Efficient dynamic simulation of pH in processes associated to biofiltration of volatile inorganic pollutants

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Abstract
This work proposes a generic methodology to include the pH as a state variable in mathematical models of bioreactors. An ordinary differential equation for pH is stated and introduced into the general model structure of a biotrickling filter. All chemical equilibriums were considered and included into the model framework. A preliminary evaluation was performed by comparing results predicted by the model with experimental data obtained from the oxidation of thiosulfate by sulfide-oxidizing bacteria under alkaline conditions. The model was able to describe adequately the evolution of the main state variables including the pH for the initial complete oxidation of thiosulfate. The methodology presented here can be easily adapted to other mathematical models dealing with biological waste treatment processes in which pH appears as a key factor.

Keywords: pH, oxidation of reduced sulfur-compounds, biofiltration model

INTRODUCTION

In most biological waste treatments, pH appears as fundamental operational variable. Indeed, the microorganisms activity is normally restricted to an optimal pH range. Also, pH plays an important role in some physical processes like absorption and stripping of gaseous compounds. However, many mathematical models oriented to simulate biological treatments do not include the pH as a state variable. In the biofiltration of volatile organic compounds, this approximation is justified since under relatively low inlet concentrations the pH remains practically constant, especially when organic packing materials acting as buffer are employed.

On the contrary, in biological reactors treating inorganic volatile compounds (i.e. ammonia or reduced sulfur compounds), significant changes of pH can be observed. In these cases, pH arises as a critical variable on model predictions due to its influence on the biokinetics parameters, equilibriums of the chemical species, and processes related to liquid–gas mass transfer. Therefore a reliable biofiltration model requires an accurate description of pH evolution

Different algorithms have been reported in the literature to dynamically predict pH evolution in biological systems. Most of them are based on the electro-neutral condition of the aqueous phase (Volcke et. al, 2005). Basically, this approach consists in solving an implicit non-linear algebraic equation within every numerical integration step of the model (Batstone et. al, 2002; Ebrahimi et. al 2005; Baquerizo et. al, 2007). This equation is referred to proton concentration $[H^+]$ and should take into account all ionic species involved, allowing to calculate the pH once the expression pH =

$log_{10}[H^+]$ is solved. In these cases, the required iterative calculations normally results in a high computing time for solving the model. Another common approach for the dynamic calculation of pH consists in considering acid/base equilibrium reactions as processes of the model and the resolution of the corresponding mass balance equation for each acid/base compounds (Musvoto et. al, 2000; Rosen and Jeppsson, 2006). Equilibrium rates are formulated in terms of forward and reverse reaction kinetics for the dissociation of each acid/bases pairs. This approach avoids the resolution of an implicit equation and thus pH is calculated explicitly from the sum of all ionic compounds, which is supposed to be zero. However, multiple different solutions from differential equations may be obtained if the rate coefficients are not properly chosen. As third approach, few models of biological systems have included the proton concentration as state variable (Campos and Flotats, 2003; Magrí et. al, 2007; Solé, 2008). Since a stiff system of differential equations is stated, model solution is conditioned to both the accurate definition of initial conditions and the numerical integration method.

The objective of this work is to develop a generic methodology to include the pH as state variable in mathematical models related to biological waste treatment processes. An ordinary differential equation for pH is stated and introduced into the general model structure. All chemical equilibriums involved are considered and included into the same model framework. This methodology is tested using experimental data obtained from biological processes normally encountered in biofiltration such as the oxidation of reduced sulfur compounds.

MATERIALS AND METHODS

Experiments were performed in a lab scale biotrickling filter packed with polyurethane foam colonized by sulfide-oxidizing microorganisms. More details of the pilot-unit can be found elsewhere (Bonilla-Blancas et. al, 2010). The reactor was operated at counter-current mode and fed with fresh air reaching an empty bed residence time (EBRT) of 10 s. The system was equipped with a detector for gaseous oxygen in gas phase (model 1000, California Analytical Instruments Inc., USA), an electrode for dissolved oxygen (OD 565.2, B&C Electronics, Italy) and a pH meter (pH 20, Conductronic, Mexico). All experiments were conducted at room temperature (25±2 ^oC).

