, it is clear that IBOL outlet concentrations correlate well with IBAL influent concentrations ($R^2 = 0.93 \ [n = 25]$ from days 39 to 93). Peak concentrations of 62 ppmv IBOL were measured at an IBAL influent concentration of 316 ppmv (2212 g/m$^3$/day). Besides IBOL, a second compound, IBAC, could be identified in the effluent gas from day 47 on, as shown in Figure 3. On days 65 and 101, respectively, IBAC peak concentrations of 61 and 71 ppmv were measured at the BF outlet. However, the gaseous IBAC concentrations were generally lower than the IBOL concentrations and were typically in the range of 10–30 ppmv. The effluent IBAC concentrations did not correlate with the influent IBAL concentrations ($R^2 = 0.0011 \ [n = 25]$ from days 47 to 93). In all three sections of the BF, a pH decrease was observed during period 2, reaching a minimum pH of 4.4–4.7 on day 86. The moisture content of the compost remained rather constant for the three BF sections, but the NH$_4^+$-N and (NO$_2^-$+NO$_3^-$)-N contents decreased to almost zero (Table 1).

In period 3 (days 87–113), the effect of higher IBAL influent loading rates, stripping of IBAC, and mineral nutrient addition was examined. A sharp peak in the influent loading rate from 1335 to 3049 g/m$^3$/day on day 87 immediately resulted in a drop of the IBAL removal efficiency from 77% to 50%. In addition, an IBOL concentration of 92 ppmv was measured in the effluent at the same time. After a decrease of the IBAL loading rate on day 89, the removal efficiency returned to previously obtained levels. On day 89 (after measurement of the gas concentrations) and day 93, respectively, 1 L and 300 mL of a nutrient solution was mixed with the BF material. The nutrient solution used contained 3 g/L NH$_4$Cl, 5 g/L KNO$_3$, 3 g/L K$_3$HPO$_4$, 3 g/L KH$_2$PO$_4$, 0.5 g/L MgSO$_4$, 7H$_2$O, 0.1 g/L FeSO$_4$, 7 H$_2$O, 57 g/L NH$_4$Cl, and 7 g/L KNO$_3$. This resulted in increased nitrogen concentrations in the compost material, as shown in Table 1. In addition, IBAL was not dosed in the influent gas from day 93 to 95, to strip the accumulated IBAC from the BF material. After this treatment, no IBAC was measured in the effluent on day 96 (Figure 3), and the pH increased slightly (Table 1). From day 96 on, loading rates up to 3811–4123 g/m$^3$/day were applied. Initially, $\eta$ increased to 99% (day 96) but decreased rapidly afterwards to 64% (day 102). In the same time period, a clear drop in moisture content (from 43 to 32% in section 1) and nitrogen content were observed (Table 1). From day 102 to 106, IBAC was stripped again from the BF. The moisture content was adjusted to 50% by adding distilled water to the compost. This resulted in high and stable elimination capacities of 1757 ± 69 g/m$^3$/day ($\eta > 95\%$) from day 107 until day 113. However, the moisture content again decreased rapidly during the removal of the high inlet concentrations, as displayed in Table 1.

### Biofiltration Experiments 2 and 3 (Influence of pH, Moisture Content, and O$_2$ Dosing)

Additional continuous biofiltration experiments were performed to investigate the effect of pH and moisture content on the biofiltration of IBAL and on the formation and/or degradation of its intermediates. By increasing the moisture content, it could be determined if increased oxygen limitation stimulated IBOL formation, because a thicker water layer reduces the oxygen transfer rate to the biofilm, compared with the IBAL transfer rate. Before these experiments were started, the BF material used in the biofiltration experiment 1 was air-stripped to remove the remaining IBAC. The removal of IBAC was demonstrated by an increase of the compost pH to 7 and by the absence of IBAC in the extracted organic acids from the air-stripped compost, as measured by GC-MS analysis. Next, 710 mL of a nutrient solution containing 10.4 g/L NH$_4$Cl and 19.7 g/L KNO$_3$ was added to each BF. Biofiltration experiment 2 was subdivided in three periods according to the IBAL influent concentrations: period 1 (days 0–7, 1268 ± 329 g/m$^3$/day), period 2 (days 7.3–12, 4659 ± 368 g/m$^3$/day), and period 3 (days 13–21, 1291 ± 305 g/m$^3$/day).

