Incorporating water chemistry into the steady-state models for wastewater treatment processes: case study anaerobic reactor in the SANI® process

I. Lizarralde*, C. J. Brouckaert**, G. A. Ekama*** and P. Grau*

* CEIT and Tecnun (University of Navarra) Manuel de Lardizábal 15, 20018 San Sebastián, Spain
(E-mail:*ilizarralde@ceit.es; pgrau@ceit.es*)
** Pollution Research Group, School of Chemical Engineering, University of KwaZulu-Natal, Durban 4041, South Africa
(E-mail: *brouckae@ukzn.ac.za*)
*** Water Research Group, Department of Civil Engineering, University of Cape Town, Rondebosch, 7700, Cape Town South Africa.
(E-mail: *george.ekama@uct.ac.za*)

Abstract
The awareness of the effect of abiotic processes in wastewater treatment and sludge treatment technologies is increasing considerably. However traditionally used mathematical models either do not represent abiotic processes, or use simplified approaches. This paper presents a mathematical model able to represent abiotic processes in the steady-state model developed for the anaerobic reactor in the SANI® process. The capability of the model to predict the water chemistry present in the system is shown with experimental data from a pilot-scale plant and finally the benefits of incorporating water chemistry into the anaerobic reactor model are shown with a theoretical exploration by simulation.

Keywords
Mathematical modelling, SANI, water chemistry

INTRODUCTION

Mathematical modelling and simulation tools have been proven to be very valuable tools to enable the comprehension of wastewater treatment processes as well as evaluating the optimum design and operation strategies. Even though since the publication of the ASM1 model in the 1980s (Henze et al, 1987) dynamic models have become more prominent, steady-state models constitute a very valuable tool for design purposes, since they allow for the sizing of design parameters, such as reactor volumes or recycle flows to be determined from explicit equations in terms of unit operation performance criteria (Ekama 2009). In this sense, different works have been published: Albizuri et al., 2010 proposes a set of equations that allow for the design of biofilms, Lizarralde et al., 2012 proposes a library of mathematical models for the design of optimum water networks in industry and Ekama 2009 that proposes a plant-wide steady-state model for urban wastewater treatment plant design.

Like in the existing dynamic models, in these steady-state models biological processes are described appropriately and nowadays the concern is focusing in describing the chemical processes. Because of the use of new and complex treatments where weak acid-base reactions (ionization), spontaneous or chemical dose-induced precipitation or liquid-gas transfer may take place, water chemistry cannot be neglected (Batstone et al., 2010). However, describing water chemistry implies numerical complexity and consequently in many cases its description has been neglected or much simplified. To overcome this, a new IWA Physico-Chemical Framework Task Group (IWA PCF TG) has recently been constituted with the goal of developing some guidelines and procedures to facilitate modellers to consider all these processes (Batstone et al., 2010).

In particular, for this work a case study has been selected, which focuses on the anaerobic reactor of a novel wastewater treatment technology, sulphate reduction, autotrophic denitrification, nitrification integrated (SANI®) process, developed by a research team in the Hong Kong University of Science and Technology (Wang et al., 2009). This technology has been developed to cope with saline wastewaters, containing particularly high concentrations of sulphates (2.2 gCOD:gSO_4^-), produced

when seawater is employed as an alternative water source for toilet flushing. A steady-state mathematical model was built to evaluate the performance of the SANI® process by Lu et al., (2012). However for this model pH prediction is based on simplified inorganic carbon and sulphide weak acid base equilibrium. The simplification of considering solely weak acid base equilibrium may not be completely correct since chemical processes play an important role in anaerobic processes. Besides, given that seawater is being used, wastewater has high ionic strength thus ionic activity needs to be considered for pH calculation.

Based on these postulates the work presented in this paper aims to upgrade the model for the anaerobic reactor in the SANI® process by incorporating water chemistry associated with the inorganic components present in the system into the biological model.

PROCEDURE TO INCORPORATE WATER CHEMISTRY INTO BIOCHEMICAL STEADY-STATE MODELS

Mathematical models built to describe biological processes comprise three steps: (1) kinetic based model description; (2) definition of process stoichiometry; and (3) water chemistry definition to predict pH (Sötemann et al., 2005). In the case of steady-state models, these three steps are calculated in a sequential way (Figure 1).

Figure 1 Model resolution procedure

The details of the model for biological sulphate reduction used to describe the anaerobic treatment in the SANI® process can be found in Poinapen and Ekama (2010). This work focuses on the third step of the procedure: the incorporation of water chemistry into the biochemical model. The specifications for the water chemistry model for the SANI® case study are presented in the following section.