Experiments began with the addition of 210 mL of low buffered mineral medium containing (g L^{-1}): Na_2CO_3 (0.25); $NaHCO_3$ (0.7); NaCl (5); K_2HPO_4 (1.0); KNO_3 (1.01); $MgCl_6 \cdot H_2O$ (0.4) providing an initial pH value of 10. Aqueous phase was continuously recycled and aerated for some hours to stabilize the biofilm. Afterwards, the reactor was closed and immediately a pulse of concentrated thiosulfate (1600 mmol $S_2O_3^{=}$ L^{-1}) was added to obtain initial thiosulfide concentrations ranged from 60 to 100 mmol $S_2O_3^{=}$ L^{-1} in the biotrickling reservoir. Both on-line data of gaseous and dissolved oxygen were monitored in a PC by means of LabJack (Lakewood, USA) acquisition software. Thiosulfate concentrations at the end of experiments were measured by titration using an iodine solution (Rodier, 1998).

MODEL DEVELOPMENT

General considerations

The biotrickling filtration process was modeled using general mass balances that include the most relevant physical and biological phenomena involved during pollutant transport and oxidation. Mass balances were stated on the basis previously described by Kim and Deshusses (2003), in which the effects of axial dispersion and mass transfer limitation in the gas phase were neglected. Also the biofilm was assumed to be fully wetted. Since experiments are of short duration, all phenomena related to biomass (i.e. biomass growth, biofilm thickness variation or biomass detachment among others) were considered invariable in the model basis.

Mass balances equations

Three phases were considered in the model: gas, liquid and biofilm (Eq. 1-3). A solid phase was not considered due to the negligible adsorption capacity of polyurethane foam. Biotrickling reservoir was also included and modeled as aqueous phase (Eq. 4). Lumped variables were employed to model the process in order to avoid stating equilibrium equations for the ionic species. This approach is supported by the fact that the diffusion coefficient of the combined variable is practically equal to the diffusion coefficient of single species involved. Therefore variables considered in the mass balances of liquid and biofilm phases were: oxygen, total thiosulfate (S_{thio}) as the sum of $S_2O_3^{=}$ and $HS_2O_3^{-}$, total sulfate (S_{SO4}) as the sum of $SO_4^{=}$ and HSO_4^{-}, total inorganic carbon (S_{IC}) as the sum of CO_2, HCO_3^{-} and $CO_3^{=}$, and total phosphate (S_{phos}) as the sum of H_3PO_4, $H_2PO_4^{-}$, $HPO_4^{=}$ and PO_4^{-3}. Since H_2CO_3 and $H_2S_2O_3$ are unstable species, they were not included as model compounds. Likewise H_2SO_4 was considered completely dissociated (i.e. high pKa) and thus it was not considered as part of total sulfate lumped variable. Additional ionic species supplied with the liquid medium such as K^+, Na^+, Mg^{+2} and Cl^- were also included in the liquid and biofilm phases for pH calculation. Regarding the gas phase, CO_2 and O_2 were considered into the mass balances. The set of partial differential equations related to packed bed was discretised in space along the bed height, and biofilm thickness.

Gas phase

$$\frac{\partial C_{g,i}}{\partial t} = -v_g \frac{\partial C_{g,i}}{\partial z} - \frac{K_L a_i}{\varepsilon_g}\left(\frac{C_{g,i}}{H_i} - C_{l,i}\right) \qquad i = O_2, CO_2 \qquad (1)$$

Liquid phase

$$\frac{\partial C_{l,i}}{\partial t} = -v_l \frac{\partial C_{l,i}}{\partial z} + \frac{K_L a_i}{\varepsilon_l}\left(\frac{C_{g,i}}{H_i} - C_{l,i}\right) + \frac{a}{\varepsilon_l} D_{b,i}\left.\left(\frac{\partial C_{b,i}}{\partial x}\right)\right|_{x=0} \qquad i = O_2, S_{thio}, S_{SO4}, S_{IC}, S_{phos} \qquad (2)$$

Biofilm phase

$$\frac{\partial C_{b,i}}{\partial t} = D_{b,i}\frac{\partial^2 C_{b,i}}{\partial x^2} - r_{b,i} \qquad i = O_2, S_{thio}, S_{SO4}, S_{IC}, S_{phos} \qquad (3)$$

