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A new general methodology for incorporating physico-chemical transformations into multiphase wastewater treatment process models



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ABSTRACT

This paper introduces a new general methodology for incorporating physico-chemical and chemical transformations into multi-phase wastewater treatment process models in a systematic and rigorous way under a Plant-Wide modelling (PWM) framework. The methodology presented in this paper requires the selection of the relevant biochemical, chemical and physico-chemical transformations taking place and the definition of the mass transport for the co-existing phases. As an example a mathematical model has been constructed to describe a system for biological COD, nitrogen and phosphorus removal, liquid–gas transfer, precipitation processes, and chemical reactions. The capability of the model has been tested by comparing simulated and experimental results for a nutrient removal system with sludge digestion. Finally, a scenario analysis has been undertaken to show the potential of the obtained mathematical model to study phosphorus recovery.

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1. Introduction

Traditionally, WWTPs have been operated to guarantee a certain effluent quality and consequently the main focus has been the biological processes taking place for COD and nutrient removal. However, nowadays, the general concern about climate change and scarcity of natural resources is encouraging operating the processes in a more sustainable and environmental-friendly way seeking the reduction of energy consumption, recovery of valuable materials and minimization of greenhouse gas emissions. With this purpose, WWTPs are incorporating novel technologies and ways of design and operation where physico-chemical and

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List of al	bbreviations	Ι
AD	Anaerobic digestion	т
ADM1	Anaerobic digestion model No 1	Г
ASM1/2d	l/3 Activated sludge model No 1, 2d and 3	г
ASMs	Activated sludge models	L
ASU	Activated sludge unit	т
BNRM	Biological nutrient removal model	I K
CEIT	Centro de estudios e investigaciones técnicas de	r k
	Gipuzkoa	k
COD	Chemical oxygen demand	-
DAE	Differential algebraic equations	k
DO	Dissolved oxygen	F
E-PWM	Extended plant-wide model	k
IAP	Ion activity coefficient	k
IWA	International water association	k
LT	List of transformations	k
NDBERP	Nitrification-denitrification biological excess	k
ODE	phosphorous removal	
DDE	Drainary differential equations	k
PAO	Phosphorous accumulating organisms	
	Polynyuloxyaikanoales	k
TAG	Total acetate	k
т цс	Total budylate	
	Total inorganic carbon	k
TIN	Total inorganic nitrogen	
TIP	Total inorganic phosphorous	k
$T-NO_{0}$	Total nitrite	N
T-NO ₂	Total nitrate	r
TPRO	Total propionate	F
TSO₄	Total sulphate	F
TVA	Total valerate	F
UCT	University of Cape Town	{
UCTADN	/P University of Cape Town anaerobic digestion	5
VFA	Volatile fatty acids	5
WIN W/W/TP	Wastewater treatment plant	ſ
** ** 11	wastewater deathent plant	
List of sy	mbols	7
а	Contact area between liquid and gaseous phases	Ż
		C
a _{ij}	Stoichiometric relationship of species 1 and	γ
	component j	ρ
A	Debye–Huckel constant	U
Ci	Concentration of component i (mol m ⁻³)	
a _B	Diameter of the bubbles (m)	

$D_{L,O_2} \\$	Diffusivity of component oxygen in liquid phase $(-2^{2} - 1)$
F	(m ⁻ d ⁻) Staishiomatry of internation between water and
L _{ghu,w}	store hold up in gas hold up
F,	Stoichiometry of interaction between water and
∟w,ghu	gas hold up in water phase
T	Ionic strength
K'	Kinetic rate for precipitation (d^{-1})
K.	Equilibrium constant (mol L^{-1})
Kab	Kinetic rate constant for chemical equilibrium
aU	(d ⁻¹)
K _H	Henry's constant (mol atm $^{-1}$ L $^{-1}$)
K _{H.i}	Henry's constant for component I (mol atm $^{-1}$ L $^{-1}$)
k _{L/G}	Mass transfer rate constant (d^{-1})
k _{L/G,i}	Mass transfer rate constant for component i (d^{-1})
$k_{L/G,NH_3}$	Mass transfer rate constant for ammonia (d ⁻¹)
k _{L/G,O2}	Mass transfer rate constant for oxygen (d^{-1})
k _G	Mass transfer rate constant limited by gaseous
	phase (d ⁻¹)
$k_{G,NH_3} \\$	Mass transfer rate constant limited by gaseous
	phase for ammonia (d $^{-1}$)
k_L	Mass transfer rate constant limited by liquid
_	phase (d^{-1})
k_{L,O_2}	Mass transfer rate constant limited by liquid
1	phase for oxygen (d ⁻¹)
K _{L,i}	Mass transfer rate constant limited by liquid
V	phase for component I (d) Supercontruction coefficient (mol L^{-1})
к _{sp}	Molality of aposics i (mol I^{-1})
n.	Total moles contained in gas hold-up (mol)
D.	Partial pressure of component i (atm)
P_h.	Pressure of gas hold-up (atm)
P gnu P goff	Pressure of contact atmosphere (atm)
{S}	Activity of species S
[S]	Molality of species S (mol L^{-1})
S _{A-}	Total anion equivalent concentration (mol L^{-1})
S_{C+}	Total cation equivalent concentration (mol L^{-1})
Tj	Molality of component <i>j</i> given by the process
	model mass balance (mol L ⁻¹)
V_{ghu}	Gas hold up volume (m³)
Z_i	Charge of species i
Greek su	mbols
Υs	Activity coefficient of S
ρ	Kinetic rate (d ⁻¹)
υ _r	Slip velocity between liquid and gaseous phase
	(m s ⁻¹)
$\psi \; k_L$	proportionality factor

chemical processes are becoming increasingly important and cannot be neglected when making decisions.

 $D_{L.i}$

Diffusivity of component i in liquid phase (m² d⁻¹)

Referring to energy consumption reduction in WWTPs, the optimization of aeration systems is a key factor as it may represent 50% of the total energy consumption in a WWTP (Olsson, 2013). Several aspects such as type and state of diffusers, reactor geometry, wastewater characteristics, operational temperature or air composition may have a great impact on aeration systems and consequently on energy consumption.

In this respect, work has been carried out to optimize aeration systems (Beltran et al., 2013; Thunberg et al., 2009) with the aim of reducing energy consumption. Another example is the use of high purity oxygen aeration as alternative to conventional aeration systems in industrial sector (Irizar et al., 2012) as a way to improve the efficiency of the process and consequently reduce energy costs (Irizar et al., 2012).

The concern of scarcity of natural resources is also driving resource recovery at WWTP. As an example, some studies

suggest that by the year 2060–2070 about half the world's current economic phosphate resources will have been used up (Driver et al.,1999). This has pushed the development of different techniques for phosphorous recovery. The work of Shu et al. (2006) shows that phosphorous recovery as struvite by means of precipitation processes is technically feasible and economically beneficial (Pastor et al., 2008).

Finally, with respect to greenhouse gas emissions, nitrous oxide (N₂O) produced in WWTP contributes significantly to global warming. Although there is still no complete consensus regarding the specific pathways for N₂O formation, it has been demonstrated that environmental conditions like DO, temperature or pH play an important role on the N₂O formation (Ni et al., 2013).

