Pre-print of: Pagans, E.; Font, X and Sánchez, A. “Adsorption, absorption and biological degradation of ammonia in different biofilter organic media” in Biotechnology and bioengineering (Ed. Wiley), vol. 97, issue 3 (June 2007), p. 515-525. The final version is available at DOI 10.1002/bit.21246

Adsorption, absorption and biological degradation of ammonia in different biofilter organic media

Estela Pagans, Xavier Font and Antoni Sánchez*

Composting Research Group

Department of Chemical Engineering

Universitat Autònoma de Barcelona

Bellaterra (Cerdanyola, 08193-Barcelona, Spain)

* Corresponding author:

Dr. Antoni Sánchez

Fax: 34-93581019

Email: antoni.sanchez@uab.cat

Abstract

A tailor-made apparatus called ammoniometer have been applied to the study of ammonia adsorption, absorption and biodegradation in five different organic materials (compost, coconut fiber, 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 1866 to 15320) than that of pure water (1498). Adsorption data was successfully fitted to Langmuir and Freundlich isotherms and maximum adsorption capacity varies from 1.06 to 1.81 mg NH_3/g dry media. Ammonia biodegradation rates for each organic material were also calculated. Biodegradation rates varied from 0.67 to 7.82 mg NH_3/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.

Key words:

Absorption, Adsorption, Ammonia, Biodegradation, Biofiltration, Organic Support.

Introduction

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. Municipal solid waste treatment plants usually treat polluted gaseous emissions by biofiltration, a suitable technology for pollution abatement, particularly for air streams with low contaminant concentration and high flow rates. In a biofilter, a contaminated/odorous 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 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; Pagans et al., 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).

The determination of the biodegradation rate of biofilter materials permits 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). However, when biodegradation rates are calculated it is necessary to consider adsorption and absorption phenomena. These phenomena are believe 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). Additionally, operation of biofilters is usually conducted at a moisture level of the packing material around 50-70% (Devinny and Deshusses, 1999), conditions in which the prevalence of adsorption or absorption mechanisms is not clear. To our knowledge, only few studies have been focused on the adsorption of some pollutants in compost or peat (Delhoménie 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).

The objective of this work is to determine the ammonia biodegradation rate and the adsorption and absorption capacity of five different organic materials (compost, coconut fiber, bark, pruning wastes and peat) used in biofilters of full-scale waste treatment plants. To fulfil this objective, a new specific apparatus called "ammoniometer" was designed and an experimental procedure was developed. The ammoniometer is essentially a batch-mode solid static respirometer (Barrena et al., 2005) in which the measure of oxygen has been substituted by ammonia. The analytical procedure is based on the monitoring of ammonia gas concentration present in the headspace of a flask containing an organic material intended for biofiltration.

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. Compost from sludge was obtained from the municipal composting plant of Jorba (Barcelona, Spain), coconut fiber 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). The materials were sampled during the period of May-December of 2005. 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.

Experimental set-up

Experimental data were obtained in a tailor-made apparatus called “ammoniometer”. 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 ppm_v). Ammonia gas (99.9% purity, Carburos Metálicos, 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 setup also included a water bath in order to carry out the experiments at a fixed value of temperature, which was set at 25ºC 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.

Adsorption, absorption and biodegradation experiments

Sample preparation

The organic materials used for adsorption experiments were previously oven-dried at 105ºC 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 to avoid direct ammonia adsorption on the organic solid material surface. In the combined adsorption-absorption experiments the moisture content was adjusted to the required value. In these experiments, the organic materials samples were previously sterilized using sodium azide (Sharlau, Barcelona, Spain) in a 10% (w/w) ratio to remove the interferences of biological activity in the adsorption-absorption measurements. The efficiency of sodium azide to sterilize the organic samples was checked by measuring the respiration index of the sample. In all cases, no respiration activity was detected for sterilized samples.

Analytical procedure of adsorption and absorption experiments

The ammoniometer flask was filled with approximately 10-20 g of each conditioned organic material. Afterwards, 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).

Analytical procedure of biodegradation experiments

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.

The Ammonia Biodegradation Rate (ABR) was determined at different equilibrium ammonia concentration 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. Additionally, the ABR was also determined for pruning waste and peat for different free ammonia (FA) concentration to determine the operational limits of the biological activity in biofiltration, since FA is considered the main responsible of inhibition of nitrifying microorganisms (Baquerizo et al., 2005; Villaverde et al., 1997).

In order to verify that the observed decrease of ammonia concentration is only due to biodegradation, parallel control biodegradation experiments with sterilized material (using sodium azide 10% w/w) were carried out for each organic material. Using sterilized 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 (Equations 1 and 2 respectively), since they are the most common patterns used for predicting adsorption performance in biofiltration (Delhoménie et al., 2002; Helminen et al., 2000). The absorption data were linearly fitted to a Henry's law equation (Equation 3), in which the fundamental parameter is the Henry coefficient expressed as a dimensionless air/water partition coefficient (K_H) (Kuhne et al., 2005). All the fitted curves and parameters of the equations were obtained using the software SigmaPlot version 8.0 for Windows (SPSS Inc. 2002).

Langmuir isotherm: $$C_S = \frac{C_{sm} K_L C_i}{1 + K_L C_i} \qquad (1)$$

where: C_s is the concentration of ammonia adsorbed on the solid (mg NH_3/g dry media), C_{sm} is the maximum adsorption capacity (mg NH_3/g dry media), C_i is the concentration of ammonia in gas phase (mg NH_3/m^3) and K_L is the equilibrium adsorption constant for Langmuir model (m^3/mg NH_3).

Freundlich isotherm: $$C_S = K_F C_i^{\,n} \qquad (2)$$

where: K_F is the Freundlich empirical constant ([(mg $NH_3)^{1-n}$ $(m^3)^n$]/g dry media) and n is the Freundlich isotherm exponent (dimensionless).

