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Industrial Electrical Engineering and Automation

Physico-Chemical Modelling (PCM)

– a literature review

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Physico-Chemical Modelling (PCM)

– A LITERATURE REVIEW

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CONTENTS

1. INTRODUCTION

This literature review is a part of the self-study course required for my PhD studies at IEA, LTH. The specific objectives of this task are to research on and critically summarize current and significant papers about physico-chemistry, especially focusing on its application to modelling wastewater treatment processes.

1.1. Physico-chemical processes

Physico-chemical refers to both physical and chemical properties/aspects, as opposed to biochemical. Physico-chemical processes are non-biologically mediated processes. They can be liquid-liquid processes (i.e. ion association/dissociation), gas-liquid processes (i.e. gas-liquid transfer), and liquid-solid processes (i.e. precipitation and solubilisation) (Batstone et al., 2012).

1.2. Applications of physico-chemical modelling

The advances in the modelling as well as data collection related to physico-chemistry are generally established in the field of geochemistry. Most of the software products about water chemistry are directed for geochemical applications.

In the field of wastewater treatment modelling, the physico-chemical models that are used are the same ones used as for geochemistry. And for this reason, publications written on physico-chemical modelling as applied to wastewater treatment modelling are, most of the time, similar. Because of the enormity of available databases and processes involved in the physico-chemical models, the main difference on these for-wastewater-treatment models would be the reduction of the database/processes depending on the specific objective/s of why these physico-chemical models were included in the first place.

1.3. Motivation for the development of physico-chemical models for wastewater treatment processes

Due to the current needs to expand the IWA models (e.g. Activated Sludge Models (Henze et al., 2000), Anaerobic Digestion Model (Batstone et al., 2002)), model formulations also need to be modified and expanded. For example, anaerobic digestion systems dealing with sulfate-rich waste streams need to account for an increase in the number of state variable being considered (Fedorovich et al., 2003; Barrera et al., 2015). In addition, one should also take into account the other relevant and significant components that are interacting with sulfur, in this case iron (Fe) (Flores-Alsina et al., 2016). In certain conditions, sulfur (in the form of sulfate) can be removed by precipitating it with S or aluminium (Al). Such precipitation reactions are physico-chemical processes. Modelling precipitation reactions should consider ion activities instead of the actual concentrations (Kazadi Mbamba et al., 2015a; 2015b) (more detail on this in the next sections) and this involves non-ideality corrections that are inherent to geochemical software. Thus, in this highly interlinking mechanism, addition of certain components on standard models would increase dramatically the number of components and submodels to be included (Solon et al., 2015; Flores-Alsina et al., 2015). Most importantly, systems with non-ideal conditions are modelled correctly when physico-chemical models are included (Batstone et al., 2012).

1.4. Available models on physico-chemistry for wastewater treatment modelling

Currently, a significant number of IWA models have been extended to include physico-chemical modelling. Flores-Alsina et al. (2015) have extended the activated sludge models ASM1, ASM2d, ASM3 with a physico-chemical framework that allows for the dynamic calculation of pH. However, it does not include precipitation yet. Solon et al. (2015) have extended the anaerobic digestion model no.1 (ADM1) as well in order to account for non-idealities. These results have shown a significant difference with the results from the original model implementation, especially for the cases where multi-valent ions are considered. The results have proved that such physico-chemical modelling is needed in order to produce accurate results. Kazadi Mbamba et al. (2015a; 2015b) have also shown using the PCM framework and together with the developed precipitation framework the effect of multiple mineral precipitation on simulation results and have further validated this extended modelling with experimental data.

Lizarralde et al. (2015) have also developed a model to describe physico-chemical transformations, which includes liquid-gas transfer and liquid-solid transfer. The acid-base equilibrium as well as the ion-pairing equilibrium are further described in a physico-chemical model. In their study, the components added in order to describe the physico-chemical reactions are dependent on the biochemical processes chosen.

Musvoto et al. (1997; 2000a; 2000b; 2000c) have also used the weak acid/base model in order to extend the applications of ASM1 in cases where pH estimation is considered important (Sötemann et al., 2005a).

2. CONTENTS OF THE PHYSICO-CHEMICAL MODELLING FRAMEWORK

A physico-chemical model involves the phase changes in the reactions products. This includes precipitation/re-dissolution reactions and gas stripping. Modelling these phase changes reactions require the use of water chemistry (acid/base and ion pairing reactions). Thus, physico-chemical modelling includes: liquid-liquid processes, liquid-solid processes, and gas-liquid processes.

