Adsorption, Absorption, and Biological Degradation of Ammonia in Different Biofilter Organic Media

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Received 28 July 2006; accepted 5 October 2006
Published online 6 November 2006 in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/bit.21246

ABSTRACT: A tailor-made apparatus called ammoniometer, which is a batch mode respirometer applied to the study of ammonia biodegradation in biofilter media, has been used to evaluate adsorption, absorption, and biodegradation in five different organic materials (compost, coconut fibre, bark, pruning wastes, and peat) obtained from full-scale biofilters in operation in several waste treatment plants. The results showed that absorption could be represented by a Henry’s law linear equation, with values of the Henry coefficient significantly higher (from 1,866 to 15,320) than that of pure water (1,498). Adsorption data were successfully fitted to Langmuir and Freundlich isotherms and maximum adsorption capacity varies from 1.06 to 1.81 mg NH₃/g dry media. Ammonia biodegradation rates for each organic material were also calculated. Biodegradation rates varied from 0.67 to 7.82 mg NH₃/kg media/d depending on the material tested. The data obtained showed important differences in the behaviour of the biofilter organic media, which has important implications in the design and modelling of these systems.


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KEYWORDS: absorption; adsorption; ammonia; biodegradation; biofiltration; organic support

Introduction

Air biofiltration is a suitable technology for pollution abatement, particularly for air streams with low contaminant concentration and high flow rates. In a biofilter, a contaminated/odoriferous gas stream passes through a biologically enriched layer of a filter material such as soil, wood chips, compost or mixed materials, followed by a biodegradation of the absorbed/adsorbed pollutant. The by-products of microbial oxidation are primarily water, carbon dioxide, mineral salts, some volatile organic compounds, and microbial biomass (Nicolai and Janni, 2001).

Municipal solid waste treatment plants usually treat polluted gaseous emissions by biofiltration. Among them, composting plants present numerous odour sources, including the reception and handling of materials, active composting, stock piling, etc. Gaseous emissions in composting facilities are variable (Eitzer, 1995), being ammonia one of the main compounds responsible for generation of offensive odours and atmospheric pollution when managing organic wastes. Although the detection and recognition thresholds for ammonia are relatively high (17 and 37 ppmv, respectively) (Busca and Pistarino, 2003) ammonia gas is found in waste treatment plants in concentrations well over the threshold limit (Beck-Friis et al., 2001; Elwell et al., 2002; Pagans et al., 2006). Ammonia gas can cause adverse effects on vegetation and can be converted to N₂O, a powerful greenhouse gas (Krupa, 2003).

The quality of the biofilter media has been reported as one of the key factors in the biofilter performance. The most common situation in municipal waste treatment plants is the use of organic materials because of their high availability and low cost (Pagans et al., 2005, 2006). Among the operational advantages of using organic materials it is pointed the presence of complex microbial communities capable of degrading several pollutants, a high water retention capacity and available organic matter and nutrients for...
microorganisms (Devinny et al., 1999). In fact, there is abundant literature on the high capacity of biofilters packed with organic materials such as compost for ammonia elimination (Liang et al., 2000; Pagans et al., 2005; Park et al., 2002; Smet et al., 2000). However, when biodegradation rates are calculated for organic filter media, it is necessary to consider adsorption and absorption phenomena. These phenomena are believed to play a key role in the performance of biofilters, especially under transient conditions or shock loading, since absorption and adsorption may act as buffer for biological activity (Barona et al., 2005; Mcnevin and Barford, 2001). To our knowledge, only few studies have been focused on the adsorption of some pollutants in compost or peat (Delhomenie et al., 2002; Mcnevin and Barford, 1998), being the absorption and the combined adsorption-absorption studies very scarce and usually conducted on synthetic or well-defined inorganic materials (Helminen et al., 2000).

Therefore, it is necessary to extend the knowledge in the determination of the biodegradation rate of biofilter materials to know the real biofiltration capacity and to anticipate the behaviour of the biofilter in the case of a flow fluctuation or a change in concentration of pollutants, especially in waste treatment plants (Lang and Lager, 1992; Schlegelmilch et al., 2005). It is also necessary to study the role of adsorption and absorption phenomena in biofilters to improve biofiltration modelling and design.

This work studies the ammonia biodegradation rate (ABR) of five different organic materials (compost, coconut fibre bark, pruning wastes, and peat) obtained from full-scale biofilters. To perform this study, a new specific apparatus, called ammoniometer, and an analytical procedure have been developed. Also, data on adsorption and absorption and combined adsorption–absorption phenomena are provided and discussed.

