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Long-term ammonia removal in a coconut fiber-packed biofilter: Analysis of N fractionation and reactor performance under steady-state and transient conditions

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ABSTRACT

A comprehensive study of long-term ammonia removal in a biofilter packed with coconut fiber is presented under both steady-state and transient conditions. Low and high ammonia loads were applied to the reactor by varying the inlet ammonia concentration from 90 to 260 ppm_v and gas contact times ranging from 20 to 36 s. Gas samples and leachate measurements were periodically analyzed and used for characterizing biofilter performance in terms of removal efficiency (RE) and elimination capacity (EC). Also, N fractions in the leachate were quantified to both identify the experimental rates of nitritation and nitratation and to determine the N leachate distribution. Results showed stratification in the biofilter activity and, thus, most of the NH_3 removal was performed in the lower part of the reactor. An average EC of 0.5 kg N-NH_3 m^{-3} d^{-1} was obtained for the whole reactor with a maximum local average EC of 1.7 kg N-NH_3 m^{-3} d^{-1}. Leachate analyses showed that a ratio of 1:1 of ammonium and nitrate ions in the leachate was obtained throughout steady-state operation at low ammonia loads with similar values for nitritation and nitratation rates. Low nitratation rates during high ammonia load periods occurred because large amounts of ammonium and nitrite accumulated in the packed bed, thus causing inhibition episodes on nitrite-oxidizing bacteria due to free ammonia accumulation. Mass balances showed that 50% of the ammonia fed to the reactor was oxidized to either nitrite or nitrate and the rest was recovered as ammonium indicating that sorption processes play a fundamental role in the treatment of ammonia by biofiltration.

1. Introduction

Ammonia is a colourless, toxic, reactive, and corrosive gas, emitted in several industrial and agricultural processes such as petrochemical refining, livestock farming or composting facilities (Chung et al., 2005; Demeestere et al., 2002; Liang et al., 2000; Pagans et al., 2005). Although ammonia scrubbing under acidic conditions is considered the most cost-effective physicochemical technique for ammonia abatement, operating costs are much higher compared to biological alternatives such as biofiltration (Kennes and Veiga, 2001), which has demonstrated to be an effective and reliable biological method to treat a wide range of pollutants (Devinny et al., 1999).

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Ammonia-treating biofilters are generally packed with organic carriers, which act as a natural source of nutrients for microorganisms. In particular, coconut fiber is one of the most used packing materials in full-scale biofilters in Europe (van Groenestijn, 2005). A large number are located in municipal solid waste treatment facilities where ammonia removal takes places in the biofilter simultaneously to other compounds such as volatile organic and reduced sulphur compounds. However, a low number of studies have been reported evaluating coconut fiber performance in ammonia-treating biofilters (Baquerizo et al., 2005; Gabriel et al., 2007). In these studies, coconut fiber provided good performance in terms of stable operation, without presenting compaction and/or degradation episodes, even if some properties such as a low water retentivity compared to inorganic packing materials and low adsorption capacities were also reported for this material.

A broad range of operating conditions has been applied in biofilters treating air streams contaminated with ammonia. The empty bed residence time (EBRT) is normally lower than 1 min, while ammonia inlet concentration is generally varied in the range of 10–300 ppm_v, even though concentrations above 2500 ppm_v have been also reported (Pagans et al., 2005). However, experimental studies dealing with long-term operation in ammonia biofiltration are significantly more limited (Chen et al., 2005; Gabriel et al., 2007; Liang et al., 2000; Yani et al., 1998; Yani et al., 2000). Usually, the main concern is to determine the maximum elimination capacity (EC) varying either the inlet concentration and/or the EBRT. ECs from 0.1 to 0.6 kg N-NH_3 m^{-3} d^{-1} with maximum values of 1 kg N-NH_3 m^{-3} d^{-1} have been obtained during short periods of time (less than 1 week). On the other hand, most of these studies show that pH control together with the maintenance of an optimal water content in the filter bed arise as key operating parameters in order to keep a stable operation. In any case, no definitive conclusions have been provided related to the maximum EC and optimal operating conditions in ammonia biofiltration.

Despite of high ECs reported in the literature, some studies have questioned the efficiency of ammonia biofiltration at relatively high inlet concentration (above 50 ppm_v) due to the sensitivity of nitrifying bacteria (Chen et al., 2005; Demeestere et al., 2002), the large ammonia solubility in water and the pH-dependant protonation, which cause that NH_3 is partially removed by sorption processes into the water fraction of the reactor and into the packing material (Shoda, 1991; Smet et al., 2000). Therefore, the role of simultaneous physical and biological processes needs to be also identified and quantified in ammonia biofilters (Pagans et al., 2006). Furthermore, excessive accumulation of nitrogen species in the reactor bed may produce inhibition effects on nitrifying bacteria diminishing the bioreactor efficiency (Baquerizo et al., 2005; Chen et al., 2005; Smet et al., 2000). Also, accumulation of ammonium, nitrite and nitrate in the carrier material and in the drain water implies that further treatment of biofilters leachate is needed.

In this study ammonia removal in a biofilter packed with coconut fiber was investigated in a continuous operation period larger than two years. The biofilter performance was studied under low and high ammonia loads. Biofilter response to transient operation varying both ammonia inlet concentration and EBRT was also investigated. A reliable and deep characterization of nitrogen fractions in the leachate is performed and used for identifying the experimental rates of nitrification as well as to assess the mass balance and to determine the degree of ammonia oxidation in the biofilter.

