European Symposium on Computer Aided Process Engineering – 15
L. Puigjaner and A. Espuña (Editors)

Development and Validation of a Dynamic Complex Model for Ammonia Removal by Gas-Phase Biofiltration

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Abstract

In this study a general dynamic biofiltration model to describe ammonia removal in a gas-phase biofilter is developed. The mathematical equations are based on discretized mass balances and detailed nitrification kinetics that include inhibitory effects caused by free ammonia (FA) and free nitrous acid (FNA). The model was able to predict experimental results operation under different loading rates (from 3.2 to 13.2 g NH_3 h^{-1} m^{-3}). In particular the model was capable of reproducing inhibition behavior caused by high inlet ammonia concentrations.

Keywords: Dynamic biofilter model; inhibition kinetics

1. Introduction

Several well known physical and/or chemical processes have been used to control polluted air emissions: incineration, oxidation, adsorption, chemical scrubbing among others. However biological treatments have attracted considerable interest in recent years.

A biofilter is a reactor normally packed with organic material where microorganisms growth developing a biofilm. Biofiltration is a technology based on the biological oxidation of pollutants using immobilized microorganism. Usually the contaminated air to be treated is fed to the reactor in up flow way where biodegradable volatile compounds are transferred into the biofilm by adsorption and subsequently diffusion and aerobic biodegradation occurs simultaneously.

In literature a significance number of experimental works can be found but theoretical studies regarding biofilter modeling are more limited. Recently Amanullah et al. (1999) studied and compared different dynamic models available in the literature. Their work demonstrated that complex and realistic models are necessary to improve knowledge of biofiltration systems.

Monod kinetic models, including substrate inhibition and oxygen limitation, have been applied with satisfactory results (Deshusses et al., 1995). In addition, many works have established bacteria inhibition as one of the factors affecting performance of ammonia

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biotreatment (Kim et al., 2000) but complete inhibition kinetics by FA and FNA have not been included in biofiltration models so far.
The main objective of this work is to develop and validate a dynamic general model to predict performance in a biofilter used to remove ammonia from air streams. The model considers most of the phenomena that occur in biofiltration and includes detailed biokinetic expressions for ammonia depletion considering all biological inhibitions occurring in the nitrification process. In addition, three different conceptual models were explored in order to include proton as a variable state due to its notable influence on equilibrium and inhibition constants.

2. Materials and Methods

Experimental data for model validation was performed in a bench-scale biofiltration unit, which is comprehensively described in Martin et al. (2004). Briefly, the overall height of the biofilter and the inner diameter are 110 cm and 10 cm, respectively, and is divided by PVC perforated plates into four equal modules. Each module was packed with 20 cm of coconut fiber as packing material. No inoculation was needed since the packing was withdrawn from a full scale plant which had been running for more than 2 years at an average ammonia inlet concentration of 40 ppmv. Four gas sampling ports were placed along the biofilter height for automated gas sampling. Gas flow rates for air and ammonia through the biofilter were measured and controlled by digital mass flow controllers. The biofilter was operated in up-flow mode. The top was equipped to sprinkle a solution of nutrients once per day.

3. Model Development

3.1 Model Equations

The model developed in this work comprises transport, physical and biological phenomena that occur during biofiltration. Processes such as advection, absorption, diffusion, adsorption and biodegradation are included in the model.
The mathematical equations of the model are based on the following assumptions:

1. Gas phase is modelled as plug flow.
2. Mass transfer resistance in the gas phase was neglected.
3. Biofilm is formed on the exterior surface of the particles. Biofilm thickness is small compared to the particle size; hence planar geometry and a perpendicular diffusion in biofilm-gas interface can be used to derivate model equations.
4. Biomass does not growth in the pores of particles.
5. Physical properties of the biofilm are assumed to be the same as in water.
6. Different biomass concentrations are considered along the bed height but there is no accumulation of biomass in the filter bed.

3.1.1 Mass balance for the bulk gas phase:

$$\frac{\partial C_g}{\partial t} = - v_z \frac{\partial C_g}{\partial z} - \frac{1}{\varepsilon} A_S N_G \qquad C_g = C_{gi}, z = 0 \tag{1}$$

where v_z is the interstitial gas velocity (m h^{-1}), C_{gi} is the inlet gas concentration (g m^{-3}), z is the position along the biofilter height (m), A_S is the specific surface area (biofilm

surface area per unit volume of biofilter, $m^2\ m^{-3}$), and N_G is the mass flux from the gas to the biofilm through the interface gas-biofilm (g $m^{-2}\ h^{-1}$). Note that N_G is given by Fick's law:

$$N_G = -D\left(\frac{\partial C_b}{\partial x}\right)\Bigg|_{x=0} \tag{2}$$

where D is the diffusion coefficient ($m^2\ h^{-1}$), C_b is the concentration in biofilm phase (g m^{-3}), and x is the position in the biofilm (m).

