

Abatement of ammonia loaded waste gases: biofiltration versus chemical precipitation

► Abstract

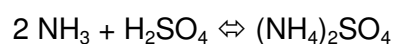
The applicability of two different techniques to control the emission of NH₃-loaded waste gases was studied, being biofiltration and the chemical precipitation as magnesium ammonium phosphate. High removal efficiencies were obtained in a compost biofilter at very high input NH₃-concentrations (up to 550 mg.m⁻³), without toxicity effects. Surprisingly, it was found that only about 50% of the NH₃ removed was nitrified (converted to NO₃⁻), while the other 50% was retained in the biofilter carrier material as NH₄⁺. As a result of this, no acidification of the biofilter carrier material was observed. The long term stability of the compost biofilter, however, was limited due to osmotic effects, caused by the accumulation of the salt ammonium nitrate (NH₄NO₃). The second NH₃-removal technique studied is the absorption of NH₃, followed by its chemical precipitation as magnesium ammonium phosphate (MAP). The influence of different parameters (pH, molar ratio NH₄⁺/Mg²⁺/PO₄³⁻,...) on the efficiency of the precipitation reaction was studied. Next to this, interference caused by other precipitation reactions was investigated. It was shown that, for a NH₄⁺-concentration of 600 mg.l⁻¹ in the scrubbing liquid, removal efficiencies of 97% could be obtained at a molar ratio NH₄⁺/Mg²⁺/ PO₄³⁻ of 1/1.5/1.5 and provided the pH was set and continuously adjusted at a value of 9. Based on these data and the fact that MAP can be used as a slow release fertiliser, the chemical precipitation of NH₄⁺ offers excellent perspectives in regenerating the liquid, obtained by scrubbing NH₃-loaded waste gases.

► Introduction

Agricultural activities, in particular livestock farming, are responsible for 95% of the ammonia emission in Flanders. The emission of waste gases with high concentrations of ammonia is also encountered in different bioindustrial processes, as e.g. rendering and composting plants. The emission of this compound should be minimised because it contributes to acid deposition and soil acidification, and because of odour pollution.

Both biotechnological and physico-chemical techniques can be used to control the emission of ammonia. Among biotechnological waste gas treatment systems, mainly biofilters have been used to control the ammonia and odour emission from bio-industrial sources. Due to the sensitivity of nitrifying micro-organisms, however, biofiltration of waste gases containing high ammonia concentrations (above 40 mg.m⁻³) has been reported to be questionable.

Among the physico-chemical abatement techniques, mainly acid scrubbers have been used to control NH₃- emission, according to e.g.:



Next to H_2SO_4 , also other acids as e.g. H_3PO_4 or HCl can be used. This process, however, also yields an ammonium loaded waste water stream, that has to be treated in a subsequent waste water treatment plant. In the literature about treatment technologies for NH_4^+ -loaded waste water streams, the technology of precipitating ammonium as magnesium ammonium phosphate (MAP) or struvite has been reported (Buchanan et al., 1994; Petlicka, 1998) :



This reaction offers some opportunities to regenerate the liquid phase, obtained by scrubbing ammonia-loaded waste gases. According to Buchanan et al. (1994), MAP-precipitation is strongly pH-dependent, with an optimal pH value of 9. Next to the pH value, the initial ammonium concentration and the molar ratio $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$ were shown to influence the precipitation efficiency (Petlicka, 1988). However, contradictory results have been obtained up to now, so there is still uncertainty about the optimal reaction conditions for MAP precipitation. An important advantage of the MAP-precipitation technique is the potential application of struvite as a slow release fertilizer. The release of nutrients from MAP appears to be enhanced by a biological nitrification mechanism, and occurs at a controlled rate over an extended period of time. It can be used as an additive nutrient to compost, garden soil or dried sewage sludge.

The scope of this work is to discuss the applicability of two different techniques to treat NH_3 -loaded waste gases with regard to both their operational limits and its long-term stability.

