Ammonia transformation in a biotrickling air filter

LARS PETER NIELSEN, MARIE LOUISE NIELSEN, MATHIAS ANDERSEN, AND ANDERS M. NIELSEN
Department of Biological Sciences, University of Aarhus, Ny Munkegade 1540, 8000 Aarhus C, Denmark

ABSTRACT

A simple, tubular biotrickling filter was designed for optimal removal of ammonia and odour in ventilation air from a pig house. The removal and transformation of ammonia was studied in detail by analysis and modelling of chemical gradients through the filter. Good correspondence between measurements and model was obtained by using conventional substrate and inhibition kinetics of ammonium and nitrite oxidizing bacteria. Highest rates of ammonia removal were observed in the central section of the filter. Near the air outlet and water inlet the process was ammonia limited, while high nitrous acid concentrations almost excluded any biological activity near the air inlet and water outlet. Nitrous acid inhibition also stabilized pH at 6.5-7 all through the filter. Being sensitive to both ammonia and nitrous acid the nitrite oxidation process occurred mainly in the filter sections near the air outlet / water inlet, and only 8% of the nitrite was turned into nitrate. Water supply only exceeded evaporation by 20% but modelling indicated that additional watering would have limited effect on filter efficiency. The filter was also robust to varying loading, as a 4-fold increase in ammonia inlet concentration only reduced filter efficiency from 86 to 76%.

1 INTRODUCTION

Ammonia emitted from animal facilities is a major contributor to acidification and eutrophication of terrestrial and aquatic environments (McCrory and Hobbs, 2001). Significant reductions of both ammonia and door emissions can be accomplished by use of biological trickling filters. The good results, however, are not sufficiently reproducible, and further optimization of design and operation is required for more widespread application.
Ammonia is a highly water soluble gas (62 M/atm at 20 °C) that is readily protonized to ammonium (NH$_4^+$) in water. In biofilters ammonia is oxidized to nitrite (NO$_2^-$) by ammonium oxidizing bacteria (AOB) and further to nitrate (NO$_3^-$) by nitrite oxidizing bacteria (NOB). The overall removal efficiency is the result of complex interactions of ammonia load, filter surface area, air and water flow, temperature, nitrifier biomasses, and inhibition kinetics. To resolve this we analyzed chemical gradients in a simple counter-current biofilter and simulated the results with a mathematical model. Long term development of nitrifier biomass and the impact of nitrification processes on the removal of organic odorants are two important aspects that will not be addressed in this paper.

2 MATERIALS AND METHODS

2.1 TUBULAR BIOTRICKLING FILTER

The first, small version of the tubular biotrickling filter optimized for studies of function is shown in Figure 1 (M. Andersen, DK Patent no. 3108_06). Contaminated air is lead into the lower end of 3 independent tubes being 5.5 meter long and with a cross-section area of 11 cm$^2$ each. The straight airflow gives a good gas-filter contact in relation to pressure drop and minimizes the risk of clogging. The inner surface of the tubes is covered with a thin layer of a fibrous material through which the water slowly percolates driven by gravity. The biofilm developing on the surface of the conductive layer is thus moisturized with fresh water from inside and in direct contact with the air stream outside. This almost eliminates a liquid film diffusion barrier thus promoting the removal of airborne contaminants that are not easily soluble in water. Details on NH$_3$ load and air and water dynamics during the experimental run are given in Table 1.