Henry's law equation: $$K_H = \frac{C_w}{C_i} \qquad (3)$$

where: K_H is the Henry's law constant (dimensionless) and C_w is the ammonia concentration in water (mg NH_3/m^3 water).

Biodegradation experiments

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

$$\textit{Ammonia biodegradation rate: } ABR = \frac{V\ P\,17\,m\,24}{R\,T\ X\ 10^6} \qquad (4)$$

where: ABR is the ammonia biodegradation rate (mg NH_3/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 (ppm_v/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 ppm_v 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 analyzed 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 1. Compost presented the highest bulk density and the lowest organic matter content, which is typical for stabilized compost (Barrena et al., 2006). The values of bulk density (0.4-0.7 g/cm^3) are similar to other organic and inorganic materials characterized in the literature as a potential biofilter media (Kim et al., 2000; Ramírez et al., 2003). Moisture data is 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 (Devinny and Deshusses, 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 analyzed 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

A summary of the results of the adsorption isotherms is shown in Table 2. 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 fiber 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 Pistarino, 2003).

It can be seen in Table 2 that bark showed a maximum 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 NH_3/m^3, 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

The results obtained for the determination of the Henry coefficient (expressed as a water/air partition coefficient at 25ºC) for the five materials are presented in Table 3, jointly with experimental data (obtained with the ammoniometer) and bibliographical data of the Henry coefficient for ammonia absorbed on pure water. 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 fiber 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 hypothesized 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. However, an attempt to correlate the Henry coefficient with two characteristic properties of the biofilm such as pH and electrical conductivity 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 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 3 and 4 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 C_{sm} is the higher the Henry coefficient is. Although more research would be necessary, this fact might indicate that there is a synergistic effect between absorption and adsorption of ammonia in organic materials with a high capacity to absorb/adsorb ammonia.

Combined effect of ammonia adsorption and absorption

An example of the results obtained for the combined adsorption-absorption experiments in the case of coconut fiber is shown in Figures 2a-2d 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 Figures 2a-2d, there is a rapid transition from adsorption governing conditions (Figure 2a) to an absorption pattern that can be observed even for low moisture levels (Figure 2b). For the normal moisture level of biofilter operation (Figure 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 3). 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 (ABR) for different organic materials

In relation to the control biodegradation experiments, Figure 3 illustrates the ammonia concentration evolution in the gas phase for a sterilized and a non-sterilized 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 hours for the sterilized 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 ABR determined at the normal operation conditions for each full-scale biofilter (ammonia concentration from 40 to 150 mg NH_3/m^3) is shown in Table 4. It can be seen that, on a weight basis, pruning presented the highest ABR (7.82 mg NH_3/kg media/d) followed by peat and coconut fiber (6.38 and 5.76 mg NH_3/kg media/d, respectively) and compost and bark presented the lowest ABR (1.92 and 0.67 mg NH_3/kg media/d, respectively). In spite of the differences found in bulk density of each organic media (Table 1), the ABR values expressed in terms of volume of media presented the same trend (Table 4). 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 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 3) 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 4), which presented the highest ammonia content (946 mg NH_3/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.

Ammonia biodegradation rate for different substrate concentration

The ABR was determined at different ammonia concentration once equilibrium was reached: from 50 to 300 mg NH_3/m^3 for pruning wastes and from 90 to 600 mg NH_3/m^3 for peat. Figure 4 shows the evolution of ABR and pH for different free ammonia (FA) concentrations present in the liquid phase for pruning wastes (Figure 4a) and peat (Figure 4b). 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 3). Then, FA content was calculated from the total ammonia content taking into account the ammonia-ammonium equilibrium for a given pH at 25ºC.

In the case of pruning wastes (Figure 4a), in the range of FA between 0 to 250 mg NH_3/L, the ABR increased with substrate concentration and a maximum ABR is measured (14.26 mg NH_3/kg media/d) for an ammonia concentration 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 fiber 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 2 and 3), it can be hypothesized 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 (Figure 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 5000 to 16700 mg N/kg dry media/d for two organic and two inorganic packing materials inoculated with night-soil sludge in the concentration range of 0-235 ppm_v; Yani et al. (1998) determined a maximum removal rate of 11400 mg N/kg dry media/d at ammonia concentrations up to 260 ppm_v 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_4^+-N/kg dry peat/d (McNevin and Barford, 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; Yani et al., 1998; Ying-xu et al., 2004). Simultaneously, it should be noted that biological ammonia removal may be attributed to absorption 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 (Liang et al., 2000; Hirai et al., 2001; Streese et al., 2005). However, most of these studies do not describe the method utilized 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 has 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 characterize rapidly organic support materials in relation to ammonia biofiltration, concerning ammonia biodegradation and both adsorption and absorption phenomena.

The results obtained in this work show that absorption 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; Mao et al., 2006).

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 availability of experimental data from full-scale biofilters is very limited. In consequence, the actual mechanisms of pollutants removal in biofilters are not known. Therefore, results presented in this work may be useful for the design and modelling of the biofiltration process and for the characterization 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) Ammonia adsorption of the five organic materials tested can be modelled by a Langmuir or a Freundlich isotherm. The maximum adsorption capacity of the materials varies from 1.06 to 1.81 mg NH_3/g dry media for the typical ammonia concentrations found in waste treatment plants.

2) Ammonia absorption can be represented by a Henry's law linear equation, with values of the Henry coefficient significantly higher (from 1866 to 15320) than that of pure water (1498). Results obtained indicate that absorption must be considered an important mechanism of pollutant removal in biofiltration. The Henry coefficient should be previously known for the modelling and design of the biofilter operation.

3) Ammonia biodegradation rates (from 0.67 to 7.82 mg NH_3/kg media/d) are considerably lower than adsorption and absorption rates. Different ammonia concentrations (250 and 500 mg NH_3/L) have been found to inhibit ammonia biodegradation, pointing that ammonia inhibition should depend on the organic material used in the biofiltration process.