In the last decades, mathematical models and simulation tools have been proven to be very valuable tools for several goals such as design, diagnosis and elaboration of optimised management strategies of WWTPs. Since the publication of the ASM1 model in the 1980s (Henze et al.,1987) mathematical models have become very prominent and in this sense different works have been published: ASMs and ADM1 (Henze et al., 2000; Batstone et al., 2002) for the description of activated sludge units and anaerobic digesters respectively. In accordance with the objectives of traditional WWTPs, the focus in these models has been the description of biological processes for COD and nutrient removal taking place in the aqueous phase and consequently, mass transport has focused on this phase considering it as a series of completely stirred reactor.

Considering all abovementioned requirements in WWTP modelling, it can be said that traditional models present some limitations in both, scope and structure. Bearing this in mind, the scientific community, practitioners and consulting and engineering firms are seeking the development of mathematical models that in addition to COD, nitrogen, phosphorus and sulphur removal and sludge digestion, describe phenomena related to energy consumption, resource recovery and greenhouse gas emissions in a plant wide context. With this purpose, biological, chemical and physico-chemical reactions need to be modelled, incorporating liquid, solid and gaseous phases and the interactions among them. In this context, in the last years several research groups proposed mathematical models or approaches along this line. Ekama et al. (2006) presented a steady-state PWM where COD and nutrient removal and anaerobic digestion are described. This work was updated by Ikumi et al. (2014a,b, 2015) to consider process dynamics and phosphorus precipitation. Barat et al. (2013) also presented a model for COD and nutrient removal and incorporated chemical reactions. Grau et al. (2007) proposed a plant-wide modelling (PWM) methodology that allows the construction of plant wide models tailored to the specific case studied guaranteeing the mass and charge continuity throughout the entire plant. Recently, this methodology was extended (E-PWM) by including enthalpy balances (Fernández-Arevalo et al., 2014) to dynamically predict temperature and heat fluxes in all unit processes of the WWTP.

However, the current situation, where novel and complex configurations need to be explored, makes it necessary to define some guidelines and procedures to facilitate modellers to construct such plant wide models in a systematic, rigorous and flexible way. With this objective in mind objective the IWA Physico-chemical Framework Task Group was constituted (Batstone et al., 2012). As part of the work done under this Task Group, this paper aims to introduce a methodology that allows constructing in a systematic and rigorous way mathematical models able to rigorously describe biochemical, chemical and physico-chemical transformations based on previous models and approaches presented by authors of this paper. First, the main steps for incorporating chemical and physico-chemical processes are indicated. Second, a modular and systematic way of describing the mass transport where gaseous, aqueous and solids phases co-exist is presented. Finally, as an illustrative example a mathematical model is built for a selected case study, showing the capabilities of the model to reproduce real data. The potential of the model is further shown by a scenario analysis.

2. Physico-chemical Plant Wide Modelling methodology (PC-PWM)

The Physico-chemical Plant Wide Modelling (PC-PWM) methodology proposed in this paper is developed in order to construct mathematical models that (i) incorporate biochemical, chemical and physico-chemical processes in a plant-wide context and (ii) describe mass transfer among phases in a systematic and modular way.

The construction of a model under the PC-PWM requires two steps:

- 1. Definition of the relevant transformations taking place in a WWTP
- 2. Construction of the unit process model

2.1. Definition of the model components and transformations

This step entails the compilation of the relevant biochemical, chemical and physico-chemical transformations that must be considered in the system under study. First the modeller selects the biochemical and physico-chemical reactions present in the system depending on the scope and goals required for the model. Second, biochemical and physico-chemical reactions determine the chemical reactions that also need to be included (Fig. 1).

The following subsections describe in detail the procedure to be followed for the selection of relevant transformations.

2.1.1. Definition of biochemical model

The biochemical model is constructed based on the processes required for the case study treatment plant (nitrification, denitrification ...). It must be pointed out that considering aquatic chemistry in WWTP mathematical models necessarily requires mass and charge characterization of all model components. This fact, together with the plant-wide scope of the models makes works proposed by Ekama et al. (2006), Grau et al. (2007b) or de Gracia et al. (2006) to be very suitable frameworks for the construction of these biochemical models.



Fig. 1 - Relation between biochemical, chemical and physico-chemical model.

Specifically, Grau et al. (2007) proposed a plant-wide modelling methodology that offers a systematic and rigorous way to construct model tailored for the WWTP under study.

With this purpose and as a preliminary step Grau et al. (2007) suggested a general List of Transformations (LT) of the most relevant transformations (Fig. 2) involved in WWTPs based on the well-known IWA models for activated sludge: ASM1, ASM2d (Henze et al., 2000) and anaerobic digestion: ADM1 (Batstone et al., 2002). A detailed description of the transformations is presented in Grau et al. (2007). This original list was expanded with additional transformations and components to represent sulphate removal in Lizarralde et al. (2010), based on the model proposed by Knobel and Lewis (2002).

All biochemical transformations included in the LT are described based on the original models but the stoichiometry and kinetics are rewritten based on the following two principles: (1) the stoichiometry is defined so that elemental mass (C, N, O, P, H, S, Mg and K) and charge conservation is guaranteed. For this purpose all components involved in transformations need to be described in terms of elemental mass and charge composition. Additionally, *source-sink* components are defined for each element to act as mass compensation terms (Reichert et al., 2001; de Gracia et al., 2006). (2) Kinetic equations incorporate the required activation/inhibition terms to represent the proper activity under every possible environmental condition considered (aerobic, anoxic or anaerobic).

2.1.2. Definition of physico-chemical model

Physico-chemical reactions involve phase changes in the reaction products. On the one hand, liquid—gas transfer is considered. On the other hand, precipitation—redissolution of the most common minerals is introduced.

2.1.2.1. Liquid–gas transfer. Liquid–gas transfer equations describe the dissolution and stripping process of the gaseous components consumed or formed during the biological activity. In a generic WWTP seven gaseous components need to be considered: O₂, CO₂, NH₃, N₂, H₂, CH₄ and H₂S.

Depending on the biochemical processes selected for the model of the system under study in the previous step, the gaseous components that need to be considered are selected (Table 1).



Fig. 2 – General List of Transformations (LT) proposed by Grau et al. (2007).

Table 1 – Selection of gaseous components depending on the biological transformations.													
	02	CO ₂	$\rm NH_3$	N_2	H_2	CH_4	H_2S						
Heterot. aer B activity	1	1	1										
Nitrifier activity	1	1	1	1									
Aer. PAO activity	1	1	1										
Heterot. B activity on NO3	1	1	1										
Heterot. B activity on NO ₂	1	1	1										
Anox. PAO activity	1	1	1										
Anammox	1	1	1										
Acidogenesis		1	1		1								
Acetogenesis		1	1		1								
Methanogenesis		1	1		1	1							
An. PAO activity		1	1		1	1							
Sulphidogenesis		1	1		1		1						

The mathematical model of the liquid—gas transfer process describes the tendency of the system to reach the equilibrium state. The kinetic rate (Eq (1)) of the process is proportional to the difference between the saturation concentration and the actual concentration of the gas dissolved in the liquid and to the contact area between the gaseous and the aqueous phase.

$$\rho = \mathbf{k}_{\mathrm{L/G}} \cdot \mathbf{a} \cdot \left(\mathbf{K}_{\mathrm{H,i}} \cdot \mathbf{P}_{\mathrm{i}} - \mathbf{C}_{\mathrm{i}} \right) \tag{1}$$

The saturation concentration of the gas in the liquid is given by Henry's law of dissolution, which states that the saturation concentration is equal to the product of Henry's constant (K_H) multiplied by the partial pressure of the gas (P_i). For gases which dissociate in aqueous solution to form ionic species (CO₂, NH₃ and H₂S), the equilibrium relationship is a little more complex. Henry's law coefficient relates gas-phase partial pressures to the concentrations of the un-ionised aqueous phase species (H₂CO₃, NH₃ and H₂S). However, these undissociated species form only a part of the total dissolved concentrations, and depend on the solution conditions, particularly the pH. These species concentration are obtained from the general aquatic chemistry model described in Section 2.1.3. The contact area of the gaseous and aqueous phase (a) depends on the reactor configuration described by the unit process model, discussed in Section 2.2.2.