Materials and Methods

Organic Materials

Experiments were conducted with five different organic materials commonly used in biofiltration units of full-scale municipal waste treatment plants. Table I presents the main properties of each organic support material. The materials were sampled during the period of May–December of 2005 from different full-scale biofilters that mainly treat ammonia and volatile organic compounds. Compost from sludge was obtained from the municipal composting plant of Jorba (Barcelona, Spain), coconut fibre and peat were obtained from a municipal waste treatment plant located in Barcelona (Spain), bark was obtained from the municipal composting plant of Botarell (Tarragona, Spain), and pruning wastes were obtained from the municipal composting plant of Castelldefels (Barcelona, Spain).

Experimental Set-Up

Experimental data were obtained in a tailor-made apparatus called "ammoniometer". It is essentially a batch-mode solid static respirometer (Barrena et al., 2005) in which the measure of oxygen has been substituted by ammonia. The apparatus consisted of a sealed flask (500 mL volume) containing the organic support and equipped with an ammonia sensor model AMT100 from Vaisala (Helsinki, Finland) connected to a data logger and a personal computer to register data of ammonia concentration in the headspace of the flask (in ppmv.). Ammonia gas (99.9% purity, Carburos Metalicos, Barcelona, Spain) was pumped through the organic support in a down-flow mode. A digital mass flowmeter model Bronkhorst Hi-Tec F-201C-RAA-11-E (Ruurlo, The Netherlands) was used to introduce an exact amount of pure ammonia in the flask. The operating range of the mass flowmeter (0.2–10 mL/min) ensured a high precision in ammonia additions. The set-up also included a water bath in order to carry out the experiments at a fixed value of temperature, which was set at 25°C for all the experiments. A scheme of the ammoniometer is presented in Figure 1.

In all the experiments ammonia concentration was recorded every 15 s and the duration of each run was 10 h for adsorption and absorption experiments and 24 h for biodegradation experiments. After the ammonia readings were finished, the total volume of free air space in each sample flask was determined by filling the flask with deionised water with 3 drops/L of Tween® 20 (Sharlau, Barcelona, Spain) to avoid the formation of air bubbles.

### Table I. Main characteristics of the five organic support materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Org. matter (%)</th>
<th>Moisture (%)</th>
<th>NH₄⁺-N (%)</th>
<th>Bulk density (g/cm³)</th>
<th>pH</th>
<th>Elec. conduc. (mS/cm)</th>
<th>Respiration index (mg O₂/g omb/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost</td>
<td>47.8</td>
<td>38.1</td>
<td>0.06</td>
<td>0.65</td>
<td>7.1</td>
<td>5.42</td>
<td>1.13</td>
</tr>
<tr>
<td>Coconut fibre</td>
<td>98.1</td>
<td>77.6</td>
<td>1.42</td>
<td>0.41</td>
<td>6.8</td>
<td>7.58</td>
<td>2.07</td>
</tr>
<tr>
<td>Bark</td>
<td>68.9</td>
<td>59.5</td>
<td>0.10</td>
<td>0.46</td>
<td>6.6</td>
<td>0.74</td>
<td>0.66</td>
</tr>
<tr>
<td>Pruning</td>
<td>55.9</td>
<td>54.3</td>
<td>0.01</td>
<td>0.58</td>
<td>7.5</td>
<td>1.52</td>
<td>0.62</td>
</tr>
<tr>
<td>Peat</td>
<td>47.0</td>
<td>69.6</td>
<td>0.01</td>
<td>0.45</td>
<td>7.0</td>
<td>0.50</td>
<td>1.44</td>
</tr>
</tbody>
</table>

adb, dry basis.

om, organic matter basis.
Adsorption, Absorption, and Biodegradation Experiments

Sampling Procedure
At least five different points of the full-scale biofilters studied were sampled at different depth. The resulting sample (5 kg) was manually mixed to obtain a homogeneous unique sample for each biofilter.

Adsorption and Absorption Experiments
Previously to these experiments, samples had to be prepared. The organic materials used for adsorption experiments were previously oven-dried at 105°C to constant weight to ensure that the material was completely dry and that absorption and biodegradation were not present. For absorption experiments, moisture content was adjusted to the field capacity of the material by adding pure water to saturation of the sample. In the combined adsorption–absorption experiments the moisture content was adjusted to the required value. In these experiments, the organic materials samples were previously sterilised using sodium azide (Sharlau) in a 10% (w/w) ratio to remove the interferences of biological activity in the adsorption–absorption measurements. The efficiency of sodium azide to sterilise the organic samples was checked by measuring the respiration index of the sample. In all cases, no respiration activity was detected for sterilised samples.

