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Biotrickling filters for the removal of gaseous ammonia emissions from livestock facilities. Theoretical prediction of removal efficiency and experimental validation

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Abstract

From theoretical calculations validated by the results of experiments, it was shown that the properties of the washing liquid that flows into biotrickling filters at livestock facilities determine the maximum ammonia removal efficiency (RE) that can be achieved. For a well-designed biotrickling filter not limited by hydrodynamic conditions, the ammonia driving force is mainly controlled by the pH, and also by the electrical conductivity (EC_L), although to a lesser extent. With the washing liquid at a given temperature, therefore, the removal efficiency depends on the gaseous ammonia concentrations to be treated (C_{Gin} ; usually lower than $20 \text{ mg}_{\text{NH}_3} \text{ m}^{-3}$) and on the values of the pair (pH, EC_L). Theoretical prediction of the maximum removal efficiency that can be achieved by simply measuring the properties of the washing liquid, in line or from samples, could be a useful diagnostic tool to identify possible failure of the apparatus and to manage the electrical conductivity to guarantee removal efficiency at a desired rate.

Keywords

Ammonia; Mass transfer; Biofiltration; Electrical Conductivity; Removal efficiency; Livestock facilities

Highlights

- The theoretical ability of a biotrickling filter to treat NH_3 is proposed
- Theoretical calculations are validated by experimental results
- The removal efficiency depends on the physical properties of the washing liquid
- pH, electrical conductivity and temperature are the main influencing parameters
- Theoretical RE could be used as a diagnostic tool to identify apparatus failure

Introduction

Biotrickling filters can be used to treat gaseous ammonia (NH_3) pollution generated by livestock facilities (pigs or poultry). In practical terms, the polluted air comes into contact with a washing liquid (water), enabling the absorption of ammonia. Both phases flow countercurrently through a plastic packing material to improve the ammonia mass transfer from air to water. In addition, the washing liquid recirculates continuously via a buffer tank containing biomass (Figure 1). Once absorbed by the washing liquid, the ammonia is converted into ammonium ions (NH_4^+). In the presence of biomass, the ammonium ions are oxidized into nitrite ions (NO_2^-) by ammonia-oxidizing bacteria (AOB), then into nitrate ions (NO_3^-) by nitrite-oxidizing bacteria (NOB). As ammonia is highly soluble in water (Table 1), high ammonia removal efficiency (RE) is expected. However, REs of between 10% and 99% are reported in the literature, indicating that biotrickling filter operations are not easy to control [1]. The wide discrepancies between the results reported may have different causes:

- (i) the characteristics of the inlet air which can change over time (daily and seasonal variations), i.e. temperature T_G , flow-rate F_G and ammonia concentration C_{Gin} (F_G and C_{Gin} defining the ammonia loading rate to be treated LR; Table 2);
- (ii) the properties of the washing liquid, i.e. temperature T_L , pH, concentration of nitrogen species ($\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-$) which can be linked to the electrical conductivity EC_L [2], presence of biomass, dust and inhibition elements in the liquid volume V_L (i.e. free NH_3 and free nitrous acid HNO_2);
- (iii) the design of the biotrickling filter, based on:

- the packing material selected to bring the gas and the liquid phases into contact: type of packing material, porosity, specific surface area a , surface S and height L ($S \times L$ being the volume of the packing bed);
- the hydrodynamic conditions via the liquid flow-rate F_L , the spraying system which influences the effective specific contact area between gas and liquid, a^0 .

These causes are discussed below. In practical terms, the maximum air flow-rate and the ammonia concentration (which depend on rearing conditions, temperature and number and type of animals at the livestock farm [3]) are the input data for the design of the biotrickling filter. It should also be noted that the design of the biotrickling filters used at livestock operations can differ significantly from the design of the absorption devices developed for chemical engineering applications in which the washing liquid does not recirculate. As a result, the simpler approach described below is usually considered. A packing material and gas velocity U_G in the device are selected first. From the maximum air flow-rate to be treated $F_{G,max}$, the surface S of the packing material is easily deduced ($S = F_{G,max}/U_G$). The height of the packing material is then arbitrarily chosen depending on the height of the packing material elements provided by manufacturers (usually, a multiple of 0.30 m or 0.45 m) and a spraying liquid flow-rate per unit of surface area (i.e. trickling density) is also chosen (e.g. $1 \text{ m}^3 \text{ h}^{-1}$ per unit surface of packing material, or more). Basically, it can be demonstrated that the total liquid flow-rate in the biotrickling filter is relatively small compared to the liquid flow-rate calculated from rigorous mass balance based on gas/liquid equilibrium, according to chemical engineering principles, even if the air flow-rate to actually be treated is far from the maximum air flow-rate used for the design. As a result, mass ratios F_L/F_G in the biotrickling filters used at livestock operations are usually small with regard to the mass ratios calculated for chemical engineering absorbers. For a given gas velocity in the biotrickling filter, the contact time between the gas and liquid phases is all the more important if the packing bed is high. This contact time, arbitrarily called EBRT (Empty Bed Residence Time; Table 1) must be long enough to promote good NH_3 mass transfer between phases. Note that determination of EBRT implies that the space occupied by the packing material is fully empty, which is not true. Nonetheless, the porosity of modern packing material is usually very high (around 96%) and consequently the actual contact time between phases is close to EBRT. The specific surface area a of the packing material, which corresponds to the ratio between the

developed surface and the volume of the packing material, is also an important parameter to take into account for mass transfer. However, this parameter must be distinguished from the interfacial area a^0 , which corresponds to the actual contact surface between the gas and liquid phases in relation to the packed volume. Thus the interfacial area a^0 can be lower than the specific surface area a if the liquid flow-rate (trickling density) is not high enough in relation to the gas flow-rate (i.e. for low values of mass ratio F_L/F_G), or if the phase flows are not well distributed in the packing material (the spraying system is therefore an important element to be considered). The volume of the washing liquid contained in the buffer tank, usually located under the packing material, depends on the surface of the packing material S and an arbitrary selected height. A large volume of washing liquid is required to limit the frequency of water renewal. Finally, the pressure drops ΔP in the biotrickling filters may be uneven depending on the type and height of the packing material selected and the flow-rates through the packed bed. Low pressure drops are required to limit the wearing of fans and pumps and reduce electricity costs. From this general description of biotrickling filter design, it can be considered that many parameters can significantly influence the operation of the apparatus and cause changes in ammonia removal efficiency.

Assuming, then, that all biotrickling filters are initially well-designed to treat the nominal pollution efficiently, it must be concluded that the wide discrepancies in RE values reported in the literature are due to the properties of the washing liquid. A drop in RE is necessarily linked to a drop in ammonia mass transfer rate (ϕ in $\text{kg}_{\text{NH}_3} \text{m}^{-3} \text{s}^{-1}$) represented by the equation:

$$\phi = K_L a^0 (C_L^* - C_L) = K_L a^0 \left(\frac{C_G}{H} - C_L \right) \quad (1)$$

in which the equilibrium between gas and liquid at the interface is defined as $C_L^* = C_G/H$, C_G is the ammonia concentration of the air ($\text{kg}_{\text{NH}_3} \text{m}^{-3}$), H is the dimensionless Henry's law constant (Table 1), C_L is the free ammonia concentration in the washing liquid ($\text{kg}_{\text{NH}_3} \text{m}^{-3}$) and $K_L a^0$ is the overall mass transfer coefficient (s^{-1}), depending mainly on the hydrodynamics of the biotrickling filter, i.e. on the design of the apparatus, and on biomass development on the packing material. Although slow changes in $K_L a^0$ can occur over time due to biomass development, the mass transfer rate is dependent mainly on the term $(C_L^* - C_L) = (C_G/H - C_L)$, known as the concentration gradient or driving force. In other words, for a well-designed biotrickling filter, the mass transfer rate is dictated by the ammonia thermodynamic equilibrium between the air and the

washing liquid. Since NH_3 concentration in the gas phase is an input parameter, which cannot be controlled, the mass transfer rate is therefore largely dependent on the ammonia concentration in the washing liquid. Surprisingly, few studies focus on the mass transfer limitation of biotrickling filters treating ammonia emissions. Ottosen et al. [4] suggest that minimum ammonia concentration at the outlet is controlled by concentrations of ammonia, nitrite and nitrate ions in the washing liquid, but this idea is not investigated further by the authors. Melse et al. [2] explored a possible mass transfer limitation due to the ammonia equilibrium between phases. They verified that the ammonia concentration measured at the outlet is in agreement with the estimated theoretical value. However, the theoretical approach is not developed. Blasquez et al. [5] investigated the limits and capacities of ammonia removal using biotrickling filtration. However, the inlet NH_3 concentrations considered in this study (from 100 to 1400 ppmv) and the EBRT (from 2.1 to 45.7 s), were so much higher than the concentration and EBRT values found in biotrickling filters operating at livestock facilities that it is not possible to benefit from the conclusions of this study. A mechanistic model of ammonia removal in a countercurrent biotrickling filter was recently proposed by [6] to study the effect of the pH and nitrogen components in the washing liquid on the driving force. To date, this work represents the most comprehensive study on the influence of these parameters on driving force limitation. The main conclusion is that an on/off pH control system could be considered where the pH is above 7.5. However, although the authors recognized the importance of the two parameters (pH and EC_L) for removal efficiency, they did not propose a mathematical formulation.