3.1.2 Mass balance for the biofilm:

$$\frac{\partial C_b}{\partial t} = D\frac{\partial^2 C_b}{\partial x^2} + r \qquad C_b = C_g / H\ ,\ x = 0 \tag{3}$$

where r is the substrate utilization rate (g $m^{-3}\ h^{-1}$) which will be explained in the next section, and H is the gas-biofilm distribution coefficient given by Henry's law.

3.1.3 Mass balance for the solid phase:

$$\frac{\partial C_s}{\partial t} = \frac{A_S N_B}{1-\varepsilon} \tag{4}$$

where C_S is the concentration in solid phase (g m^{-3}), and N_B is the mass flux from the biofilm to the solid through the interface biofilm-solid (g $m^{-2}\ h^{-1}$). Note that N_B is given by:

$$N_B = -D\left(\frac{\partial C_b}{\partial x}\right)\Bigg|_{x=\delta} \tag{5}$$

where δ is the biofilm thickness (m).

3.2 Microkinetics

A detailed model of the nitrification process developed by Carrera et al. (2003) was used to describe the biodegradation rate.

The kinetic model considers oxidation from ammonium to nitrite (nitritation) and oxidation from nitrite to nitrate (nitratation). Nitritation and nitratation processes were modeled considering inhibition by FA and FNA. A Haldane model was used to describe substrate inhibition while nitritation inhibition by FNA and nitratation inhibition by FA were modeled as non-competitive inhibitions. Oxygen limitation is also included in the kinetic model. Since biomass growth (accumulation) is not considered in the model, no decay processes for ammonium- and nitrite-oxidizing biomass are considered. The kinetic parameters and stoichiometric coefficients used for model validation are comprehensively described elsewhere (Carrera et al., 2003).

3.3 pH model

The general assumption that the pH remains approximately constant may be not valid in a widespread of biological systems i.e. treating organic waste with a high nitrogen concentration or operating with a low buffer capacity (Musvoto et al., 2000). In order to include proton as a state variable in the general model, three different conceptual models were tested to describe equilibrium between ammonia/ammonium inside the biofilm without considering biological reaction.

In the first model a simple kinetic model was employed to describe the equilibrium (equation 6). The model describes equilibrium in terms of the kinetics of the forward and reverse reaction. Considering the dissociation for the ammonia/ammonium according to:

$$NH_4^+ \Leftrightarrow H^+ + NH_3 \tag{6}$$

the forward rate expression is given by

$$r_f = K_f \left[NH_4^+\right] \tag{7}$$

where r_f is the rate of the forward reaction; K_f the specific rate constant for the forward reaction .The rate of the reverse expression is:

$$r_r = K_r \left[NH_3\right]\left[H^+\right] \tag{8}$$

where r_r is the rate of the reverse reaction; K_r the specific rate constant for the reverse reaction.

The dissociation of ammonia/ammonium is represented by the above two half reactions and both kinetics equations are included in the conceptual model as separate process. Given that H^+ is included as a state variable in the model and also in the kinetic expressions, its value at equilibrium can be computed.

The second model assumes total nitrogen diffusing through the biofilm meanwhile a fixed proton concentration is established in gas-biofilm interface. Therefore this conceptual model is based on a predefined pH profile in the interface. Finally the third model is derived from a complex algorithm where ammonia and ammonium concentration are recalculated in each integration step as a function of total nitrogen and proton concentration in the previous integration step. A Sketch of the third algorithm is shown in figure 1.

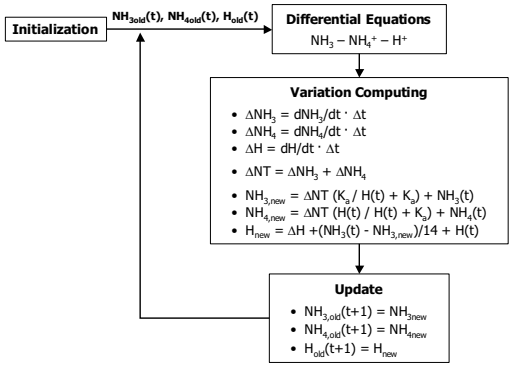

Figure 1. Algorithm scheme used in the third conceptual model

3.4 Numerical Solution

To build the model the following variables were used: in both biofilm and solid phase total ammonia (NTnh) as the sum of ammonia and free ammonium, total nitrite ($NTno_2$) as the sum of nitrite and nitrous acid, total nitrate ($NTno_3$) as the sum of nitrate and nitric acid and oxygen were included. Regarding gas phase, ammonia, nitrous acid, nitric acid and oxygen were considered. Although HNO_3 will never be present in the gas

phase due to its equilibrium constant, it was convenient to include it as a state variable in the model from a programming point of view.
The set of partial differential equations was discretized in space along the bed height and biofilm thickness. The resulting set of ordinary differential equations was solved using MATLAB in a home-made modelling environment. Initial conditions for all the state variables were set equal to zero.