► Materials and methods

• Biofilter set-up

The biofilter consisted of a Plexiglass column with an internal diameter of 0.195 m. Gas sampling was possible in the influent and effluent and at a height of 25 and 50 cm of the filled part of the biofilter. At a height of 25 and 50 cm, circular rings with internal diameter 0.135 m and outer diameter 0.195 m were installed in order to minimise preferential air flow along the walls. The air was humidified in a scrubber before adding the volatile compounds and before entering the biofilter. The compost used as a carrier material was not older than 2 months and was produced from source-separated municipal organic waste processed by the so-called double process, i.e. it was treated in an anaerobic thermophilic digester and subsequently subjected to an aerobic treatment. Ammonia was dosed using a cylinder containing the liquified gas, a back pressure regulator and a flow controller.

• MAP experiments

Experiments on MAP-precipitation were done batchwise, using 0.5 l erlenmeyer flasks. Ammonium chloride (NH_4Cl) was used as an ammonium source. Magnesium sulphate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) or magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was used as a magnesium source. Sodium phosphate ($\text{Na}_3\text{PO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) was added as a phosphate source. The molarity of all solutions used was 0.1 N, except in the experiment studying the influence of the molar ratio $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$. Demineralized water was used in all experiments. The pH of the solutions was set by means of NaOH or HCl . The time period used to mix the NH_4^+ , Mg^{2+} and PO_4^{3-} solutions is different and mentioned in 'Results'. The precipitate was filtered from the solution using Ederol-Qual 15 (125 mm) filters, followed by washing the precipitate with about 50 ml of demineralized water.

- **Analysis**

Ammonia in the gas phase was analysed using Gastec detector tubes (3L, 3LA, 3M). These tubes have an accuracy tolerance of 25%. For the MAP experiments, analysis of the $\text{NH}_4^+\text{-N}$ content of the filtrate and the precipitate was performed according to standard methods. Before analysis, the precipitate was air-dried during 24 h. Assuming all nitrogen in the precipitate was in the form of MAP (molecular weight = $245 \text{ g}\cdot\text{mol}^{-1}$), the amount of $\text{NH}_4^+\text{-N}$ analysed in the precipitate was multiplied by a factor 17.5 to calculate the amount of MAP in the precipitate.

► **Results**

BIOFILTRATION OF NH_3

- **Ammonia removal in a compost biofilter**

The biofilter was filled over a height of 0.8 m with fresh compost material ($V = 24 \text{ l}$). The carrier material was previously inoculated by mixing it with 1 l nitrifying culture ($\text{VS } 0.82 \text{ g}\cdot\text{l}^{-1}$), obtained in an enrichment experiment using biowaste compost as the inoculum. The surface loading rate of the filter was $22 \text{ m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, corresponding to a superficial gas residence time t of 131 s. Due to the physico-chemical interaction of NH_3 with the carrier material, no start-up period was observed since complete NH_3 -removal is obtained from day 0 on (Figure 1). A 100% removal efficiency is obtained at a loading rate (LR) of $55 \text{ g NH}_3\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ (NH_3 -concentration $\pm 75 \text{ mg}\cdot\text{m}^{-3}$) (day 0-11) while an average removal efficiency of 94% is obtained at a LR of $140\text{-}225 \text{ g NH}_3\cdot\text{m}^{-3}\cdot\text{d}^{-1}$ (NH_3 -concentration $190\text{-}310 \text{ mg}\cdot\text{m}^{-3}$) (day 11-30). Upon increasing the surface loading rate to $72 \text{ m}^3\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ($t = 40 \text{ s}$) on day 30, the NH_3 -removal efficiency dropped to an average value of 64%. After re-installing the original surface loading rate on day 38, however, the biofilter recovered its original high removal efficiency for a short time (4 days). The NH_3 -removal in the biofilter resulted in a strong increase of both the ammonia and nitrite/nitrate content of the compost, while the pH of the compost material slightly increased (Table 1).