4) There is an important lack of experimental data from full-scale biofilters. The ammoniometer developed in this work can be useful for the design and operation of biofilters.

Acknowledgements

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

References

Baquerizo G, Maestre JP, Sakuma T, Deshusses MA, Gamisans X, Gabriel D, Lafuente J. 2005. A detailed model of a biofilter for ammonia removal: model parameters analysis and model validation. Chem Eng J 113:205-214.

Barona A, Elías A, Amurrio A, Cano I, Arias R. 2005. Hydrogen sulphide adsorption on a waste material used in bioreactors. Biochemical Eng J 24:79-86.

Barrena R, Vázquez F, Gordillo MA, Gea MT, Sánchez A. 2005. Respirometric Assays at Fixed and Process Temperatures to Monitor Composting Process. Bioresource Technol 96:1153-1159.

Barrena R, Vázquez F, Sánchez A. 2006. The Use of Respiration Indices in the Composting Process: A Review. Waste Manage Res 24:37-47.

Busca G, Pistarino C. 2003. Abatement of ammonia and amines from waste gases: a summary. J Loss Prevent Proc 16:157-163.

Davison BH, Barton JW, Klasson KT, Francisco AB. 2000. Influence of high biomass concentrations on alkane solubilities. Biotechnol Bioeng 68:279-284.

Delhoménie M, Bibeau L, Heitz M. 2002. A study of the impact of particle size and adsorption phenomena in a compost-based biological filter. Chem Eng Sci 57:4999-5010.

Devinny JS, Deshusses MA, Webster, TS. 1999. Biofiltration for Air Pollution Control. Lewis Publishers, Boca Raton, USA.

Eitzer BD. 1995. Emissions of volatile organic chemicals from municipal solid waste composting facilities. Environ Sci Technol 29:896-902.

Gabriel D, Deshusses MA. 2003. Retrofitting existing chemical scrubbers to biotrickling filters for H_2S emission control. PNAS USA 100:6308-6312.

Gea MT, Barrena R, Artola A, Sánchez A. 2004. Monitoring the Biological Activity of the Composting Process: Oxygen Uptake Rate (OUR), Respirometric Index (RI) and Respiratory Quotient (RQ). Biotechnol Bioeng 88:520-527.

Helminen J, Helenius J, Paatero E, Turunen I. 2000. Comparison of Sorbents and Isotherm Models for NH_3-Gas Separation by Adsorption. Aiche J 46:1541-1555.

Hirai M, Kamamoto M, Yani M, Shoda M. 2001. Comparison of the biological removal characteristics among four inorganic packing materials. J Biosci Bioeng 91:428-430.

Kim NJ, Hirai M, Shoda M. 2000. Comparison of organic and inorganic packing materials in the removal of ammonia gas in biofilters. J Hazard Mater B72:77-90.

Kuhne R, Ebert R, Schuurmann G. 2005. Prediction of the Temperature Dependency of Henry’s Law Constant from Chemical Structure. Environ Sci Technol 39:6705-6711.

Lang ME, Lager RA. 1992. Odor control for municipal sludge composting. Biocycle 33:76-85.

Liang Y, Quan X, Chen J, Chung JS, Sung JY, Chen S, Xue D, Zhao Y. 2000. Long-term results of ammonia removal and transformation by biofiltration. J Hazard Mater 80:259-269.

Mao I-F, Tsai C-J, Shen S-H, Lin T-F, Chen W-K, Chen M-L. 2006. Critical components of odors in evaluating the performance of food waste composting plants. Sci Total Environ Available on line: doi:10.1016/j.scitotenv.2006.06.016.

Mcnevin D, Barford J. 1998. Modelling adsorption and biological degradation of nutrients on peat. Biochem Eng J 2:217-228.

McNevin D, Barford J, Hage J. 1999. Adsorption and biological degradation of ammonium and sulfide on peat. Wat Res 33:1449-1459.

McNevin D, Barford J. 2000. Biofiltration as an odour abatement strategy. Biological Eng J 5:231-242.

Mcnevin D, Barford J. 2001. Inter-relationship between adsorption and pH in peat biofilters in the context of a cation-exchange mechanism. Wat Res 35:736-744.

Omur-Ozbek P, Dietrich AM. 2005. Determination of Temperature-Dependent Henry's Law Constants of Odorous Contaminants and Their Application to Human Perception. Environ Sci Technol 39:3957-3963.

Pagans E, Barrena R, Font X, Sánchez A. 2006. Ammonia emissions from the composting of different organic wastes. Dependency on process temperature. Chemosphere 62:1543-1542.

Pagans E, Font X, Sánchez A. 2005. Biofiltration for ammonia removal from composting exhaust gases. Chem Eng J 113:105-110.

Park KJ, Choi MH, Hong JH. 2002. Control of composting odor using biofiltration. Compost Sci Util 10:356-362.

Ramírez E, Corona J, Dendooven L, Rangel P, Thalasso F. 2003. Characterization of five agricultural by-products as a potential biofilter carriers. Bioresource Technol 88:259-263.

Sander R. 2006. Compilation of Henry’s Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry. URL: www.henrys-law.org.

Schlegelmilch M, Streese J, Biedermann W, Herold T, Stegmann R. 2005. Odour control at biowaste composting facilities. Waste Manage 25:917-927.

Smet E, Van Langenhove H, Maes K. 2000. Abatement of high concentrated ammonia loaded waste gases in compost biofilters. Water Air Soil Poll 119:177-190.

Streese J, Schlegelmilch M, Heining K, Stegmann R. 2005. A macrokinetic model for dimensioning of biofilters for VOC and odour treatment. Waste Manage 25:965-974.

US Department of Agriculture and US Composting Council. 2001. Test methods for the examination of composting and compost. Edaphos International, Houston, USA.