LIQUID-LIQUID PROCESSES

2.1. Acid-base reactions (chemical equilibrium dissociation)

Stumm and Morgan (1996) give the general principle of dissociation reactions:

$$\mathrm{HA} \leftrightarrow \mathrm{H}^{+} + \mathrm{A}^{-} \qquad \text{Eq. 2.1.1}$$

The chemical equilibrium is solved either with ordinary differential equations (ODEs) or algebraic equations (AEs). The dissociation processes of acid/base reactions and ion pairing reactions can be described using ODEs. They are given high kinetic rate constants to show that these reactions occur instantaneously (Musvoto et al., 1997; 2000a; 2000b).

2.2. Ion speciation/pairing

The Tableau method (Morel and Hering, 1993) shows an organized way of representing all equations required for acid/base and ion pairing reactions. It allows to easily determine the expression for a solution (represented by the total), given the components. Components are the basic building blocks from which all species are formed. This can be organised using the Tableau method, which is basically a table of stoichiometric coefficients, where each column represents an individual component, and each row represents a separate species. The composition of the solution is written in terms of the components.

In a proper component set:

1. All species can be expressed stoichiometrically as a function of the components, the stoichiometry being defined by the chemical reactions.
2. Each species has a unique stoichiometric expression as a function of the components.
3. H_2O should always be chosen as a component. Although it is omitted from the Tableau, it is implicitly included in the component set.
4. H^+ should always be chosen as a component.

In some cases, there are also non-electrostatic interactions between ions, which form ionic complexes as new chemical species. These ion pairs or ion complexes are different from the free ions (such as a biphosphate ion, HPO_4^{2-}, which is different from free orthophosphate, PO_4^{3-}) in solution. For this reason, ion complexes can increase or decrease the chemical driving force for a specific reaction to occur, depending on whether the free-form (such as phosphate precipitating as struvite) or the ion complex (such as ammonium precipitating as struvite) is the chemical species that participates in the particular reaction. Ion pairing effects on pH predictions are considered significant in systems with high total dissolved solids concentrations (Musvoto et al., 2000a), indicating high ionic strengths such as in high-strength anaerobic digestion liquors, sea water, and concentrated industrial wastewater (Table 2.2.1).

Table 2.2.1. Non-ideality corrections (Batstone et al., 2012) to achieve a pH error of less than 5%.

LEVEL	IONIC STRENGTH (M)	WASTEWATER TYPE	APPROACH
1	< 0.001	drinking water clean natural fresh water	no correction required – assume ideal
2	< 0.1	weak industrial wastewater all domestic wastewater	non-iterative simple correction
3	< 1 (only ion activity)	sea water anaerobic digesters	full iterative calculation of ion activity
4	< 1 (activity with non-valents)	as above, with gas transfer	similar to level 3, using non-valent form of Extended Debye-Hückel equation
5	< 5	strong industrial wastewater landfill leachate RO brine	similar to level 4, but including ion pairs

A sub-model containing the most common ion pairs present in wastewater is set-up to describe ion-pairing behaviour (see some examples in Table 2.2.2). This is implemented in a similar fashion as weak acid/base reactions where an algebraic procedure (Ikumi et al., 2011) is used based on the assumption that ion pairs are in a state of equilibrium at all times. Total concentrations are determined by mass balances and subsequently, the ionic concentrations are calculated iteratively using a speciation sub-routine from a set of algebraic mass balances and equilibrium constant relationships (Tait et al., 2012).

Table 2.2.2. Common ion-pair reactions taken from Musvoto et al. (2000a).

Ion pair reactions		
$Ca^{2+} + OH^- \leftrightarrow CaOH^+$	$Ca^{2+} + PO_4^{3-}$	$Mg^{2+} + OH^- \leftrightarrow MgOH^+$
$Ca^{2+} + CO_3^{2-}$	$Ca^{2+} + H_2PO_4^-$	$Mg^{2+} + CO_3^{2-}$
$Ca^{2+} + HCO_3^- \leftrightarrow CaHCO_3^+$	$Mg^{2+} + HPO_4^{2-}$	$Mg^{2+} + HCO_3^-$
$Ca^{2+} + HPO_4^{2-}$	$Mg^{2+} + PO_4^{3-}$	