The mass transfer rate constant $(k_{L/G})$ is calculated for each gaseous component. The method used for its calculation depends on the solubility of the gas considered. The values of Henry's constant (Table 2) show the solubility of the gaseous components considered in this paper. Based on these values, it can be said that all gases included in the model are low solubility gases except for NH₃.

For gases with low solubility, the mass transfer mechanism of the gas is controlled by the liquid phase resistance (Lewis and Whitman, 1924). Thus the overall gas transfer rate constant ($k_{L/G}$) is limited by the gas transfer rate constant in the liquid phase (k_L). This k_L constant is calculated with a proportionality factor (Ψ) from the k_L of the reference compound oxygen (k_{L,O_2}). The proportionality factor of the mass transfer rate constants is given by Eq (2) (Munz and Roberts, 1988). The proportionality factor depends on the relation of the diffusivity of the gas in the liquid (D_{L,O_2}).

Table 2 $-$ Values of Henry's constant at 25 $^\circ$ C.												
Gas	Henry's constant at 25 °C	Unit	Reference									
O ₂	0.0013	mol/atm l	Perry and Chilton (1973)									
CO_2	0.035	mol/atm l	Perry and Chilton (1973)									
NH_3	59	mol/atm l	Perry and Chilton (1973)									
N_2	0.00061	mol/atm l	Perry and Chilton (1973)									
H_2	0.00078	mol/atm l	Perry and Chilton (1973)									
CH_4	0.0014	mol/atm l	Perry and Chilton (1973)									
H_2S	0.001	mol/atm l	Perry and Chilton (1973)									

$$\psi = \frac{\mathbf{k}_{\text{L/G,i}}}{\mathbf{k}_{\text{L/G,O}_2}} = \frac{\mathbf{k}_{\text{L,i}}}{\mathbf{k}_{\text{L,O}_2}} = \left(\frac{\mathbf{D}_{\text{L,i}}}{\mathbf{D}_{\text{L,O}_2}}\right)^n \tag{2}$$

For aqueous phase controlled mass transfer different studies propose different values for the exponent n. The most likely values expected are 1/2, 2/3 or 1, however the proposed values range between 0.1 < n < 0.8.

The mass transfer rate of oxygen (k_{L,O_2}) is calculated based on Higbie's penetration theory (Higbie, 1935), which states that the mass transfer rate constant depends on the diffusivity of oxygen in the liquid phase (D_L), the slip velocity between the gaseous phase and the aqueous phase (v_r) and is inversely proportional to the diameter of the bubbles (d_b).

$$k_{L/G,O_2} = k_{L,O_2} = \sqrt{\frac{D_{L,O_2} \cdot v_r}{\pi d_b}}$$
 (3)

For very soluble gases, such as NH_3 , mass transfer is limited by the diffusion in the gaseous phase and consequently the overall gas transfer rate is controlled by the gas transfer rate in the gaseous phase (k_G). Based on the penetration theory the mass transfer rate constant depends on the diffusivity of NH_3 in the gaseous phase (D_G) and the diameter of the bubbles (d_b).

$$\mathbf{k}_{\mathrm{L/G,NH_3}} = \mathbf{k}_{\mathrm{G,NH_3}} = \sqrt{\frac{\mathbf{D}_{\mathrm{G}} \cdot v_{\mathrm{r}}}{\pi d_b}} \tag{4}$$

However, the slip velocity is often not measurable and consequently, this mass transfer rate needs to be calibrated based on experimental results.

Values reported for the mass transfer rate constant for oxygen and ammonia (k_{L,O_2}, k_{G,NH_4}) are gathered in Table 3:

2.1.2.2. Corrections to the saturation concentration. The kinetic rate presented is valid for the conditions for which the model was proposed, i.e. standard conditions and clean water. However, the transfer rate depends on operational conditions and, thus, correction factors need to be incorporated into the transfer rate. These correction factors need to consider temperature, type and state of the aeration system, process water

Table 3 – Values for k_{L,O_2} and $k_{G,NH_3}.$												
Constant at $T=20\ ^\circ C$	Value	Reference										
k_{L,O_2} (m/d) k_{G,NH_2} (m/d)	0.074 0.18–0.54	Vogelaar et al. (2000). Arogo et al. (1999).										

and atmospheric characteristics. All these corrections can be found in the work of Beltran et al. (2013).

2.1.2.3. Precipitation—redissolution. The precipitation—redissolution reactions considered in this paper are those identified by Musvoto et al. (2000a,b) as the most likely to occur in a WWTP. The precipitated minerals that result from these reactions are: CaCO₃, MgCO₃, Ca₃(PO₄)₂, struvite (MgNH₄PO₄·6H₂O), k-struvite (MgKPO₄·6H₂O) and newberyite (MgHPO₄·3H₂O). Besides, the utilization of ferric chloride for coagulation or chemical phosphorous removal makes it necessary to include FePO₄ and Fe(OH)₃ as precipitated compounds in the system. The reactions describing the precipitation of the cited minerals are:

 $Ca^{2+} + CO_3^{=} \leftrightarrow CaCO_3$

 $Mg^{2+} + CO_3^{=} \leftrightarrow MgCO_3$

• Ca₃(PO₄)₂

 $3Ca^{2+} + 2PO_4^{3-} \leftrightarrow Ca_3(PO_4)_2$

Struvite

 $\mathrm{Mg}^{2+} + \mathrm{NH_4}^+ + \mathrm{PO_4}^{3-} + \mathrm{6H_2O} \! \leftrightarrow \! \mathrm{MgNH_4PO_4} \! \cdot \! \mathrm{6H_2O}$

• K-struvite

 $Mg^{2+} + K^{+} + PO_4^{3-} + 6H_2O \leftrightarrow MgKPO_4 \cdot 6H_2O$

• Newberyite

 $Mg^{2+} + HPO_4^{=} + 3H_2O \leftrightarrow MgHPO_4 \cdot 3H_2O$

• FePO₄

 $Fe^{3+} + PO_4^{3-} \leftrightarrow FePO_4$

• Fe(OH)₃

 $Fe^{3+} + 3OH^- \leftrightarrow Fe(OH)_3$

If the precipitation process is relevant in the case under study the methodology proposes to select all reactions suffested in Musvoto et al. (2000a,b). FePO₄ and Fe(OH)₃ should be included when chemical phosphorus removal needs to be described.

The mathematical model adopted in this paper for the precipitation—redissolution reactions is based on the models developed by Koutsoukos et al. (1980). First, at each time step, the model checks the condition of supersaturation and

depending on whether the solution is supersaturated or not precipitation or dissolution occurs.