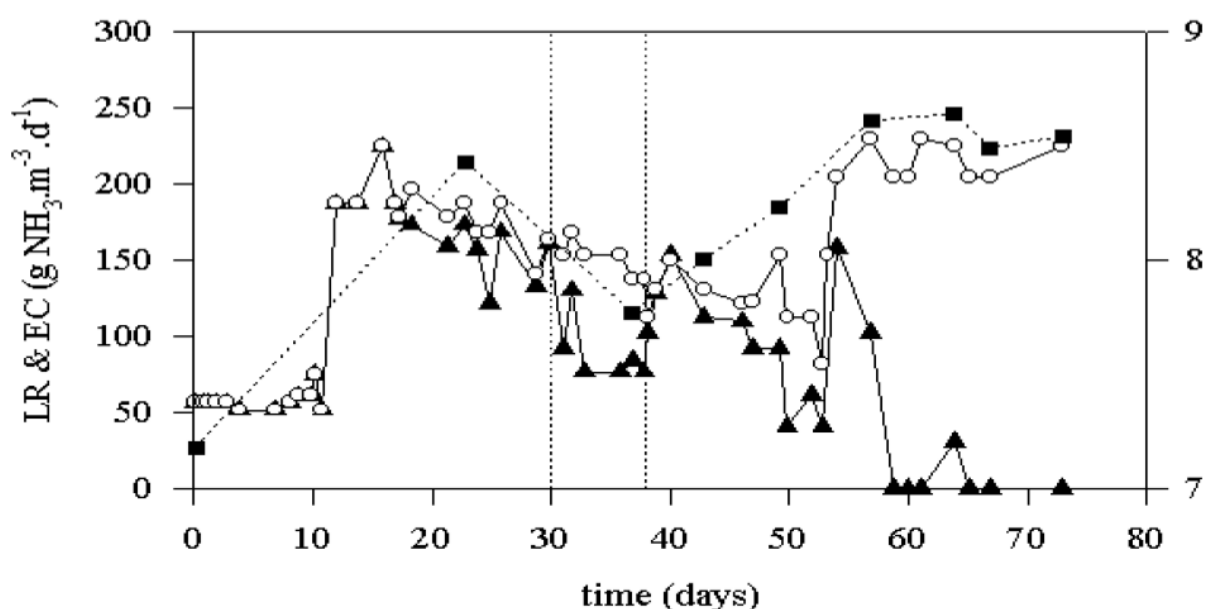


Figure 1. Loading rate (LR) and elimination capacity (EC) ($\text{g NH}_3\cdot\text{m}^{-3}\cdot\text{d}^{-1}$) of the inoculated biofilter as a function of time (days), together with the pH of the carrier material (n). From day 30 to 38 (vertical lines), superficial gas residence time was reduced from 131 s to 40 s.

Table 1. pH, $\text{NH}_4^+\text{-N}$, (NO_2^- and NO_3^-)-N, molar ratio ($\text{NO}_x^-/\text{NH}_4^+$) and moisture content (%) of the carrier material during the biofilter experiment

day	0	42	57	67	73
pH	7.2	8.0	8.6	8.5	8.5
$\text{NH}_4^+\text{-N}$ (g.kg^{-1})	0	2.5	3.3	3.5	3.3
($\text{NO}_2^- + \text{NO}_3^-$)-N (g.kg^{-1})	1.1	3.2	3.5	3.6	3.3
$\text{NO}_x^-/\text{NH}_4^+$ (mol/mol)	---	1.3	1.1	1.0	1.0
moisture content (%)	38	42	37	35	39

From day 42 on, the EC for NH_3 gradually decreased, while the pH of the carrier material increased to a value of 8.5. The temporary slight increase in EC on day 54-56 can be explained by the increased physico-chemical sorption due to the increased influent NH_3 -concentration. From day 58 on, the pH of the compost remained unaffected (pH 8.5) while the NH_3 -removal completely stopped. In accordance with this, no increase in ammonia and nitrite/nitrate content of the compost was observed from day 57 on (Table 1). The cumulative NH_3 -removal over this 73-day experiment was $6550 \text{ g NH}_3.\text{m}^{-3}$ or $9.3 \text{ g NH}_3\text{-N.kg}^{-1}$ compost. The total amount of $\text{NH}_4^+/\text{NO}_2^-/\text{NO}_3^-$ -N that accumulated in the compost material over this period was 5.5 g.kg^{-1} compost (Table 1), corresponding to 59% of the cumulative NH_3 -removal.