The objective of this study is therefore to demonstrate that, for a well-designed biotrickling filter with no mass transfer limitation for hydrodynamic reasons, the pH and electrical conductivity of the washing liquid determine the ability of the biotrickling filter to remove ammonia. Theoretical calculations validated by the results of experiments are developed for this purpose. Good practices for use are then proposed.

Table 1. Henry's law solubility constants at 298.15 K [7]

Substance	$H = C_{\text{Gas}}/C_{\text{Liquid}}$ (dimensionless)
Ammonia (NH ₃)	$6.84 \cdot 10^{-4}$
Nitrogen (N ₂)	63.1
Nitrous oxide (N ₂ O)	1.68
Nitric oxide (NO)	21.2
Nitrogen dioxide (NO ₂)	2.88
Nitrogen trioxide (NO ₃)	1.06
Nitrous acid (HNO ₂)	$8.41 \cdot 10^{-4}$
Nitric acid (HNO ₃)	$1.92 \cdot 10^{-7}$

Table 2. Operational parameters used in biotrickling filtration

Loading Rate	$LR = \frac{F_G}{S L} C_{Gin}$	$\text{g}_{\text{NH}_3} \text{h}^{-1} \text{m}^{-3} \text{ packing material}$
Removal Capacity	$RC = \frac{F_G}{S L} (C_{Gin} - C_{Gout})$	$\text{g}_{\text{NH}_3} \text{h}^{-1} \text{m}^{-3} \text{ packing material}$
Removal Efficiency	$RE = 100 \frac{(C_{Gin} - C_{Gout})}{C_{Gin}}$	%
Empty Bed Residence Time	$EBRT = \frac{S L}{F_G}$	s
Gas velocity	$U_G = \frac{F_G}{S} = \frac{L}{EBRT}$	m s^{-1}

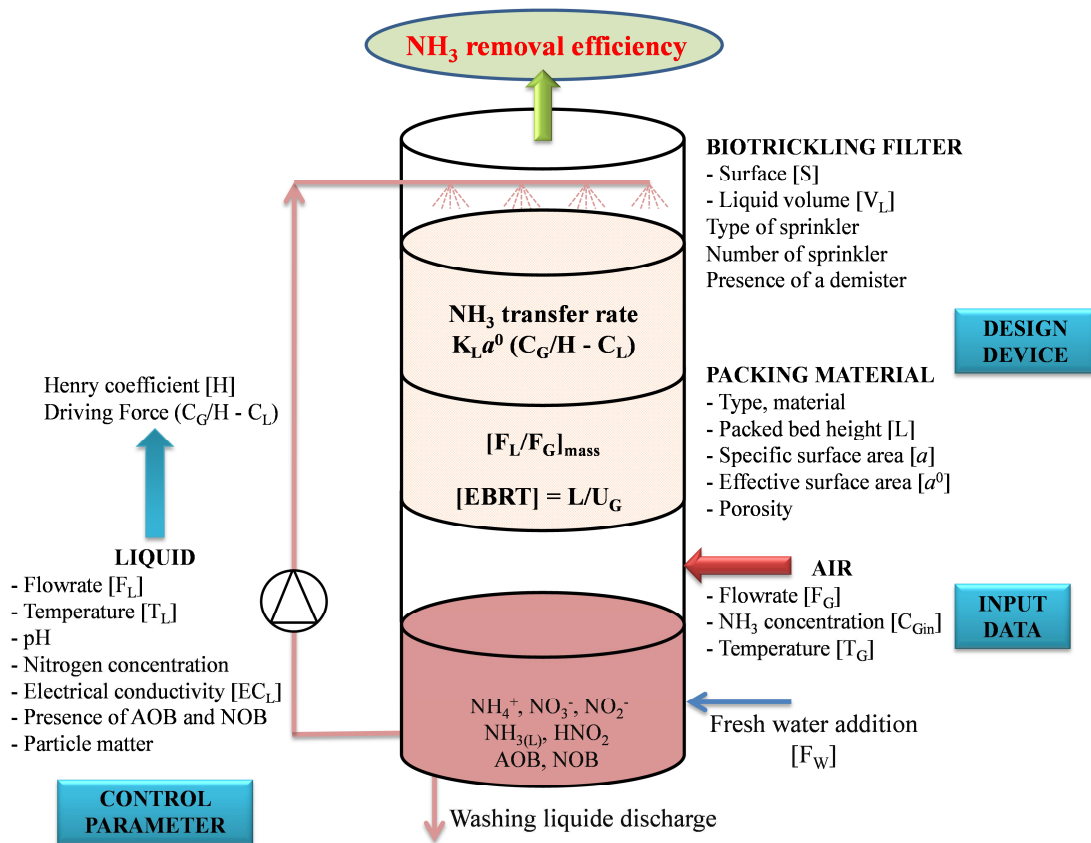
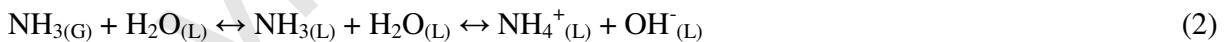


Figure 1 Schematic sketch of biotrickling filter used at livestock operations

2. Theoretical consideration

Once transferred into the washing liquid, NH_3 is ionized into ammonium ion (NH_4^+) by the following reaction, which consequently leads to an increase in the pH of the water (OH^- production):



The chemical equilibrium between ammonium and free ammonia ($\text{NH}_{3(\text{L})}$) in the liquid depends on the pH and acid dissociation constant (pK_a). The proportion of free ammonia in the liquid is represented by the following equation [8]:

$$\frac{\text{NH}_{3(\text{L})}}{\text{NH}_{3(\text{L})} + \text{NH}_4^+} = \frac{10^{-\text{pK}_a}}{10^{-\text{pH}} + 10^{-\text{pK}_a}} \quad (3)$$

Hence, the proportion of ammonia in the water, close to 0 at $\text{pH} = 6.5$, increases with pH to 0.2% at $\text{pH} = 7$, 2.3% at $\text{pH} = 8$ and 18.9% at $\text{pH} = 9$ ($T = 15^\circ\text{C}$; Figure 2). The increase is more

pronounced for higher water temperatures. As a result, an increase in the pH and ammonium concentration in the water thermodynamically leads to a decrease in the ammonia driving force between the gas and liquid phases. Without biomass, it was observed that the ammonia mass transfer between phases dropped rapidly due to a pH increase (not shown).

In aerobic conditions and in the presence of biomass, ammonium ions are oxidized into nitrite ions then nitrate ions according to these reactions (nitrification process):



The nitrification process requires chemolithoautotrophic bacteria with the ability to use ammonium (ammonia-oxidizing bacteria, AOB) or nitrite (nitrite-oxidizing bacteria, NOB) as the only energy source and CO_2 to satisfy the carbon requirement. According to Eq (4), two protons H^+ are then formed, leading to a decrease in the pH of the washing liquid. Since NH_4^+ is the only cation available to balance the produced anions ($\text{NO}_2^- + \text{NO}_3^-$), only half of the ammonia absorbed in the washing liquid is oxidized while the other half remains dissolved as ammonium [4]. Consequently, the amount of H^+ formed counter-balances the amount of OH^- formed due to ammonia ionization, and a pH equilibrium is consequently achieved. Thus, the pH equilibrium values for experiments reported in the literature are usually around neutral (between 6.7 ± 0.2 and 7.6 ± 0.2) [3,9,10]. This range of pH values is favorable for the growth of microorganisms [4].

As illustrated in Figure 3, nitrous oxide (N_2O) can also potentially be formed during the nitrification process, either via the oxidation of hydroxylamine (NH_2OH) or the reduction of NO_2^- [11]. Additionally, N_2 and NO_x can potentially be produced, but none of these nitrogen species (N_2O , NO_x and N_2) dissolve easily in water and are consequently emitted into the air. Ammonium and nitrite and nitrate ions are therefore the main ionic species dissolved in the washing liquid. As the washing liquid is continuously recirculating in the biotrickling filter, the concentrations of NH_4^+ , NO_2^- and NO_3^- increase constantly over time, which is easily evidenced by periodic measurement of the electrical conductivity of the water (EC_L). However, the accumulation of ammonium ions in the washing liquid, i.e. the accumulation of free ammonia, progressively hinders the ammonia mass transfer and some of the liquid has to be replaced regularly to maintain the performance of the apparatus. In biotrickling filters installed at pig or poultry

facilities, the correlation between ionic nitrogen concentration (in $\text{g}_\text{N} \text{L}^{-1}$) and electrical conductivity (in mS cm^{-1}) is represented by the following equation, in which $\beta = 0.22$ according to [2,12]:

$$\Sigma(\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-) = \beta \text{EC}_\text{L} \quad (6)$$

$$\text{NH}_4^+ = \beta/2 \text{EC}_\text{L} \quad (7)$$

Combining Eq (3) and Eq (7), it can be deduced that:

$$\text{NH}_{3(\text{L})} = \text{NH}_4^+ 10^{(-\text{pK}_\text{a}+\text{pH})} = \beta/2 \text{EC}_\text{L} 10^{(-\text{pK}_\text{a}+\text{pH})} \quad (8)$$