IBAL loading rates and inlet concentrations are given in Figure 4a, whereas the IBAL removal efficiencies are summarized in Table 2. From Table 2 it is clear that in BF 2, the removal efficiency was as good as in the control BF during period 1, but after day 7, after increasing the inlet concentration, $\eta$ decreased compared with that of the control BF. BF 3 needed a period of adaptation to the low pH value, but after 12 days, the removal efficiency was about equal to that in the control BF. The pH values of the different BFs are shown in Figure 5. The pH decreased sharply when high IBAL loads are applied from day 7, although this decrease was reversible if the IBAL loads decreased again from day 12. The moisture content in BFs 1–3 remained quite constant, at 32 ± 3%, 53 ± 2%, and 37 ± 2% for BF 1, 2, and 3, respectively. Table 2 shows that the IBAL removal efficiencies during period 3 were the lowest in BF 2, meaning that in the long term, a moisture content >51% appeared to have a more negative effect on the IBAL removal efficiency than pH values as low as 4.

During period 1, no IBOL was detected in the effluent of BF 1 and 2 (Figure 4b and Table 2). In BF 3, however, IBOL emissions were higher than 9 ppmv, from day 0 on and increased with increasing IBAL influent concentrations. Table 2 shows that after the sharp increase in IBAL influent concentration in period 2, IBOL was measured in the effluent of all three of the BFs, although the concentration was
much higher for BF 3 than for BF 1 and BF 2. For the calculation of the mean and standard deviation of the IBOL concentration during period 2 in Table 2, the value from day 7.3 was not used because of the delay in the IBOL production after the IBAL inlet concentration increase on day 7. At the end of period 3 (days 20 and 21), after an increase of the influent IBAL concentration, the IBOL effluent concentrations were 4 ppmv and 8–9 ppmv for BF 2 and 3, respectively, whereas no IBOL was detected in the effluent of BF 1 (Figure 4b). IBAC was measured in the effluent from day 9 in all of the BFs (17–27 ppmv). From day 12 on, the IBAC concentrations started to decrease until it was no longer detected in the effluents of BF 1 and BF 3 (days 13 and 14) and later of BF 2 (between days 14 and 19).

In a third short, continuous biofiltration experiment (data not shown), it was shown that the IBAL degradation and the IBOL formation were the same when air (21% O₂) or pure O₂ (during 4 hr) was supplied to the BF. Upon air supplementation, 322 ppmv IBAL was removed for 95%, whereas upon oxygen supplementation, 285 ppmv IBAL was also removed for 95%. The IBOL formation was ~5% in both cases.

**Batch Degradation Experiments**

The results of the batch experiments are summarized in Table 3. The reference compost is compost with pH 8.4

---

**Table 2.** Summary of the IBAL loading rate, the IBAL removal efficiency and the IBOL formation during biofiltration experiment 2 (mean ± standard deviation).