Once the sample was prepared, the ammoniometer flask was filled with approximately 10–20 g of each organic material. Afterward, a known amount of ammonia gas was introduced to the system and the drop of ammonia concentration in the headspace was monitored until the equilibrium was reached (ammonia concentration constant). Several ammonia inputs were introduced for each experiment in order to obtain different equilibrium data of ammonia concentration in the organic media (solid phase) and the flask headspace (gas phase).

Biodegradation Experiments
The biodegradation experiments were carried out immediately after the sampling of the full-scale biofilter to minimise possible material disturbance.

The ammoniometer flask was filled with approximately 10–20 g of each organic material. A known amount of ammonia gas was introduced to the system and the drop of ammonia concentration in the headspace was monitored until the equilibrium was reached. After reaching the adsorption and absorption equilibrium conditions, there was a linear decline in ammonia concentration as a result of the biodegradation of ammonia. In order to verify that the observed decrease of ammonia concentration is only due to biodegradation, parallel control biodegradation...
experiments with sterilised material (using sodium azide 10% w/w) were carried out for each organic material. Using sterilised samples, ammonia concentration remained constant once the adsorption and absorption equilibrium was reached.

**Numerical Procedures**

**Adsorption and Absorption Experiments**

The equilibrium parameters were determined by plotting the equilibrium data of ammonia concentration in the solid and gas phase. The adsorption experimental data were fitted to Langmuir and Freundlich isotherms (Eqs. 1 and 2 respectively), whereas the absorption data were linearly fitted to a Henry’s law equation (Eq. 3). All the fitted curves and parameters of the equations were obtained using the software SigmaPlot version 8.0 for Windows (SPSS Inc., Chicago, IL, 2002).

\[
\text{Langmuir isotherm: } C_s = \frac{C_{sm}K_FR_i}{1 + K_FR_i} \quad (1)
\]

where, \(C_s\) is the concentration of ammonia adsorbed on the solid (mg NH₃/g dry media), \(C_{sm}\) is the maximum adsorption capacity (mg NH₃/g dry media), \(C_i\) is the concentration of ammonia in gas phase (mg NH₃/m³) and \(K_F\) is the equilibrium adsorption constant for Langmuir model (m³/mg NH₃).

\[
\text{Freundlich isotherm: } C_s = K_FC_i^n \quad (2)
\]

where, \(K_F\) is the Freundlich empirical constant ([(mg NH₃)\(^{1-n}\) (m³)\(^n\)]/g dry media) and \(n\) is the Freundlich isotherm exponent (dimensionless).

\[
\text{Henry's law equation: } K_{HI} = \frac{C_w}{C_i} \quad (3)
\]

where, \(K_{HI}\) is the Henry’s law constant (dimensionless) and \(C_w\) is the ammonia concentration in water (mg NH₃/m³ water).

**Biodegradation Experiments**

The ABR was calculated from the slope in a linear segment on the chart of ammonia concentration in gas phase (ppmv) versus time, by using Equation (4), after the adsorption/absorption equilibrium was reached.

\[
\text{Ammonia biodegradation rate: } ABR = \frac{VP17m24}{RTX10^6} \quad (4)
\]

where, ABR is the ammonia biodegradation rate (mg NH₃/kg organic material/d), \(V\) is the volume of air in flask (mL), \(P\) is the atmospheric pressure at elevation measurements (atm), 17 corresponds to the molecular weight of ammonia, \(m\) is the slope of change in ammonia concentration (ppmv/h), 24 is the conversion factor from minutes to days, \(R\) is the ideal gas constant (0.08206 L atm/mol/K), \(T\) is the temperature (K), \(X\) is the wet weight of organic material (g) and 10\(^6\) is the conversion factor from ppmv to absolute value.

For all the experiments (adsorption, absorption, and biodegradation), several replications were carried out for each experimental condition tested. Experimental error for the calculated parameters was never higher than 10%.

**Analytical Methods**

Physico-chemical properties of the organic support materials were analysed for the determination of moisture content, organic matter content, bulk density, pH, electrical conductivity and NH\(_4\)\(^+\)–N content according to the standards procedures (US Department of Agriculture and US Composting Council, 2001). Respiration index, which measures the rate of oxygen consumption of the biomass and it is used as a measure of the biological activity of a sample, was determined using a static respirometer previously described (Barrena et al., 2005; Gea et al., 2004). Briefly, respiration index is a measure of oxygen uptake rate expressed as g of oxygen consumed per kg of organic matter and hour.