When this biofilter experiment was repeated without inoculation of the compost material, a similar result was observed. At an influent concentration of $\pm 550 \text{ mg.m}^{-3}$ NH_3 , very high EC were obtained during the first 18 days. From day 18 on, however, a strong reduction in EC was obtained, while a complete NH_3 breakthrough was observed on day 27. The cumulative NH_3 -removal of the biofilter in this experiment was $5560 \text{ g NH}_3.\text{m}^{-3}$ or $7.9 \text{ g NH}_3\text{-N.kg}^{-1}$ compost.

- **Supplementation of ammonium nitrate to a compost biofilter**

Finally, the biofilter was filled over a height of 0.7 m with fresh compost material ($V = 21 \text{ l}$) and the surface loading rate was $28 \text{ m}^3.\text{m}^{-2}.\text{h}^{-1}$ ($t = 90 \text{ s}$). No inoculation of the fresh compost material was applied. After a 4-day period with 100% NH_3 -removal efficiency, the compost material was mixed with 0.5 l of a 456 g.l^{-1} NH_4NO_3 -solution, corresponding to a nitrogen supplementation of $3 \text{ g NH}_4^+\text{-N.kg}^{-1}$ compost and $3 \text{ g NO}_3^-\text{-N.kg}^{-1}$ compost. The NH_3 -removal in the biofilter strongly dropped from day 4 on and the NH_3 -removal completely stopped on day 10. The cumulative NH_3 -removal over this 10-day experiment was $1175 \text{ g NH}_3.\text{m}^{-3}$ or $1.7 \text{ g NH}_3\text{-N.kg}^{-1}$ compost. The calculated ($\text{NO}_x^- + \text{NH}_4^+$)-N content of the compost material at the end of this experiment is 8 g N.kg^{-1} (sum of NH_3 -removal and NH_4NO_3 -supplementation).

MAP PRECIPITATION

- **Effect of pH on the amount and composition of the precipitate**

The influence of the pH on the precipitation reaction was investigated using a stepwise procedure. First, the pH of the mixture of the three salts was set at a value of 6.0. After a mixing period of 10 minutes, the mixture was filtered and the precipitate was air-dried during a 24-hour period. The filtrate was reused and its pH-value was increased up to a value of 6.5 for a new precipitation reaction. This procedure was repeated and at every step, the pH was increased with 0.5 units up to pH 10. At every pH-value, the extra amount of precipitate formed by the pH increase was determined and the N-content of the precipitate was analysed (Figure 2). The maximum amount of MAP that stoichiometrically could be formed under these conditions was 1.227 g (see horizontal line in Fig. 2). As shown in Figure 2, both the amount of precipitate and the amount of MAP strongly increase at pH values > 6.5 . At all pH values tested, more precipitate than MAP is formed. However, contrary to the precipitate production, the MAP production strongly drops at pH-values exceeding pH 8. At a pH > 8 , more precipitate is formed than the maximum amount of MAP expected on a stoichiometric basis, illustrating the presence

of interfering salts. Next to this, only 0.973 g of MAP is formed at a pH 10, illustrating a maximum NH_4^+ precipitation efficiency of 79% in the system used. When this experiment was repeated replacing the NH_4^+ -solution by demineralized water, precipitate formation was observed at a pH > 8 (Figure 3). The most probable explanation for this is the formation of magnesium phosphate and magnesium hydroxide. When both the NH_4^+ -solution and the PO_4^{3-} -solution were replaced by demineralized water, precipitation of magnesium hydroxide was observed at a pH > 10.5. The formation of these salts must be taken into account as interference during MAP precipitation.