Biotrickling Reservoir

$$\frac{d C_{l,i}^{res}}{dt} = \frac{Q_L}{V_l^{res}}\left(C_{l,i}^{bottom} - C_{l,i}^{res}\right) \qquad i = O_2, S_{thio}, S_{SO4}, S_{IC}, S_{phos} \qquad (4)$$

where $C_{g,i}$, $C_{l,i}$, and $C_{b,i}$ are the concentrations of the component i in the bulk gas phase, bulk liquid phase and biofilm respectively (g m^{-3}); $C_{l,i}^{bottom}$ is the liquid concentration of the component i at the bottom of the packed bed (g m^{-3}); $C_{l,i}^{res}$ is the liquid concentration of the component i in the liquid recycling tank (g m^{-3}); Q_L is the liquid volumetric flow rate passing through the packed bed (m^3 h^{-1}); v_g, and v_l are the interstitial velocities for gas and liquid in the packed bed, respectively (m h^{-1}); V_l^{res} is the reservoir volume (m^3); ε_g, and ε_l are the volume fractions occupied by the gas and liquid in the packed bed, respectively (m^3 m^{-3}); K_La_i is the mass transfer coefficient of the component i (h^{-1}); H_i is the gas/liquid partition coefficient of component i (dimensionless); $D_{b,i}$ is the diffusion coefficient of component i in the biofilm (m^2 h^{-1}), a is the specific surface area per volume of reactor bed (m^2 m^{-3}); x is the thickness position in the biofilm (m); z is the position along the reactor height (m); $r_{b,i}$, is the consumption rate of component i in the biofilm (g m^{-3}h^{-1}).

pH modeling

A general differential equation describing the pH evolution in the liquid and biofilm phase was developed and included in the model framework. The dynamic calculation of pH was based on the charge balance equation (Eq. 5) once the main equilibriums occurring in the system were identified (Table 1). Dissociation equations were assumed to occur instantaneously and to be affected by temperature conditions.

$$\begin{aligned}\varphi = {} & 2[S_2O_3^{=}] + 2[SO_4^{=}] + [HCO_3^{-}] + 2[CO_3^{=}] + [H_2PO_4^{-}] + 2[HPO_4^{=}] + \\ & 3[PO_4^{-3}] + [NO_3^{-}] + [Cl^{-}] - [K^{+}] - [Na^{+}] - 2[Mg^{+2}] + [OH^{-}] - [H^{+}]\end{aligned} \qquad (5)$$

Table 1. Equilibriums considered in the model

Compounds	Equilibrium
Thiosulfate	$HS_2O_3^{-} \xleftrightarrow{K_{thio}} S_2O_3^{=} + H^{+}$
Sulfate	$HSO_4^{-} \xleftrightarrow{K_{so4}} SO_4^{=} + H^{+}$
Inorganic carbon	$CO_2 + H_2O \xleftrightarrow{K_{IC1}} HCO_3^{-} + H^{+} \xleftrightarrow{K_{IC2}} CO_3^{=} + 2H^{+}$
Phosphate	$H_3PO_4 \xleftrightarrow{K_{phos1}} H_2PO_4^{-} + H^{+} \xleftrightarrow{K_{phos2}} HPO_4^{=} + 2H^{+} \xleftrightarrow{K_{phos3}} PO_4^{-3} + 3H^{+}$
Water	$H_2O \xleftrightarrow{K_w} OH^{-} + H^{+}$

Concentration of ionic species associated to lumped compounds can be expressed as a function of: concentration of the corresponding lumped variables, the respective dissociation constants and the proton concentration. As an example, concentration of carbonate ion can be computed as follows (Eq. 6):

$$[CO_3^{=}] = S_{IC} \cdot \frac{K_{IC1}K_{IC2}}{[H^{+}]^2 + K_{IC1}[H^{+}] + K_{IC1}K_{IC2}} \qquad (6)$$

where S_{IC} corresponds to the concentration of total inorganic carbon.