**Results and Discussion**

**Organic Materials Tested**

The main characteristics of the five organic materials studied are presented in Table I. Compost presented the highest bulk density and the lowest organic matter content, which is typical for stabilised compost (Barrena et al., 2006). The values of bulk density (0.4–0.7 g/cm³) are similar to other organic and inorganic materials characterised in the literature as a potential biofilter media (Kim et al., 2000; Ramirez et al., 2003). Moisture data are referred to the moisture content at the moment of material sampling. The pH near-neutral values were similar among the organic materials tested and in the typical range for packing materials with a wide variety of bacterial activity (Devlin et al., 1999). However, the electrical conductivity presented significant differences, which may be an indication of a different biofilm composition in the organic supports, since the determination of electrical conductivity in solid samples is based on an aqueous extract.

The biological activity of the organic materials was analysed by the respiration index, a common technique to determine the aerobic activity of biologically active materials (Gea et al., 2004). The results showed some differences among the materials tested, nevertheless, the five materials can be considered biologically active and suitable for biofiltration (Barrena et al., 2006).
Adsorption of Ammonia on Organic Materials

Ammonia adsorption experiments were conducted for the five organic materials selected previously dried (compost, coconut fibre, bark, pruning wastes, and peat) at 25°C. Experimental data were fitted to Langmuir and Freundlich isotherm models, since they are the most common patterns used for predicting adsorption performance in biofiltration (Delhommé et al., 2002; Helminen et al., 2000). A summary of the results of the adsorption isotherms is shown in Table II. In the case of compost, pruning wastes and peat, the experimental data could be fitted to a Langmuir isotherm, whereas in the case of coconut fibre the Freundlich isotherm model provided a better correlation coefficient. Bark adsorption pattern admitted both Langmuir and Freundlich fitting, although the correlation coefficient was low in both cases. The results obtained in this work are in accordance with recent results on the adsorption of hydrogen sulphide and toluene on organic materials, which have also shown that both Langmuir and Freundlich isotherms can represent adsorption experimental data (Barona et al., 2005; Mcnevin and Barford, 1998). This fact has been also observed in the ammonia adsorption on inorganic materials (Busca and Pistorino, 2003).

As it can be seen in Table II, it is remarkable that there are significant differences in the maximum adsorption capacity ($C_{\text{fm}}$) for the five materials, especially in the case of bark, which showed an adsorption capacity one order of magnitude higher than those found for the other materials. However, it must be pointed that the plateau of the adsorption isotherm curve (adsorption saturation) could not be reached in some experiments due to the limitation of the ammonia sensor. Nevertheless, the data used in this work for adsorption modelling was determined for a range of 0–800 mg NH₃/m³, which is the typical operational range of ammonia concentration for biofilters of waste treatment plants (Schlegelmilch et al., 2005).

Absorption of Ammonia in Organic Materials

Ammonia absorption experiments using the five materials studied were conducted under conditions that ensured that absorption was the predominant active mechanism to remove ammonia from the gas phase. The materials were sterilised using sodium azide to prevent biological degradation of ammonia and moistened to the field capacity of the material (maximum capacity of water retention) to avoid direct ammonia adsorption on the organic solid material surface. In this case, all the experimental data could be properly fitted to a linear Henry’s law equation, in which the fundamental parameter is the Henry coefficient expressed as a dimensionless air/water partition coefficient ($K_{\text{H}}$) (Kuhne et al., 2005).