<table>
<thead>
<tr>
<th>Period</th>
<th>Days 1–7</th>
<th>Days 7.3–12</th>
<th>Days 13–21</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBAL loading rate (g/m²/d)</td>
<td>1268 ± 329</td>
<td>4659 ± 368</td>
<td>1291 ± 305</td>
</tr>
<tr>
<td>IBAL removal efficiency (%)</td>
<td>BF 1 97 ± 1</td>
<td>75 ± 18</td>
<td>91 ± 6</td>
</tr>
<tr>
<td></td>
<td>BF 2 97 ± 5</td>
<td>56 ± 20</td>
<td>62 ± 10</td>
</tr>
<tr>
<td></td>
<td>BF 3 61 ± 12</td>
<td>40 ± 22</td>
<td>92 ± 4</td>
</tr>
<tr>
<td>IBOL emission (ppmv)</td>
<td>BF 1 0 ± 1</td>
<td>47 ± 3ᵃ</td>
<td>2 ± 2</td>
</tr>
<tr>
<td></td>
<td>BF 2 0</td>
<td>46 ± 7ᵃ</td>
<td>4 ± 2</td>
</tr>
<tr>
<td></td>
<td>BF 3 13 ± 4</td>
<td>139 ± 9ᵃ</td>
<td>4 ± 3</td>
</tr>
</tbody>
</table>

ᵃResults are from days 8–12.
and 36% moisture content. The first series of batch degradation experiments was performed to investigate the biodegradation of IBAL, IBOL, and IBAC as single compounds in the compost material. At reference conditions, the removal rate of IBAL (0.050 \text{ min}^{-1}) was higher than for IBOL (0.025 \text{ min}^{-1}). At pH 5.2 the IBOL removal rates decreased to 0.001 \text{ min}^{-1}, which was lower than when only sorption was determined (0.008 \text{ min}^{-1}). The latter can be attributed to the higher sorption of VOCs at low pH. For IBAC, no biodegradation was observed during the studied time interval of 94 min (data not shown). A second set of batch degradation tests was performed to determine if the addition of electron acceptors (O2 and nitrate) would decrease the IBOL formation during IBAL degradation. In these experiments, bottles containing compost (reference), compost after flushing for 72 hr with oxygen, and compost with 0.2 mL of 5-g NO3^-/L were used. The IBAL removal was slightly faster for the control test (0.0060 \text{ min}^{-1}) compared with the bottles with increased O2 (0.0050 \text{ min}^{-1}) and nitrate (0.0045 \text{ min}^{-1}) concentrations, but no positive effect from adding electron acceptors was observed. The IBOL production rate during IBAL degradation was 0.11 g/m^3/hr for the reference, whereas after addition of O2 or nitrate, values of 0.11 g/m^3/hr and 0.10 g/m^3/hr were measured, respectively. When the ratio of the IBOL production and the IBAL degradation were compared (Table 3), it was clear that no reduction of the IBOL formation was observed upon the addition of electron acceptors after normalizing the data for the IBAL degradation.

**DISCUSSION**

**Biofiltration of IBAL**

The immediate high elimination efficiencies (>99%) in biofiltration experiment 1 demonstrate that the compost BF required no adaptation period to remove medium influent concentrations of IBAL (30–112 ppmv). Other authors, on the contrary, have found that it took at least 2–3 days before maximum removal efficiencies of 85% and 97% were obtained for 10-ppmv, hexanal\textsuperscript{13} or butanal\textsuperscript{14} in a wood-bark BF. It is not clear, however, if these longer adaptation periods were caused by lower influent concentrations, differences in BF material, or other reasons. The possibility that low influent concentrations cause a slow startup can be supported by the occurrence of a diffusion-controlled regime.\textsuperscript{19} In this case, a larger portion of the biofilm is exposed to VOCs if higher influent concentrations are applied, which can lead to a more rapid development of the actively degrading biofilm. This hypothesis is additionally supported by other authors, who explained higher VOC elimination capacities at increased gas concentrations (for the same loading rate) by an increased microbial activity induced by the increased VOC concentrations.\textsuperscript{20} For other VOCs, reported adaptation periods range from a few hours for methanol (400 ppmv) to 7–10 days for α-pinene (30–35 ppmv).\textsuperscript{21}