WATER CHEMISTRY FOR THE ANAEROBIC REACTOR OF THE SANI® PROCESS

In order to describe the water chemistry in the system under study, 15 components and 50 species were selected (Table 1). Species are chemical entities taken to be physically present in the system, and components are a linearly independent set of stoichiometric elemental ratios which span the entire compositional space of interest to the model. (That is, the elemental amounts present in any composition of interest can be uniquely specified as a linear combination of component concentrations). Chemical equilibrium modelling consists basically of formulation of the material balance and equilibrium relationships which determine species concentrations from a mixture composition specified in terms of component concentrations.

Table 1. List of species and components selected for the SANI® process

Components			Species									
Sac	Shs	Sca	Ac	H	NH_3	PO_4	CaH_2PO_4	$CaPO_4$	HAc	$KHPO_4$	MgH_2PO_4	MgPr
Spr	Sso4	Scl	Pr	K	NH_4	SO_4	$CaHCO_3$	$CaSO_4$	HCO_3	KSO_4	$MgHCO_3$	$MgSO_4$
Sco3	Sh	Smg	Ca	HS	NO_2	CO_3	$CaHPO_4$	H_2CO_3	HPO_4	Mg	$MgHPO_4$	$NaCO_3$
Snh4	Sno2	Sna	Cl	Mg	NO_3	CaAc	$CaNO_3$	H_2PO_4	HS	MgAc	MgOH	$NaHPO_4$
Spo4	Sno3	Sk	Pr	Na	OH	$CaCO_3$	CaOH	H_2S	K	$MgCO_3$	$MgPO_4$	$NaSO_4$

The principles of ionic speciation calculations are set out in Stumm and Morgan (1996). The

equilibrium relationships are formulated in terms of species activities (e.g. Eq1), which are related to their concentrations by activity coefficients (e.g. Eq2). Activity coefficients were modelled using the Davies equation (Eq3 and Eq4).

$$K_a = \frac{\{H^+\}\{A^-\}}{\{HA\}} \quad \text{(Eq1)} \qquad \{H^+\} = \gamma_{H^+} \cdot [H^+] \quad \text{(Eq2)} \qquad I = \frac{1}{2}\sum_i C_i \cdot z_i^2 \quad \text{(Eq3)} \qquad \log(\gamma_i) = -Az_i^2\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right] \quad \text{(Eq4)}$$

Where,

Ka: equilibrium constant
{*S*}: activity of species *S*
[*S*]: concentration of species *S*
γ_S: activity coefficient of species *S*
I: Ionic strength
C_i: concentration of species i
Z_i: charge of species i
A:Debye-Huckel constant

The mass conservation equation is applied to all ionic components considered. The relationship can be expressed as follows:

$$\sum_i a_{ij} C_i - T_j = 0$$

Where,

a_{ij}: stoichiometric relationship of species *i* and component *j*;
C_i: concentration of species *i*; and
T_j: concentration of component *j* given by the process model mass balance.

Combining these mass conservation equations and the equilibrium constraints, a set of simultaneous equations is obtained which can be solved for all the species concentrations. Since the equations are non-linear, an iterative numerical solution was used.

The mathematical model described above was implemented in WEST (www.mikebydhi.com), which is a user-friendly modelling environment adapted to wastewater systems.

MODEL VERIFICATION AND EXPLORATION BY SIMULATION

The objective of this verification study was to check the capability of the model to reproduce the real performance of the anaerobic tank, considering both sulphate and COD removal efficiency and water chemistry, and a simulation scenario was defined for this purpose. In the present study, the configuration and operating conditions of the reactor were taken from a pilot plant reactor presented by Lu et al., (2012) (Table 2). The values for the stoichiometric and kinetic parameters were adopted from Poinapen and Ekama (2010).

Table 2. Influent wastewater characteristics and operational conditions

Influent wastewater characteristic		Operating conditions	
Q (m^3/d)	10	HRT (h)	16.3
tCOD (gDOD/d)	431.1	SRT (d)	90
$SO_4^=$ ($gSO_4^=$ /m^3)	195.7	T (ºC)	25

Results and discussion

The comparison between the experimental data and results obtained with the new model in Table 3 show reasonable agreement with respect to COD removal, sulphate removal and pH.

As an example of the capability of the model, an exploration study by simulation has been carried out with the aim of predicting the competition between sulphate reducing bacteria and methane producing bacteria and pH values under different inflow alkalinity values is shown in Figure 2. It can be seen that the pH increases as influent alkalinity increases, which is coherent with the process behaviour. Regarding the competition of sulphate reducing bacteria and methanogenic bacteria for COD it can be

seen that it is dependent on pH values. The variables fMPB and fSRB represent the fraction of inflow COD consumed by methanogenic bacteria or sulphate reducing bacteria respectively. The vertical line represents the operating point of the pilot-scale reactor. At pH values below 6.9 sulphate reducing bacteria are inhibited thus methanogenic bacteria out-compete sulphate reducing bacteria, whereas for higher pH values sulphate reducing bacteria are able to consume all the COD present in the reactor. This behaviour matches to the behaviour presented by Visser et al., 1996.