The results obtained for the determination of the Henry coefficient (at 25°C) for the five materials are presented in Table III, jointly with experimental data (obtained with the ammoniometer) and bibliographical data of the Henry coefficient for ammonia absorbed on pure water. In Table III, the Henry coefficient is expressed as a water/air partition coefficient to show the ammonia absorption capacity for a given material. It can be observed again that there are significant differences in the Henry coefficients for the five materials tested. Bark presented the high absorption capacity, but the other three materials (compost, coconut fibre and pruning wastes) also showed higher capacities than that of ammonia on pure water (either determined experimentally or obtained from literature). Only in the case of peat the Henry coefficient is similar to that of water. These results are in contradiction with theoretical considerations, because thermodynamically, as both phases (air and water) and the pollutant gas (ammonia) are the same, the Henry coefficient should only depend on temperature (Omur-Ozbek and Dietrich, 2005). This finding is an important fact related to organic materials, which according to these results can act as more efficient absorbers than pure water (for instance, in chemical scrubbers). Although the reason for this is not clear, it can be hypothesised that since water in an organic matrix is present in the form of a biofilm, the absorption capacity and thus the Henry coefficient can be altered according to the chemical composition of the biofilm, which can contain soluble organic and inorganic materials. This is in accordance with the important differences found in the electrical conductivity of the materials (Table I), which can be attributed to a different biofilm composition. However, an attempt to correlate the Henry coefficient with pH and electrical conductivity of the organic materials (two properties that depend on biofilm composition) did not show a well-defined tendency. Anyway, it can be concluded that absorption capacity is likely to depend on the specific chemical composition of the biofilm in organic materials intended for biofiltration. Recently, other authors have found similar results of

Table II. Summary of the results obtained for adsorption experiments.
significant difference in the solubility and Henry's law constants of some pollutants at different biofilm composition (Davison et al., 2000; Omur-Ozbek and Dietrich, 2005).

As can be inferred from Tables II and III a linear correlation ($r^2 = 0.98$) between maximum adsorption capacity ($C_{sm}$) and Henry coefficient can be obtained (data not shown), indicating that the higher the $C_{sm}$ the higher the Henry coefficient. Although more research would be necessary, this fact might indicate that absorption and adsorption of ammonia might be interrelated phenomena in biofiltration based on organic supports.

### Combined Effect of Ammonia Adsorption and Absorption

Operation of biofilters is usually conducted at a moisture level of the packing material around 50–70% (Devinyin et al., 1999). Lower levels of moisture result in a decrease of the biological activity, whereas higher moisture contents can provoke a decrease in the porosity of the material leading to several adverse consequences for the biofilter performance (increase of the pressure drop, low oxygen transfer, presence of anaerobic zones, etc.) (Devinyin et al., 1999). For this reason, biofilters usually operate in conditions in which the prevalence of adsorption or absorption mechanisms is not clear. To clarify this aspect, the five materials studied were moistened to different moisture levels and incubated with ammonia gas at different concentrations. An example of the results obtained for coconut fibre is shown in Figure 2a–d jointly with the theoretical absorption and adsorption curves. Four levels of moisture were tested: (a) 0%: corresponding to adsorption conditions; (b) 37.5%: corresponding to a biofilter with a low level of moisture; (c) 65.8%: a normal moisture level for the biofilter, and (d) 88.1%: field capacity of the material, corresponding to absorption conditions. As can be seen from the equilibrium curves shown in Figure 2a–d, there is a rapid transition from adsorption governing conditions (Fig. 2a) to an absorption pattern that can be observed even for low moisture levels (Fig. 2b). For the normal moisture level of biofilter operation (Fig. 2c) the equilibrium curve appears as a linear Henry-type model, and the Henry coefficient obtained ($K_H = 3363$, correlation coefficient 0.99) is very similar to that of field capacity ($K_H = 2903$, Table III). These results are similar to those obtained with the other four tested materials (data not shown).

These observations confirm that under the normal operational conditions of a biofilter, absorption may be considered as the predominant mechanism for ammonia transfer from the gas phase to the biofilm. In this case, this fact can be explained by the high solubility of ammonia in water, which is enhanced in the biofilm of the materials tested (high values of the Henry coefficient compared to pure water). This fact has important implications in biofilter modelling and design since absorption is not commonly considered in biofiltration studies.

### Biological Degradation

**Ammonia Biodegradation Rate for Different Organic Materials**

ABR was determined for the five organic materials selected from different full-scale biofilters. Inoculation was not considered since the full-scale biofilters had been treating ammonia from municipal waste treatment exhaust gases during a period from 1 to 4 years.