For a general equilibrium reaction:

$$xM^{v+} + yA^{v-} \leftrightarrow M_xA_y$$

x and y are the numbers of cations and anions and v_+ and v_- are the valences. If the ion activity product (IAP, Eq (5)) is higher than the solubility product, the solution is supersaturated and precipitation takes place; when the system is not supersaturated, the reverse reaction is assumed to take place.

$$\mathsf{IAP} = \left\{\mathsf{M}^{\mathsf{v}+}\right\}^{\mathsf{x}} \cdot \left\{\mathsf{A}^{\mathsf{v}-}\right\}^{\mathsf{y}} \tag{5}$$

2.1.2.3.1. Precipitation. The kinetic rate (ρ) proposed for precipitation in this paper (Eq (6)) describes three of the four main steps involved in the formation of solids: (i) development of supersaturation; (ii) nucleation and (iii) growth. The kinetic rate is based on the one proposed by Koutsoukos et al. (1980) but upgraded to consider spontaneous nucleation.

$$\rho = K' \cdot \left(IAP^{1}_{v} - K_{sp}^{1} \right)^{n} \cdot (A_{SO} + A_{XTSS} + A_{SN})$$
(6)

where k' is the kinetic rate for the precipitation reaction and A_{SO} , A_{XTSS} and A_{SN} are activation terms that are calculated as follows:

$$A_{SO} = s_o \frac{\left[M_x A_y\right]}{\left[M_x A_y\right]_O + K_2}$$
⁽⁷⁾

$$A_{\rm XTSS} = \frac{X_{\rm TSS}}{X_{\rm TSS} + K_3} \tag{8}$$

$$A_{SN} = \frac{[M^{v+}]^{x} \cdot [A^{v-}]^{y}}{[M^{v+}]^{x} \cdot [A^{v-}]^{y} + K_{1}}$$
(9)

 A_{SO} and A_{XTSS} are the terms included in the original equation proposed by Koutsoukos et al. (1980) and represent the growth of crystals when support material is added, s_o in an adimensional parameter that represents the growth of interfacial area concentration assuming a constant size distribution. A_{SN} is the new term added to reproduce crystal growth when no seed material is added. When no seed material is added, at the beginning of the process the predominant term is A_{SN} . As precipitation takes place, crystals grow and A_{SO} becomes the dominant term. K_1 , K_2 and K_3 are constants with a very low value included to guarantee numerical stability.

2.1.2.3.2. Dissolution. In the case of elevated mineral concentration the kinetic rate (ρ) describes that dissolution takes place until equilibrium is reached or until the activation term due to crystals existing in the reactor is zero. Mathematically, this is expressed with Eq (10).

$$\rho = -K' \cdot \left(IAP^{1}_{\nu_{v}} - K^{1}_{sp} \right)^{n} \cdot (A_{SO})$$
(10)

The dissolution is considered the inverse of the precipitation kinetic with the difference in the terms $A_{\rm XTSS}$ and $A_{\rm SN}$, since they can speed up the precipitation reaction but do not affect the redissolution. 2.1.3. Definition of the general aquatic chemistry model Once the biochemical and physico-chemical models are defined, the general aquatic chemistry model is built.

The aquatic chemistry model presented in this paper thoroughly describes the relevant acid—base and ion-pairing equilibrium reactions that take place in a pH-range between 5.0 and 9.0. The construction of the aquatic chemistry model is done in two steps:

- 1. Selection of the relevant chemical components and species.
- 2. Model development.

2.1.3.1. Selection of relevant chemical components, chemical reactions and species. In order to describe the general aquatic chemistry, first the relevant chemical components and species need to be determined. Species are chemical entities taken to be physically present in the system, and components are selected so that all species can be expressed as linear combination of these components. This paper proposes a compilation of relevant chemical components, reactions and species which may occur in a generic WWTP taking into account traditional and novel processes that occur in WWTPs (Fig. 3).

Based on the list proposed by Henze et al. (2008), twenty components have been selected to describe the most relevant chemical components to simulate WWTPs. The main source of information regarding the most relevant chemical reactions involved in a WWTP is the MINTEQA2 software (Allison et al., 1991). With the defined components, the chemical reactions selected are those that may take place in a pH range between 5.0 and 9.0. This list is expandable if more chemical components, reactions or species need to be considered depending on wastewater characteristics or novel technologies to be considered.

Having this generic list defined, the modeller is able to select those chemical components, reactions and species that are relevant for the specific WWTP under study depending on the biochemical and physico-chemical reactions selected in the previous step following the systematic procedure suggested below.

a) First, the biochemical processes determine the relevant components required in the description of the specific WWTP (Table 4). Analogously, the relevant chemical component selection must be done by taking into account the physico-chemical reactions included in the model. Table 5 compiles the selection of relevant chemical components depending on the physico-chemical reactions.

Additionally, all components that contribute to the ionic strength of the system need to be considered. These can only be neglected when their concentrations are low, and consequently their effect on the ionic strength is small.

- b) Second, having the components determined, chemical reactions are selected from Fig. 3. The relevant chemical reactions are those positioned in the columns and rows of the selected components.
- c) Finally, from these reactions, those species are selected, which represent any chemical entity taken to be physically present in the system.

Once the model components, reactions and species are selected the chemical model is developed.

						Cationic c	omponents			
c	omponent		н,	TIN	Ca	Mg	Na	к	Fe ³⁺	Fe ²⁺
						Chemical reacti	ons and species			
	H ₂ O		1.H₂0++H⁺+OH'	17.NH4*++H*+NH3	19.Ca0H⁺↔Ca ²⁺ +0H'	31.MgOH⁺↔Mg ² *+OH'	41.NaOH++Na*+OH'	47.K ⁺	51.Fe0H ² *↔Fe ³ *+OH ⁻ 52.Fe(OH) ₂ *↔Fe ³ *+20H ⁻ 53.Fe(OH) ₃ ↔Fe ³ *+30H ⁻	64.FeOH*↔Fe ²⁺ +OH 65.Fe(OH) ₂ ↔Fe ²⁺ +2OH
	тіс		2.H₂CO₃↔H*+HCO₃ ⁻		20.CaCO₃↔Ca ²⁺ +CO₃*	32.MgCO ₃ ↔Mg ²⁺ +CO ₃ *	42.NaCO3 ↔Na++CO3*			66.FeHCO1*↔Fe ²⁺ +HCO1
			3.HCO3*=H*+CO3* 4.H1;PO4=+H*+H1;PO4* 5.H1;PO4*=H*+HPO4* 6.HPO4*=H*+HPO4* ³ 7.504*=-504* 18.NH4504*=+NH4*+504*		21.CaHCO3 +→Ca2++HCO3	33.MgHCO3*↔Mg ² *+HCO3	43.NaHCO₃↔Na*+HCO₃'			
	TIP				22.CaH ₂ PO ₄ *++Ca ²⁺ +H ₂ PO ₄ * 23.CaHPO ₄ ++Ca ²⁺ +HPO ₄ * 24.CaPO ₄ *++Ca ²⁺ +PO ₄ * ³	34.MgH2PO4*↔Mg ²⁺ +H2PO4 [*] 35.MgHPO4↔Mg ²⁺ +HPO4* 36.MgPO4 [*] ↔Mg ²⁺ +PO4 ^{*3}	44.NaHPO4 [*] ↔Na*+HPO4*	48.KHPO4 [*] ↔K [*] +HPO4 [*]	54.FeH2PO4 ⁺² ++Fe ³⁺ +H2PO4 ⁺ 55.FeHPO4 ⁺ ++Fe ³⁺ +HPO4 ⁺	67.FeH2PO4 ⁺ ↔Fe ²⁺ +H2PO4 ⁺ 68.FeHPO4 ⁺ ↔Fe ²⁺ +HPO4 ⁺
ts	T-504	species			25.CaSO₄↔Ca ²⁺ +SO₄*	37.Mg5O₄↔Mg ²⁺ +SO₄*	45.NaSO4 ↔Na +SO4	49.KSO4 [*] ↔K ⁺ +SO4*	56. FeSO₄ ⁺ ↔Fe ³⁺ +SO₄ ⁺ 57. Fe(SO₄)₂ ⁻ ↔Fe ³⁺ +2SO₄ ⁺	69.FeSO₄↔Fe ²⁺ +SO₄*
componen	T-HS	tions and	8.H2S++H*+HS' 9.HS'++H*+S*							70.Fe(HS) ₂ ↔Fe ²⁺ +2HS ⁻ 71.Fe(HS) ₃ ⁻ ↔Fe ²⁺ +3HS ⁻
ionic	T-N03	read	10.NO3'↔NO3'		26.CaNO3*++Ca2++NO3				58.FeNO3 ²⁺ ↔Fe ³⁺ +NO3 ⁻	
An	T-N02	mica	11.NO2 ↔NO2							
	TAc	Che	12.HAc++H*+Ac*		27.CaAc*↔Ca ²⁺ +Ac	38.MgAc*↔Mg ²⁺ +Ac*	46. NaAc⊷Na⁺+Ac'	50.KAc++K*+Ac'	59.Fe(Ac)₃↔Fe ¹⁺ +3Ac	72.FeAc ⁺ ++Fe ²⁺ +Ac ⁻ 73.FeAc ⁺² ++Fe ²⁺ +Ac ⁻ 74.Fe(Ac) ₂ ++Fe ²⁺ +3Ac ⁻
	TBu		13.HBu↔H*+Bu		28.CaBu*⇔Ca²++Bu	39.MgBu*↔Mg ²⁺ +Bu ⁻				
	TProp		14.HProp++H*+Prop		29.CaProp*++Ca2++Prop*	40.MgProp*++Mg2*+Prop			60.FeProp ⁺² ++Fe ³⁺ +Prop ⁻	
	TVa		15.HVa↔H⁺+Va		30.CaVa*↔Ca ² *+Va					
	сι		16.CI						61.FeCl ⁺² ↔Fe ¹⁺ +Cl' 62.FeCl ₂ ⁺ ↔Fe ¹⁺ +2Cl'	
									63.FeCl3↔Fe ³⁺ +3Cl	