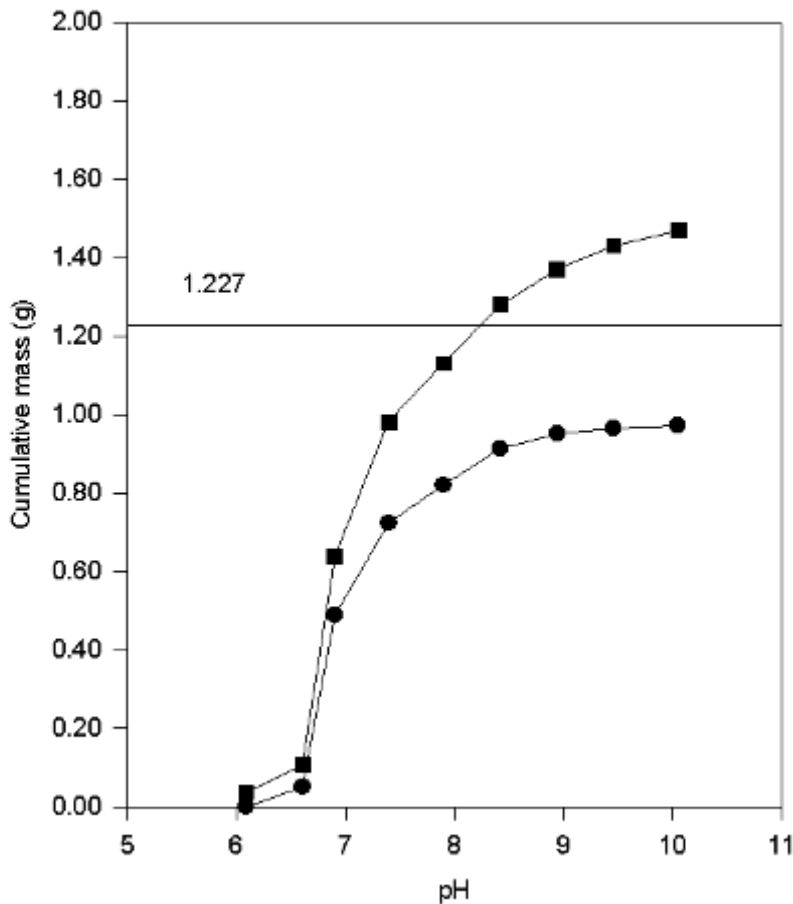


Figure 2. Cumulative weight of precipitate and MAP formed as a function of the pH. The horizontal line represents the maximum amount of MAP that could be formed (1.227 g).