In relation to the control biodegradation experiments, Figure 3 illustrates the ammonia concentration evolution in the gas phase for a sterilised and a non-sterilised sample of compost. As expected, after a pulse of ammonia gas was pumped into the system, ammonia concentration decreased until the equilibrium concentration was reached (in this case at 150 mg NH$_3$/m$^3$). As can be seen in Figure 3, the equilibrium concentration was stable during 10 h for the

<table>
<thead>
<tr>
<th>Material</th>
<th>Ammonia biodegradation rate (mg NH$_3$/Kg/d)</th>
<th>Ammonia concentration (mg NH$_3$/m$^3$)</th>
<th>Ammonia concentration (mg NH$_3$/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost</td>
<td>1.92</td>
<td>1279</td>
<td>41.1</td>
</tr>
<tr>
<td>Coconut fibre</td>
<td>5.76</td>
<td>1744</td>
<td>150</td>
</tr>
<tr>
<td>Bark</td>
<td>0.67</td>
<td>307.9</td>
<td>61.7</td>
</tr>
<tr>
<td>Pruning</td>
<td>7.82</td>
<td>4191</td>
<td>92.1</td>
</tr>
<tr>
<td>Peat</td>
<td>6.38</td>
<td>2877</td>
<td>109</td>
</tr>
</tbody>
</table>

*a* Considering the Henry coefficient obtained at field capacity.

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**Table III.** Summary of the results obtained for absorption experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Field capacity (%)</th>
<th>Henry coefficient (at field capacity)</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost</td>
<td>61.0</td>
<td>2,885</td>
<td>0.99</td>
</tr>
<tr>
<td>Coconut fibre</td>
<td>88.1</td>
<td>2,903</td>
<td>0.96</td>
</tr>
<tr>
<td>Bark</td>
<td>67.8</td>
<td>15,320</td>
<td>0.94</td>
</tr>
<tr>
<td>Pruning</td>
<td>69.0</td>
<td>3,923</td>
<td>0.82</td>
</tr>
<tr>
<td>Peat</td>
<td>79.6</td>
<td>1,866</td>
<td>0.82</td>
</tr>
<tr>
<td>Pure water (this work)</td>
<td>100.0</td>
<td>1,795</td>
<td>0.99</td>
</tr>
<tr>
<td>Pure water (Sander, 2006)</td>
<td>100.0</td>
<td>1,498</td>
<td>—</td>
</tr>
</tbody>
</table>

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**Table IV.** Ammonia biodegradation rate of the five organic support materials determined at different substrate concentration.

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DOI 10.1002/bit
sterilised sample. On the contrary, in the case of the active sample, after reaching the same initial adsorption/absorption equilibrium, there was a significant decrease in the ammonia concentration, attributable to the biological degradation of ammonia. This behaviour is in accordance with some studies that show that adsorption of ammonia on organic media is instantaneous in relation to biological growth (McNevin and Barford, 1998). Since similar results were obtained for all the organic materials tested, it can be concluded that the experimental apparatus designed is suitable to distinguish between biologically and physico-chemically (adsorption and absorption) removed ammonia.

A summary of the results for the ammonia biodegradation experiments is shown in Table IV. It should be mentioned that in Table IV the ABR were determined at different equilibrium ammonia concentration. The concentrations varied from 40 to 150 mg NH₃/m³ and they had been selected in relation to the normal operational conditions for each biofilter in order to obtain a representative rate of ammonia biodegradation in the full-scale biofilter.

As it is shown in Table IV, on a weight basis, pruning presented the highest ABR (7.82 mg NH₃/kg media/d) followed by peat and coconut fibre (6.38 and 5.76 mg NH₃/kg media/d, respectively) and compost and bark presented the lowest ABR (1.92 and 0.67 mg NH₃/kg media/d, respectively). In spite of the differences found in bulk density of each organic media (Table I), the ABR values expressed in terms of volume of media presented the same trend (Table IV). According to Smet et al. (2000), compost biofilters present higher metabolic activities in comparison with other materials (such as peat, bark, etc.) due to their

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**Figure 2.** Influence of moisture content in the combined adsorption-absorption phenomena jointly with the theoretical adsorption (solid line) and absorption (dotted line) curves in the case of coconut fibre: (a) moisture: 0% (adsorption); (b) moisture: 37.5%; (c) moisture: 65.8%; (d) moisture: 88.1% (field capacity).
superior nutritional level. However, it must be pointed that strong differences in a compost biofilter performance are to be expected depending on the type of compost (composting process, waste source, etc.) and on the maintenance and operation of the biofilter.

The ammonia content in the liquid phase for each ABR can be estimated considering the Henry coefficient obtained at field capacity (Table III) and the ammonia gas concentration. It is remarkable to note that there are important differences in ammonia content in the liquid phase among the organic materials, especially in the case of bark (Table IV), which presented the highest ammonia content (946 mg NH₃/L). Therefore, this concentration might provoke some inhibitory effects on microbial activity and could be responsible for the low ABR observed, as it is discussed in the following section.