2. Materials and methods

2.1. *Experimental setup and analytical methods*

Ammonia biofiltration was conducted in a laboratory-scale reactor as shown in Fig. 1. A PVC cylindrical biofilter with an inner diameter of 0.1 m and an overall height of 1 m was divided into 4 equal modules of 0.2 m of packing material height, with a total volume of the filter bed of 6.3 L. Each section was supported by sieve plates and packed with coconut fiber as carrier material, which characteristics can be found elsewhere (Baquerizo et al., 2005). A total of 308 g of dry coconut fiber were used in the biofilter. Also, the rationale behind the selection of the bed height of the biofilter was based on the real bed height usually found in full-scale biofilters packed with classical organic packing materials (Devinny et al., 1999). Five gas sampling points were located along the reactor height including the reactor inlet and outlet ports. Biofilter was operated in up-flow mode. A nutrient solution used for bed watering, prepared according to the following composition (in g L^{-1}): KH_2PO_4 1.0, K_2HPO_4 1.0, NaCl 1.0, $MgSO_4$ 0.2 and $CaCl_2$ 0.02, was supplied six times per day at a flowrate of 0.756 L d^{-1} from the top of the biofilter. The bottom of the reactor was conditioned by means of an electrovalve to collect the drain.

The gaseous inlet stream was obtained by mixing air and pure ammonia (Fig. 1). The air stream was previously humidified by bubbling it through a PVC humidification column (1 m height), while pure ammonia was supplied from a gas cylinder. Two digital mass flow controllers (Bronkhorst, NL) were used for air and ammonia flows to adjust the empty bed residence time (EBRT) and to ensure an accurate ammonia inlet concentration. A home-made supervisory system (WinCC, Siemens) together with a PLC (Simatic 300, Siemens) was used for automating and monitoring the pilot plant. Details of automation structure can be found elsewhere (Baquerizo et al., 2005).

Inlet gas relative humidity was kept in the range of 95–100% along the entire operation period, while the biofilter was operated at 24 ± 2 °C on average. The packing material was withdrawn from a full-scale biofilter which had been running for more than 2 years at an average ammonia inlet concentration of 40 ppm_v (Gabriel et al., 2007). Thus, no inoculation was required since nitrifying biomass was already grown in the coconut fiber. The biofilter was operated continuously for more than two years (i.e. 795 days) under steady-state and transient conditions. The reactor was sporadically stopped for a maximum of 1 day in order to carry out maintenance tasks. In general, operational parameters and conditions varied between values typically found in full-scale ammonia-treating biofilters. Along the experimental period, the inlet

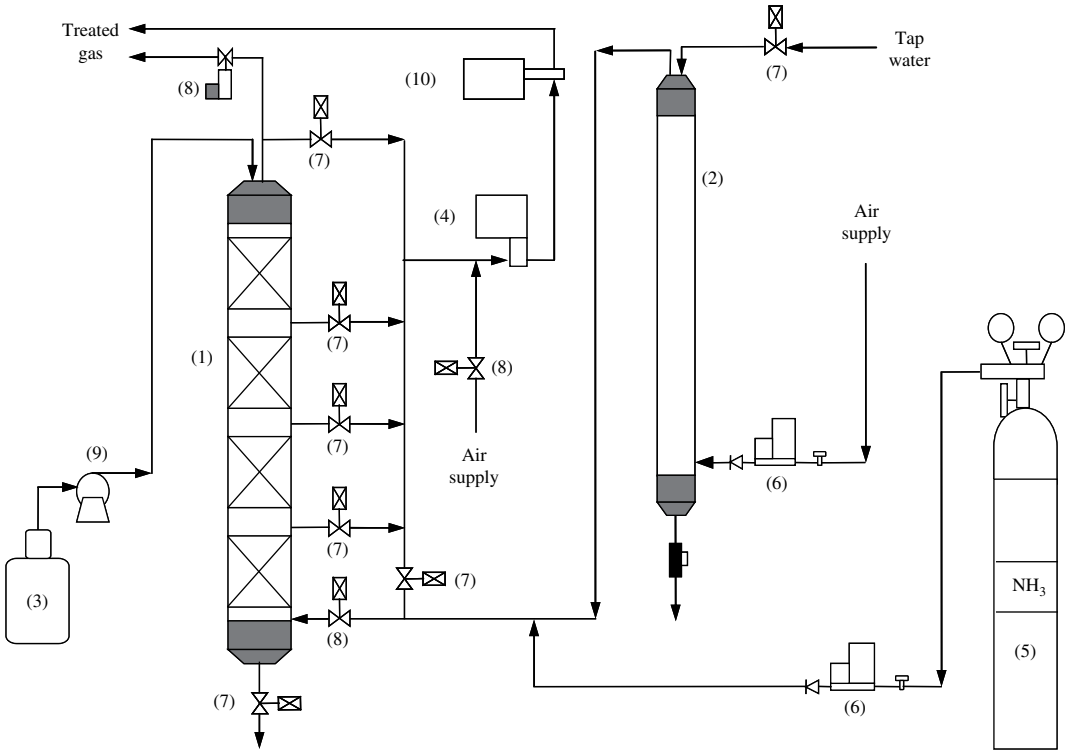

Fig. 1 – Schematic of the laboratory-scale plant: (1) biofilter, (2) humidification column, (3) nutrients reservoir, (4) relative humidity and temperature sensor, (5) ammonia gas cylinder, (6) mass flow controllers, (7) normally closed valve, (8) normally opened valve, (9) diaphragm pump, (10) ammonia gas sensor.

ammonia concentration was varied from 45 to 260 ppm_v, while the EBRT was changed between 20 and 36 s.