During period 2, an EC\textsubscript{max} of 1695 g/m^3/day (1130 g VOC-C/m^3/day) was obtained for IBAL (η = 90%). This is lower than EC\textsubscript{max} values reported for the degradation of other readily biodegradable VOCs in BFs, such as 4200 g/m^3/day for ethanol (2191 g VOC-C/m^3/day, η = 95%)\textsuperscript{22} and 10,150 g/m^3/day for methanol (3806 g VOC-C/m^3/day, η = 91%),\textsuperscript{18} even if expressed as g VOC-C/m^3/day to standardize for stoichiometric oxygen demand. This lower EC can partly be attributable to the fact that branching usually reduces the rate of biodegradation.\textsuperscript{23,24}

Furthermore, during period 3 it was shown that the long-term stability of a compost BF degrading relatively high IBAL loading rates (1335–4123 g/m^3/day) may be limited by three important factors: shortage of mineral nutrients, pH decrease, and dehydration. The importance of the first two factors was shown after nutrient addition and stripping of the IBAC from the compost by omitting IBAL from the influent. Both treatments were efficient in improving the BF performance, because η increased to 97 ± 2% at 1820 ± 86 g/m^3/day IBAL (days 107–113) compared with 85 ± 4% at 1646 ± 177 g/m^3/day IBAL (between days 58 and 86). However, during the elimination of the highest IBAL influent loading rates (3811–4123 g/m^3/day), the pH decreased quickly because of IBAC formation, and drying out of the BF was very significant, mainly in section 1 where the largest part of the IBAL was removed. Dehydration of the compost bed at high VOC influent concentrations was previously described. van Lith et al.\textsuperscript{25} calculated that moisture removal because of heat formation during bio-oxidation becomes significant as VOC inlet concentrations and volumetric elimination capacities approach 0.5 g/m^3.

**Table 3. Summary of the results from the batch degradation experiments.**

<table>
<thead>
<tr>
<th>Comparison of Batch Degradation</th>
<th>Dry (Sorption) pH 5.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBAL degradation</td>
<td>0.050</td>
</tr>
<tr>
<td>IBOL degradation</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>IBAL degradation</td>
<td>0.025</td>
</tr>
<tr>
<td>IBOL degradation</td>
<td>0.008</td>
</tr>
<tr>
<td>IBAL degradation</td>
<td>0.001</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Addition</th>
<th>Reference + Oxygen + Nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBAL degradation</td>
<td>0.0060 0.0050 0.0045</td>
</tr>
<tr>
<td>IBOL production</td>
<td>0.11 0.11 0.10</td>
</tr>
<tr>
<td>IBOL production/IBAL degradation</td>
<td>18 22 22</td>
</tr>
</tbody>
</table>

*Note: The IBAL and IBOL removal rates are expressed in min^{-1}. IBOL formation is expressed in g/m^3/hr.*
and 1200 g/m³/day, respectively. These conditions were largely exceeded in this BF during period 3.

A closer inspection of the concentration profile of IBAL along the BF (Figure 2) revealed that the inlet concentration of BF section 1 in period 1 (97 ± 14 ppmv; days 24–36) is similar to the inlet concentration of section 3 in period 2 (83 ± 14 ppmv; days 44–86). Nevertheless, the removal efficiency obtained in section 3 (26 ± 7% between days 44 and 58 and 54 ± 8% between days 59 and 86) is lower than that observed in section 1 (72 ± 6% between days 24 and 36). The lower performance of section 3 could be caused by different factors, like the occurrence of an adaptation period, low pH, toxicity of intermediates, inadequate moisture content, and oxygen and/or nutrient limitation.

The lack of adaptation and a too low pH value are unlikely causes for the lower performance, because in section 1 they did not limit the IBAL degradation during the first period of biofiltration experiment 1. Adaptation of the microorganisms to low pH can occur either by adaptation of the indigenous microbiota or by a shift to a more acidotolerant IBAL degrading microbial community. Preliminary denaturing gradient gel electrophoresis analysis of the microbial communities as a function of time indicated that a different microbial community developed gradually. However, more thorough research will be necessary to indicate if the new microbial community was a more acidotolerant one. Because the compost pH and IBAC concentrations are dependent of each other, a prolonged inhibitory effect because of IBAC toxicity is not likely for the same reason as mentioned for the pH.

