DYNAMIC MODELING OF AMMONIA BIOFILTRATION FROM WASTE GASES

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ABSTRACT

A dynamic model to describe ammonia removal in a gas-phase biofilter was developed. The mathematical model is 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 caused by high inlet ammonia concentrations. Also elimination capacity was accurately predicted. Experimental data was also used to optimize certain model parameters such as the concentration of ammonia- and nitrite-oxidizing biomass.

INTRODUCTION

Ammonia is a highly odorous gas produced by organic waste treatment facilities and other industrial sources. Common air pollution control processes for polluted emissions are physical and/or chemical. Biofiltration has been successfully applied for treating large volumes of air streams with low ammonia concentrations (Kim et al., 2000). Biofiltration is a complex process that involves several physical, chemical and biological interactions. A large number of experimental studies have demonstrated that biofiltration is an efficient biological process to remove polluted air emissions. However, theoretical studies regarding biofilter modeling are relatively limited. 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.

The main objective of this work is to develop 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. Mathematical equations are obtained from general mass balances. The model includes detailed biokinetic expressions for ammonia considering all biological inhibitions occurring in the nitrification process. The model is validated using experimental data obtained in a pilot-scale biofilter.

MATERIALS AND METHODS

Experimental data for model validation was obtained in a bench-scale biofiltration unit, which is comprehensively described in Martin et al. (2004). In short, 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 25 cm modules. Each module was packed with 20 cm of coconut fiber as packing material. 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.

The moisture content of the biofilter was controlled by humidifying the waste gas before entering the reactor. The relative humidity of the gas stream was maintained at near 100% because levels under 90% might cause a rapid loss of biodegradation activity in the biofilter. Measured variables included temperature, relative humidity, ammonia gas, and leachate composition.

THEORY

Microkinetics

The degradation of ammonia in the biofilter is described by a dynamic model based on mass balances combined with the detailed model of the nitrification process described by Carrera et al. (2003). A schematic representation of the model is shown in Figure 1.

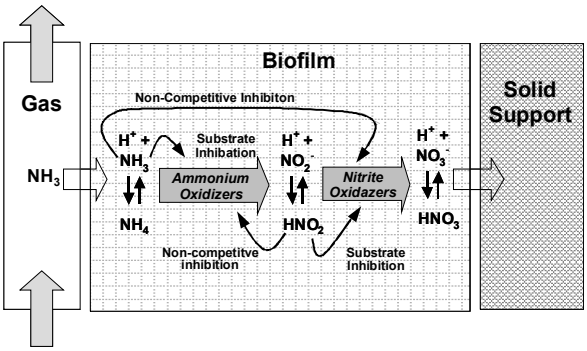

Figure 1. *Scheme of the nitrification process including substrate and non-competitive inhibitions.*

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 Free Ammonia (FA) and Free Nitrous Acid (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 is not considered in the model, no decay processes for ammonium- and nitrite-oxidizing biomass are considered. Therefore, the rate expressions for nitritation (r_A) and nitratation (r_N) are given by:

$$r_A = \mu^A_{\max} \cdot \frac{S_{O_2}}{K^A_{S,O_2} + S_{O_2}} \cdot \frac{S_{NH_4}}{K^A_{S,NH_4} + S_{NH_4} + S^2_{NH_4} / K^A_{I,NH_4}} \cdot \frac{K^A_{I,NO_2}}{K^A_{I,NO_2} + S_{NO_2}} \cdot X_A \qquad r_N = \mu^N_{\max} \cdot \frac{S_{O_2}}{K^N_{S,O_2} + S_{O_2}} \cdot \frac{S_{NO_2}}{K^N_{S,NO_2} + S_{NO_2} + S^2_{NO_2} / K^N_{I,NO_2}} \cdot \frac{K^N_{I,NH_4}}{K^N_{I,NH_4} + S_{NH_4}} \cdot X_N$$

where S_{NH4}, S_{NO2} and S_{O2} are the biofilm concentration of ammonium, nitrite and oxygen, respectively (g m^{-3}), X_A is the ammonia-oxidizing biomass (g COD m^{-3}), and X_N is the nitrite-oxidizing biomass (g COD m^{-3}). The kinetic parameters and stoichiometric coefficients used for model validation are comprehensively described elsewhere (Carrera et al., 2003). The same values optimized by Carrera et al. (2003) for a nitrifying activated sludge pilot-plant were used herein for model simulations.

Material Balance

The material balance equations were described on the basis of the following assumptions:

1.- The flow pattern of the bulk gas was plug flow.

2.- Mass transfer resistance in gas phase was neglected.

3.- Biofilm is formed on the external surface of the packing material. Biomass does not growth in the pores of particles and thus no reactions occur in the pores.

4.- The biofilm grows as patches over the packing material. The surface extension of the patches is much larger than deep, and ammonia and oxygen transport through the side of the surface can be neglected.

5.- Physical properties of the biofilm are assumed to be the same as in water

6.- There is no accumulation of biomass in the filter bed.