During the first 100 days of operation, ammonia in the gas phase was determined by bubbling gaseous samples through an acid solution (pH 4) in which ammonia was absorbed. Thereafter, ammonia gas was measured on-line by using an ammonia electrochemical sensor (Vaisala AMT102). During routine operation, the leachate volume collected after watering was drained on a daily basis even if not daily leachate samples were analyzed. Ammonium in both the leachate and that absorbed in the acid trap were determined in a continuous flow analyzer (Baeza et al., 1999). Nitrite and nitrate collected from leachate were determined by capillary electrophoresis in a Quanta 4000E unit (Waters). Leachate pH was measured with a Crison MicropH 2001 probe.

2.2. *Nitrification rates and nitrogen mass balances*

Nitrification can be described as a two-step process: oxidation from ammonium to nitrite (*i.e.* nitritation) and oxidation from nitrite to nitrate (*i.e.* nitratation). Additionally, nitrification rates may be determined from local biofilm kinetics through modelling of the entire system (Baquerizo et al., 2005). However, accurate nitrification rates are tough to determine due to the difficulty to experimentally determine both yield and kinetic parameters in the biofilm. In this study, nitritation and nitratation rates are calculated according to the Equations (1) and (2), which are directly derived from nitrite and nitrate measurements in the leachate.

$$R_1 = \frac{NO_{2(leach)}}{\Delta t \cdot V} + R_2 \quad (1)$$

$$R_2 = \frac{NO_{3(leach)}}{\Delta t \cdot V} \quad (2)$$

where R_1 is the nitritation rate (g N-NO_x produced $m^{-3}\,d^{-1}$), $NO_{2(leach)}$ is the mass of nitrite (g N-NO_2) collected in the leachate during the time interval Δt (d) over two leachate sampling events, and V is the reactor bed volume (m^3). R_2 is the nitratation rate (g N-NO_3^- produced $m^{-3}\,d^{-1}$), and $NO_{3(leach)}$ is the mass of nitrate (g N-NO_3) collected in the leachate during the time interval Δt (d).

It is worth mentioning that R_1 can be calculated based on Equation (3) which is derived from ammonium measurements in the leachate and ammonia measurements in the gas phase.

$$R_1^{alt} = \frac{(NH_{4(abs)} - NH_{4(leach)})}{\Delta t \cdot V} \quad (3)$$

where R_1^{alt} is the nitritation rate (g N-NH_4^+ consumed $m^{-3}\,d^{-1}$) based on ammonia and ammonium measurements, $NH_{4(abs)}$ is the mass of ammonium (g N-NH_4) absorbed in the packed bed during the time interval Δt over two leachate sampling events, $NH_{4(leach)}$ is the mass of ammonium (g N-NH_4) collected in the leachate during the time interval Δt (d), and V is the reactor

bed volume (m^3). $NH_{4(abs)}$ is calculated according to Equations (4) and (5).

$$NH_{4(abs)} = (NH_3 + NH_4)_{abs} \cdot \frac{10^{-pH}}{10^{-pH} + K_{eq}} \quad (4)$$

$$(NH_3 + NH_4)_{abs} = \left(NH_{3(in)} - NH_{3(out)}\right) \quad (5)$$

where $NH_{3(in)}$ is the mass of ammonia gas fed to the reactor during the time interval Δt (g N-NH_3), $NH_{3(out)}$ is the mass of ammonia gas leaving the reactor during the time interval Δt (g N-NH_3) and K_{eq} is the ionization constant for the NH_3-NH_4^+ equilibrium. A value of 5.5×10^{-10} was used in the present work (Perry and Green, 1997). However, a statistic analysis based on a paired Student's *t*-test was performed to compare R_1 and R_1^{alt} (data not shown). The *t*-test at 5% level of significance revealed that R_1 is never affected by absorption effects that may take place in the biofilter because of transient operation. Instead, R_1^{alt} is strongly affected by, for example, watering rate changes, ammonia load increments or during the start-up of a biofilter. Thus, R_1^{alt} can only be used for nitritation rate calculation during long periods under steady-state conditions.