Because the maximum removal efficiency in section 3 was obtained at day 71, in other words, when the compost moisture content was maximal (58%), moisture content can also not be the limiting factor. Furthermore, the moisture content of section 3 remained between 47 and 58% (periods 1 and 2), which is in the range usually considered to be optimal for organic BF materials.

To assess the possibility of oxygen limitation, the maximum biofilm VOC concentration (S_{IBAL}) at the air-biofilm interface, at which no oxygen limitation occurs, was calculated. Assuming that IBAL is the sole electron donor and given that S_{O2} = 8.27 mg/L (maximum solubility in water at 25 °C with conductivity = 1820 µS/cm), oxygen limitation within the biofilm will occur if

\[
S_{VOC} > \left[ \frac{v_{VOC}}{v_{O2}} \right] \left[ \frac{D_{O2}}{D_{VOC}} \right] \left[ \frac{MW_{VOC}}{MW_{O2}} \right] S_{O2}
\]

\[
= \left[ \frac{1}{5.5} \right] \left[ \frac{2.42 \times 10^{-5}}{1.09 \times 10^{-5}} \right] \left[ \frac{8.27}{32.0} \right] \left[ \frac{72.1}{1820} \right] \left[ \frac{1}{8.27} \right] = 0.01 g \text{ biomass-C/g substrate C and cell composition} \]

In eq 1, \(v\), MW, and D represent stoichiometric coefficients, molecular weights, and diffusion coefficients (2.42 \times 10^{-5} cm²/sec for O₂ and 1.09 \times 10^{-5} cm²/sec for IBAL in water at 25 °C, calculated according to the equations of Wilke and Chang, respectively. According to eq 1, O₂ limitation occurs if \(S_{IBAL}\) is 7.51 mg/L, corresponding with ~18.5 ppmv, as an equilibrium gas phase concentration (with Henry’s law constant = 0.00736). In our experiments, the inlet IBAL concentrations in section 3 always exceeded this concentration, and, consequently, O₂ shortage will limit the IBAL biodegradation. It cannot, however, explain the lower IBAL degradation efficiency compared with section 1 during period 1, because O₂ will be limiting in both cases.

A last important factor is the nutrient content of the filter material and, mainly, the inorganic nitrogen (N) content. Table 1 shows that on day 71, NH₄⁺-N and (NO₂⁻ + NO₃⁻)-N concentrations in section 3 were both 0.04 and 0.01 g N/kg DW, respectively. This low compost N content indicates that N limitation is probably limiting the IBAL removal in this BF section. This can also be illustrated by calculating the approximate cumulative removed carbon (C; 164 g C/kg DW) and the corresponding N demand (15.4 g N/kg DW, based on a cell yield coefficient \(Y = 0.4 \text{ g biomass-C/g substrate C and cell composition} = C_{6}H_{12}O_{5}N\), until day 71. Because the N demand is much larger than the initially present compost N content (1.39 g N/kg DW), N will be quickly depleted, and N limitation will occur. In this case, microorganisms can only use nitrogen recycled from dead biomass. According to Cherry and Thompson, all BFs normally operate under these stationary phase conditions, without net growth of the microorganisms, unless N is regularly supplied. This is also in accordance with the results of Demeestere et al., who found that N limitation occurred in a methanol-degrading BF at nitrate concentrations <0.09 g NO₃⁻-N/kg compost. The latter authors regarded this concentration as the threshold for the amount of microbial available nitrate, because lower nitrate concentrations were not measured. This threshold corresponds with the start of the stationary phase as mentioned by Cherry and Thompson. Furthermore, it is believed that the IBAL removal in all of the BF sections was limited by a low compost N content, because from day 71, (NO₂⁻ + NO₃⁻)-N and NH₄⁺-N concentrations were mostly <0.05 g N/kg DW. Nitrogen limitation is additionally supported by the increase of the total IBAL removal efficiency after adding a nutrient solution to the compost material during period 3.