The variables considered in the biofilm and solid phase are: 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. In the gas phase: ammonia, nitrous acid, nitric acid and oxygen are considered. These assumptions result in the following set of equations:

Mass balance for the bulk gas phase: $$\frac{\partial C_g}{\partial t} = -v_z \frac{\partial C_g}{\partial z} + \frac{1}{\varepsilon} A_S N \qquad C_g = C_{gi}\,,\, z = 0$$

where v_z is the interstitial gas velocity (m hr^{-1}), C_{gi} is the inlet gas concentration (gr m^{-3}), z is the position along the biofilter (m), A_S is the specific surface area (biofilm surface area per unit volume of biofilter, m^2 m^{-3}), and N is the mass flux into the biofilm interface (gr m^{-2} hr^{-1}). Note that N is given by Fick's law.

Mass balance for the biofilm: $$\frac{\partial C_b}{\partial t} = D \frac{\partial^2 C_b}{\partial x^2} + r \qquad C_b = C_g / m_d\,,\, x = 0$$

where r is the substrate utilization rate (gr m^{-3} hr^{-1}), and m_d is the gas-biofilm distribution coefficient given by Henry's law.

Mass balance for the solid phase: $$\frac{\partial C_s}{\partial t} = \frac{A_S D}{1-\varepsilon} \left(C_{b|x=\delta} - C_s \right)$$

Set of partial differential equations was discretized in space along the bed height and biofilm thickness. Twelve points were used along the bed length, and 4 points were used along the biofilm thickness. The resulting set of ordinary differential equations was solved with MATLAB.

RESULTS AND DISCUSSION

The biofilter was operated at a constant gas flow of 10,67 L min^{-1} (EBRT of 36 s). Four experiments were carried out varying the inlet concentration of ammonia (45, 123, 244 and 184 ppm_v), which corresponded to ammonia loadings between 3.2 and 13.2 gr NH_3 hr^{-1} m^{-3}. The inlet concentration was changed once the steady-state was verified (*c.a.* every 3-4 days). Ammonium and nitrite concentrations measured in the leachate up to 1200 g $N\text{-}NH_4^+$ m^{-3} and 480 g $N\text{-}NO_2^-$ m^{-3} indicated that inhibitory conditions developed during the 244 ppm_v feeding period and remained thereafter.

Model parameters were determined from both experimental data and the literature. In addition to this, biomass concentrations in each module were optimized assuming a decrease in the direction of flow. As expected, ammonia gas concentration measured along the bed height (Figure 2a and 2b) indicated a trend for the elimination capacity to decrease in the direction of flow, but a sharper decrease in the ammonia concentration observed in the first module indicated that a higher concentration of biomass had been developed in the module closer to the inlet of the biofilter. Ammonia-oxidizing biomass and nitrite-oxidizing biomass densities in the biofilm were optimized following the ratio given by Carrera et al. (2003). Experimental and simulated results were plotted as a function of the biofilter dimensionless height. As shown in figure 2a and 2b, the model is capable of predicting accurately predict the behaviour along the bed height of the reactor for both low and high inlet concentrations, the later under inhibitory ope-

rating conditions, thus suggesting that inhibitory effects have been included satisfactorily in the biodegradation reaction model.

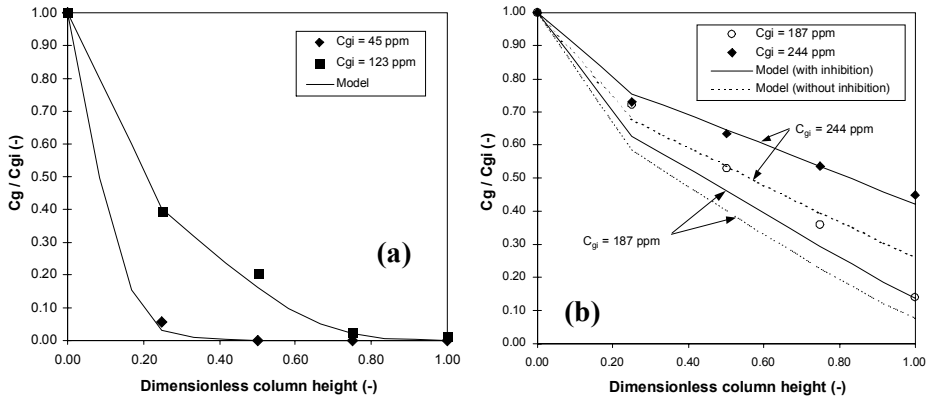

***Figure 2**. Gas concentration profile along the biofilter bed for low ammonia inlet concentration (a) and high ammonia inlet concentration (b).*

It's worth mentioning that ammonia concentration along the bed height is not well predicted for the 187 ppm_v inlet ammonia concentration (Figure 2b). The model predicted lower concentrations with and without inhibition than experimentally observed. This is most probably due to the real difficulty of biomass to recover its biodegradation activity once inhibitory conditions have affected the cells. Normally, more than a week might be necessary to recover biomass degradation capacity after an inhibition episode

In any case, the mathematical model presented herein including most of the phenomena occurring in a biofilter 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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