Therefore the charge balance equation can be expressed as a function of single and lumped variables besides the proton concentration (Eq. 7).

$$\varphi(H^{+}) = f(S_{thio}, S_{SO_4}, S_{IC}, S_{phos}, S_{NO3}, S_{Cl}, S_K, S_{Na}, S_{Mg}, S_{OH^-}, S_{H^+}) = 0 \qquad (7)$$

where S_{thio}, S_{SO4}, S_{IN} and S_{phos} correspond to the concentration of total thiosulfate, total sulfate, total inorganic nitrogen and total phosphate in the aqueous phases (i.e. liquid and biofilm phases) respectively. S_{H+} represents the proton concentration $[H^+]$. Previous expression can then be derived to obtain the following equation:

$$\frac{\partial\varphi}{\partial t} = \frac{\partial\varphi}{\partial S_{thio}}\frac{\partial S_{thio}}{\partial t} + \frac{\partial\varphi}{\partial S_{SO_4}}\frac{\partial S_{SO_4}}{\partial t} + \frac{\partial\varphi}{\partial S_{IC}}\frac{\partial S_{IC}}{\partial t} + \ldots + \frac{\partial\varphi}{\partial S_{OH^-}}\frac{\partial S_{OH^-}}{\partial t} + \frac{\partial\varphi}{\partial S_{H^+}}\frac{\partial S_{H^+}}{\partial t} = 0 \quad (8)$$

Considering the expression of pH dependent on $[H^+]$ (i.e. pH = $-\log_{10} S_{H+}$), and $S_{OH^-} = K_W / S_{H+}$, previous equation was rearranged as:

$$\frac{\partial pH}{\partial t}\left(-10^{-pH}\ln(10)\right)\left(\frac{\partial\varphi}{\partial S_{H^+}} + \frac{K_w}{S_{H^+}^2}\right) = -\frac{\partial\varphi}{\partial S_{thio}}\frac{\partial S_{thio}}{\partial t} - \cdots - \frac{\partial\varphi}{\partial S_{IC}}\frac{\partial S_{IC}}{\partial t} \qquad (9)$$

Terms related to derivates of function φ with respect to state variables (except for proton) are algebraic expressions that can be directly obtained from the charge balance equation. The derivative of function φ with respect to proton can be calculated accounting for the corresponding individual derivatives of dissociation factors. Remainder expressions correspond to mass balance equations of total compounds.

Free thiosulfate and oxygen were considered as the unique limiting substrates for sulfide-oxidizing bacteria according to a double Monod-type kinetic expression (Eq. 10). Other substrates (i.e. inorganic carbon or inorganic nitrogen) were not considered rate-limiting since their concentrations were assumed to be in excess during experiments.

$$r = \mu_{\max} X \left(\frac{S_{b,O_2}}{S_{b,O_2} + K_{S,O_2}} \right) \left(\frac{S_{b,S_2O_3^=}}{S_{b,P} + K_{S,S_2O_3^=}} \right) \quad (10)$$

where μ_{max} is the maximum specific growth rate for biomass (h^{-1}), X is the biomass concentration ($g\ m^{-3}$), $S_{b,i}$ is the concentration of the component i in the biofilm ($mol\ L^{-1}$),and $K_{S,i}$ is the half saturation constant for the component i ($mol\ L^{-1}$).

Yield coefficients for oxygen and thiosulfate were computed from the stoichiometric equation (Eq. 11) assuming that the composition of sulfide-oxidizing biomass was represented by $CH_{1.625}N_{0.24}O_{0.375}$.

$$S_2O_3^= + 1.5719\,O_2 + 0.4151\,HCO_3^- + 0.1038\,NH_4^+ + 1.6887\,OH^- \rightarrow 0.4151\,CH_{1.625}N_{0.24}O_{0.375} + 2\,SO_4^= + 0.9222\,H_2O \quad (11)$$

RESULTS AND DISCUSSION

The validation of the dynamic model was performed by comparing results predicted by the model with experimental data obtained from the oxidation of thiosulfate by sulfide-oxidizing bacteria under alkaline conditions. Experimental data used correspond to 21 operating-hours of the biotrickling filter under dynamic conditions with an initial thiosulfate concentration in the liquid phase of 68.6 mmol $S_2O_3^=\ L^{-1}$. Monitoring of dissolved oxygen at biotrickling reservoir and gaseous oxygen at biotrickling top was performed periodically during the experiment (i.e. every 5 sec.).