Fig. 3 – List of chemical reactions and species for each ionic component.

Table 4 – Selection of chemical components based on biochemical processes.																		
		Components																
	H ₂ O	H^+	TIC	TIN	TIP	T-NO ₃	T-NO ₂	TVA	TBU	TPRO	TAC	T-HS	T-SO ₄	Ca	Mg	Κ	Fe ³⁺	Fe ²⁺
Heterotrophic B activity	1	1		1	1													
Nitrifier activity	1	1		1	1	1												
Aer. PAO activity	1	1		1	1									1	1	1		
Heterotrophic B activity on NO ₃	1	1		1	1	1	1											
Heterotrophic B activity on NO ₂	1	1		1	1	1	1											
Anox. PAO activity	1	1		1	1	1								1	1	1		
Anammox	1	1		1	1	1	1											
Acidogenesis	1	1		1	1			1	1	1	1							
Acetogenesis	1	1		1	1			1	1	1	1							
Methanogenesis	1	1		1	1			1	1	1	1							
Anaer. PAO activity	1	1		1	1	1								1	1	1		
Sulphidogenesis	1	1		1	1	1	1			1	1	1	1					

2.1.3.2. Model development. The principles of water chemistry modelling are set out in Stumm and Morgan (1996). Given the following generic dissociation reaction:

$HA \leftrightarrow H^+ + A^-$

the chemical equilibrium reaction can be described using either ordinary differential equations or algebraic equations.

2.1.3.2.1. Ordinary differential equations. In the ordinary differential equations approach, the model is constructed in order to describe the forward and the reverse dissociation of the acid/base and ion pairing reactions. In this approach it is necessary to define the stoichiometry and the kinetic vector of the reactions. The kinetic rate equations are based on those proposed in Musvoto et al. (2000a,b). The kinetic rate for the general reaction has the following mathematical expression:

$$\rho = k_{ab} \left(K_a \cdot [HA] - [H^+] \cdot [A^-] \right)$$
(11)

The kinetic rate constant (k_{ab}) for these reactions is selected as a very high value to ensure that species present in the system reach the chemical equilibrium virtually instantaneously. Combining these very fast reactions with the slow bioprocess and precipitation reactions creates very stiff models which lead to long run times and possibly to numerical instability during model simulation (see section 2.3 below).

2.1.3.2.2. Algebraic equations. In the case the algebraic equations approach is adhered to, the equilibrium relationships are formulated in terms of species activities (e.g. Eq (12)), which are related to their concentrations by activity coefficients (e.g. Eq (13)). In this work, activity coefficients were modelled using the Davies equation (Eq (14) and Eq (15)). The mass conservation equation can be expressed either to (i) guarantee electroneutrality, i.e. guarantee that the sum of cations equals the sum of anions (Eq (16)) or (ii) using the alkalinity–acidity continuity, this is formulating proton conservation equations (Eq (17)). Combining these mass conservation equations and the mass action relationships, a set of simultaneous nonlinear implicit equations is obtained which can be solved for all the species concentrations.

Table 5 – Selection of chemical components based on physico-chemical processes.																		
	Components																	
	H_2O	H^+	TIC	TIN	TIP	T-NO ₃	T-NO ₂	TVA	TBU	TPRO	TAC	T-HS	$T-SO_4$	Ca	Mg	Κ	$\mathrm{Fe}^{\mathrm{3}+}$	Fe^{2+}
Liquid–gas transf	er																	
H ₂ O evaporation	1																	
CO ₂			1															
NH ₃				1														
Precipitation-redi	issolut	ion																
CaCO ₃			1											1				
MgCO ₃			1												1			
$Ca_3(PO_4)_2$					1									1				
Struvite				1	1										1			
k-Struvite					1										1	1		
Newberite					1										1			
FePO ₄					1												1	
Fe(OH) ₃	1																1	

(12)

$$K_a = \frac{\{H^+\}\{A^-\}}{\{HA\}}$$

Where,

K_a: equilibrium constant {S}: activity of species S

$$\left\{ \mathbf{H}^{+}\right\} =\gamma_{\mathbf{H}^{+}}\cdot\left[\mathbf{H}^{+}\right] \tag{13}$$

Where,

[S]: molality of species S γ_{s} : activity coefficient of S

$$I = \frac{1}{2} \sum_{i} M_i \cdot z_i^2 \tag{14}$$

Where,

I: Ionic strength M_i: molality of species i

$$log(\gamma_i) = -Az_i^2 \left[\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right]$$
 (15)

Where,

Z_i: charge of species i

A: Debye–Huckel constant

$$\sum S_{C^{+}} - \sum S_{A^{-}} = 0 \tag{16}$$

where,

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

$$\sum_{i} a_{ij}M_i - T_j = 0 \tag{17}$$

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.

This methodology proposes the use of alkalinity-acidity continuity, formulating the proton conservation using the Tableau method (Morel and Hering, 1993). The Tableau method offers a systematic way to represent all equations required for every acid-base and ion-pairing reactions considered in the general list proposed in this section.

2.1.4. Model implementation procedure

This methodology offers a systematic way for constructing a mathematical model for any system. Fig. 4 illustrates the work flow for the construction of a model following this methodology, relations among the different model and the interrelations of the different tables (Fig. 5).