4. Results and Discussion

Continuous experiments were carried out for model validation operating the bench-scale biofilter under different inlet loads at a constant gas flow of 0.63 $m^3 h^{-1}$, meaning an empty bed residence time of 36 seconds. Four different ammonia inlet concentrations were used (45.0, 123.2, 244.2 and 187.4 ppm_v). The four in a row experiments where simulated under dynamic conditions described above. Model parameters were set from both experimental data and from the literature and their values can be found in Baquerizo et al. (2004). Computing time as well as feasibility was assessed for the three proton conceptual models. Results indicated that the second model is the most suitable in terms of robustness and computing time consuming. First model demonstrated to be unstable for a wide range of values of K_f and K_r and strongly depending on the MATLAB software algorithm used for solving equations. By the other hand, good results were obtained from the third model but an extremely high computing time was needed.
The experimental data and model predicted profiles for outlet ammonia concentration considering both inhibitions by FA and FNA and considering no inhibition are shown in figure 2. The model predictions are in good agreement with experimental results indicating that inhibition kinetics are necessary to reproduce the outlet concentration under high ammonia load periods and that inhibitions effects are included satisfactorily in the model.

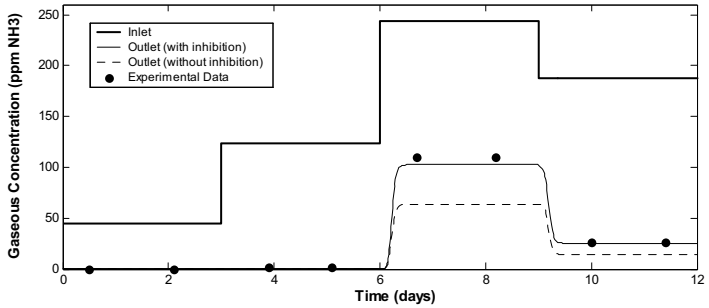

Figure 2. Dynamic simulation of ammonia outlet concentration predicted by the model (with and without inhibition) compared against experimental data

In figure 3 experimental and simulated profiles are plotted as a function of the biofilter dimensionless height. This figure indicates that the model is capable of accurately predict the behaviour along the bed height of the reactor for both low and high inlet concentrations, the later under inhibitory operating conditions.

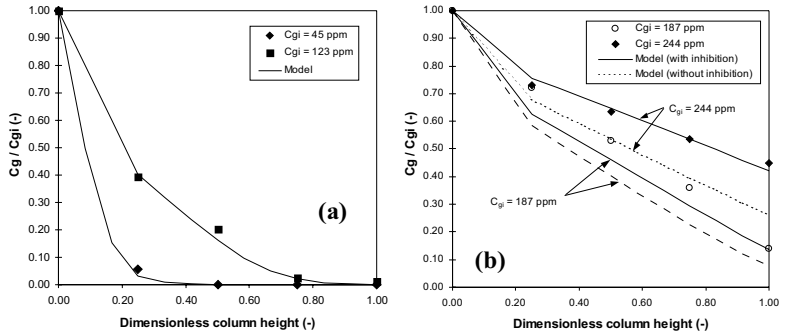

Figure 3. Gas concentration profiles along the biofilter bed for low ammonia inlet concentration (a) and high ammonia inlet concentration (b).

Preliminary results indicates that a complex dynamic model to predict the performance in a biofilter used to removal ammonia from air streams has been successfully develop. The model includes most of the phenomena occurring in a biofilter and it is able to describe the ammonia removal in a gas phase bioreactor by predicting removal profiles and ammonia outlet concentrations under inhibitory and non-inhibitory operating conditions.

Of particular importance was the inclusion of detailed nitrification kinetics that takes into account inhibition of free ammonia and free nitrous acid. Thus, the model is able to predict ammonia load shocks and bioreactor behavior under inhibitory conditions but still needs further refining for describing the lag phase for biomass recovery after an inhibition period.

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