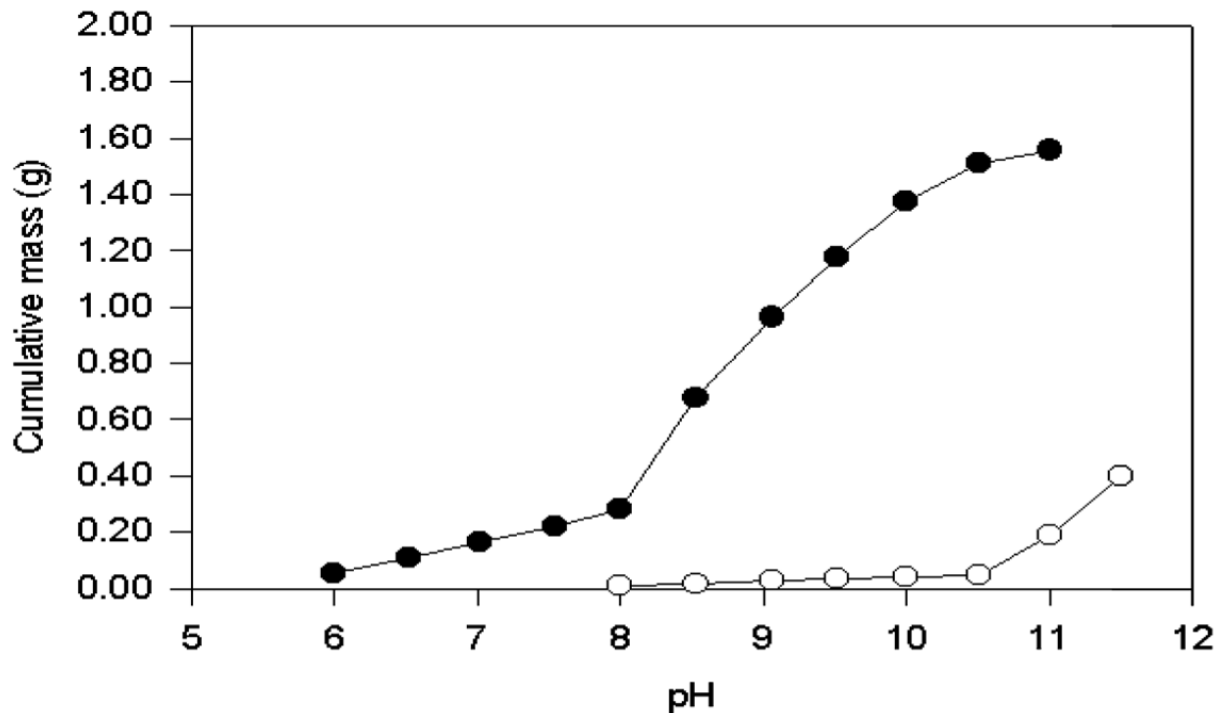


Figure 3. Cumulative weight of precipitate formed by replacing the NH_4^+ -solution by demineralized water and replacing both the NH_4^+ - and PO_4^{3-} -solution by demineralized water at stepwise increasing pH-values

- **Control of the pH during the precipitation reaction**

Upon the precipitation of MAP, a pH-decrease is observed. Also the precipitation of magnesium phosphate will result in the release of protons. Because the amount of MAP formed is limited at low pH values, it was checked whether the MAP precipitation can be increased by continuously controlling the pH at a fixed value during the reaction. Both the mass of MAP formed and the ammonium removal efficiency strongly increased by controlling the pH during the reaction. While only 0.40 g MAP was formed at an initial pH 8.0 using no pH control during the reaction, up to 0.90 g of MAP was formed when the pH was continuously adjusted to 8.0 during the reaction. However, even with pH adjustment, the theoretically maximum amount of MAP (1.227 g) was not obtained at pH 10. By consequence, the precipitation of interfering salts consuming part of the magnesium and phosphate available hinders a maximum MAP precipitation.

- **Influence of the molar ratio $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$**

In this experiment, the influence of the molar ratio $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$ on the precipitation efficiency was investigated. To obtain solutions with different molar ratios $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$, 50 ml of NH_4Cl 0.1N and 50 ml of both $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$ at varying concentrations were mixed (Figure 4). The pH of these solutions was preset at 9.0 and NaOH was added to control the pH during the reaction. In Figure 4, it can be seen that the combination of pH control during the reaction and the addition of Mg^{2+} and PO_4^{3-} in excess to NH_4^+ makes it possible to achieve high ammonium removal efficiencies. A maximum ammonium removal efficiency of 97.2% was obtained by controlling the pH at 9.0 during the reaction and by applying a molar ratio $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$ of 1/1.5/1.5. A small percentage (< 4%) of the added ammonium was not recovered neither in the filtrate, nor in the precipitate. This can probably be explained by analytical losses or volatilization of NH_3 during drying of the precipitate.