2.2. Mass transport definition for a multi-phase model of WWTP

Traditionally, since mainly the aqueous phase is considered, the state-vector (M) of the ASM models involves all state variables in the aqueous phase and analogously, the Gujer matrix (E) and the kinetic vector (ρ) involve all the transformations considered in the model. Taking into account new processes and goals to be reached in WWTPs, more than one phase must be considered. The PC-PWM proposes a *phase-based* modelling approach, first selecting the phases present in the system and then including the transformations occurring in each phase. This way of distinguishing the different phases will allow the modeller to construct mathematical models as complex as required in a systematic and modular way. The construction of the modular extended PWM consists of the three following consecutive steps:

2.2.1. Definition of phases

In this first step the modeller defines the phases depending on the processes along the plant configuration and the objectives



Fig. 4 – Schematic representation of the construction of the mathematical model.



Fig. 5 - Schematic representation of the phases that coexist in a unit process.

of the model. As an example, taking as a reference a generic biological reactor, four different phases may coexist within a unit process: (i) The aqueous phase: this corresponds to the volume of the mixed liquor. The aqueous phase is included in any unit process modelled. (ii) The off-gas phase: this represents the gaseous phase in contact with the free surface of the mixed liquor. The off-gas phase is included in all unit processes. This can be a phase with constant composition, e.g. in an open reactor when the aqueous phase is in contact with the atmosphere. Alternatively, it can be modelled to have a timevarying composition for example in an anaerobic closed reactor, where the composition of the gaseous phase depends on the biological activity (iii). The gas hold-up phase: this symbolizes the gas phase physically contained in the aqueous phase. This phase needs to be taken into consideration for example when the unit process is aerated because the gasphase composition is changing along the reactor, or when modelling an autothermal thermophilic aerobic digestion or in a denitrification reactor where CO₂ is produced, and (iv) The solid phase: this is the phase representing the precipitates formed during the processes. The solid phase is included when precipitation is relevant in the unit process that is being modelled.

2.2.2. Definition of reactions inside and interactions among phases

For the phases defined in the previous section, the transformations and interactions identified are (Fig. 6a):

- Transformations in the aqueous phase
- Liquid–Gas off transfer
- Liquid–Gas hold-up transfer
- Liquid–Solid transfer

It is assumed that no reactions take place in the gaseous and solid phases. And there is no mass transfer between the gaseous phases and the solid phase. The separation of the unit processes in different phases involves re-structuring the traditional unique state-vector, Gujer matrix and kinetic vector approach. The PC-PWM proposes defining as many state-vectors (M), Gujer matrices (E) and kinetic vectors (ρ) as existing phases and interactions among them (Fig. 6b).

With regard to the notation, E sub-matrixes and ρ subvectors include two phase subscripts to specify the involved phases in the transformations, "w" for aqueous phase, "off" for the off-gas phase, "ghu" for the gas hold-up phase and "s" for the solid phase. Subscripts whose letters are different mean an interaction between two different phases whereas subscripts whose two letters are the same refer to transformations that take place in a single phase. Moreover, given a certain $E_{i,j}$ sub-matrix, the first letter i represents the phase in which $E_{i,j}$ is defined and the second one represents the phase with which it interacts. For example, $E_{w,ghu}$ and $E_{ghu,w}$ represent in both cases the interaction between the water and the gas hold-up. In particular, $E_{w,ghu}$ represents the stoichiometry of these transformations in the aquesou phase and $E_{ghu,w}$

2.2.2.1. Transformations in the aqueous phase. Transformations taking place in the aqueous phase are all biochemical and chemical reactions considered in the transformation list presented in Section 3.2.1.1 and in Section 3.2.1.3.

2.2.2.2. Liquid—gas off transfer. Liquid gas off transfer represents the mass transfer between the aqueous phase and the free atmosphere in contact with the liquid. This transfer is driven with the kinetic rate explained in Section 3.2.1.2:

$$\rho = k_{L} \cdot a \cdot (K_{H,i} \cdot P_{goff,i} - C_{i})$$
(18)

The interfacial area (a) of the contact between the aqueous and off-gas phase is the area of the reactor under study. In the



case of transfer between the liquid phase and the off-gas phase the partial pressure of the gaseous component (Pgoff,i) is calculated as the molar fraction of the gaseous component in the contact atmosphere multiplied by the total pressure.

2.2.2.3. Liquid-gas hold-up transfer. Liquid gas hold up transfer represents the mass transfer between the aqueous phase and the gaseous phase contained inside the liquid phase, i.e. the bubbles. This transfer is driven with the kinetic rate given in Section 3.2.1.2:

$$\rho = \mathbf{k}_{\mathrm{L}} \cdot \mathbf{a} \cdot \left(\mathbf{K}_{\mathrm{H},\mathrm{i}} \cdot \mathbf{P}_{\mathrm{ghu},\mathrm{i}} - \mathbf{C}_{\mathrm{i}} \right) \tag{19}$$

The interfacial area (a) is the total contact surface between liquid and gaseous phase. This area is calculated assuming spherical bubbles with constant diameter (d_b) along the reactor. There are various models to calculate the interfacial area in literature, however, this paper models this area using the particle model, which mathematically models the area with the following expression:

$$a = \frac{6 \cdot V_{ghu}}{d_b}$$
(20)

The volume of the gas hold-up phase (V_{ghu}) is calculated using the ideal gas expression:

$$V_{ghu} = \frac{n_{ghu} \cdot \mathbf{R} \cdot \mathbf{T}}{P_{ghu}}$$
(21)

n_{ghu} represent the total number of moles of gas contained in the gas hold-up phase. P_{ghu} is the pressure of the gas hold-up phase, which is assumed to be equal in the entire gas hold-up phase and its value is an average value at the middle of the height of the reactor. P_{ghu} is calculated as the sum of the pressure of the contact atmosphere (P_{goff}) and the pressure exerted by the column of water above the middle point:

$$P_{ghu} = P_{goff} + \frac{1}{2} \cdot \frac{V_L}{A_{tan k}} \cdot \frac{1}{10.33}$$
(22)

Finally, the partial pressure of the gaseous component in the gas hold-up phase $(P_{ghu,i})$ is calculated as the product of the molar composition of the gas in the gas hold-up phase by the total pressure of the gas hold-up (P_{ghu}) phase.

2.2.2.4. Liquid-solid transfer. Liquid-solid transfer describes the phase change between liquid and solid phase. The stoichiometric matrix and kinetic vector for this transfer are the ones presented in Section 3.2.1.2 in this paper.