Measurements of the different N species collected in the leachate were used for calculating the degree of ammonia oxidation occurring in the biofilter as well as for assessing nitrogen mass balances. The nitrogen mass balance was carried out for the gas and the liquid phases according to Equation (6).

$$\sum NH_{3(in)} = \sum NH_{3(out)} + \sum NH_{4(leach)} + \sum NH_{3(leach)} + \sum NO_{2(leach)} + \sum NO_{3(leach)} \quad (6)$$

where $NH_{3(in)}$ is the mass of gaseous ammonia (g N-NH_3) fed to the reactor during a time interval in which the mass balance is assessed, $NH_{3(out)}$ is the mass of gaseous ammonia (g N-NH_3) leaving the reactor, while $NH_{4(leach)}$, $NH_{3(leach)}$, $NO_{2(leach)}$ and $NO_{3(leach)}$ are the mass of ammonium (g N-NH_4), free ammonia (g N-NH_3), nitrite (g N-NO_2) and nitrate (g N-NO_3), respectively, collected in the leachate for the time during the same time interval. The error associated to the mass balance is defined by Equation (7).

$$\text{error}\ (\%) = \frac{\sum NH_{3(in)} - \sum N_{(out)}}{\sum NH_{3(in)}} \cdot 100 \quad (7)$$

where

$$\sum N_{(out)} = \sum NH_{3(out)} + \sum NH_{4(leach)} + \sum NH_{3(leach)} + \sum NO_{2(leach)} + \sum NO_{3(leach)} \quad (8)$$

3. Results and discussion

3.1. *Overall performance of the biofilter*

Fig. 2a and b shows the overall performance results obtained during the entire experimental period. Since the packing

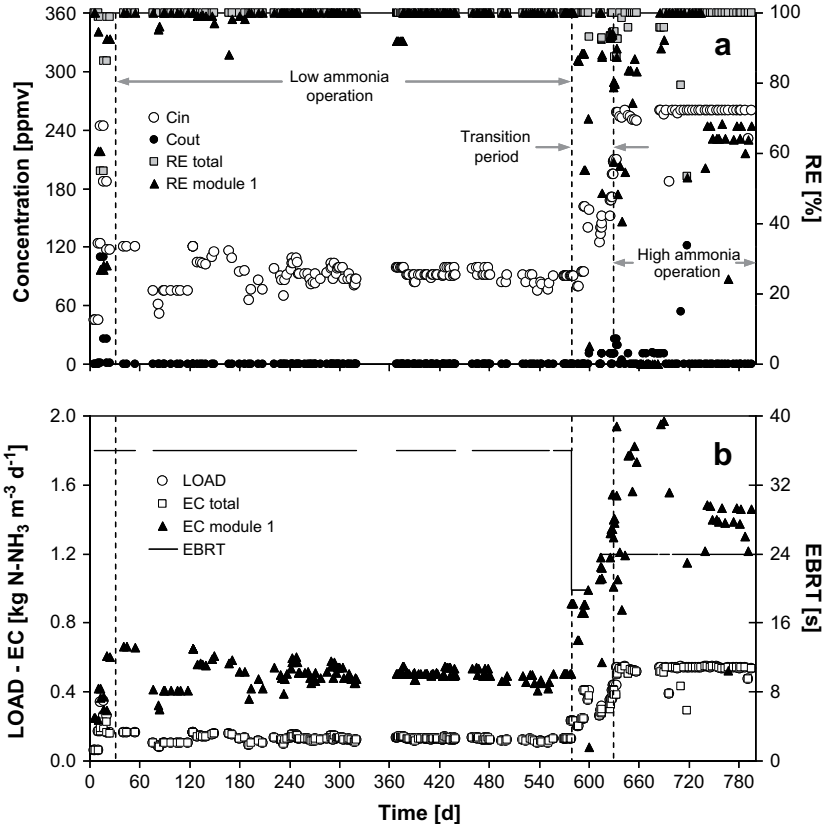

Fig. 2 – Performance of gas-phase parameters in the biofilter for 26 months of operation corresponding to the whole period under study: (a) inlet and outlet concentrations of ammonia, removal efficiencies in the overall reactor and in module 1, (b) EBRT, ammonia load and elimination capacity in the overall reactor and in module 1.

material was already inoculated, the biofilter was operated under variable inlet concentrations (45–240 ppm_v) for the first 30 days as described in Baquerizo et al. (2005). After the first 30 days period, two stationary periods were identified to characterize reactor operation (Fig. 2). In addition, a transient period between stationary periods was also analyzed. In the first steady-state period, namely low ammonia load operation (LALO) period, a constant EBRT of 36 s and average inlet ammonia concentration of 90 ppm_v were employed from day 30 until day 580 (average ammonia load of 0.13 kg N-NH_3 m^{-3} d^{-1}). Throughout the second steady-state period, namely high ammonia load operation (HALO) period, the inlet concentration was maintained at 260 ppm_v from day 632 until day 795 to study the reactor performance under high ammonia loads. By setting the EBRT at 24 s, the average ammonia load was 0.54 kg N-NH_3 m^{-3} d^{-1}.

Almost complete NH_3 removal was attained in both steady-state periods. An average removal efficiency (RE) of 99.1 ± 1.3% was achieved for the LALO period (Fig. 2a). A similar performance was obtained for the HALO period with an average RE of 97.8 ± 8.0%. Thus, the total EC overlapped the load as can be seen in Fig. 2b. In both steady-state periods, gas measurements along the reactor showed that most of the ammonia abatement took place in the first module (bottom), which is close to the reactor entry. Indeed, RE of 99.2 ± 2% and 77.0 ± 20.1% were achieved in the first module (*i.e.* module 1) for LALO and HALO periods, respectively (Fig. 2a). Results agree with stratification in biofilters found in several works (Chen et al., 2005; Chung and Huang, 1998; Joshi et al., 2000).