Villaverde S, Fernandez MT, Truena MA, Fdz-Polanco F. 1997. Influence of substrate concentration on the growth and activity of nitrifying biofilm in a submerged biofilter. Environ Technol 18:921-928.

Yani M, Hirai M, Shoda M. 1998. Removal kinetics of ammonia by peat biofilter seeded with night soil sludge. J Ferment Bioeng 85:502-506.

Ying-Xu Ch, Jun Y, Shi F. 2004. Biological removal of air loaded with hydrogen sulphide and ammonia mixture. J Environ Sci 16:656-661.

Tables

Table 1: Main characteristics of the five organic support materials.

Material	Org. matter (%, db*)	Moisture (%)	NH_4^+-N (%, db*)	Bulk density (g/cm^3)	pH	Elec. conduc. (mS/cm)	Respiration index (mg O_2/g om**/h)
Compost	47.8	38.1	0.06	0.65	7.1	5.42	1.13
Coconut fiber	98.1	77.6	1.42	0.41	6.8	7.58	2.07
Bark	68.9	59.5	0.10	0.46	6.6	0.74	0.66
Pruning	55.9	54.3	0.01	0.58	7.5	1.52	0.62
Peat	47.0	69.6	0.01	0.45	7.0	0.50	1.44

*db: dry basis; **om: organic matter basis

Table 2: Summary of the results obtained for adsorption experiments.

Material	Langmuir isotherm parameters			Freundlich isotherm parameters		
	C_{sm} (mg NH_3/g dry media)	K_L (m^3/mg NH_3)	r^2	K_F ($[(\text{mg } NH_3)^{1-n}(m^3)^n]$/ g dry media)	n (dimensionless)	r^2
Compost	1.22	0.0039	0.99	-	-	-
Coconut fiber	1.06	0.0121	0.92	0.0994	0.3688	0.98
Bark	11.4	0.0013	0.85	0.0631	0.6718	0.86
Pruning	1.81	0.0011	0.98	-	-	-
Peat	1.59	0.0027	0.99	-	-	-

Table 3: Summary of the results obtained for absorption experiments.

Material	Field capacity (%)	Henry coefficient (at field capacity) (dimensionless)	r^2
Compost	61.0	2885	0.99
Coconut fiber	88.1	2903	0.96
Bark	67.8	15320	0.94
Pruning	69.0	3923	0.82
Peat	79.6	1866	0.82
Pure water (this work)	100.0	1795	0.99
Pure water (Sander, 2006)	100.0	1498	-

Table 4: Ammonia biodegradation rate of the five organic support materials determined at different substrate concentration.

Material	Ammonia Biodegradation Rate (mg NH_3/Kg/d)	Ammonia Biodegradation Rate (mg NH_3/m^3/d)	Ammonia concentration Gas phase (mg NH_3/m^3)	Ammonia concentration Liquid phase (mg NH_3/L)*
Compost	1.92	1279	41.1	118
Coconut fiber	5.76	1744	150	434
Bark	0.67	307.9	61.7	946
Pruning	7.82	4191	92.1	361
Peat	6.38	2877	109	203