**ABR for Different Substrate Concentration**

Since free ammonia (FA) is considered the main responsible of inhibition of nitrifying microorganisms (Baquerizo et al., 2005; Villaverde et al., 1997), the determination of ABR for different FA concentrations is essential to know the operational limits of the biological activity in biofiltration. The amount of FA has been determined considering that the total ammonia content in the liquid phase could be estimated by the experimental Henry coefficient obtained at field capacity (Table III). Then, FA content was calculated from the total ammonia content taking into account the ammonia–ammonium equilibrium for a given pH at 25°C.

The experiments were carried out using two support materials: pruning waste and peat, with a previous similar ABR (7.82 and 6.38 mg NH₃/kg media/d, respectively) (Table IV). The ABR was determined at different ammonia concentration once equilibrium was reached: from 50 to 300 mg NH₃/m³ for pruning wastes and from 90 to 600 mg NH₃/m³ for peat. The data were obtained from 15 ammonia biodegradation tests for each organic material. Figure 4 shows the evolution of ABR and pH for different FA concentrations present in the liquid phase for pruning wastes (Fig. 4a) and peat (Fig. 4b).

In the case of pruning wastes (Fig. 4a), in the range of FA between 0 and 250 mg NH₃/L, the ABR increased with substrate concentration and a maximum ABR is measured (14.26 mg NH₃/kg media/d) for an ammonia concentration

![Figure 4](https://example.com/figure4.png)
in the gas phase of 240 mg NH$_3$/m$^3$. For values of FA higher than this concentration, ABR dropped to 5.80 mg NH$_3$/kg media/d. The decrease in ABR may be explained by a toxicity effect of ammonia on microbial activity. These results have been previously observed in modelling works. For instance, Baquerizo et al. (2005) developed a model of a coconut fibre biofilter for ammonia removal which reported that FA in the support material can strongly inhibit the biological activity of a biofilter. According to the authors, FA began to accumulate after a long period in which the concentration of ammonia was 100 mg NH$_3$/m$^3$.

In reference to peat, the ABR measured showed the same behaviour. From Figure 4b it can be seen that ABR increased approximately linearly with FA when the concentration was below 500 mg NH$_3$/L. The maximum ABR value measured was 37.95 mg NH$_3$/kg media/d for an ammonia concentration in the gas phase of 420 mg NH$_3$/m$^3$. Beyond this concentration, peat presented lower ABR (17.77 mg NH$_3$/kg media/d), which again indicated an inhibition of the biological activity.

It must be pointed that peat showed not only higher values of ABR but also presented inhibition at higher ammonia concentration. Therefore, peat showed a superior performance when compared to pruning wastes in relation to ammonia biodegradation and its capability to work under high ammonia concentration conditions (420 mg NH$_3$/m$^3$). At the same time, since pruning wastes showed an adsorption and absorption capacity higher than peat (Tables II and III), it can be hypothesised that during the long-term operation of the biofilter, the organic materials with high adsorption/absorption capacity could be inhibited at low ammonia concentration in the gas phase.

On the other hand, the exact cause of inhibition is not clear. Although it is highly probable that microbial activity was inhibited by high FA concentrations, another phenomena, such as pH changes or the generation of toxic by-products, could be responsible for the drop observed in ABR. For instance, pH control is important in maintaining high ammonia removal capacity because optimal pH range for the growth of autotrophic nitrifying bacteria is 5.8–8.5 (Yani et al., 1998). In the case of pruning wastes, for instance, ABR values in the case of inhibition were determined at pH values over 8.5 (Fig. 4a).

To our knowledge, only few studies have been focused on kinetic data for ammonia removal by biofiltration. Several studies found in literature report that research on ammonia biofiltration is limited because nitrifying bacteria responsible for the oxidation of ammonia exhibit slow growth rates. However, some values found in literature show extremely high removal rates of ammonia. Kim et al. (2000) reported maximum removal rates of ammonia ranging from 5,000 to 16,700 mg N/kg dry media/d for two organic and two inorganic packing materials in the concentration range of 0–235 ppmv. Yani et al. (1998) determined a maximum removal rate of 11,400 mg N/kg dry media/d at ammonia concentrations up to 260 ppmv, in a peat biofilter seeded with nitrifying bacteria; and the rate of biological degradation of ammonium on peat in a perfusion column was found to vary between 240 and 1920 mg NH$_3$–N/kg dry peat/d (McNevin et al., 1999). However, several works have demonstrated that ammonia in the biofilters is mainly removed by physical and chemical adsorption on the packing material and by absorption to the water fraction of the biofilter media, and the biological removal rate for ammonia in biofilters is in fact low (Kim et al., 2000; Sheridan et al., 2002; Yani et al., 1998; Ying-Xu et al., 2004). Simultaneously, it should be noted that biological ammonia removal may be attributed to adsorption in moisture present in the biofilter and adsorption onto the surface of the organic filter material if the system has not achieved a long-term steady state (McNevin and Barford, 2000). The adaptation phase of microbial communities in biofilters found in literature vary from few hours to months, depending on the contaminants and the packing material investigated (Hirai et al., 2001; Liang et al., 2000; Streese et al., 2005). However, most of these studies do not describe the method utilised to check if the system is under limitation of biological activity and, in consequence, the calculated ammonia removal may not be due to the biological activity only. The results showed in this study present an experimental procedure to ensure that the biological activity measured corresponds to the situation of a biofilter material at steady operation, since physico-chemical phenomena have been studied separately.