2.2 ANALYTICAL METHODS

Ammonia in the air was sampled in acid solution and analyzed by spectrophotometer (Bower and Holm-Hansen, 1980). Water was sampled with filter paper sticks through the sampling ports, and after dilution NO$_2^-$ and NO$_3^-$ was analyzed by HPLC and NH$_4^+$ as above. pH was determined by pH sticks. Concentrations of HNO$_2$ and NH$_3$ were calculated from pH and concentrations of NO$_2^-$ and NH$_4^+$ using pKa values of 3.4 and 9.4 respectively. Evaporation was calculated from the concentration gradient of a bromide tracer added to the water supply and analyzed by HPLC.
Figure 1. The experimental tubular biotrickling filter. The 5 sample points divide the filter in 4 sections of equal length.
Table 1.
Parameters of the model and the experimental filter. Values apply to one filter tube. The terms AOB and NOB stands for ammonium and nitrite oxidizing bacteria, respectively.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet NH\textsubscript{3} concentration</td>
<td>8.6 ppm</td>
</tr>
<tr>
<td>Airflow</td>
<td>19400 L/h</td>
</tr>
<tr>
<td>Water flow</td>
<td>63 mL/h</td>
</tr>
<tr>
<td>Air volume per section</td>
<td>4.65 L</td>
</tr>
<tr>
<td>Water volume per section</td>
<td>23 mL</td>
</tr>
<tr>
<td>Evaporation, section 3</td>
<td>23 mL/h</td>
</tr>
<tr>
<td>Evaporation, section 4</td>
<td>30 mL/h</td>
</tr>
<tr>
<td>Air/water mass transfer coefficient per section</td>
<td>5 mL/s</td>
</tr>
<tr>
<td>Substrate limitation factors</td>
<td>C/(C+Km)</td>
</tr>
<tr>
<td>NH\textsubscript{3} inhibition factor for AOB</td>
<td>e\textsuperscript{(-C/Ki)}</td>
</tr>
<tr>
<td>Other inhibition factors</td>
<td>1/(1+(Ci/Ki))</td>
</tr>
<tr>
<td>Km of NH\textsubscript{3} for AOB</td>
<td>786 \textmu M</td>
</tr>
<tr>
<td>Km of HNO\textsubscript{2} for NOB</td>
<td>114 \textmu M</td>
</tr>
<tr>
<td>Ki of NH\textsubscript{3} for AOB</td>
<td>2000 \textmu M</td>
</tr>
<tr>
<td>Ki of NH\textsubscript{3} for NOB</td>
<td>168 \textmu M</td>
</tr>
<tr>
<td>Ki of HNO\textsubscript{2} for AOB &amp; NOB</td>
<td>1.14 \textmu M</td>
</tr>
<tr>
<td>AOB capacity</td>
<td>50 x NH\textsubscript{3} load</td>
</tr>
<tr>
<td>NOB capacity</td>
<td>20 x NH\textsubscript{3} load</td>
</tr>
<tr>
<td>Model iteration frequency</td>
<td>100/s</td>
</tr>
<tr>
<td>Model runtime</td>
<td>20 h</td>
</tr>
</tbody>
</table>

2.3 Model

The mathematical model was programmed in JAVA and followed in most aspects a new, more general biofilter model (Nielsen et al., in preparation). The model filter was divided in 4 sections according to Figure 1 with fully mixed air and water phases and fixed biomass. In each iteration the changes of gaseous NH\textsubscript{3}, total NH\textsubscript{4}\textsuperscript{+}, total NO\textsubscript{2}\textsuperscript{−}, and total NO\textsubscript{3}\textsuperscript{−} were calculated from air/water NH\textsubscript{3} mass transfer, nitrification rates and water and air transport between sections. Subsequently the pH was calculated by solving a charge balance equation using a two-step Newton-Raphson approximation as described by Volcke et al. (2005). Inlet ammonia concentrations, air and water flow and evaporation were set to observed values in the experimental filter (Table 1). Compared to NH\textsubscript{3} the concentration of organic compounds in the ventilation air was an order of magnitude lower and transformations of organics were ignored in the present model version. Model parameters, kinetic equations, and initial values are
Figure 2. Concentration gradients from the water inlet at the top of the filter to the air inlet at the bottom showing NH$_3$ in the air (a) and NO$_3^-$, NH$_4^+$, NO$_2^-$, HNO$_2$, NH$_4$, and pH in the water (b-g). Lines are model simulation results and symbols are measured averages with standard errors (n=3).
listed in Table 1. Many different kinetic constants are found in the literature, but the general patterns of the model output were quite robust to variations in kinetic constants. The chosen values were mainly derived from Anthonisen et al. (1976). Notice that the uncharged species NH$_3$ and HNO$_2$ and not NH$_4^+$ and NO$_2^-$ were considered the real species for substrate uptake and inhibition of nitrifiers (Anthonisen et al., 1976). Chemical equilibrium constants for the inorganic nitrogen and carbon species at 20 °C were obtained from table values.

3 RESULTS

3.1 Chemical Gradients

Of the water supplied 86% evaporated in the two lower sections (Table 1). Good correspondence between measured and modelled chemical gradients was obtained after proper adjustment of ammonium oxidation capacity and the results are shown together in Figure 2. Ammonia content of the air declined throughout the filter to an outlet concentration of 1 ppm corresponding to 85% overall removal. Most of the removal, 78%, occurred in the two central sections while the upper and lower section only accounted for 21 and 1% respectively. Concentrations of NO$_2^-$ and NH$_4^+$ increased down the filter with final steep increases up to about 300 mM in the evaporation zone (Figure 2c-d). Concentrations of NO$_3^-$ were much lower and both measured and simulated data showed that virtually all nitrite oxidation occurred in the upper two sections (Figure 2b). The discrepancy between simulated and measured NO$_3^-$ concentrations could be ascribed to under estimation of the nitrite oxidation capacity. Despite the absence of any chemical buffer or pH regulation, the pH values remained between 6.5 and 7 (Figure 2g). By comparison with the Km and Ki values the concentrations of free NH$_3$ and HNO$_2$ indicated strong substrate limitation of AOB in the upper sections and strong HNO$_2$ inhibition of both AOB and NOB in the lower section (Figure 2e-f, Table 1).