Simulation of the experimental period was performed assuming that concentrations of ionic species provided with the mineral medium remained constant except for the inorganic carbon. Model parameters were both determined by separated experiments and taken from literature. In this sense, abiotic experiments were conducted for estimating K_La. Biokinetic parameters were previously determined by means of biotic experiments (Bonilla-Blancas et. al, 2010). Model was implemented using Matlab (The Mathworks, USA) in a home-made modeling environment. In Fig. 1, gaseous and liquid oxygen concentration predicted by the model are plotted and compared to experimental data. Consumption of oxygen by sulfide-oxidizing bacteria was satisfactorily predicted by the model in both gas and liquid phase. Moreover, consumption of thiosulfate was also well predicted by comparing sulfate concentration at the end of the experiment (i.e. 45.7 mmol $S_2O_3^=\ L^{-1}$) with model calculation (i.e. 41.1 mmol $S_2O_3^=\ L^{-1}$).

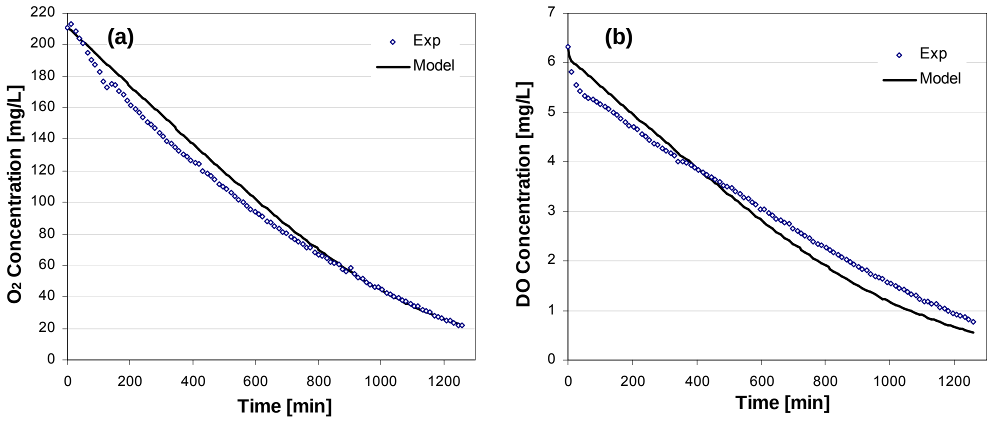

Figure 1. Oxygen consumption during oxidation of thiosulfate in (a) gas phase and (b) liquid phase

Regarding pH, an expected decrease in pH was observed along the operating period since low buffered mineral medium was employed. Experimental data and model predicted results for pH are depicted in Fig. 2. A good model fitting was observed for the first 10 operating hours. However the model predicted lower pH values after 10 hours than those observed experimentally. This can be explained by the fact that model considers sulfate as the only product from the aerobic thiosulfate oxidation under experiments conditions (Eq. 11). Nevertheless, it is well known that elemental sulfur may also be generated from the oxidation of reduced sulfur compounds by sulfide oxidizing microorganisms especially under oxygen limiting conditions (Eq. 12). The formation of each species is conditioned to the availability of dissolved oxygen (Janssen et. al, 1995).

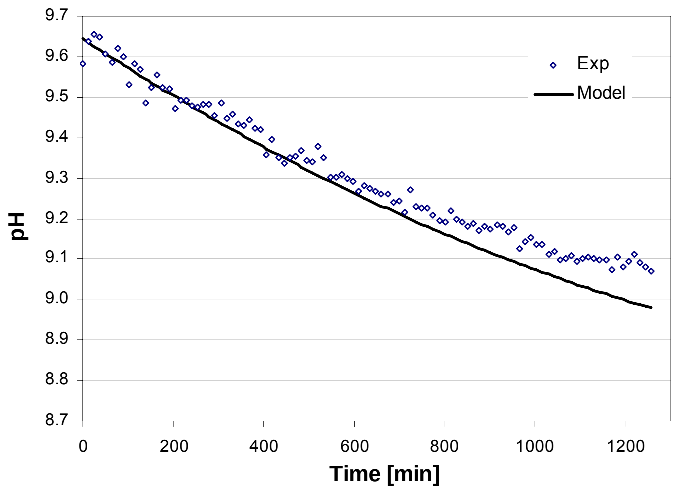

Figure 2. Dynamic evolution of pH predicted by the model compared to experimental data for thiosulfate oxidation

$$S_2O_3^{=} + \frac{1}{2} O_2 \rightarrow SO_4^{=} + S^0 \qquad (12)$$

Thus, oxygen limiting conditions in the biofilm after 10 hours of operation probably led the system towards the formation of elemental sulfur. This fact results in a slower decrease of pH than model predictions. Accuracy of model prediction might be improved if both metabolic paths (i.e. production of sulfate and elemental sulfur) were included as a function of oxygen concentration.