The influence of the loading rate on the EC for both the total reactor volume and the module 1 section was calculated by averaging the EC calculated for several pseudo steady-state periods (Fig. 3). The ammonia EC in the total reactor volume showed a linear relationship over the entire range of ammonia load (Fig. 3a), which indicates that the biofilter never reached its maximum EC under steady-state conditions. Several studies have reported similar results in biofilters packed with both organic and inorganic materials treating ammonia at inlet concentrations lower than 100 ppm_v (Chen et al., 2005; Joshi et al., 2000; Weckhuysen et al., 1994; Yani et al., 1998). However, ECs based on the module 1 volume can be also calculated to assess the maximum EC since ammonia removal is mainly attained in this reactor section (Deshusses and Johnson, 2000). In module 1, an average EC of 1.7 ± 0.4 kg N-NH_3 m^{-3} d^{-1} was achieved during the HALO period (Fig. 3b). It is interesting to notice that such ECs corresponded to an EBRT equal to a fourth part of the overall EBRT, *i.e.* 6 s, which indicates that the system has the potential to reach such EC in a packed bed biofilter of 1 m of height treating four times the actual flowrate. Such results are slightly above the larger ECs in biofilters found in the literature, which are about 1.4 kg N-NH_3 m^{-3} d^{-1} in biofilters packed with organic and inorganic materials at inlet ammonia concentration of 1000 ppm_v or higher (Kanagawa et al., 2004; Pagans et al., 2005). However, the main inconvenient of most reported studies is that the biofilter efficiency is analyzed in terms of ammonia EC, which is restricted to evaluate the gas phase performance. Thus, and despite of the EC obtained, the main concern in ammonia biofiltration is the nitrification capacity of the system, which can be analyzed through the examination of leachate concentrations.

3.2. *Analysis of steady-state conditions: nitrification capacities and nitrogen mass balances*

Monitoring results for nitrogen species in the leachate and nitrification rates for the entire operation period are depicted in Fig. 4. Also, nitritation (R_1) and nitratation (R_2) rates were assessed for both stationary periods (*i.e.* LALO and HALO) and compared with the corresponding inlet load. Average R_1 were 0.064 kg N m^{-3} d^{-1} and 0.243 kg N m^{-3} d^{-1} along the LALO and HALO periods, respectively; while average R_2 were 0.053 kg N m^{-3} d^{-1} and 0.115 kg N m^{-3} d^{-1} along the LALO and HALO periods, respectively.

Almost identical values for R_1 and R_2 were assessed during the LALO period (from day 30 to 580, Fig. 3b) confirming that the ammonium oxidized was subsequently oxidized to nitrate (average value of 1093 ± 257 mg N-NO_3^- kg^{-1} dry packing). Thus, nitrite accumulation was irrelevant during the LALO period with concentrations lower than 300 mg N kg^{-1} dry packing. On the other hand, similar concentrations of ammonium and nitrate were obtained in the LALO period, indicating that around a 50% of the total ammonia fed to the reactor was not biodegraded. Under operation at low inlet concentrations, a stable pH of 7.45 ± 0.5 was observed for 550 operating days (Fig. 4a). Low variations in pH values for ammonia biofiltration were explained as a consequence of the

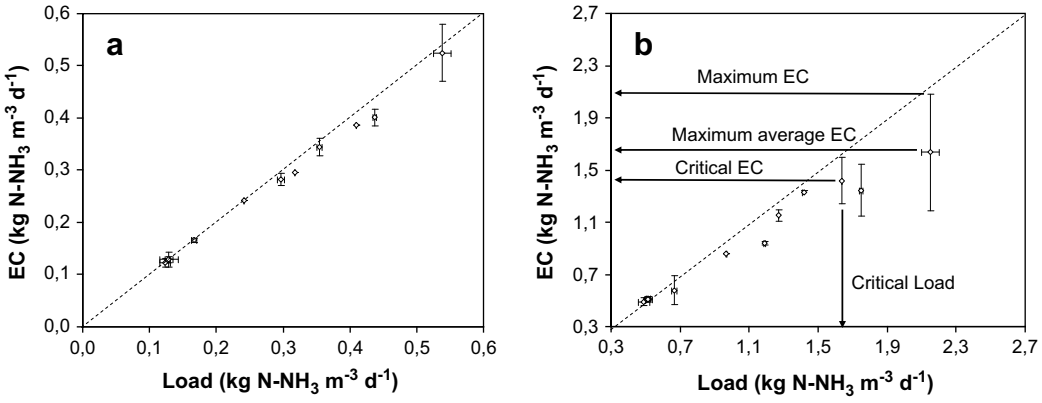

Fig. 3 – Inlet load versus elimination capacity for (a) total reactor and (b) module 1.