2.2.3. Mass transport definition

Each phase included in the model is considered to be a completely stirred reactor. Mass balances are applied to each phase present in the model and have the following expressions: Mass balance in the aqueous phase

$$\begin{split} \frac{dM_{w}}{dt} &= \overline{\vec{m}}_{w,in} - \overline{\vec{m}}_{w,out} + \tilde{E}_{w,w}^{T} \cdot \overline{\rho}_{w,w} + \tilde{E}_{w,off}^{T} \cdot \overline{\rho}_{w,off} + \tilde{E}_{w,ghu}^{T} \cdot \overline{\rho}_{w,ghu} \\ &+ \tilde{E}_{w,s}^{T} \cdot \overline{\rho}_{w,s} \end{split}$$

Mass balance in the off-gas

$$\frac{d\overline{M}_{off}}{dt} = \overline{\vec{m}}_{ghu,off} - \overline{\vec{m}}_{off,out} + \widetilde{E}_{off,w}^{T} \cdot \overline{\rho}_{off,,w}$$

Mass balance in the gas hold-up

$$\frac{d\overline{M}_{ghu}}{dt} = \overline{\dot{m}}_{ghu,in} - \overline{\dot{m}}_{ghu,off} + \tilde{E}_{ghu,w}^{T} \cdot \overline{\rho}_{ghu,,w}$$

Mass balance in the solid phase

$$\frac{d\overline{M}_{s}}{dt} = \overline{\dot{m}}_{s,in} - \overline{\dot{m}}_{s,off} + \tilde{E}_{s,w}^{T} \cdot \overline{\rho}_{s,w}$$

2.3. Numerical solution procedure

When combining biochemical and physico-chemical processes with chemical reactions, numerical resolution is a critical step, because of the stiffness that arises when considering reactions with very different dynamics. There are two possible resolution procedures: (i) the ordinary differential equation (ODE) approach or (ii) the differential algebraic equations approach.

2.3.1. Ordinary Differential Equations (ODE)

In the ODE approach, chemical equilibrium reactions are described using ordinary differential equations. With this approach (Fig. 7) all reactions are calculated simultaneously as in Musvoto et al. (2000a,b), Sötemann et al. (2005a,b) and Poinapen and Ekama (2010) (Fig. 8).

In the ODE approach, all chemical species are included in the state vector, thus stoichiometry and kinetics are defined in terms of species.

2.3.2. Differential Algebraic Equations (DAE)

In the DAE approach, the slow reactions are represented by differential equations and the fast reactions are assumed to reach equilibrium instantaneously and are calculated algebraically (DAE) at each iteration step (Fig. 7) as in ADM1 (Batstone et al., 2002; Volcke et al., 2005; Rosen et al. 2006 or UCTADMP Brouckaert et al., 2010, Ikumi et al., 2011, 2014b, 2015). As a consequence, equilibrium is guaranteed in chemical reactions.

In the DAE approach, components are included in the state vector and are calculated using the differential equations. Consequently, the stoichiometry of the biochemical and physico-chemical models is written in terms of chemical components. However, the chemical species of each chemical component are calculated at each iteration step using algebraic equations. The concentration of the species is used to calculate the kinetics of the biochemical and physicochemical transformations. In the DAE approach, the modeller can choose between using 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., 1991; Barat et al., 2013).

A comparative analysis of the different methods presented above was carried out in Lizarralde et al. (2014) showing the benefits of using the DAE approach with a tailored code for aquatic chemistry resolution. This comparison shows that different approaches reach very comparable simulation results. However, the DAE approach with tailored code for aquatic chemistry solution showed the lowest simulation times. Therefore, this methodology suggests the use of the tailored approach.

3. Example: construction of a model for the NDBEPR system

Once the methodology to construct mathematical models considering biochemical, physico-chemical and chemical processes has been defined, a tailored model can easily be built. As an illustrative example of the usefulness of the methodology, this paper presents the construction of an integrated model for the nitrification—denitrification biological excess phosphorous removal system combined with an anaerobic sludge digester (NDBEPR-AD) under the methodology presented in this paper. The model results are compared with the experimental results presented in Ikumi et al. (2014).

3.1. Description of NDBEPR-AD system

A NDBEPR system has been set up using the UCT configuration with sequential anaerobic, anoxic and aerobic reactors. The waste activated sludge is fed to an anaerobic digester (Fig. 9). The dimensions of the reactors, inflow characteristics and operating conditions correspond to a pilot plant and are those presented in Ikumi et al. (2014). The most descriptive characteristics are summarized in Table 6.



Fig. 7 – Model solution procedure using the ordinary differential equations (ODE approach).



Fig. 8 — Model solution combining differential and algebraic equations (DAE approach).



Fig. 9 - Configuration of the NDBEPR-AD case study.

3.2. Construction of the model based on the PC-PWM methodology

The construction of the model to represent the NDBEPR-AD system has been done following the methodology presented in the previous section.

3.2.1. Definition of the model components and transformations

3.2.1.1. Definition of biochemical model. According to the configuration of the system under study, biochemical transformations were selected from Fig. 2. In this case the selected intracellular transformations are 1-2-3-4-6-8-9-10 and 12. Additionally, extracellular transformations to describe disintegration, hydrolysis and endogenous respiration (13–14–15) were selected.

3.2.1.2. Definition of physico-chemical model. Based on the biochemical transformations selected in the previous section, liquid gas transfer transformations were selected. Based on Table 1, six gases need to be included in the model for the NDBEPR-AD system: O₂, CO₂, NH₃, N₂, H₂ and CH₄. Regarding the liquid—solid transfer reactions, the most relevant ones proposed by Musvoto et al. (2000a,b) are the ones selected, i.e. CaCO₃, MgCO₃, Ca₃(PO)₄, struvite, k-struvite and newberyite.

3.2.1.3. Definition of the chemical model. Having the biochemical and physico-chemical reactions defined, components and species that need to be considered were selected following the methodology presented in Section 2.1.3.1. Biochemical and physico-chemical reactions determine the chemical components that need to be included in the model.

In this case study the components selected from Tables 4 and 5 were: TIC, TIN, TIP, H, N–NO₃, TVA, TPRO, TBU, TAC, Ca, Mg, K, Na and Cl. Once the components were defined, the selection of chemical reactions was straightforward from Fig. 3. The chemical reactions selected for this study are: 1 to 6, 10, 12–17, 19–24, 26–36, 38.40–43, 46–48 and 50. In total for the system under study, 14 components, 39 chemical reactions and 50 species were included in the aquatic chemistry for the system under study.

3.2.2. Construction of unit process models

The unit process models were built for the NDBEPR system and for the anaerobic digester. In the case of the unit processes of the NDBEPR system three phases were considered. One of them represents the aqueous phase, another represents the open atmosphere and the last one represents the gas hold-up phase describing in the aerobic reactor the air flow rate introduced and in the anaerobic and anoxic reactors the gaseous phase formed due to biological activity. All transformations take place in the aqueous phase and there is interaction between the phases. For the model of the digester, three phases coexist: the aqueous phase, the off-gas with a closed atmosphere and a solid phase. Interactions are defined between the aqueous phase with the gaseous phase and with the solid phase.

3.3. Experimental model validation and result discussion

Using the conditions presented above a simulation under steady state conditions has been run in order to check the capability of the model to reproduce the experimental results.

Table 6 – Characte	Table 6 — Characteristics of the experimental set-up.														
Volume (L)			Influent ch	aracteristics		Operating conditions									
Anaerobic	19	Q (l/d)	150	TIC (mg C/l)	183.54	Recycle ratio	1.3:1								
Anoxic	21	COD (mg/l)	800	K (mg K/l)	175.73	External recycle ratio	3:1								
Aerobic	35	TIN (mg N/l)	44.3	Mg (mg Mg/l)	90.32	Anaerobic digester inflow (l/d)	1.6								
Anaerobic digester	20	TIP (mg P/l)	51.6	Ca (mg Ca/l)	24.74										

Table 7 – Composition of the gas hold-up and the off-gas phase in all reactorsreactors of the NDBEPR-AD case study.