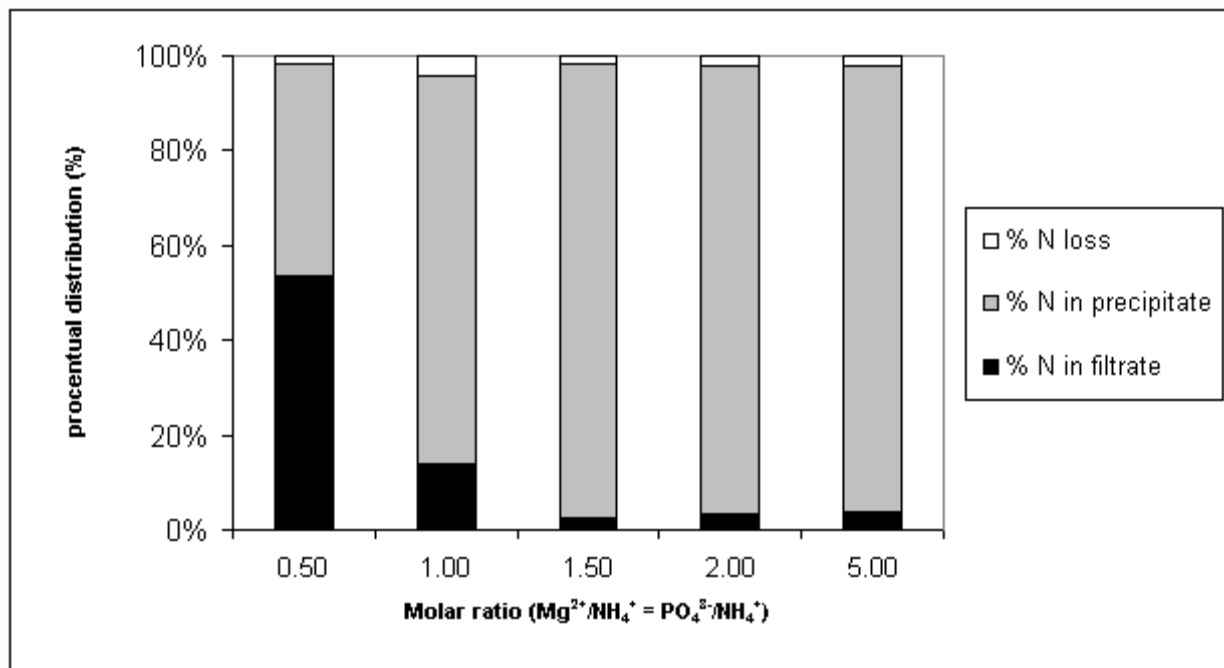


Figure 4. Procentual distribution of added nitrogen over filtrate, precipitate and residual losses at different molar ratios $NH_4^+/Mg^{2+}/PO_4^{3-}$ and at pH 9.0 with pH control

► Discussion

Due to significant physico-chemical retention phenomena of ammonia on the compost carrier material, no startup period was detected during the biofiltration of NH_3 (Figure 1). No effect on the NH_3 -removal in the compost biofilter was observed by inoculating it with a nitrifying culture since high elimination capacities (up to $350 \text{ g } NH_3 \cdot m^{-3} \cdot d^{-1}$) were obtained in both the inoculated and the non-inoculated biofilter. Apparently, the fresh compost material used in this study is already a good inoculum for nitrifying micro-organisms. The EC obtained in the compost biofilters strongly exceeded maximum removal capacities obtained by others using wood bark and peat as a carrier material (Terasawa et al., 1986; Van Langenhove et al., 1988; Weckhuysen et al., 1994). These findings are in accordance with other biofilter experiments performed on ammonia (Don, 1985) and volatile organic sulphur compounds (Smet et al., 1996) and can be explained by the higher nutritional level of compost in comparison with the other materials mentioned. However, high superficial gas residence times ($t > 90 \text{ s}$) were required to obtain high ($> 87\%$) removal efficiencies at a loading rate exceeding $150 \text{ g } NH_3 \cdot m^{-3} \cdot d^{-1}$. Contrary to others (Don, 1985; Hartikainen et al., 1996), no toxicity effect of ammonia was observed on the nitrifying activity of the biofilter, even at NH_3 -concentrations up to $550 \text{ mg} \cdot m^{-3}$. In accordance with Don (1985), analysis of the compost material revealed that only 50% of the NH_3 -input in the biofilter was nitrified, while the other 50% remained in the filter as NH_4^+ (Table 1). As a result of this, a molar NO_x^-/NH_4^+ ratio of ± 1 was observed in the compost material. Due to the equilibrium between microbiological and physico-chemical removal, no acidification of the carrier material is observed (day 0-42: pH 7-8) (Figure 1).