As a result, at a given washing liquid temperature, the ammonia driving force is controlled directly by the electrical conductivity and pH. It can therefore be calculated that the driving force becomes nil for the following expression of gaseous ammonia concentration in the biotrickling filter (corresponding to $C_{\text{Gout}}/\text{H} = C_{\text{L}} = \text{NH}_{3(\text{L})}$) with C_{Gout} in $\text{mg}_{\text{NH}_3} \text{m}^{-3}$:

$$C_{\text{Gout}} = \frac{17}{14} 10^6 \text{H} \frac{\beta}{2} \text{EC}_\text{L} 10^{(-\text{pK}_\text{a}+\text{pH})} \quad (9)$$

Given that $\text{RE} = 100 (C_{\text{Gin}} - C_{\text{Gout}})/C_{\text{Gin}}$, the maximum RE value that can be achieved according to the gaseous ammonia concentration to be treated is (for $C_{\text{Gin}} \geq C_{\text{Gout}}$ in $\text{mg}_{\text{NH}_3} \text{m}^{-3}$):

$$\text{RE} = 100 \left(1 - \frac{17}{14} 10^6 \frac{\text{H} \beta \text{EC}_\text{L} 10^{(-\text{pK}_\text{a}+\text{pH})}}{2 C_{\text{Gin}}} \right) \quad (10)$$

Bear in mind that this value, controlled by the thermodynamic conditions, corresponds to the maximum attainable value for a well-designed biotrickling filter, i.e. for an apparatus not limited by hydrodynamic conditions. In case of mass transfer limitation by hydrodynamic conditions, the RE could not achieve the values given in Eq (10).

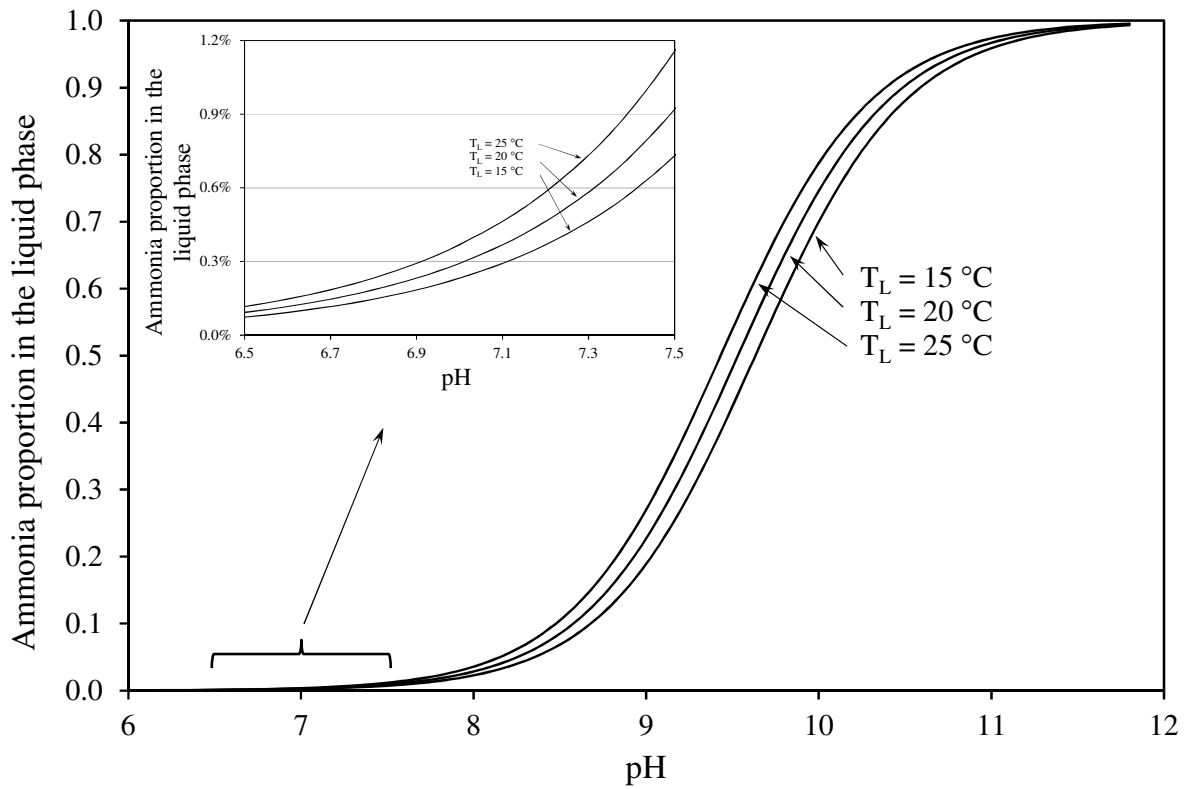


Figure 2 Proportion of ammonia in water according to pH value ($pK_a = -\log_{10}(1.1630 \cdot 10^{-10} \exp(0.0463 T))$; T_L in $^{\circ}\text{C}$; [8]).

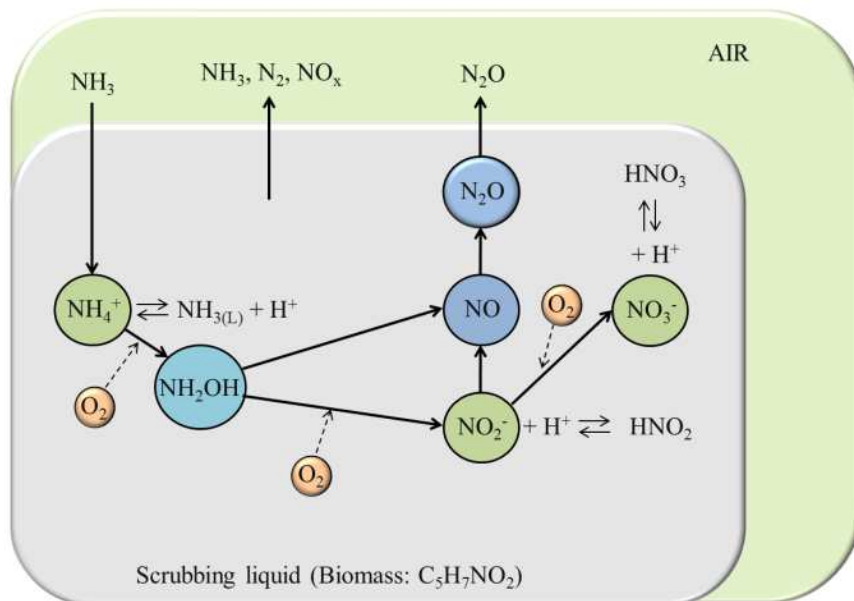


Figure 3 Nitrification process in aerobic condition

The theoretical mutual influence of the electrical conductivity and pH of the washing liquid on the minimum possible value of ammonia gaseous concentration that can be achieved at the outlet of the biotrickling filter is reported in Figure 4. It can be observed that C_{Gout} is mainly influenced by the pH (power-law change), and to a lesser extent by EC_L (linear change). These changes in C_{Gout} directly impact removal efficiency, as highlighted in Figure 5 for 3 C_{Gin} values (10 and 20 $mg_{NH_3} m^{-3}$ respectively, in accordance with NH_3 concentrations that usually have to be treated by biotrickling filters at livestock facilities). The theory postulates, therefore, that with $pH > 7.2$, an RE higher than 70% can only be achieved for low EC_L values (for instance $< 20 mS cm^{-1}$ if $C_{Gin} = 20 mg_{NH_3} m^{-3}$). In other words, with high EC_L values, the biotrickling filter is only efficient under acidic conditions.

Although pH and EC_L are the main influencing parameters, the dependence of RE on pKa and H values must be assessed. The pKa is mainly influenced by temperature ($pK_a = -\log_{10}(1.1630 \cdot 10^{10} \exp(0.0463 T))$; T in °C [8]) while the Henry coefficient can be influenced by both the temperature and the ionic strength of the washing liquid (i.e. EC_L influence). For pure aqueous solutions at atmospheric pressure, it is well known that the Henry coefficient is mainly influenced by temperature. The equation used in this paper (provided by [13]) is therefore $H = 12.19 / (T \exp[-8.09694 + 3917.507/T - 0.00314 T])$ (T in Kelvin). As observed in Figure 4 and Figure 5, a small change in the temperature of the washing liquid (e.g. from 17° to 19°C, i.e. $18^\circ \pm 1^\circ C$, which consequently modifies the pKa and H values concomitantly), has a definite influence on the theoretical values of C_{Gout} and RE. However, this moderate influence does not alter the overall evolution of the RE. In addition, the influence is less pronounced at higher RE values than at lower RE values. Nonetheless, the precise temperature of the washing liquid must be known to avoid bias in the calculation of RE.