	Ana	aer	An	ox	Ae	er	Digester		
	Ghu	Off	Ghu	Off	Ghu	Off	Off		
%O ₂	_	20	_	20	19.7	20	_		
%N ₂	10.3	79	8.3	79	79	79	_		
$%NH_3$	55.4	_	4.7	_	_	_	_		
%CO ₂	34.3	1	87	1	1.3	1	35.9		
%CH4	-	-	-	-	_	-	65.1		

Table 8 – k_{La} values of the gas hold-up and the off-gas phase of components in all reactors of the NDBEPR-AD case study.

	Ana	aer	An	ox	A	er	Digester
	Ghu	Off	Ghu	Off	Ghu	Off	Off
k_{La,O_2}	_	7.8	_	7.8	103	16.8	-
k_{La,CO_2}	1.5	7.2	1.5	7.2	91	15.2	2.9
k_{La,N_2}	1.4	6.9	1.4	6.9	89 14.4		2.7

The model parameters have been adopted from Ikumi et al. (2011, 2014b) and those that describe phosphorus removal were modified following the guidelines given in Larrea et al. (2002). The comparison between experimental and simulation results is shown in Fig. 10 where it can be seen that there is reasonable correspondence experimental and simulation results (Figs. 11 and 12).

It can be seen that the model is able to reproduce COD and nutrient (N and P) removal by means of biochemical processes under different environmental conditions. The main mismatches between the experimental and simulated data are in the calculation of TIP and pH in the anaerobic digester. These could be caused by an excess orthophosphate release predicted by the model in comparison to the real system. This can also explain the lower biogas production in the anaerobic digester predicted by the model, since the VFAs are used for PHA accumulation rather than for biogas production. The physico-chemical and chemical processes modelled are able to reproduce phenomena like pH evolution at each point of the plant and struvite precipitation that is dependent on pH. In this respect, the importance of considering two different gaseous phases for the correct prediction of aquatic chemistry, and consequently of all biological and precipitation processes that depend on it, must be highlighted. Being able to describe gas stripping correctly, particularly CO₂, allows predicting pH correctly, since the accumulation of the total dissolved carbonate system is avoided. Thus, the distribution of the carbonated species is done correctly. The following table shows the different gaseous compositions in the gas hold-up phase in all reactors. The main differences between gas hold-up and off phases are observed, obviously, in nonaerated reactors where CO2 and NH3 composition are considerably higher in comparison with off-gas due to biological activity taking place in the reactors. Although at a first glance one could think that N₂ composition in bubbles formed in anoxic reactors should be higher the main transfer is done with the off-gas phase, so most of the N₂ formed is transferred to the atmosphere (Table 7).

Besides, separating the traditionally used k_La value into a k_L parameter and a variable representing the specific interface area enables reproducing the transfer of the oxygen and the rest of the gases independently. For example, in the reactors which are not aerated the contact area of the oxygen is null, whereas if the traditional approach would be used the k_La of other gases would need calibration, whereas with this new approach, k_L of all gases is calculated through the k_L of the oxygen but the area is calculated independently (Table 8).

Additionally, the model is able to predict phosphorous precipitation as struvite, showing the benefits of incorporating a solid phase. Finally, the model is capable of predicting the biogas production in the anaerobic digester because a gaseous phase is explicitly modelled in the anaerobic digester.

3.4. Exploration by simulation

Once the capability of the model to reproduce the real behaviour of the NDBEPR process under study was checked, a scenario analysis was carried out to illustrate the potential of the model to study the behaviour of different plant configurations or operational scenarios.



Fig. 10 - Comparison between experimental and simulation results for the NDPEBPR-AD case study.



Fig. 11 – Effect of reactor height oxygen percentage in gas hold-up when using air or pure oxygen for aeration.

To have a more realistic case study regarding the physical characteristics of a full-scale WWTP the case validated in the previous section has been updated by scaling the reactor dimensions and flow rates to 1:100,000, incorporating a recycle from the anaerobic digestion supernatant to the influent of the WWTP and reducing the influent phosphorus concentration to more realistic values. This new plant configuration has allowed the analysis of two main facts related to the contents of this paper.

1. Influence of reactor dimensions, specifically effect of reactor height on oxygen mass transfer efficiency.

For this case study, different heights have been analysed (Fig. 13), and evaluated for aeration either with air or pure oxygen. It can be seen that the model is able to predict the influence of reactor height in the composition of the pas phase. It is interesting to note that in the taller reactors, the percentage of O_2 present in the gas hold-up is lower, showing higher transfer efficiencies. This shows the benefits of using this methodology for case studies where tall reactors are present.

2. Assessment of different plant configurations: addition of novel technologies and plant operating strategies.

In this example, two different scenarios have been compared to the updated baseline scenario: in Scenario (A) a precipitation unit has been added to treat the supernatant of the digester and in Scenario (B) the aerobic reactor in Scenario (A) is aerated with pure oxygen.

Fig. 12 shows the effluent quality in terms of TIP. It can be seen than when the precipitation unit is included it is not only possible to recover struvite but also the effluent quality in terms of TIP is improved. No difference is observed when the system is aerated with pure oxygen.

Fig. 13 shows the variation of TIN in the effluent when comparing the different plant configurations. The difference from one scenario to the other is small, because in all cases the aeration is controlled to maintain oxygen at 2 mg/l.

Discussing the aeration requirements, the addition of a precipitation unit leads to lower aeration needs in Scenario (A). This is caused by the lowered ammonia in the influent, as



Fig. 12 - Comparison of TIP in effluent in the baseline case, in Scenario A and in Scenario B.



Fig. 13 - Comparison of TIN in effluent in the baseline case, in Scenario A and in Scenario B.



Fig. 14 — Comparison of aeration requirements in the baseline case, in Scenario A and in Scenario B.

part of it has been removed in the precipitation unit. Finally, the aeration is lowest when pure oxygen is used to aerate the aerobic reactor (Fig. 14).

Even though the aeration requirement is lower and consequently pumping costs may be reduced, the high costs of pure oxygen makes this alternative non appropriate for urban WWTPs. However, in some cases pure oxygen may be used in combination with air. In this case, it would be necessary to add a second gas hold-up phase, which is straightforward thanks to the proposed methodology.

All these examples have shown the capability of the model to reproduce biochemical, chemical and physico-chemical processes and the benefit of the methodology that enables the incorporation of new technologies in a straightforward way.

4. Conclusions

This paper presents a general methodology to integrate biochemical, chemical and physico-chemical models for describing wastewater and sludge treatment processes. The description of the model components in terms of elemental mass according the Plant-Wide Modelling methodology proposed by Grau et al. (2007) offers a suitable framework to incorporate chemical and physico-chemical transformations in a straightforward way. Additionally, the proposed methodology enables representing in systematic and modular way unit processes where liquid, gaseous and solid phases co-exist including the mass transport among them. Three additions are especially useful: 1) the multiphase extension of the Gujer compact model representation, 2) separating gas hold-up and off-gas transfer processes, and 3) separating "k_L" and "a" in the mass transfer coefficients. This permits the systematic incorporation of all transformations to be considered for any plant layout.

If additional biochemical transformations need to be considered or the kinetics of the processes are to be updated the methodology offers a flexible framework to incorporate these modifications easily.

The case study illustrates the procedure to build a model based on the PC-PWM methodology. Additionally the comparison of the mathematical model results with the experimental data shows the capability of the model obtained to reproduce real data. The scenario analysis shows the benefits of using this methodology to study WWTPs as a whole when considering of the biochemical, chemical and physicochemical transformations. Finally, it also shows the usefulness of the methodology since it facilitates the incorporation of new processes without any conversions or without altering the model conceptually.

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