Incorporating aquatic chemistry into wastewater treatment process models: A critical review of different approaches

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INTRODUCTION
In recent years the awareness of the effect of abiotic processes in wastewater and sludge treatment technologies has increased rapidly (Batstone *et al.,* 2012). In the field of municipal wastewater treatment for example, chemical processes play an important role in the performance of different technologies present throughout the plant. Besides, pH has an important impact on other processes that may take place in wastewater treatment such as precipitation or liquid gas transfer. Such processes will be critical in the future of these facilities as there are attempts to operate them in a sustainable and environmentally-friendly way. For example, there is a general concern about scarcity of some natural resources and the recovery processes of these resources often rely on physico-chemical processes (Vanrolleghem, 2013). Another example is the need to reduce greenhouse gas emissions that originate in the processes occurring at the wastewater treatment plant. Therefore, an appropriate description of the abiotic processes is of high importance in the development of models for the description of wastewater treatment technologies.

Traditional mathematical models, widely used for wastewater and sludge treatment, have different levels of detail for the calculation of pH. In the models proposed for wastewater treatment (ASMs) it is considered that the buffering capacity is sufficient, therefore there is no rigorous calculation of pH included (Henze *et al*., 1987). In the case of models describing anaerobic digestion (ADM1) (Batstone *et al*., 2002), models describing river water quality (RWQM1) (Reichert *et al*., 2001) or the plant wide modelling (PWM) methodology proposed by Grau *et al*., (2007) pH calculation from chemical equilibria is included; however, these models do not consider ionic activity in the calculation, which makes the models only valid for dilute systems, with low ionic strength (Batstone *et al.,* 2012). In the UCTADM of Sötemann *et al.,* (2005a) ion pairing was included but the fast equilibrium and speciation processes were included as dynamic processes along with the slow biological and precipitation processes, causing slow calculation times and/or numerical instability. In the model proposed for biological nutrient removal N2 (BNRM2) by Barat *et al*., (2013) water chemistry is calculated using a commercial software tool MINTEQA2 (Allison *et al.,* 2009). Finally, the UCTADMP, upgrade of the anaerobic digestion UCTADM proposed by Ikumi

(2011) describes chemical reactions using an algebraic speciation model (Brouckaert *et al.,* 2010).

As a result it has been recognised that these traditional models should be updated and rewritten in order to include abiotic phenomena. To address this, the IWA Physico-Chemical Framework Task Group (IWA PCF TG) has recently been constituted with the goal of developing guidelines and procedures to assist modellers to consider all these processes (Batstone *et al.*, 2012). One particular aspect is that, from a numerical point of view, the inclusion of acid-base equilibrium and the subsequent pH calculation in biochemical models can lead to the appearance of some degree of stiffness, caused by the different conversion rates considered. This may introduce numerical instabilities and slow down the simulation speed. Tackling this problem requires analysis and testing of numerical methods that deal with combined algebraic and differential equations.

Based on these postulates, the work presented in this paper aims to introduce a methodology for incorporating aquatic chemistry into models representing wastewater treatment processes, based on different approaches found in literature for the description of aquatic chemistry and its numerical resolution. A simulation scenario has been defined in order to carry out a comparative analysis of the different approaches in terms of the accuracy of the results and the simulation time.

METHODOLOGY TO INCORPORATE WATER CHEMISTRY INTO WASTEWATER TREATMENT PROCESS MODELS

The construction of dynamic mathematical models comprises of: (1) the selection and description of the relevant biological and physico-chemical processes in the system under study and (2) the definition of water chemistry to predict pH tailored to the model defined in the first step (Figure 1).
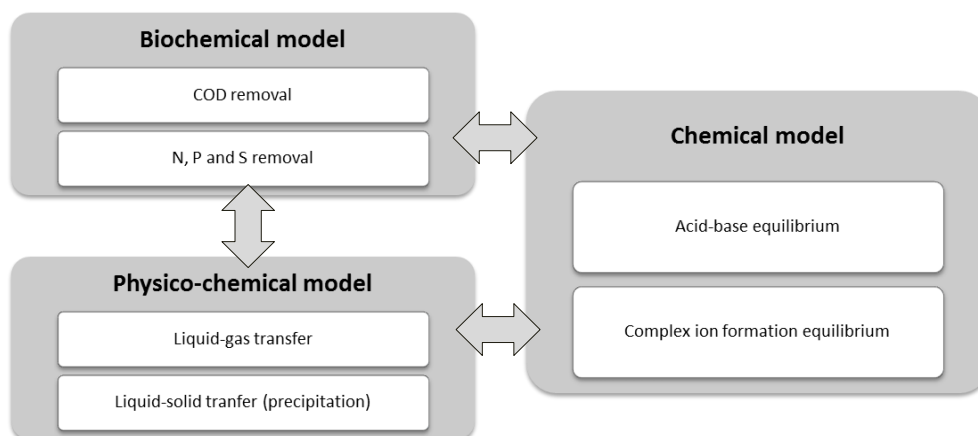
Figure 1. The selection of the chemical model depends on biological and physico-chemical model