It is also important to determine whether the presence of dissolved nitrogen ions as well as the presence of biomass in the water has a significant or marginal influence on the H value compared to that of the temperature. Basically, the presence of salts in the water may increase (salting-in) or decrease (salting-out) the solubility of compounds. In practical terms, it would be useful to have information on the change in Henry coefficient as a function of EC_L . A large amount of literature exists which describes the solubility of ammonia in various electrolytes in terms of the Pitzer thermodynamic model [14–16]. However, the ionic composition of the solution must be known in

order to predict the Henry coefficient. Thus, Clegg & Brimblecombe [13] studied the solubility of ammonia in pure aqueous and multicomponent solutions to assess the influence of different ions, using partial pressure, salt solubility and NH_3 partitioning data. According to these authors, the presence of NH_4^+ and NO_3^- in water has a very slight influence on NH_3 partial pressure. Another interesting finding was reported by Lang et al. [17] who studied the solubility of ammonia at 37°C and low ammonia partial pressure (0.02-1 mmHg) in pure water, in aqueous isotonic salt solutions (0.155 M; NH_4Cl + NaCl solution; HCl + NaCl solution; pure weak acid + NaCl solutions) and in human plasma. The solubility of ammonia was $46.7 \pm 0.4 \text{ mM mmHg}^{-1}$ in pure water (the average of three different methods), $46.8 \pm 0.8 \text{ mM mmHg}^{-1}$ in aqueous isotonic salt solutions and $42.0 \pm 0.7 \text{ mM mmHg}^{-1}$ in human plasma. As a result, this study allowed the possible salting-in effect due to the presence of proteins in plasma to be separated from the presence of ions. The presence of ions has therefore no influence on ammonia solubility, whereas the presence of proteins leads to a 10% decrease. Consequently these results suggest, in a first approach, that the accumulation of ammonium, nitrite ions and nitrate ions in the washing liquid (as well as the presence of other secondary elements such as SO_4^{2-} , Ca^{2+} , Mg^{2+} , Cl^- , CO_3^{2-} , HCO_3^- , etc. naturally present in fresh water, depending on the ground water) have only a limited impact on the Henry coefficient. However, based on results obtained with human plasma, the presence of biomass could have a negative influence but in the same order of magnitude as that for the change in liquid temperature of $\pm 1^\circ\text{C}$.

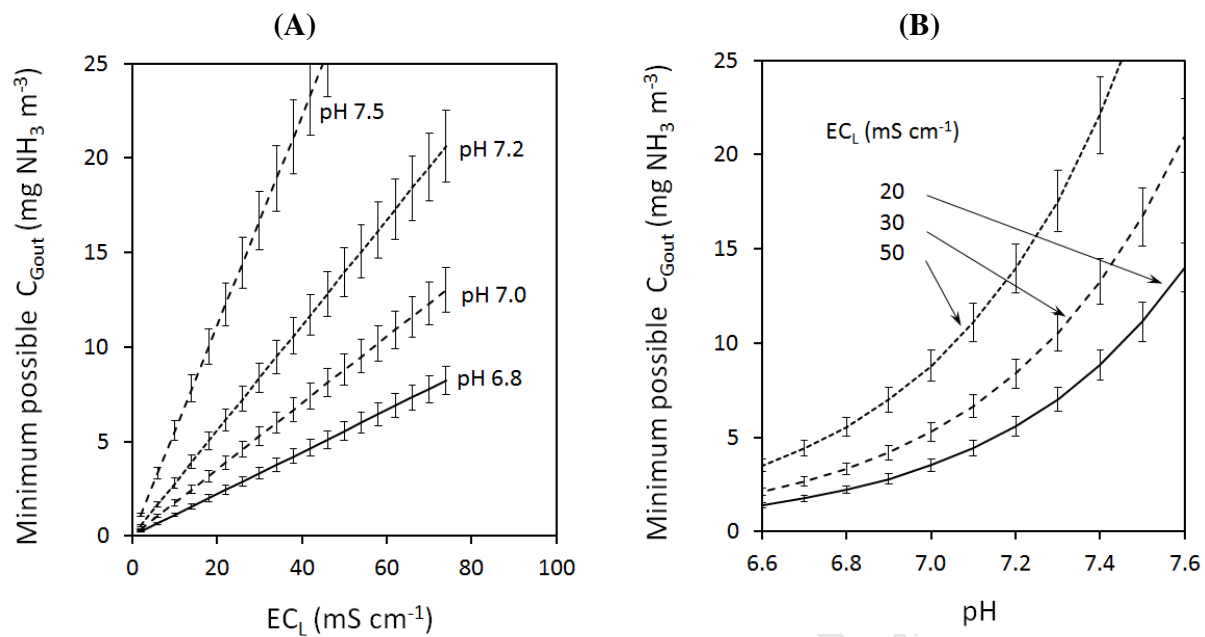


Figure 4 Theoretical influence of electrical conductivity of washing liquid and pH on the minimum value of ammonia gaseous concentration that can be obtained at the outlet of the biotrickling filter (temperature of washing liquid: 18°C). Error bars: influence of the change in the temperature of the washing liquid (from 17°C to 19°C , i.e. $18 \pm 1^\circ\text{C}$) on pKa and H calculations, simultaneously.

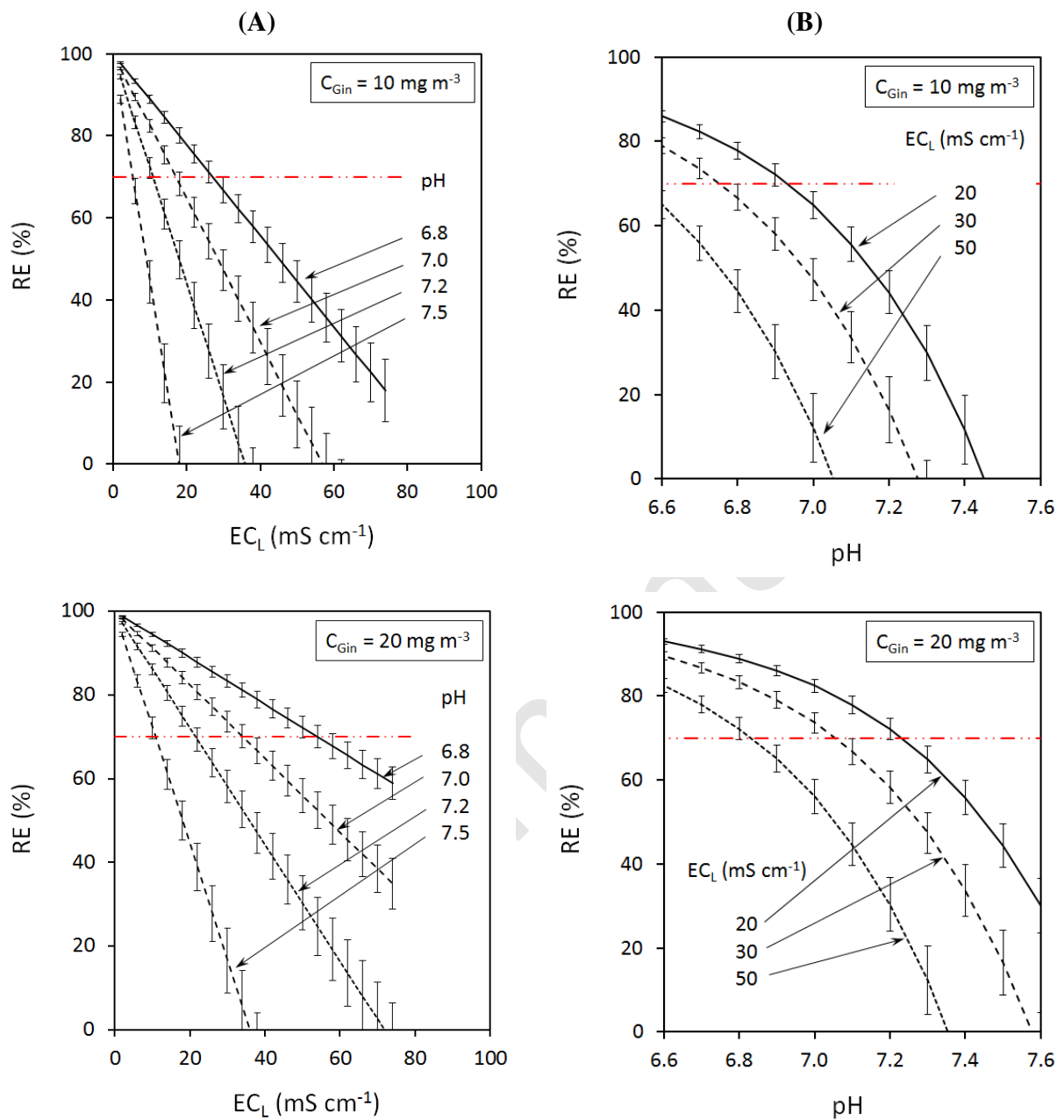


Figure 5 Ammonia removal efficiencies that can be reached (theoretical values) according to (A) the electrical conductivity of the washing liquid and (B) the pH (temperature of the washing liquid: 18 °C). Error bars: influence of the change in the temperature of the washing liquid (from 17°C to 19°C, i.e. $18 \pm 1^\circ C$) on pKa and H calculations, simultaneously.