*Considering the Henry coefficient obtained at field capacity

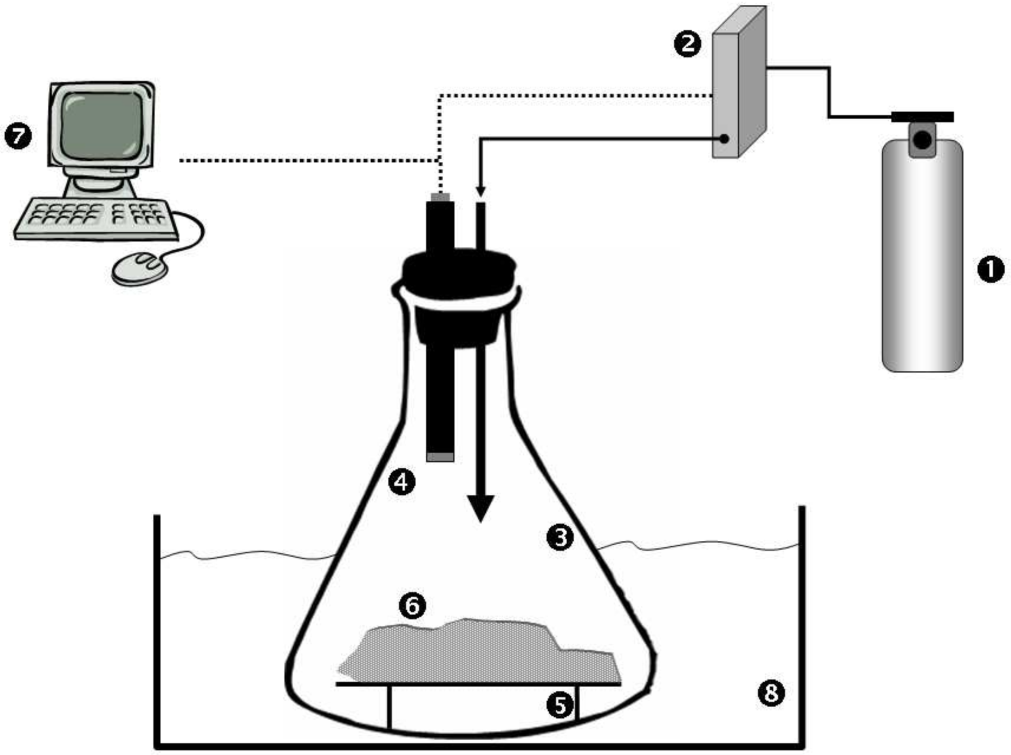
Legends to Figures

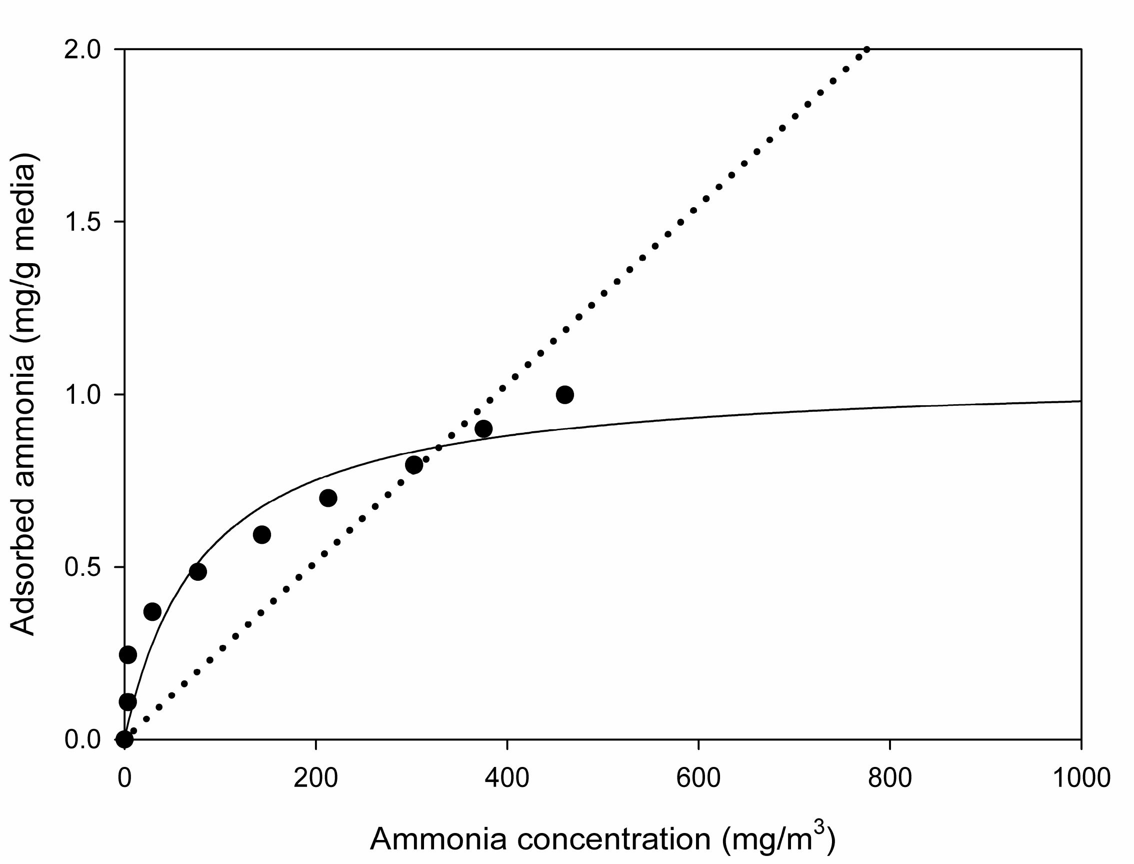
Figure 1: Scheme of the ammoniometer: 1: Ammonia tank, 2: Mass flowmeter, 3: Flask, 4: Ammonia sensor, 5: Plastic mesh, 6: Organic material (sample), 7: Personal computer, 8: Water thermostatic bath.

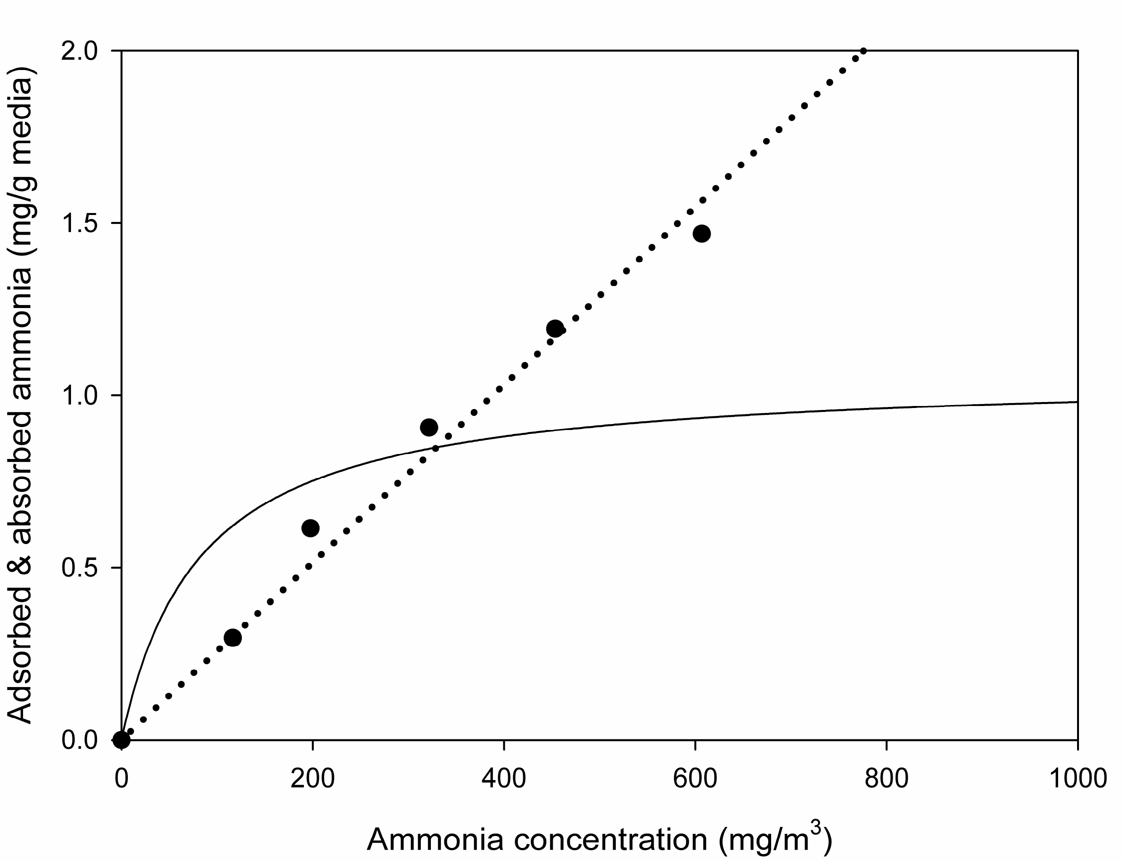
Figure 2: Influence of moisture content in the combined adsorption-absorption phenomena jointly with the theoretical adsorption (solid line) and absorption (dotted line) curves in the case of coconut fiber: a) Moisture: 0% (adsorption); b) Moisture: 37.5%; c) Moisture: 65.8%; d) Moisture: 88.1% (field capacity).