CONCLUSIONS

The mathematical model developed here was able to describe adequately the evolution of the main state variables, including pH in a biotrickling filter aimed at the oxidation of thiosulfate by sulfide-oxidizing bacteria under alkaline conditions. Probably model predictions could be improved if the formation of elemental sulfur would be included into the stoichiometry equation for thiosulfate oxidation.

In any case, the methodology used here can be easily adapted to other biological models in which pH appears as a key factor. Model adaptation is conditioned to the proper identification of different ionic species that contribute to pH variation in the system. On the other hand, future improvements are related to considering ionic activities of chemical species according to the ionic strength of the medium rather than their concentrations.

REFERENCES

Baquerizo, G.; Gamisans, X.; Gabriel, D. and Lafuente J. (2007) A dynamic model for ammonia abatement by gas-phase biofiltration including pH and leachate modeling. *Biosystems Engineering* 97(4): 431-440.

Batstone, D.J.; Keller, J.; Angelidaki, I.; Kalyuzhnyi, S.V.; Pavlostathis, S.G.; Rozzi, A.; Sanders, W.T.M.; Siegrist, H. and Vavilin V.A. (2002) The IWA Anaerobic Digestion Model No 1 (ADM1). *Water Science & Technology* 45(10): 65-73.

Bonilla-Blancas, W.C.; Baquerizo, G.; Gonzalez-Sanchez, A. and Revah, S. (2010) Characterization of packing bed from an operating biofilter by respirometry. *In Proceedings of Conference on Biofiltration for Air Pollution Control*. October 2010, Washington, USA.

Campos, E. and Flotats, X. (2003) Dynamic simulation of pH in anaerobic processes. *Applied Biochemistry & Biotechnology* 109(1-3): 63-76.

Ebrahimi, S.; Picioreanu, C.; Kleerebezem, R.; Heijnen, J.J. and van Loosdrecht, M.C.M. (2005) Rate based modeling of a sulfite reduction bioreactor. *A.I.Ch.E. Journal* 51(5): 1429-1439.

Janssen, A.J.H.; Ruitenberg, R. and Buisman, C.J.N. (2001) Industrial applications of new sulphur biotechnology. *Water Sci. & Technol*. 44(8): 85-90.

Kim, S. and Deshusses, MA. (2003) Development and experimental validation of a conceptual model for biotrickling filtration of H_2S. *Environ. Prog.* 22(2): 119-128.

Magrí, A.; Corominas, Ll.; López, H.; Campos, E.; Balaguer, M.; Colprim, J. and Flotats, X. (2007) A model for the simulation of the SHARON process: pH as a key factor. *Environmental Technology* 28(3): 255-265.

Musvoto, E.V.; Wentzel, M.C.; Loewenthal, R.E. and Ekama, G.A. (2000) Integrated chemical-physical processes modelling –I. Development of a kinetic-based model for mixed weak acid/base systems. *Water Research* 34(6): 1857-1867.

Rodier J. (1998) Análisis de las aguas. Ediciones Omega. Barcelona, Spain.

Rosen, C. and Jeppsson, U. (2006) Aspects on ADM1 implementation within the BSM2 framework. Department of Industrial Electrical Engineering and Automation, Technical Report, Lund University. Lund, Sweden.

Solé, J. (2008) Development of a Model for an Absorption Filter (*in catalan*). University of Lleida. Master Thesis. Lleida, Spain.

Volcke, E.I.P.; Van Hulle, S.; Deksissa, T.; Zaher, U. and Vanrolleghem P. (2005) Calculation of pH and concentration of equilibrium components during dynamic simulation by means of a charge balance. University of Gent. Internal Report. Gent, Belgium.