3. Material and methods

The experiments were carried out continuously for 48 days (January - March 2020) using a pilot-scale biotrickling filter (

Figure 6) consisting of a cylindrical plastic column (0.305 m inlet diameter) filled with a channel-structured polypropylene packing material (WAT NET 150 NC 20/48 purchased from WaluTech, Germany; specific surface area: $125 \text{ m}^2 \text{ m}^{-3}$; packing height: 1.15 m; packing volume: 0.084 m^3). Synthetic polluted air was obtained by mixing clean air flow from a centrifugal air fan (VCP HP 75 Europe Environment, France) with pure ammonia gas flow from an NH_3 storage tank. The pure ammonia gas flow-rate was controlled by a mass flow meter (Bronkhorst, Netherlands). The inlet ammonia concentration was kept constant at 15 ppm (i.e. $C_{\text{Gin}} = 10.5 \text{ mg m}^{-3}$) throughout the experiment. To avoid mass transfer limitation due to hydrodynamic conditions, the polluted air flow-rate entering the biotrickling filter was fixed at $112 \text{ m}^3 \text{ h}^{-1}$ (EBRT = 2.7 s; gas velocity 0.43 m s^{-1} ; NH_3 loading rate: $14 \text{ g m}^{-3} \text{ packing material h}^{-1}$; Table 2) and the washing liquid flow-rate was fixed at $0.16 \text{ m}^3 \text{ h}^{-1}$ (washing liquid density: $2.2 \text{ m}^3 \text{ h}^{-1} \text{ m}^{-2} \text{ packing material}$; ammonia absorption factor $F_L/(F_G H)$: 3.0). The washing liquid was stored in a closed tank (volume 100 L; washing liquid volume: 80 L) and continuously recirculated in the biotrickling filter using a centrifugal pump (SERMES, Netherlands). Due to possible evaporation of the washing liquid in the biotrickling filter, the addition of tap water was regulated and monitored to maintain the washing liquid at a constant level in the storage tank. The washing liquid was inoculated at the beginning of the experiment with 10 L of activated sludge from a wastewater treatment plant (Nantes, France). The temperature and pH of the washing liquid were not controlled during the experiment and no nutritive solution was added.

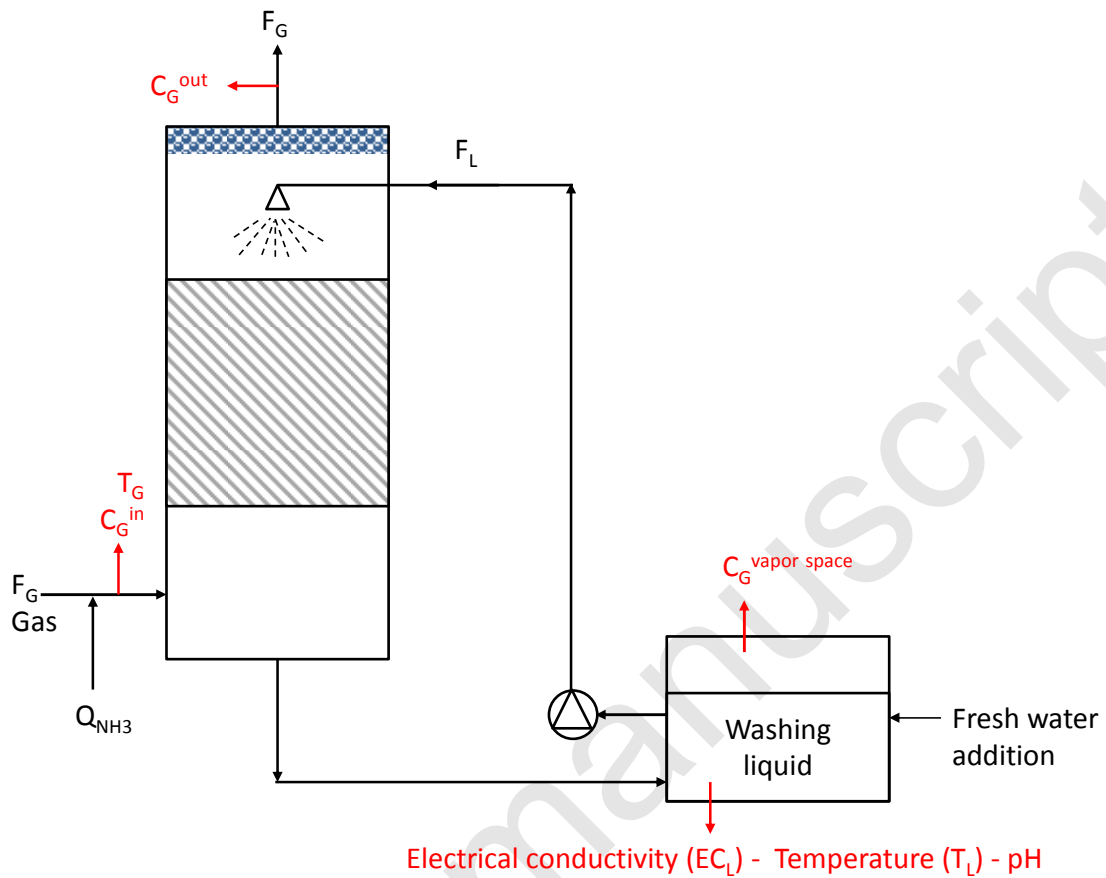


Figure 6 Schematic sketch of the biotrickling filter

During the experiments, the parameters (i) temperature and (ii) NH_3 concentrations were measured daily in the gas phase at the inlet and outlet of the biotrickling filter and in the vapor space of the water storage tank. Gaseous concentrations were measured by a Fourier Transform InfraRed (FTIR) gas analyzer (GasetTM DX-4030, Environment SA). For the washing liquid, the parameters (i) temperature, (ii) pH and (iii) electrical conductivity (EC_L) were also measured daily. EC_L and pH were measured using a multi-channel analyzer consort C834 (Consort bvba, Turnhout, Belgium) with temperature correction. From the electrical conductivity, the concentrations of NH_4^+ were deduced using Eq (7) and the concentration of $\text{NH}_{3(L)}$ in the washing liquid was calculated according to pH and temperature values using Eq (8). The pK_a and Henry coefficient of the ammonia were calculated from the equations given in Section 2.

4. Results and discussion

4.1. Theory validation

The row results obtained are shown in Figure 7. Two phases can be distinguished according to the pH value. The first phase corresponds to the acclimation period of the biomass. At the beginning of the experiment, the pH of the washing liquid was constant for 15 days (at around 9) indicating that the biomass introduced into the water tank was not able to oxidize ammonium ions into nitrite ions. A significant drop in pH was then observed, confirming that the nitrification process had started in the biotrickling filter ($\text{NH}_4^+ + \frac{3}{2}\text{O}_2 \rightarrow \text{NO}_2^- + 2\text{H}^+ + \text{H}_2\text{O}$). The acclimation period can be considered as ending at day 22. From days 22 to 48, i.e. the second phase corresponding to the operating period with acclimated biomass, the pH remained roughly constant between 7.0 and 7.4. It is interesting to note that for the first 15 days of the acclimation period, the ammonia removal efficiency calculated from NH_3 concentrations at the inlet and outlet of the biotrickling filter was around 10-20%, which may seem high considering the pH values. The ammonia measurements carried out in the vapor space of the water tank may explain this; as observed in Figure 7, significant values for ammonia concentration in the vapor space of the water tank were recorded, indicating that some of the NH_3 entering the biotrickling filter was transferred to the washing liquid in the packing material but was re-emitted into the atmosphere via the water tank. Only a fraction of the ammonia was therefore actually converted into ammonium ions, as confirmed by the small increase in the electrical conductivity of the washing liquid. In other words, the actual ability of the biotrickling filter to remove ammonia was appreciably lower than the RE values calculated. Between day 15 and day 22, the ammonia concentration in the vapor space of the water tank pH dropped close to zero in relation to the drop in pH and the biomass activity. As a result, it can be reasonably concluded that the ammonia transferred from the gas phase was largely accumulated in the washing liquid under different nitrogen forms, and only a small amount of NH_3 was re-emitted to the atmosphere.

Once the biomass had acclimated, high removal efficiency values were recorded for some days (up to 85%) but a decrease was observed from day 29. At the end of the experiment, the RE dropped to 20%. The drop in RE due to the increase in ammonia concentration at the biotrickling filter outlet (since the inlet concentration was set at a constant value) was concomitant with the increase in electrical conductivity of the water, i.e. the accumulation of nitrogen ions in the washing liquid. According to the theory set out in section 2, a linear increase in C_{Gout} with EC_{L} ,

and consequently a linear decrease in RE with EC_L , were expected (Figure 4A and Figure 5A, respectively). From Figure 8, showing that a linear trend exists between C_{Gout} and EC_L for $EC_L > 12 \text{ mS cm}^{-1}$, it can be concluded that the theory is clearly confirmed (it can be reasonably assumed that the mass transfer coefficient $K_L a^0$ remained constant throughout the short time of the experiment). Nonetheless, for EC_L values between 6 and 12 mS cm^{-1} (i.e. between day 22 and day 29), the C_{Gout} remained at a constant minimum value of $1.7 \text{ mg}_{\text{NH}_3} \text{ m}^{-3}$, whereas lower values were expected. In this case, the mass transfer limitation could be also due to hydrodynamic conditions occurring in the biotrickling filter. However, the results in Figure 9 clearly demonstrate that the ammonia mass transfer was also limited by the thermodynamic conditions for this range of EC_L values. According to this figure, showing the experimental RE values and theoretical RE values (Eq 10) calculated from the temperature and the pH of the washing liquid recorded each day and the C_{Gin} values measured at the same time, it can be observed that the theoretical RE values also present a plateau for this range of EC_L values. In other words, according to the operating parameters in the apparatus (pH, T_L , EC_L), the theoretical value of C_{Gout} could not be lower than $2 \text{ mg}_{\text{NH}_3} \text{ m}^{-3}$ and consequently the theoretical value of RE could not be higher than 80%. Therefore, the results of the experiment are also in agreement with the theory for EC_L values of between 6 and 12 mS cm^{-1} .