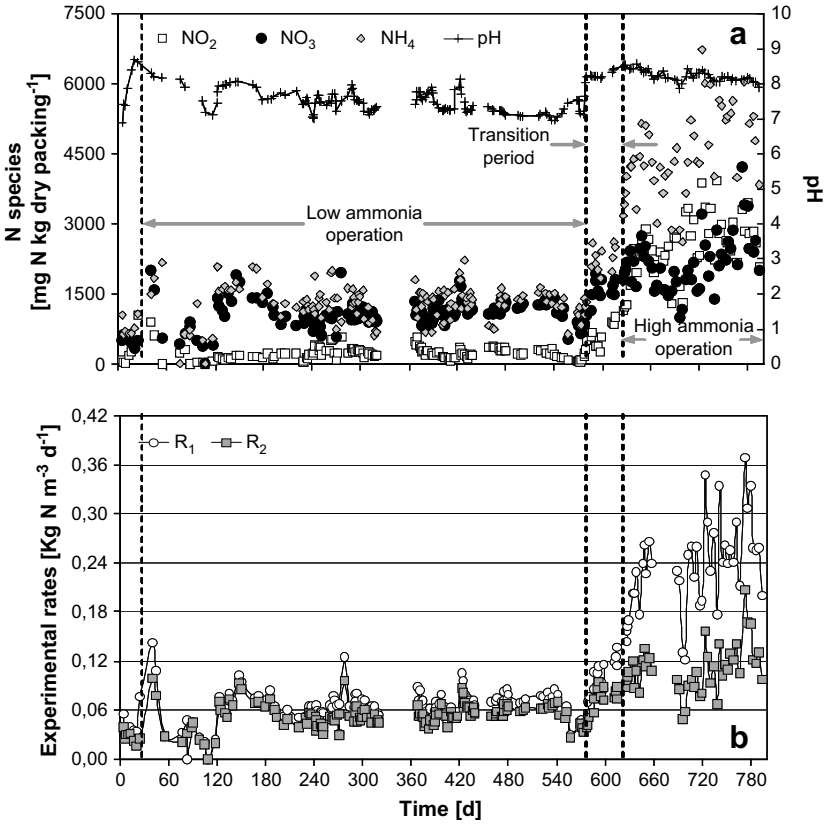

Fig. 4 – Evolution of the main liquid-phase parameters: (a) leachate analyses: ammonium, nitrite, nitrate and pH, (b) experimental nitritation (R_1) and nitratation (R_2) rates.

equilibrium between partial nitrification and sorption processes (Togashi et al., 1986).

In the HALO period, leachate ammonium concentrations varied from 3000 to 6000 mg N kg^{-1} dry packing (average value of 4742 ± 1110 mg N-NH_4^+ kg^{-1} dry packing) as a consequence of the absorption process at high inlet ammonia concentrations (*i.e.* 260 ppm_v) and due to nitrification inhibition, which lead to average nitrite and nitrate concentrations of 2629 ± 573 and 2175 ± 636 mg N kg^{-1} dry packing, respectively. Incomplete nitrification was also assessed by calculating average nitrification rates. The average nitratation rate reached values of about 50% of the nitritation rate, indicating that nitrite-oxidizing bacteria (NOB) are much more sensible to inhibition than ammonium-oxidizing bacteria (AOB). Under this condition, a decrease of RE in module 1 was detected (Fig. 2) confirming that module 1 had reached its maximum EC and that was operating under inhibitory conditions. However, and despite of nitrogen species accumulation in the filter bed and reduced RE in module 1, ammonia removal in the gas effluent was still accomplished along the HALO period with a constant RE close to 100% for 150 operating days. According to the results, nitrogen removal in ammonia biofiltration can be questioned if only gas-phase data are reported. Instead, leachate analysis and nitrification rates are crucial to assess bioreactors performance.

The mass distribution percentage in the leachate was assessed for both periods (Fig. 5). Mass balances revealed that in both cases around 50% of the total nitrogen was accumulated as ammonium into the packed bed, which is subsequently removed in the leachate. Such results are in concordance with several other biofilters works in which a 50% of the ammonia removed was nitrified and the other 50% was retained in the packed bed as ammonium in biofilters under similar operating conditions as in the present study (Chen et al., 2005; Smet et al., 2000; Don, 1985). It is worth noticing that the nitrate to ammonium mass distribution ratio was close to 1:1 during the LALO period while a ratio close to 2:1 was detected for ammonium to nitrate and ammonium to

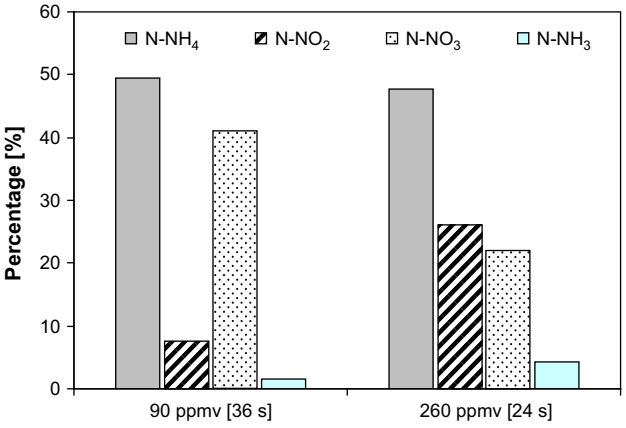

Fig. 5 – Mass percentage distribution in the leachate under steady-state operating conditions (FNA fraction not plotted since it was close to 0% in both periods).

nitrite ratios during the HALO period. Thus, results confirmed that NOB were largely inhibited than AOB.