Both in the non-inoculated and the inoculated biofilter, however, a sharp reduction in NH_3 -removal was observed after a cumulative NH_3 -removal of $\pm 6000 \text{ g } NH_3 \cdot m^{-3}$. According to Hunik et al. (1992), no NH_4^+ -inhibition is to be expected for *Nitrosomonas europaea* and *Nitrobacter agilis* in concentrated waste streams, while also NO_2^- - and NO_3^- -inhibition is not to be expected at a pH-value of 8.5. However, osmotic pressure due to high salt concentrations was found to inhibit mainly the activity of *Nitrosomonas europaea* according to (Hunik et al., 1992):

$$\frac{V}{V_{\max}} = 0.994 - 0.00187 \cdot (C_{\text{salt}})$$

with V = activity of *Nitrosomonas europaea*

V_{\max} = maximum activity of *Nitrosomonas europaea*

C_{salt} = salt concentration (mmol salt.l⁻¹)

Upon substitution of the NH_4NO_3 -concentration analysed in the compost material on day 73 ($6.6 \text{ g NH}_4\text{NO}_3\text{-N.kg}^{-1} = 16.9 \text{ g NH}_4\text{NO}_3\text{-N.l}^{-1}$) (Table 1) in this equation, a complete (100%) inhibition in nitrification activity due to osmotic effects is found. This was confirmed by the supplementation of $6 \text{ g NH}_4\text{NO}_3\text{-N.kg}^{-1}$ to the biofilter, resulting in an immediate reduction in NH_3 -removal of the biofilter.

With regard to the MAP precipitation reaction, it was shown in this work that the pH has an influence on both the amount of precipitate formed, the composition of the precipitate and the ammonium removal efficiency. More MAP is formed at higher pH-values. However, at pH-values > 8 , several other precipitation reactions were shown to occur next to the MAP-precipitation. As a result of this, an optimal pH-value of ± 8 was found yielding a good NH_4^+ -removal efficiency and a limited precipitation of interfering salts.

As a result of the MAP precipitation reaction, a pH drop is observed in the liquid phase. It was shown in this work that the efficiency of the MAP formation can be strongly increased by controlling the pH during the reaction. It was also observed that adding Mg^{2+} and PO_4^{3-} in excess to NH_4^+ contributes to an increased MAP precipitation efficiency, although the percentage of MAP in the precipitate decreases at higher excess amounts of magnesium and phosphate. The optimal molar ratio $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$ was found to be 1/1.5/1.5. Upon controlling the pH at a value of 9 during the reaction, an ammonium removal efficiency of 97% was obtained at NH_4^+ -concentrations of 600 mg/l at a molar ratio $\text{NH}_4^+/\text{Mg}^{2+}/\text{PO}_4^{3-}$ of 1/1.5/1.5.

It can be concluded that the MAP process offers perspectives in regenerating the liquid phase, obtained by scrubbing ammonia loaded waste gases. Indeed, according to the low Henry's law coefficient of ammonia ($H_{20^\circ\text{C}} = 5.6 \cdot 10^{-4}$), an efficient transfer of NH_3 from the air to a water phase can be obtained in a scrubbing system. Moreover, the pH-increase of the scrubbing liquid due to the absorption of NH_3 into the water phase will optimise the MAP-precipitation reaction. With regard to the biofiltration of ammonia, it can be concluded that high NH_3 -removal efficiencies can be obtained in compost biofilters, even at input NH_3 -concentrations up to 550 mg.m^{-3} . Due to the accumulation of toxic NH_4NO_3 -concentrations, however, regular renewal of the compost material in the biofilter has to be applied.

► References

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