According to Figure 9, the theoretical and experiment RE values are in close agreement for EC_L values up to 20 mS cm^{-1} , and there is a gap for EC_L at around 30 mS cm^{-1} . For these EC_L values, the theory indicates that the RE should be close to 0, whereas the RE values measured were around 20%. As discussed in section 2, the theoretical prediction of C_{Gout} , and consequently RE, is strongly dependent on pH and to a lesser extent on temperature. It was observed, therefore, that the influence of these parameters is more pronounced at low RE values than at high RE values (Figure 5). To illustrate the influence of pH, the theoretical RE values were also calculated using the pH values measured in Eq. 10: -0.1 and +0.1 respectively (dashed lines in Figure 9). As observed, experiment and theoretical values are in very close agreement when pH -0.1 is used for the calculation (in this case, $RE_{\text{theory}} = 1.03 RE_{\text{experiment}} - 1.94$; $R^2 = 0.98$, not shown). Conversely, when pH +0.1 is used for the calculation, a large discrepancy is observed for EC_L at around 30 mS cm^{-1} , theoretical RE values being around -30%. This finding confirms that a theoretical assessment of the removal efficiency of a biotrickling filter is possible (Eq 10) provided that the parameters in the liquid phase (temperature, pH and electrical conductivity) are measured *in situ*.

However, the pH has to be measured accurately to avoid large errors. Additionally, the inlet ammonia concentration to be treated must also be known, which is rarely the case in real conditions.

Revised manuscript

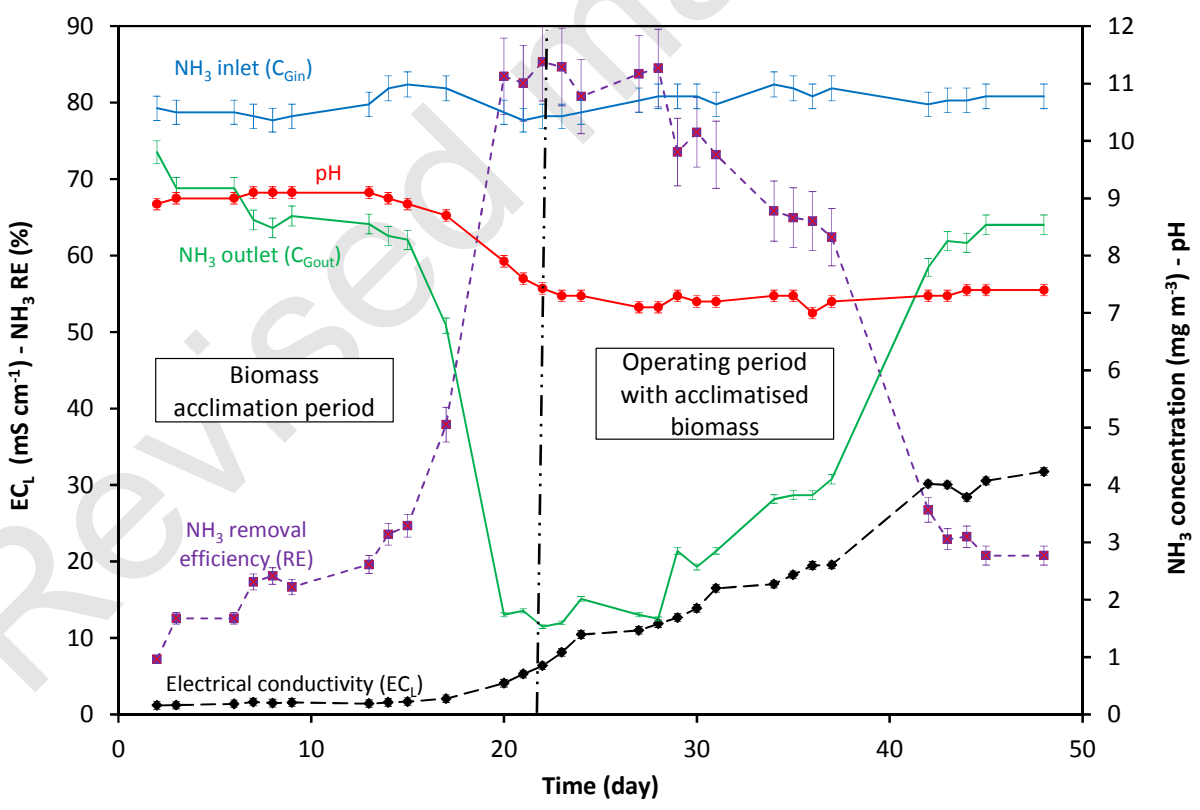
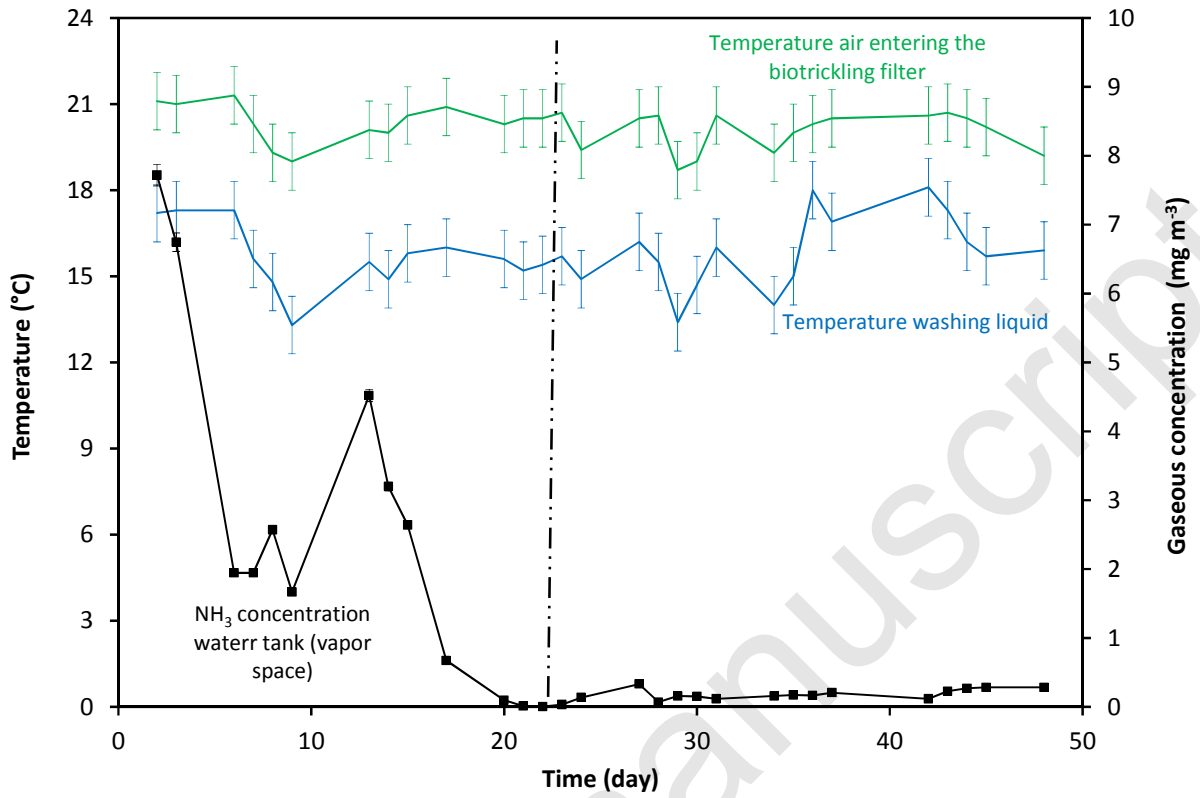