It should be stressed that inhibition of AOB and NOB are due to both free ammonia (FA) and free nitrous acid (FNA) rather than to ammonium and nitrite. Thus, the impact on nitrification rates must be assessed in terms of the former species. On average, concentrations of FA and FNA in the leachate were 26 ± 54 mg N-NH_3 L^{-1} and $1.4 \times 10^{-2} \pm 1.8 \times 10^{-2}$ mg N-HNO_2 L^{-1}, respectively, along the LALO period and 215 ± 94 mg N-NH_3 L^{-1} and $2.7 \times 10^{-2} \pm 1.7 \times 10^{-2}$ mg N-HNO_2 L^{-1}, respectively, along the HALO period. Standard deviations are explained as a consequence of inlet load variations coupled to analytical limitations of the methods employed. However, data compiled for different cases on inhibiting boundary concentrations of FA and FNA on AOB and NOB (Anthonisen et al., 1976) indicated that the main cause for the inhibition in the biofilter was the accumulation of FA, particularly during the HALO period. FNA concentrations were out of the reported limits to affect both nitrification rates because of the relatively high pH of operation in the biofilter (generally above 7) coupled to the low equilibrium constant of the HNO_2-NO_2^- pair (2.5×10^{-3}, Perry and Green, 1997). Although only a 4% of the total mass of nitrogen species in the biofilter leachate collected in the HALO period corresponded to FA (Fig. 5), this was enough to cause a nitrite accumulation and a decrease of the nitratation rate of about 50% in comparison to the nitritation rate in the LALO period.

A nitrogen mass balance performed in both periods showed errors of 6% during the LALO period and 5% during the HALO period. Mass balance errors of about 30% are often found in biofiltration of ammonia (Chen et al., 2005; Malhautier et al., 2003; Sakuma et al., 2008). Some studies have associated the error in the nitrogen mass balance to nitrogen species not included into the analyses as organic nitrogen from biomass and gaseous nitrogen (Chen et al., 2005; Joshi et al., 2000). Therefore, and according to the nitrogen mass balance, the denitrification process was discarded in the experiments conducted during this study.

Clearly, the amount of ammonium collected in the leachate and/or accumulated in the packed bed must be reduced to improve the effective ammonia removal in the biofilter. In this sense, a balance between nitritation and nitratation rates should be attained to avoid inhibitory effects due to the accumulation of nitrogen species and to achieve both large nitrification rates. Even if not tested in the present work, such accumulation of FA and FNA may be reduced by changing the amount of water added to the reactor, which is the sole manipulated variable to control the inhibitory by-products wash-out. Although reduced EC and RE are obtained as a consequence of a deficient water supply (Gabriel et al., 2007), an excessive watering may increase the fraction of ammonia recovered as ammonium. Also, nitrification rates may be improved by decreasing the pH of the watering solution which will reduce the FA fraction in the biofilm. However, viability of both alternatives needs further research.

3.3. *Study of reactor performance under inlet ammonia variations*

The transition period from LALO to HALO periods in the biofilter (Fig. 2) was also analyzed. Higher ammonia loads were achieved by decreasing the EBRT from 36 to 20 s coupled to a systematic increase of the ammonia inlet concentration from 90 to 260 ppm_v (Fig. 6a). Overall, an increase on the pH, ammonium, nitrite and nitrate concentrations in the leachate was detected (Fig. 4a) while slightly lower ammonia RE were encountered compared to non-transient periods (Fig. 2a). As depicted in Fig. 6a, the RE of the whole biofilter decreased showing that the system was not able to face relatively high inlet load peaks in a short period of time. The minimum RE (88%) was attained at inlet concentrations of 260 ppm_v, even if complete RE was again obtained on day 636 and remained around this value most of the time during the HALO period.

Fig. 6b indicates that a non-stable operation was reached throughout variations of the ammonia inlet load with a considerable increase in all nitrogen species. Most significant increases were related to nitrite (162%), and ammonium and FA (125%) while nitrate only increased by a 39%. Also, nitritation and nitratation rates remained relatively constant until day 626 irrespectively of the ammonium increase (Fig. 6c). From day 626, in which the inlet load was stepwise increased to a maximum value of 0.54 kg N-NH_3 m^{-3} d^{-1}, a larger capacity of ammonium and nitrite oxidation was encountered in the reactor. Conversely, the nitratation rate slightly increased in this period, which leaded to a progressive increase of the nitrite concentration in the reactor bed. One would expect that a larger mass of ammonia being transferred from the gas to the liquid phase would cause a pH increase and, consequently, to a reduction in the nitrification rates because of NH_3 accumulation. The opposite behaviour found in the biofilter from day 626 on might indicate that nitrification was more predominant than titration of the ionic species (Chen et al., 2005; Joshi et al., 2000). Thus, a concomitant reduction of FA in the liquid/biofilm phase probably provoked the increase in the nitritation rate and, to a shorter extent, in the nitratation rate, which confirmed again that AOB are notably less affected by FA than NOB.

Results obtained herein suggest that the pH regulation may be the key factor to improve the nitrification rates by reducing the amount of FA and, in consequence, reducing the large ammonium fractions that generally accumulate in biofilters. Operation and long-term stability of biofilters treating high ammonia inlet concentrations seem to be restricted to the application of a continuous watering load, which needs to be optimized, to remove the excess of inhibitory species as well as to maximize the nitrification rates. Additionally, if no enough biological activity is found in the biofilter or FA is already accumulated, as for example during the start-up of the bioreactor, an acidification agent could be an alternative to reduce the possible impact of large amounts of FA. Due to their configuration and controllability, biotrickling filters appear as a better alternative to biofilters when ammonia is the main pollutant to be treated (Sakuma et al., 2008). In any case, the critical ammonia load, pH and watering rate to obtain a minimum recovery of ammonium must be optimized case-by-case in biofilters because of the major impact of the packing material in the reactor performance.