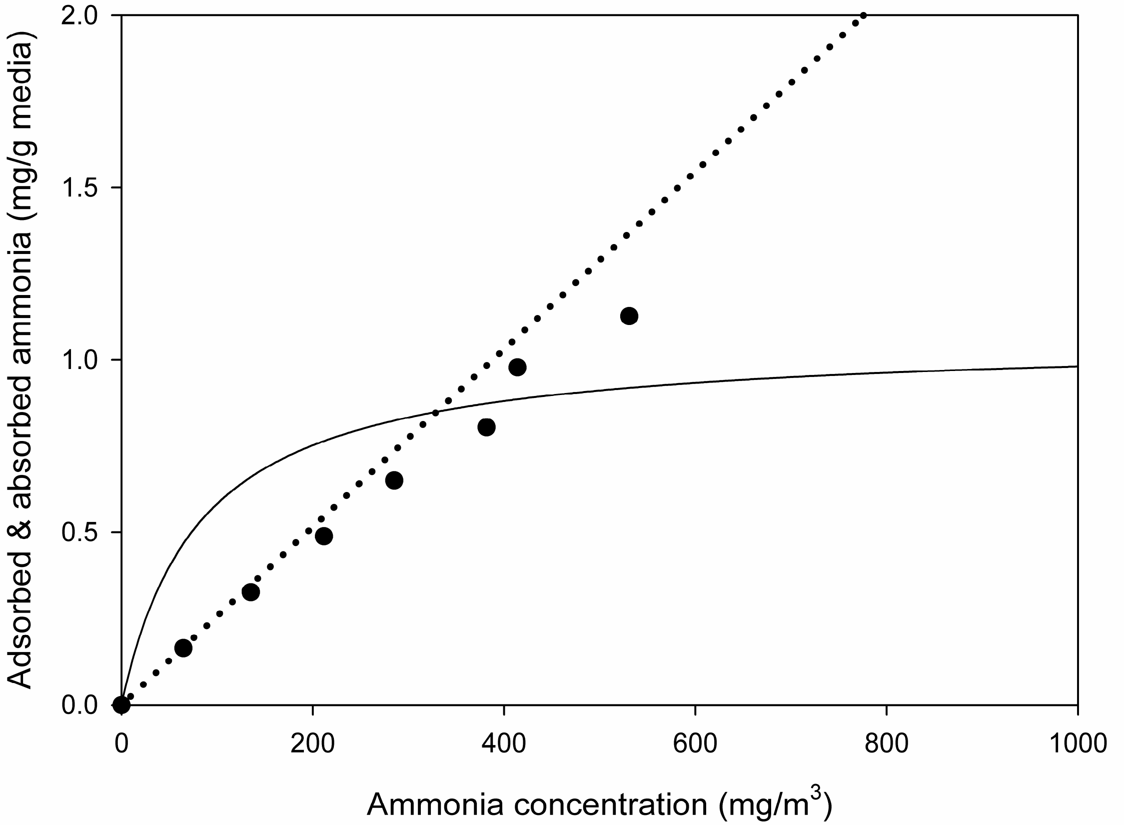
Figure 3: Ammonia concentration evolution for sterilized sample of compost (circles) and non-sterilized sample of compost (solid circles).

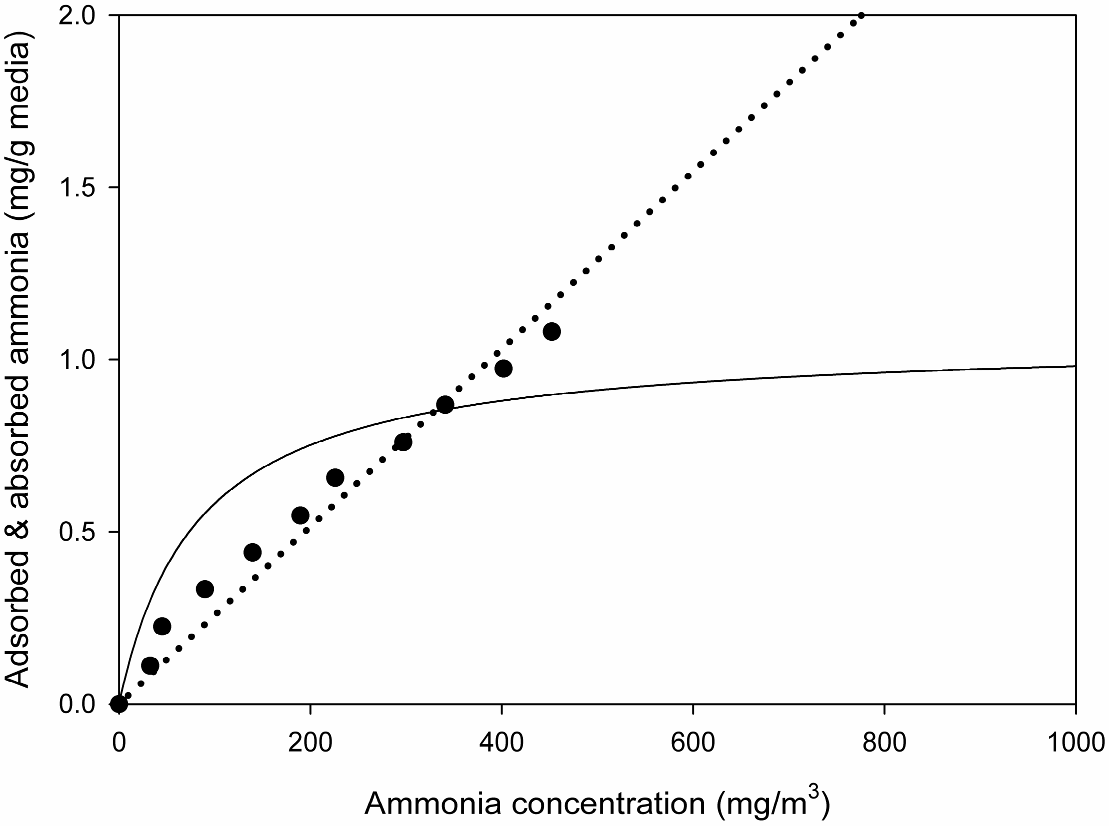
Figure 4: Evolution of ammonia biodegradation rate (circles) and pH (triangles) versus free ammonia concentration present in the liquid phase for: a) pruning wastes; b) peat.