4 DISCUSSION

There are many ways to examine the regulation of ammonia transformations in a biological airfilter, and some interesting points can actually be derived without running any models or experiments.

One point is that if the maximum capacity of the ammonium oxidizer biomass exceeds the NH$_3$ load, the process will have to be restricted accordingly by NH$_3$ limitation and/or inhibitors. As long as the overall NH$_3$ removal efficiency is good, a high inhibitor level is therefore not an indicator of a critical filter situation but rather
an indicator of excess nitrifier biomass. In the present case the maximum capacity in
the model was set to 50 times the NH₃ load, and therefore the kinetics somehow had
to reduce ammonium oxidation to less than 2% of the capacity. The results showed
that this was accomplished mainly by HNO₂ inhibition in the lower half of the filter
with concentrations up to 170 times the inhibition constant, and by NH₃ limitation in
the upper end of the filter with concentrations 15-80 times lower than the Km value
(Figure 2e-f, Table 1). The point that inhibitor level and substrate limitation is essentially
determined by the biomass/loading ratio has other perhaps counter-intuitive
implications; including that inhibitor level must decrease significantly with higher
NH₃ loading but not with enhanced watering. Model perturbations indeed showed
that a 6 times increase in NH₃ inlet concentration only reduced filter efficiency from
86 to 76% (Figure 3a).

Another general point is that in time only half of the NH₃ taken up in a biofilter
will be oxidized, while the other half will remain in solution as NH₄⁺ (Smet et al.,
2000). This is simply because NH₄⁺ in reality is the only cation available to balance
the produced anions NO₂⁻ and NO₃⁻ when concentrations are up in tens to hundreds of
mM N. The measurements confirmed this by perfect charge balances, i.e. 310 mM
NH₄⁺ versus 320 mM NO₂⁻ + NO₃⁻ in the outlet (Figure 2). Another way to address
the general point of half-way nitrification is to consider pH: If the nitrifiers tried to generate
just 1 mM NO₂⁻ + NO₃⁻ more in excess of NH₄⁺ the anion excess would have to be
balanced by H⁺, thus implying a pH drop to around 3 which would stop the bacteria
long before. In the present filter with significant NO₂⁻ accumulation, the immediate
effect of lowering pH was the protonization of NO₂⁻ to form the highly inhibitory
HNO₂. In that way kinetics of HNO₂ inhibition of ammonium oxidation served as a

Figure 3. Modelled NH₃ removal efficiency as a function of inlet NH₃ concentration (a)
and water supply (b). All other parameters are as shown in Table 1.
biological pH buffer ensuring that pH nowhere dropped below 6.5, despite the continuous uptake of a strong base, NH$_3$, and conversion to a moderately strong acid, HNO$_2$ (Figure 2). In other filters with well-established nitrite oxidation and therefore accumulation of NO$_3^-$ in place of NO$_2^-$ pH may drop below 5, as the HNO$_2$ block is not operating (L.B. Guldbreg, unpublished).

In biological airfilters there must be some water run off removing the generated nitrogen salts. Not only in order to sustain NH$_3$ removal but also to avoid emission of the detrimental gasses NO and N$_2$O as observed in poorly watered biofilters (Trimborn et al., 2003). The cost of handling the wastewater, however, makes it relevant to consider how the run off can be minimized. Of the 63 ml supplied every hour to each filter tube 53 ml evaporated in the lower part of the filter and only 10 ml drained off. This means that microorganisms in the upper half of the filter were blessed with more than 6 times the flow of water that eventually was discharged wastewater. The lowest section essentially served as a waste condenser with poor biological conditions due to nitrous acid accumulation. Osmotic stress might have been another important limiting factor at these high salinities (Smet et al., 2000). Model perturbations (Figure 3b) showed that the overall removal efficiency would only increased from 85% to 95% following a doubling of the water supply to 126 mL/h and thereby the generation of about 7 times more wastewater ((63 mL + 10 mL)/10mL). On the other hand a reduction of the water supply by 16% to 53 mL or less would leave no wastewater and the filter would stop working. The major ambition with the modelling studies partly presented here is actually to develop better algorithms for optimization of water supply and biomass management in response to varying ammonia and door loading, air flow, temperature, humidity, etc.

5 ACKNOWLEDGEMENTS

The Danish Ministry of Food, Agriculture and Fisheries funded this work.

REFERENCES