**Formation and Degradation of Intermediates**

During the biofiltration of IBAL, the formation of IBOL, as well as IBAC, was observed. Also, other studies have previously mentioned the formation of intermediates during the biofiltration of VOCs. For example, ethanol production was observed during biofiltration of ethyl acetate (at
~2600 ppmv, influent concentrations), butyric acid was measured in the effluent during biofiltration of butyraldehyde, although the concentration at which this occurred was not specified. Also, acidification of a BF treating formaldehyde was experienced, but no data were given with respect to pH values and aldehyde concentrations. Others associated rapid ethanol degradation with the production of acetaldehyde, acetic acid, and ethyl acetate and, consequently, also with pH reduction, inhibiting optimal VOC treatment. The main reason for the formation of byproducts at high loads was found to be oxygen limitation, although other authors mentioned nutrient limitation as a possible reason. In this study, pH was shown to be most important with respect to the formation of IBOL. Low pH values increased IBOL emissions, although adaptation occurred, resulting in less IBOL emissions over time.

In biofiltration experiment 1, IBAC was measured in the effluent a few days after increasing the influent IBAL concentrations to ~300 ppmv (day 47). Although no statistically significant correlation was observed between IBAC effluent and IBAL influent concentrations, a relation between both concentrations was observed. This is illustrated by the temporary increased IBAC effluent concentrations after IBAL peak loadings at days 87 and 100, although with some delay. The low correlation with the influent IBAL concentrations was probably because of accumulation of IBAC in the filter bed, indicated indirectly by the continuous pH decrease until day 86. This accumulation can be explained by the low Henry’s Law coefficient (1.26 × 10⁻⁶ atm·m³/mol at 25 °C) and the low biodegradability of IBAC. The latter was shown in batch degradation experiments and is in accordance with the low removal efficiencies previously observed for butyric acid in a wood bark BF (72–80% at 6 ppmv influent concentration, EC = 37–41 g/m³/day), being much lower than that of butyraldehyde in the same BF (EC = 2160 g/m³/day). In biofiltration experiment 2, the IBAL influent concentrations were proportional with the IBAC effluent concentrations (again with some delay of the IBAC change) and inversely proportional with the pH. Moreover, this relation was reversible, because the pH increased again after the IBAL influent concentration decreased on day 13. It is probably because of the more controlled influent IBAL concentrations in biofiltration experiment 2 (three periods with large concentration differences and small internal concentration variability) that this relation was more pronounced than in biofiltration experiment 1. The pH increase at low IBAL influent concentrations (when no additional IBAC is produced) can be caused by stripping and/or microbial degradation of IBAC, although the latter was expected to be slow. Furthermore, it was shown that IBAC concentrations were not largely affected by the moisture content and pH of the BF material.

IBOL was measured as a second intermediate during IBAL biofiltration, mostly at higher effluent concentrations than IBAC. The majority of the IBOL measurements showed increasing concentrations in the consecutive BF sections. This indicated that the IBOL production rate was higher than its degradation rate. In contrast with IBAC formation, the IBOL production from IBAL is the result of a reduction process. This suggests that IBAL can be used as an electron donor as well as an electron acceptor in the BF, even when the BF is operated under aerobic conditions (21% O₂ in incoming air). No higher production of IBOL was measured, however, at 51% compared with 36% moisture content. To confirm that O₂ limitation was not important for the IBOL formation, IBAL was dosed in air with 21% oxygen in a short third BF experiment (data not shown). After dosing IBAL in pure oxygen for 4 hr, neither the IBAL nor the IBOL effluent concentrations decreased. Also, batch experiments could not prove a decreased IBOL formation when increased electron acceptor concentrations were available. The pH was a more important factor controlling the IBOL production, as was shown in biofiltration experiment 2. A low pH (5.2 compared with 8.4) resulted in higher IBOL emissions the first 12 days of BF experiment 2. Thereafter, adaptation to low pH occurred, but when the inlet IBAL concentration increased again, higher IBOL emissions were measured for the BF at low pH. Also, batch degradation experiments revealed a very slow IBOL degradation rate at pH 5.2 compared with pH 8.4.