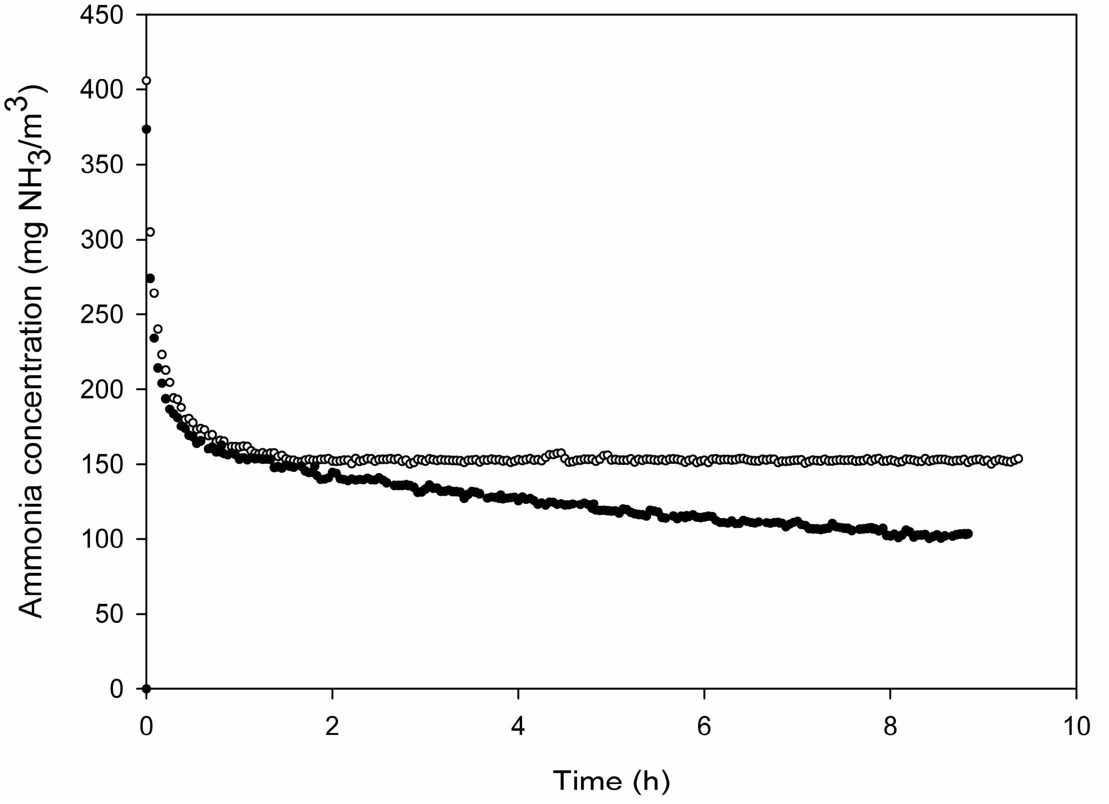

❷
❼
❶
❹
❸
❻
❽
❺

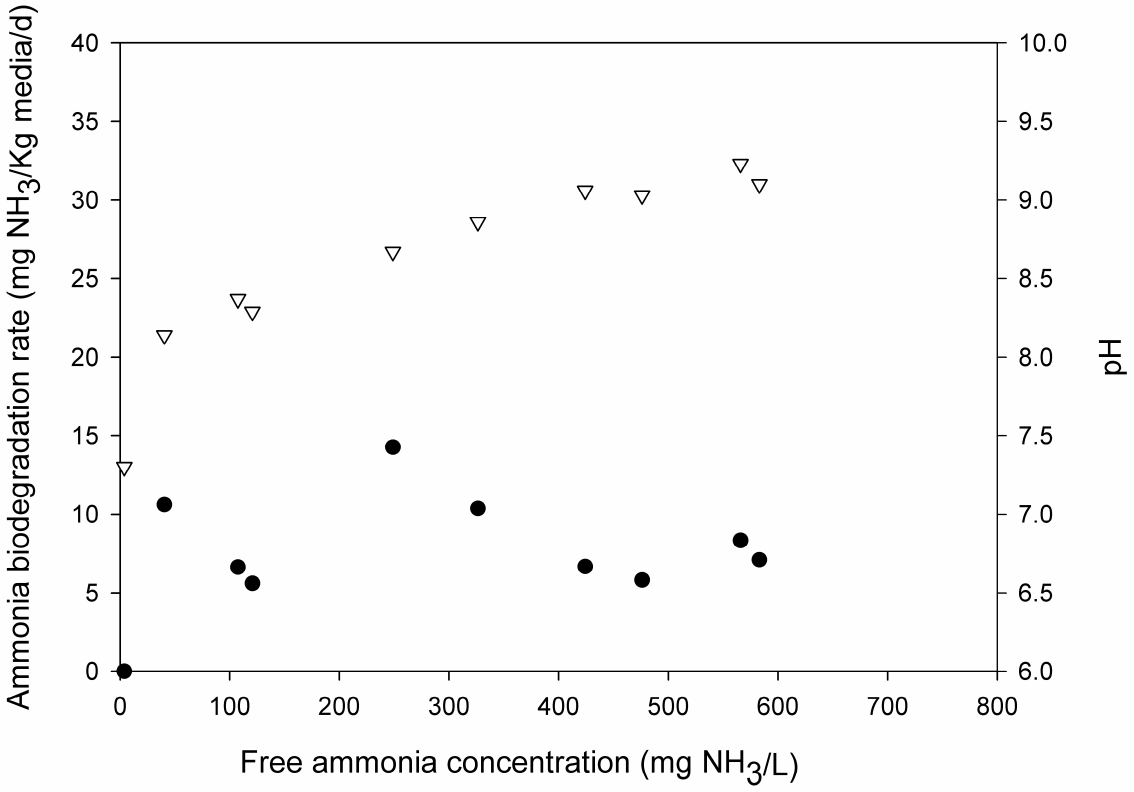

2.0
1.5
1.0
0.5
0.0
Adsorbed ammonia (mg/g media)
0
200
400
600
800
1000
Ammonia concentration (mg/m^3)

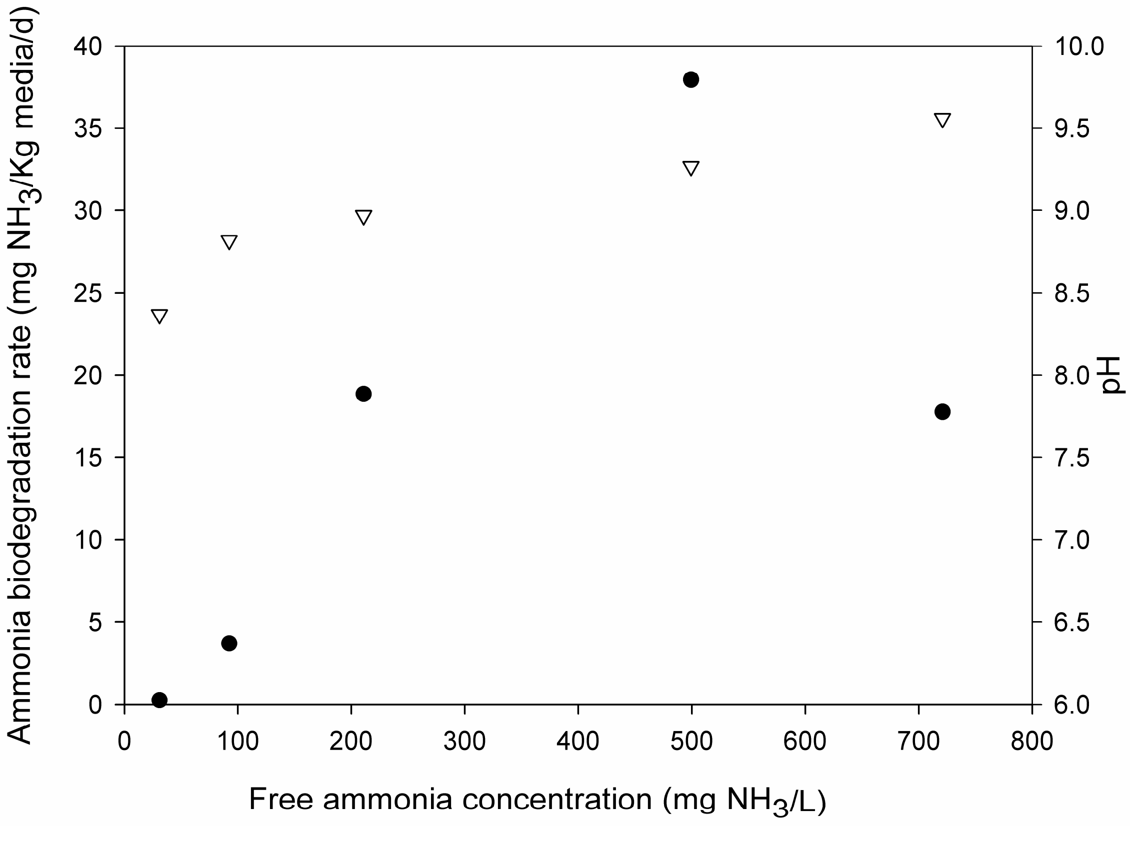

Adsorbed & absorbed ammonia (mg/g media)
0.0
0.5
1.0
1.5
2.0
0
200
400
600
800
1000
Ammonia concentration (mg/m^3)


Adsorbed & absorbed ammonia (mg/g media)
0.0
0.5
1.0
1.5
2.0
0
200
400
600
800
1000
Ammonia concentration (mg/m^3)


Adsorbed & absorbed ammonia (mg/g media)
2.0
1.5
1.0
0.5
0.0
0
200
400
600
800
1000
Ammonia concentration (mg/m3)


Ammonia concentration (mg NH3/m3)
450
400
350
300
250
200
150
100
50
0
0
2
4
6
8
10
Time (h)


Ammonia biodegradation rate (mg NH3/Kg media/d)
0
5
10
15
20
25
30
35
40
pH
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
0
100
200
300
400
500
600
700
800
Free ammonia concentration (mg NH3/L)


Ammonia biodegradation rate (mg NH3/Kg media/d)
0
5
10
15
20
25
30
35
40
pH
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
0
100
200
300
400
500
600
700
800
Free ammonia concentration (mg NH3/L)