### Implications on Research of Ammonia Biofiltration Using Organic Materials

The complexity of most organic support materials, with irregular shapes and different origins, and their frequent overwhelming development of biomass hamper the research on reliable measures for the evaluation of the performance of a particular biofilter when biodegradation takes place. Therefore, it is necessary to conduct experiments at conditions similar to the intended industrial applications in relation to concentration range, packing material, gas composition, and other parameters. These studies are time consuming and imply complex equipment and high cost. On the contrary, the experimental apparatus presented in this work is an inexpensive method to characterise rapidly organic support materials in relation to ammonia biofiltration, concerning ammonia biodegradation and both adsorption and absorption phenomena.

Few works in literature can be found on the study of adsorption, absorption, and biodegradation patterns for polluted gases on organic complex materials. Usually, biofiltration is explained as an initial step of adsorption followed by biodegradation (Chung et al., 2005; McNevin et al., 1999). The results obtained in this work show that adsorption must be considered as an important mechanism of pollutant removal in biofiltration, especially when highly soluble pollutants are treated. Although this is relevant for biofilters in the typical range of operational moisture, it is
even more important in biotrickling filters, which operate with a continuous supply of an aqueous stream to provide nutrients for biological activity, and they are expected to operate near the field capacity of the material (Gabriel and Deshusses, 2003).

Finally, it is important to mention that the high adsorption and absorption capacities found in organic materials give the biofilter a significant buffering capacity to protect against surges in loading. However, according to the results obtained, it should be taken into account that the rate of ammonia biodegradation could be low during the biofilter long-term operation.

The results presented in this work may be useful for the design and modelling of the biofiltration process and for the characterisation of organic support materials in real, transient or shock loading conditions. Moreover, the apparatus developed can be useful to compare the performance characteristics of various biofilters with different packing material, seeding source, detection of dead zones, etc., and permit to predict microbial activity and possible inhibition conditions.

Conclusions

From the work presented, the following conclusions can be obtained:

(1) An experimental procedure has been developed to determine adsorption and absorption capacities and biodegradation rates of organic materials used for biofiltration. This protocol has been used to characterise five common materials used in biofilters of full-scale waste treatment plants.

(2) In relation to adsorption it can be concluded that:

- Ammonia adsorption of the five organic materials tested can be modelled by a Langmuir or a Freundlich isotherm.
- The isotherms obtained can be used for the prediction of adsorption capacities of the materials working at the typical range of ammonia concentration found in waste treatment plants.

(3) In relation to absorption it can be concluded that:

- Ammonia absorption can be represented by a Henry’s law linear equation. However, values of the Henry coefficient are significantly higher than that of pure water. This indicates that the biofilm properties are important to predict the maximum absorption capacity of an organic material intended for biofiltration.
- Absorption must be considered an important mechanism of pollutant removal in biofiltration. This is important for biofilters in the typical range of operational moisture (50–70%), and crucial for biotrickling filters. Absorption parameters for a given organic material (Henry coefficient) should be previously known for the modelling and design of the biofilter operation.

(4) In relation to ammonia biodegradation it can be concluded that:

- The ammoniometer is suitable to distinguish between biological and physico-chemical removal phenomena.
- Ammonia biodegradation rates are considerably lower than adsorption and absorption rates.
- Depending on the material tested, different ammonia concentrations have been found to inhibit ammonia biodegradation, pointing that ammonia inhibition should depend on the organic material used in the biofiltration process.

Financial support was provided by the Spanish Ministerio de Ciencia y Tecnología with FEDER support (Project REN2003-00823).

References