The following sections focus on (1) the construction of the chemical model to describe chemical processes taking place in the system under study with the selected biological and physico-chemical processes; and (2) the introduction of different numerical resolution procedures to couple chemical models with biological and physico-chemical processes.

Modelling water chemistry

In order to describe the water chemistry in the system first the components and species have to be defined; as an example the 12 components and 38 species given in Table 1 were

collected for the case study presented below. Species are chemical entities taken to be physically present in the system, and for the given set of species, components are selected so that all species can be expressed as linear combination of components, and no component can be written as combination of other components. Chemical equilibrium modelling consists basically of formulation of the material balance and mass action law which determine species concentrations from a mixture composition specified in terms of component concentrations.

Table 1. List of species and components selected

Components			Species									
S_h	S_{TVA}	S_{Ca}	H	Mg	H_2CO_3	H_2PO_4	Hac	Hpro	CaH_2PO_4	MgH_2PO_4	$MgCO_3$	$NaHPO_4$
S_{IP}	S_{TBU}	S_{Mg}	Na	OH	HCO_3	HPO_4	Ac	Pro	$CaHCO_3$	$MgHCO_3$	$MgPO_4$	NaOH
S_{IN}	S_{TPRO}	S_{Na}	Ca	NH_3	CO_3	PO_4	Hbu	Hva	$CaHPO_4$	$MgHPO_4$	$NaCO_3$	
S_{IC}	S_{TAC}	S_{Cl}	Cl	NH_4	$CaCO_3$	CaOH	Bu	Va	$CaPO_4$	MgOH	$NaHCO_3$	

The principles of water chemistry modelling 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). The mass conservation equation can be expressed either to (i) guarantee electroneutrality, i.e. guarantee the sum of cations equals the sum of anions (Eq5) or (ii) using the alkalinity-acidity continuity, this is formulating proton conservation equations (Eq6). Combining these mass conservation equations and the mass action relationships, a set of simultaneous equations is obtained which can be solved for all species concentrations.

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

Where,

K_a: equilibrium constant $[S]$: molality of species S I: Ionic strength Z_i: charge of species i
$\{S\}$: activity of species S γ_S: activity coefficient of S M_i: molality of species i   A:Debye-Huckel constant

$$\sum S_{C+} - \sum S_{A-} = 0 \text{ (Eq5)}$$

Where,
S_{C+}: represents total cation equivalent concentration; and
S_{A-} : represents total anion equivalent concentration.

$$\sum_i a_{ij}M_i - T_j = 0 \qquad \text{(Eq6)}$$

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

Numerical resolution procedure
When combining biological and chemical reactions, numerical resolution is a critical step, because of the stiffness that arises when considering reactions with very different conversion rates. In the case of dynamic models, there are two possible resolution procedures:

(i)   All reactions are calculated simultaneously using ordinary differential equations (ODE) as in Musvoto *et al.* (2000a,b) and Sötemann *et al.* (2005a,b).
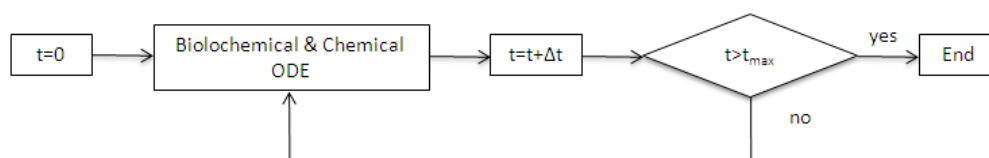
Figure 2. Model resolution procedure using the ordinary differential equations (ODE approach)