Figure 7 Main parameters recorded during the experiment

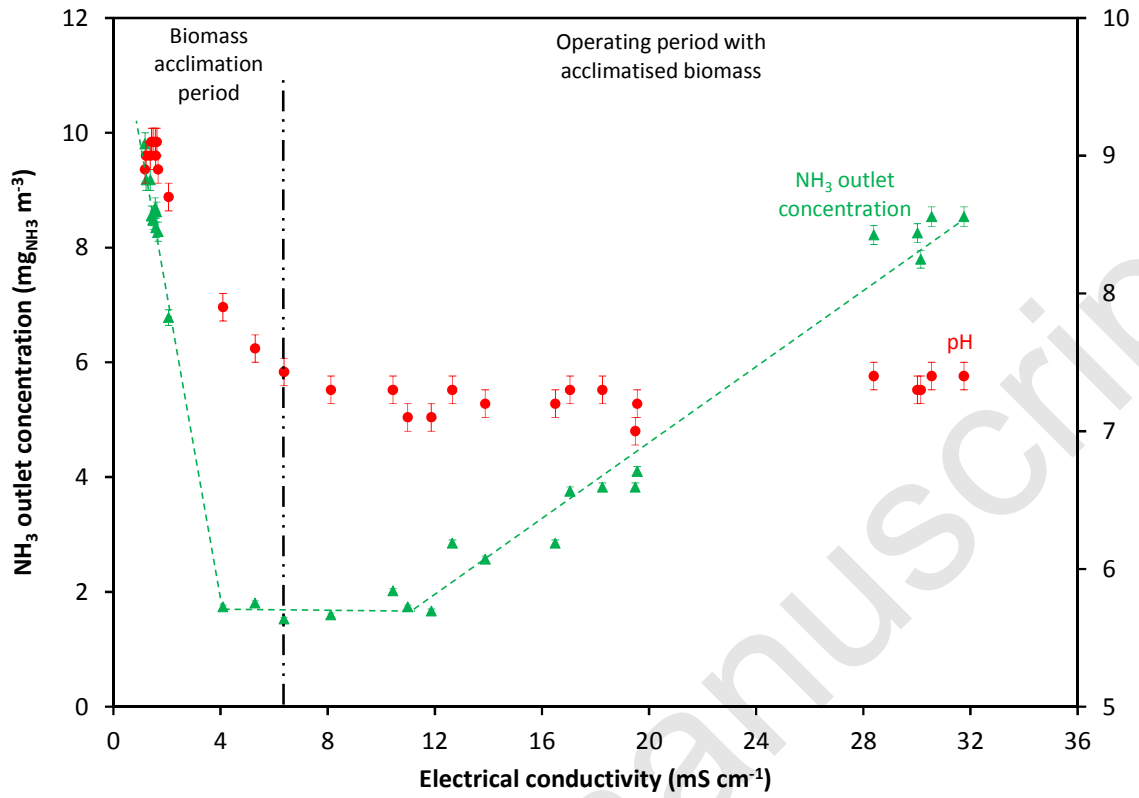


Figure 8 Change in ammonia concentration at the outlet of the biotrickling filter with EC_L

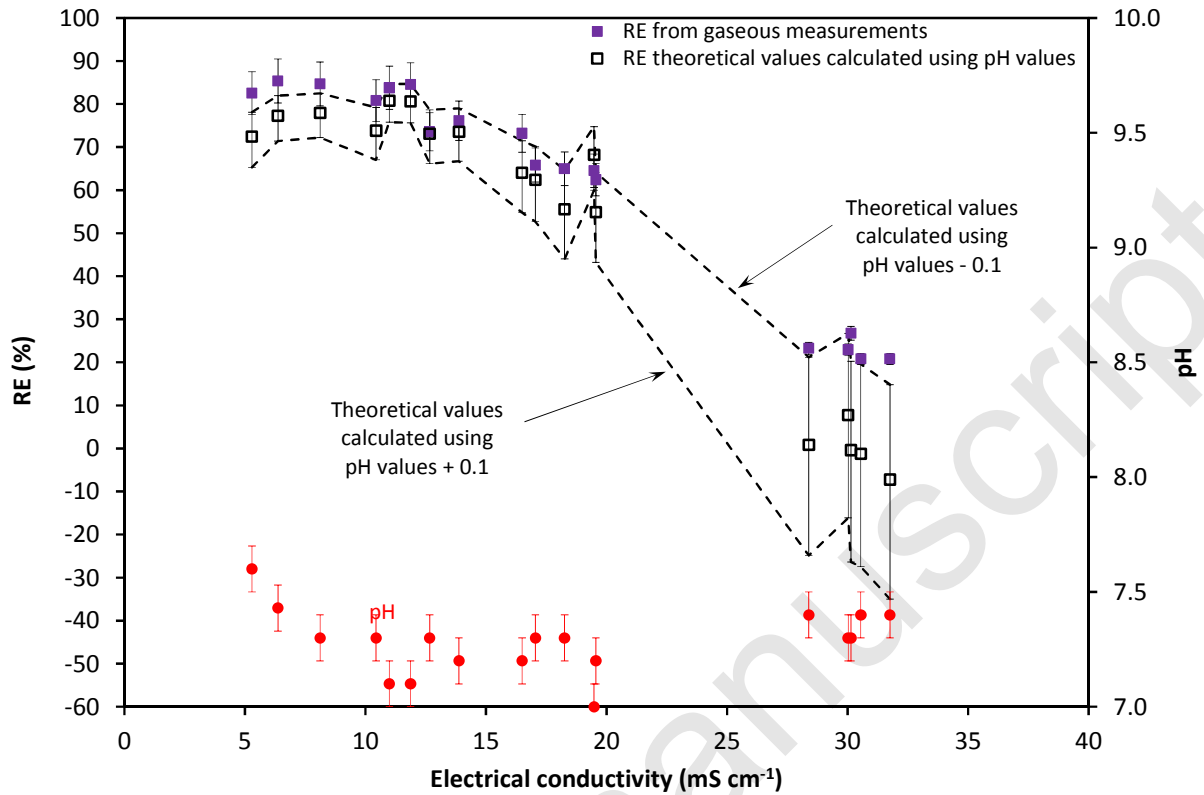


Figure 9 Comparison between experimental RE values and theoretical RE values calculated from temperature, pH and C_{Gin} values recorded for each point, using Eq (10). Error bars correspond to theoretical RE values calculated using measured pH values ± 0.1 (biomass acclimation period not represented).

4.2. Biomass inhibition

Taking into account the large amount of nitrogen ions in the washing liquid at the end of the experiment (up to $7 \text{ g}_N \text{ L}^{-1}$), the possible limitation of RE due to biomass inhibition must be considered. Thus, the ammonia-oxidizing bacteria (AOB) can be inhibited by the presence of free ammonia $\text{NH}_{3(L)}$, calculable using Eq (8), whereas the nitrite-oxidizing bacteria (NOB) can be inhibited by the presence of free nitrous acid $\text{HNO}_{2(L)}$, calculable using the correlation given by Anthonisen et al. [18], i.e. $(\text{HNO}_2)_{\text{gHNO}_2/\text{L}} = (46/14) 10^{-\text{pH}} (\text{NO}_2^-)_{\text{gN}/\text{L}} / \exp(-2300/T)$. The range of inhibition values reported in the literature is wide [4], for instance between 10 and $150 \text{ mg}_{\text{NH}_3} \text{ L}^{-1}$ and between 0.22 and $2.8 \text{ mg}_{\text{HNO}_2} \text{ L}^{-1}$ for AOB and NOB respectively, according to Anthonisen et al. [18]. Concerning AOB inhibition, the free ammonia concentrations calculated ranged between 5 and $26 \text{ mg}_{\text{NH}_3} \text{ L}^{-1}$ during the operating period with acclimated biomass. However, these values correspond to the values for canceling the driving force, since $C_{Gout}/H =$

$C_L = \text{NH}_3(L)$ and consequently free ammonia directly governs the RE via the following equation, deduced from Eq (8) and Eq (10):

$$\text{RE} = 100 \left(1 - \frac{17}{14} 10^6 H \frac{\text{NH}_3(L)}{C_{\text{Gin}}} \right) \quad (11)$$

As there is close agreement between the experiment and theoretical RE values, it can be concluded that mass transfer was limited by the thermodynamic conditions due to the accumulation of NH_4^+ , and proportionally the accumulation of $\text{NH}_3(L)$, although the accumulation of NH_4^+ could have been limited by AOB inhibition. In other words, whether there was AOB inhibition or not, it is the amount of NH_4^+ in the washing liquid (i.e. EC_L) that determines the efficiency of the biotrickling filter. Concerning NOB inhibition, the minimum and maximum values of free HNO_2 concentration in the washing liquid can be calculated by assuming (i) that $\text{NO}_2^- = \text{NO}_3^-$ and consequently $[\text{NO}_2^-]_{\text{gN/L}} = \frac{1}{2}[\text{NH}_4^+]_{\text{gN/L}}$; (ii) that $\text{NO}_2^- \gg \text{NO}_3^-$ and consequently $[\text{NO}_2^-]_{\text{gN/L}} \rightarrow [\text{NH}_4^+]_{\text{gN/L}}$. The correlation given by Anthonisen et al. [18] can therefore be adapted under the following forms (in which $\beta=0.22$):

$$\min(\text{HNO}_2) = \frac{46}{14} \frac{\beta}{4} \frac{\text{EC}_L}{\exp(-2300/T)} 10^{-\text{pH}} \quad (12)$$

$$\max(\text{HNO}_2) = 2 \min(\text{HNO}_2) \quad (13)$$

From Eqs. (12-13), assessments of free HNO_2 concentrations in the washing liquid during the experiment ranged between 0.07 and 0.95 $\text{mg}_{\text{HNO}_2} \text{L}^{-1}$, i.e. within the range of inhibition values reported by Anthonisen et al. [18]: between 0.22 and 2.8 $\text{mg} \text{L}^{-1}$. As a result, NOB inhibition probably occurred in the washing liquid. At a given temperature and constant pH, free HNO_2 concentration increases in line with the electrical conductivity of the washing liquid. In addition, free HNO_2 concentration decreases with increased pH. For instance, at $T = 18 \text{ }^\circ\text{C}$ and $\text{pH} = 7.2$, the minimum free HNO_2 concentration is 0.031 EC_L ; consequently, NOB inhibition could probably occur for an EC_L of between 10 and 20 mS cm^{-1} . Given that EC_L values in biotrickling filters treating ammonia emissions at livestock facilities are within this order of magnitude or higher, it can be argued that NOB inhibition usually occurs in the washing liquid. According to the literature, NO_2^- ions usually dominate NO_3^- ions, representing the typical situation for biotrickling filters [4]. For instance, studying 13 field-scale biotrickling filters located in northern