CONCLUSIONS

Biodegradation of IBAL in a compost BF was possible at >99% removal efficiencies for volumetric influent loading rates up to 785 g/m³/day (112 ppmv, 36 sec EBRT). At higher influent concentrations (~200–300 ppmv), the removal efficiency decreased initially but stabilized at 86 ± 2% (Bₘ = 1670 ± 160 g/m³/day) for at least 20 days. Inspection of the operational parameters, however, revealed that at these higher loading rates, mineral nutrient limitation and low pH decreased the IBAL removal efficiencies. After nutrient addition, elimination capacities up to 1835 g/m³/day were obtained (η = 95%). At even higher loading rates (3811–4123 g/m³/day), dehydration occurred rapidly in addition to nutrient limitation and a pH decrease. The pH decrease was caused by production and accumulation of IBAC. The formation of intermediates (IBOL and IBAC) was observed at IBAL influent concentrations higher than ~140 ppmv. Low pH was an important factor controlling the emissions of IBOL, although adaptation to low pH values occurred. The persistence of intermediates in the effluent was caused by a slow degradation rate of these compounds in the compost material.

A combination of the results of both the continuous and batch experiments leads to the overall conclusion that
degradation of medium to high IBAL loading rates in a compost BF results in acidification of the filter material, caused by the accumulation of IBAC. Also, nutrient limitation is quickly observed at high elimination capacities. Consequently, IBAL degradation decreases, and IBOL is formed as a by-product, resulting in decreasing VOC elimination capacities in the BF. Therefore, it is recommended to include a pH buffer for the treatment of medium influent loads of IBAL and possibly also for other aldehydes. Besides pH buffering and moisture control, regular addition of mineral nutrients is necessary if higher VOC elimination capacities have to be obtained.

ACKNOWLEDGMENTS

This work was supported by a scholarship from the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen). The authors acknowledge Peter Machilse at IGEAN for providing the compost material. 

REFERENCES


5. Smet, E.; Van Langenhove, H.; De Bo, I. The Emission of Volatile Compounds During the Aerobic and the Combined Anaerobic/Aerobic Composting of Bio- waste; Atmos. Environ. 1993, 52, 1295-1303.


22. Togna, A.P.; Singh, M. Biological Vapor-Phase Treatment Using Biofilter and Biotrickling Filter Reactors—Practical Operating Regimes; Environmental Progress 1994, 13, 94-97.


27. van Groenestijn, J.W.; Hesselink, P.G.M. Biotechniques for Air Pollution Control; Biodegradation 1993, 4, 283-301.


About the Authors

Herman Van Langenhove is a professor of Environmental Chemistry and Technology at the Department of Organic Chemistry, Faculty of Bioscience Engineering, Ghent University. Bram Sercu and Kristof Demeestere are both Ph.D. students in this same department. Hans Baillieul is a former MSc student of Prof. Van Langenhove. Willy Verstraete is a professor of Microbial Ecology and Technology at the Department of Biochemical and Microbial Technology. Address correspondence to: Herman Van Langenhove, Department of Organic Chemistry, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653 B-9000 Gent, Belgium; phone: +32-926-54-59-53; fax: 329-264-62-43; e-mail: herman.vanlangenhove@ugent.be.