Table 3. Comparison between experimental and simulated result

Variable	Description	Experimental data	Simulated
Δ_{COD}	COD removed ($gCOD/m^3$)	332.1	342.8
$\Delta_{SO4=}$	$SO_4^=$ removed ($gSO_4^=/m^3$)	130.3	171.4
pH	pH	7.20	7.32

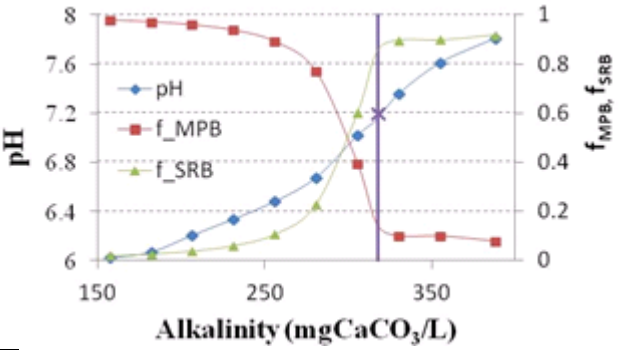

Figure 2. Effect of influent alkalinity on pH and competition between BMP and SRB

CONCLUSIONS

The importance of the pH and abiotic processes in the performance of the biological process has been demonstrated, and therefore the necessity of calculating the pH value in the models representing these biological processes has been proven. A mathematical model able to reproduce and compute water chemistry related phenomena has been developed and successfully implemented in the simulation software WEST.

ACKNOWLEDGEMENTS

The authors wish to thank the European Commission for financing the EU-Project Aquafit4use (grant number 211534) within the VII Framework Program. Water Research Commission for financing the collaboration between the authors

REFERENCES

Albizuri, J, Santamaría, A and Larrea, L (2010). IFAS process for Nitrogen Removal with HRT of 4 Hours. Proceedings of WEF/IWA Biofilm Reactor Technology Conference 2010.

Batstone D.J., Amerlinck Y., Ekama G., Goel R., Grau P., Johnson B., Kaya I., Steyer J-P., Takács I., Vanrolleghem P.A. and Volcke E. (2010). Towards a Generalized Physicochemical Framework. *Wat. Sci. Tech*. **66**(6) 1147-1161.

Ekama, G.A. 2009. Using bioprocess stoichiometry to build a plant-wide mass balance based steady-state WWTP model. Water Research **43** (2009). 2101-2120.

Henze, M., Grady, C. P. L., Gujer, W., Marais, G. V. R. and Matsuo, T. 1987. *Activated Sludge Model Nº1*. I.S.A.T.R. Nº1,

Lizarralde, I., Claeys, F., Ordóñez, R., de Gracia, M., Sancho, L. and Grau, P. 2012. Water Network Cost Optimization in a Paper Mill Based on a New Library of Mathematical Models. Water Science and Technology **65** (11) pp. 1929-1938.

Lu, H., Ekama, G.A., Wu, D., Feng, J., van Loosdrecht, M.C.M. and Chen, G. 2012. SANI® process realizes sustainable saline sewage treatment: Steady state model-based evaluation of the pilot-scale trial of the process. *Water Research* **46** 475-490.

Poinapen, J. and Ekama, G.A. 2010. Biological sulphate reduction with primary sewage sludge in an upflow anaerobic sludge bed reactor – Part 5: Steady-state model. Water SA 36 (3) 193-202.

Sötemann, S.W., Ristow, N.E., Wentzel, M.C. and Ekama, G.A. 2005. A steady state model for anaerobic digestion of sewage sludges. Water SA **31** (4) 511-527.

Stumm W. and Morgan J. J. 1996. *Aquatic Chemistry: Chemical equilibria and rates in natural waters.* John Wiley & Sons Inc. New York.

Visser, A., Hulshoff Pol, L.W. and Lettinga, G 1996. Competition of methanogenic and sulphidogenic bacteria. Water Science and Technology **33**(3) 99-110.

Wang, J., Lu, H., Chen, G., Lau, G.N and Tsang, W.L. 2009. A novel sulphate reduction, autotrophic denitrification, nitrification integrated (SANI) process for saline wastewater treatment. Water Research 43 (2009) 2363-2372.