Germany, Liu et al. [9] reported only 2 cases where $\text{NO}_2^-/\text{NO}_3^- < 1$, whereas for the 11 other cases, $\text{NO}_2^-/\text{NO}_3^-$ ratios ranged between 3.7 and 30.1 (recorded pH and EC_L values being roughly the same for the 13 sets of apparatus). Mechanisms controlling repartition between NO_2^- and NO_3^- in biotrickling filters are still studied, but the findings obtained in the present study suggest the following possible mechanism: once absorbed by fresh washing liquid, ammonia is converted into NH_4^+ ions which are oxidized into NO_2^- then NO_3^- ions. The equilibrium between NO_2^- and NO_3^- (i.e. ratio $\text{NO}_2^-/\text{NO}_3^- = 1$) would be satisfied up to a critical EC_L value dependent on the pH value. Once the critical value is reached, NOB inhibition would limit the oxidation of nitrite ions into nitrate ions, leading to an imbalance between NO_2^- and NO_3^- ($\text{NO}_2^- > \text{NO}_3^-$) while maintaining the electrical balance between the cation and the anions. The imbalance would increase with the increase in EC_L values until the accumulation of free ammonia in the washing liquid, in equilibrium with the accumulated NH_4^+ ions, halted the ammonia absorption between phases. At a given pH, the higher the electrical conductivity value, the greater the imbalance between the anions. Therefore, further investigations are needed to confirm this mechanism.

4.3. Good practice for an efficient biotrickling filter treating ammonia emissions

In terms of the theory and its validation by the experiment as detailed above, it can be concluded that biotrickling filters could be the right choice for gaseous ammonia removal only if the water quality is assured in terms of pH and ionic strength. On the one hand, the pH must be close to neutral to promote both the transfer of ammonia and the biological process of nitrification. On the other hand, the electrical conductivity of the washing liquid can be controlled by regular discharge and replacement of the water. However, it seems that there are only a few regulations governing EC_L control. According to the Flanders regulations, the maximum nitrogen content allowed for washing liquid is $3.2 \text{ g}_N \text{ L}^{-1}$, corresponding to $\text{EC}_L = 15 \text{ mS cm}^{-1}$ [10]. In northern Germany, half the volume of washing liquid is discharged once $\text{EC}_L > 22 \text{ mS cm}^{-1}$ [19]. Basically, the amount of fresh water needed to keep EC_L at a given value (F_W in $\text{m}^3 \text{ h}^{-1}$) is represented by the following equation [20]:

$$F_W = F_G \text{ RE} \frac{(14/17) C_{Gin} 10^{-6}}{\beta \text{ EC}_L} \quad (14)$$

According to this equation, the higher the air flow rate to be treated (F_G in $\text{m}^3 \text{h}^{-1}$) and the higher the pollutant concentration at the inlet (C_{Gin} in $\text{mg}_{\text{NH}_3} \text{m}^{-3}$), the higher the desired efficiency towards 1, and the lower the EC_L limit value, the greater the amount of fresh water needed. As a result, an efficient biotrickling filter requires large amounts of fresh water. At livestock facilities, ground water is generally used to feed biotrickling filters and its initial composition can be determined. A ground water pH significantly lower than 7.0 is advantageous from the point of view of driving force but is disadvantageous for the nitrification process, since high values of free HNO_2 concentration in the washing liquid lead to NOB inhibition. A pH value close to neutral is desirable. In the scenario where the initial pH of the ground water is higher than the desired pH value for ammonia removal, the amount of sulfuric acid ($F_{\text{H}_2\text{SO}_4}$ in $\text{m}^3 \text{h}^{-1}$) that has to be added to reach this pH value (called pH final) is:

$$F_{\text{H}_2\text{SO}_4} = \frac{2 F_W (10^{-\text{pH final}} - 10^{-\text{pH initial}})}{\text{Molarity}} \quad (15)$$

As a result, the cost of adding sulfuric acid could be prohibitive if acid has to be purchased, which depends on the initial pH value of the ground water. A possible solution to reduce costs would be to use acidic water produced *in situ*. For instance, the acidic water produced by an anoxic bioprocess treating the H_2S from biogas could be considered (Figure 10) since anaerobic digestion systems are installed at livestock facilities. In an anoxic bioprocess, the nitrite and nitrate ions would be used as electron acceptors instead of oxygen for H_2S oxidation [21]. The pairing of an aerobic biotrickling filter treating NH_3 with an anoxic biotrickling filter treating H_2S would therefore be beneficial for removing the pollutants generated by the two bioprocesses, H_2SO_4 and $\text{NO}_2^- + \text{NO}_3^-$ [22]. However, the potential presence of NH_4^+ in the acidic water produced by the anoxic biotrickling filter treating H_2S could be detrimental to the aerobic biotrickling filter treating NH_3 . In theory therefore, the ammonium ions should be removed beforehand, using photobioreactors to feed the anoxic bioprocess treating the H_2S with water containing nitrites and nitrates ions only (Figure 10). Clearly, more studies must be carried out to test the feasibility of the pairing of bioprocesses.

To conclude, good practice for an efficient biotrickling filter treating ammonia emissions is to measure the pH of the washing liquid accurately to determine the electrical conductivity value that must not be exceeded. Depending on the pH value and the ammonia concentration to be

treated, $RE > 70\%$ could be obtained for higher EC_L values than are recommended, provided the biotrickling filter is well designed, i.e. mass transfer is not limited by hydrodynamic conditions.

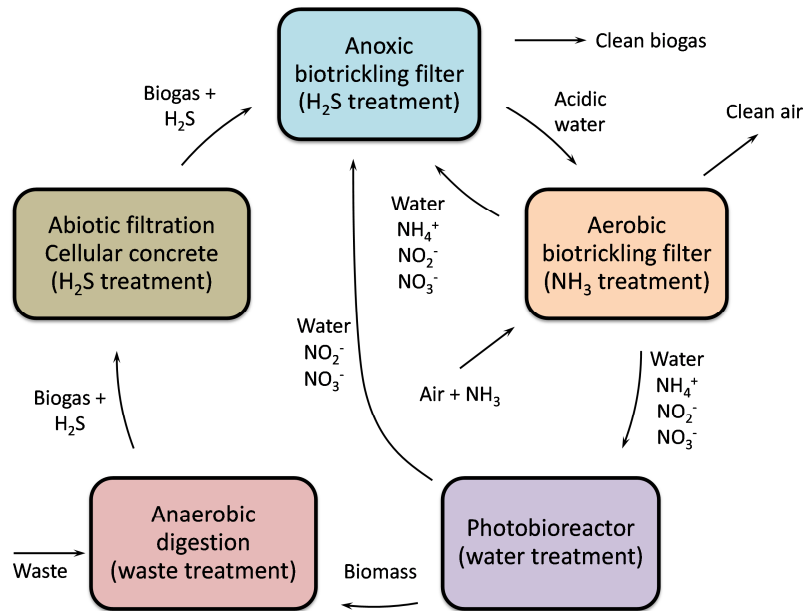


Figure 10 Pairing of bioprocesses for simultaneous removal of H_2S and nitrogen ions at livestock facilities

4. Conclusion

The maximum removal efficiency (RE) of a biotrickling filter treating ammonia emissions at livestock facilities was theoretically predicted for the first time. It was demonstrated that RE is controlled by thermodynamic conditions, i.e. the ammonia driving force between the gas phase and the liquid phase. For a given gaseous ammonia concentration to be treated (C_{Gin}), the maximum removal efficiency depends on the physical properties of the washing liquid, i.e. pH, electrical conductivity and temperature. The maximum RE value, easily calculable using Eq (10), can only be achieved by a well-designed biotrickling filter not limited by hydrodynamic conditions. Limitation of the driving force by thermodynamic conditions is mainly due to the low ammonia concentrations that are usually to be treated (C_{Gin} usually lower than $20 \text{ mg}_{NH_3} \text{ m}^{-3}$).

Although it is desirable to determine the removal efficiency of operational biotrickling filters by measuring the gaseous ammonia concentration at the inlet and outlet of the apparatus (which is a difficult task), the theoretical prediction of the maximum removal efficiency that can be achieved

by simply measuring the properties of the washing liquid, in line or from samples, can be beneficial as a diagnostic tool to identify the possible failure of the apparatus. In addition, the theoretical prediction can be used to manage renewal of the washing liquid. Depending on the measured pH of the liquid, the limit value for electrical conductivity could be adapted to guarantee removal efficiency at a desired rate.

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Conflict of interest

The authors declare no conflict of interest.

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