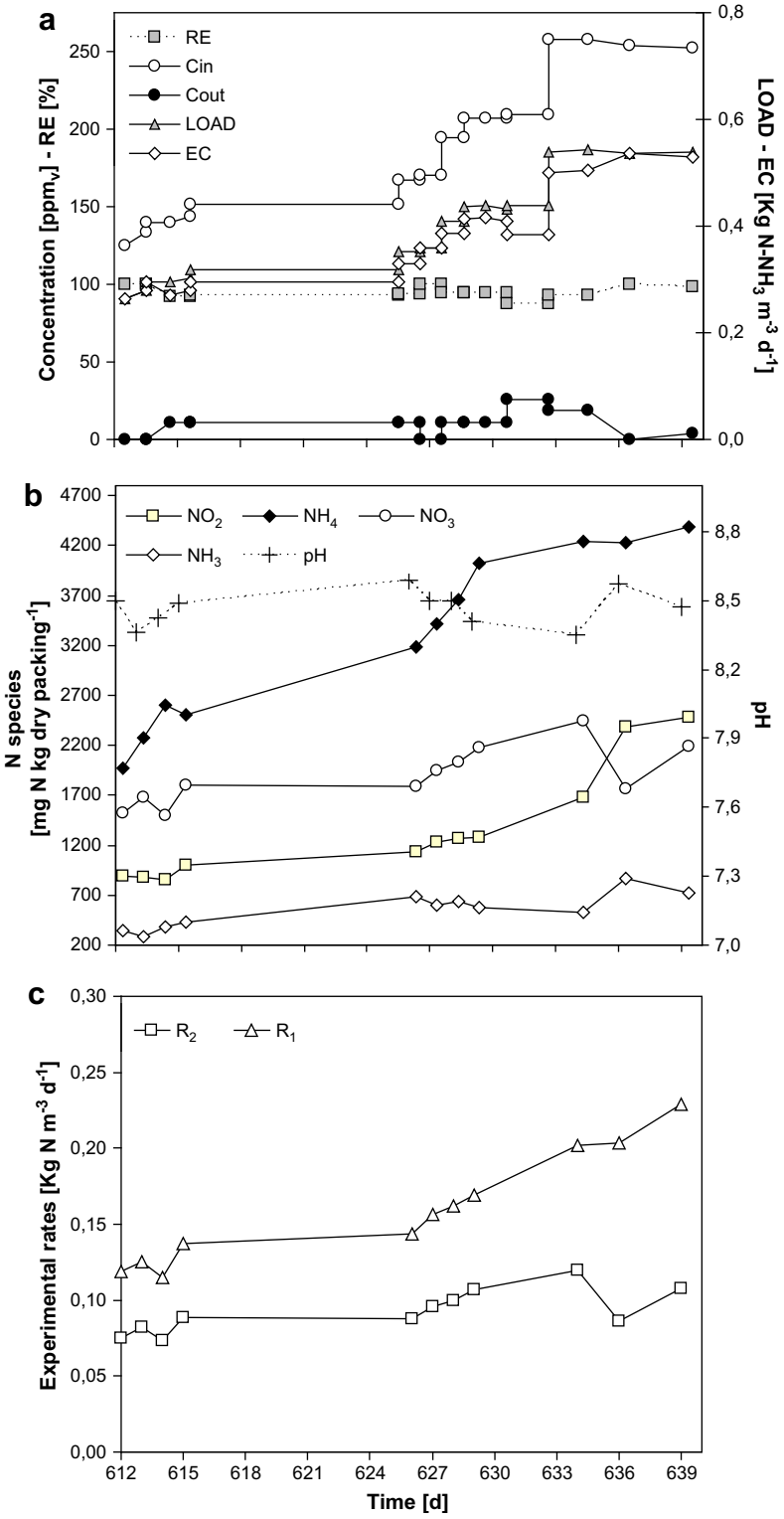

Fig. 6 – Biofilter performance during the last 3 weeks of the transition period: (a) inlet and outlet concentrations of ammonia, inlet load, EC and RE for the overall reactor, (b) concentration of nitrite, nitrate, ammonium and pH in the leachate, and (c) experimental nitritation and nitratation rates.

4. Conclusions

Long-term stable and continuous operation under low and high ammonia loads of a biofilter treating ammonia in waste gases has been presented. Results showed that analyses of the drain are needed to explain the nitrogen cycle and sink of the NH_3 removed from the gas phase since absorption plays a key role on NH_3 removal. Drain analyses revealed that free ammonia was the sole responsible for the accumulation of

high concentrations of ammonium and nitrite in the filter bed affecting the nitratation rate to a larger extent than the nitritation rate. Even if a ratio of 1:1 for ammonium and nitrate was obtained under low ammonia load operating conditions, a 2:1 ratio was found under high ammonia load operating periods. Also, transient operation brought light to other alternatives that may be implemented to improve the performance of biofilters by means of pH regulation. Either optimization of the watering rates or external addition of acidic solutions to the packed bed is warranted to maximize the nitrification potential of the biofilter.

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