(ii)   The slower reactions are represented by differential equations and the fast reactions are calculated algebraically (DAE) at each iteration step (Figure 3) as in ADM1 (Batstone

et al., 2001), Volcke *et al.,* (2005), Rosen *et al.* (2006) or UCTADMP (Brouckaert *et al.,* 2010; Ikumi *et al.,* 2011). In the DAE approach, the modeller can choose between having a tailored code to solve water chemistry or using an external software tool such as PhreeqC+ (Parkhurst and Appelo 2013) or MINTEQA2 (Allison *et al.,* 2009; Barat *et al.,* 2013) at each iteration step.
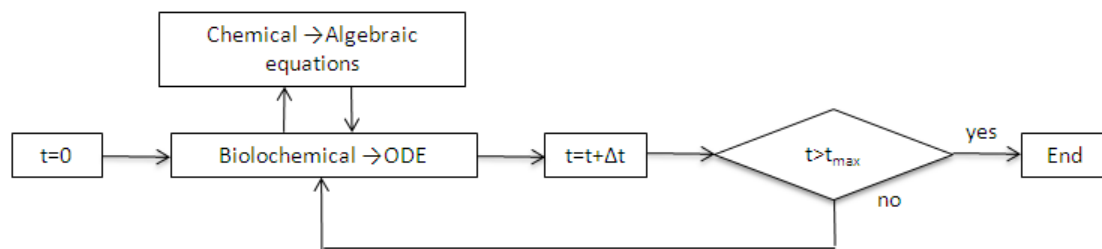
Figure 11. Model resolution combining differential and algebraic equations (DAE approach)

COMPARISON OF DIFFERENT RESOLUTION APPROACHES

The objective of this study was (i) to check the capability of the model presented in the previous section to calculate aquatic chemistry equilibrium, and (ii) to carry out a comparison of the different approaches in terms of results accuracy and simulation speed. For this purpose, the anaerobic reactor in the Benchmark Simulation Model No 2 (BSM2) (Jeppson et al., 2007) was selected as the simulation test case.

Results and discussion

Using the conditions presented above, a dynamic simulation for a period of 365 days was run in order to check the capabilities of the different models. When running the simulations, different integrators and kinetic parameters have also been tested. The comparison between results obtained with different approaches regarding simulation time, and accuracy of results is shown in Table 2. For the ODE approach, the CVODE solver was used, and two values for the equilibrium kinetic rate have been compared: 10^{12} and 10^6. It is seen that when using the kinetic rate of 10^{12} the simulated results are more accurate, since the result is closer to equilibrium. Nevertheless, higher kinetic rates slow down the simulation speed. The DAE approach using a tailored code for equilibrium calculation showed the shortest simulation time. Finally, when simulating the scenario with the external software Phreeq C+, the highest number of species was considered, but the simulations were the slowest (in designing the tailored code, species which had insignificant impact under the conditions found in anaerobic digesters were excluded to improve the simulation speed). A more detailed comparison using the full BSM2 will be presented in a forthcoming paper.

Table 2. Simulation of the anaerobic reactor in BSM2 under dynamic conditions for a period of 365 days

	Evaluation criteria			Evaluation criteria	
	Simulation time (sec)	$\sum \left(K_a \cdot \{HA\} - \{H^+\}\{A^-\} \right)^2$		Simulation time (sec)	$\sum \left(K_a \cdot \{HA\} - \{H^+\}\{A^-\} \right)^2$
ODE-Kab 10^{12}	6.25	7.61^{-05}	DAE-Tailored	0.96	0
ODE-Kab 10^6	3.82	7.85^{-05}	PhreeqC+	23.36	0

The results show that the optimum resolution procedure depends on the objectives of the simulation study. However, this work shows that the methodology proposed using a tailor-made equilibrium calculation using algebraic equations, and incorporating it into the biological ODE system gave the most effective methodology, based on the simulation times of the different approaches.

CONCLUSIONS

Different approaches for calculating chemical equilibrium have been presented and a critical review has been undertaken. Based on this comparison a methodology is proposed for incorporating water chemistry into biological models.

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