2.3. Ion activity

The effect of ionic strength, also known as ion activity ($S_{\{i\}}$), is defined as the effective concentration of any particular kind of ion in solution and is caused by electrostatic interactions between ions. It is calculated by multiplying the concentration of ion i ($S_{[i]}$) by a correction factor which is called the activity coefficient (γ_i):

$$S_{\{i\}} = \gamma_i \cdot S_{[i]} \qquad \text{Eq. 2.3.1}$$

Considering a chemical equilibrium reaction:

$$bB + cC \leftrightarrow dD \qquad \text{Eq. 2.3.2}$$

In infinitely dilute solutions, the ion activities can be approximated by the concentrations, as the activity coefficient approaches unity. The equilibrium constant (K_{eq}) is expressed as:

$$K_{eq} = \frac{S_{[D]}{}^{d}}{S_{[B]}{}^{b} \cdot S_{[C]}{}^{c}} \qquad \text{Eq. 2.3.3}$$

However, for non-ideal solutions K_{eq} is calculated as:

$$K_{eq} = \frac{S_{\{D\}}{}^{d}}{S_{\{B\}}{}^{b} \cdot S_{\{C\}}{}^{c}} = \frac{\left(\gamma_D \cdot S_{[D]}\right)^{d}}{\left(\gamma_B \cdot S_{[B]}\right)^{b} \cdot \left(\gamma_C \cdot S_{[C]}\right)^{c}} \qquad \text{Eq. 2.3.4}$$

There have been numerous studies on this topic, which have developed empirical correlations of experimental data that allow prediction of activity coefficients at various solution conditions (see Table 2.3.1). All of these expressions have shown that ion activity is dependent on the ionic strength (I) of the solution, which can be determined as follows:

$$I = \frac{1}{2} \sum S_{[i]} \cdot z_i^2 \qquad \text{Eq. 2.3.5}$$

where z_i is the charge of ion i.

The calculated activity should be used in equilibrium equations as well as weak acid/base pairing and ion complexation reactions.

The current physico-chemical models applied for wastewater treatment process modelling has used the Davies equation (Davies, 1939; Merkel and Planer-Friedrich, 2008) to describe the activity of the components instead of the concentrations. This is because this equation is simple and does not need other constants unlike the extended and WATEQ Debye-Hückel equation (Truesdell and Jones, 1973). In addition, the Davies equation is valid for a larger range of ionic strength. The differences between the different ion activity correction equations and their relationship with ionic strength and ion types (i.e. monovalent, divalent, etc.) are shown in Figure 2.3.1. It would have been better to use the WATEQ Debye-Hückel equation since it is valid for the widest range of ionic strength, however, it requires two additional parameters for each ion type considered which are not always available in literature. Thus, the Davies equation seems to be the most fitting choice.

Table 2.3.1. Expressions for calculating activity coefficients and their corresponding range of applicability.

EQUATION NAME	EQUATION	APPLICABILITY
Debye-Hückel (Debye and Hückel, 1923)	$\log \gamma_i = -A \cdot z_i^2 \cdot \sqrt{I}$	$I < 0.005 \frac{mol}{L}$
Extended Debye-Hückel (Debye and Hückel, 1923)	$\log \gamma_i = -A \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + B \cdot \alpha_i \cdot \sqrt{I}}\right)$	$I < 0.1 \frac{mol}{L}$
Güntelberg (Guntelberg, 1926)	$\log \gamma_i = -A \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}}\right)$	$I < 0.1 \frac{mol}{L}$
Davies (Davies, 1939)	$\log \gamma_i = -A \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3 \cdot I\right)$	$I < 0.5 \frac{mol}{L}$
WATEQ Debye-Hückel (Truesdell and Jones, 1973)	$\log \gamma_i = -A \cdot z_i^2 \cdot \left(\frac{\sqrt{I}}{1 + B \cdot \alpha_i \cdot \sqrt{I}} + \beta_i \cdot I\right)$	$I < 1 \frac{mol}{L}$

where:

γ_i	Activity correction coefficient of ion i;
A, B	Temperature-dependent constants;
z_i	Charge of ion i;
α_i, β_i	Ion-specific parameters;
I	Ionic strength.

Another technique for determining activity coefficients is the Pitzer equation (Pitzer, 1973). It is applicable for predicting activity coefficient values of ions in solution with very high ionic strength. It implements a specific ion interaction model, wherein both ionic strength and the characteristics of the solution are considered. This means that this is a more precise modelling of mean activity coefficient data and equilibrium constants. However, there is a much greater number of parameters included in Pitzer equations which means that they are more difficult to calibrate based on available measurements.

As an example of typical ions present in wastewater, Na^+ and Mg^{2+} are shown in Figure 2.3.1. In solutions with low ionic strength (I < 0.1 mol/L), the activity corrections applied to the concentrations are precise for the different expressions when used within their ionic strength validity range. However, correction factors become very different at higher ionic strengths even when used within their valid ranges, and can be observed by the curves corresponding to Davies and WATEQ Debye-Hückel equations.

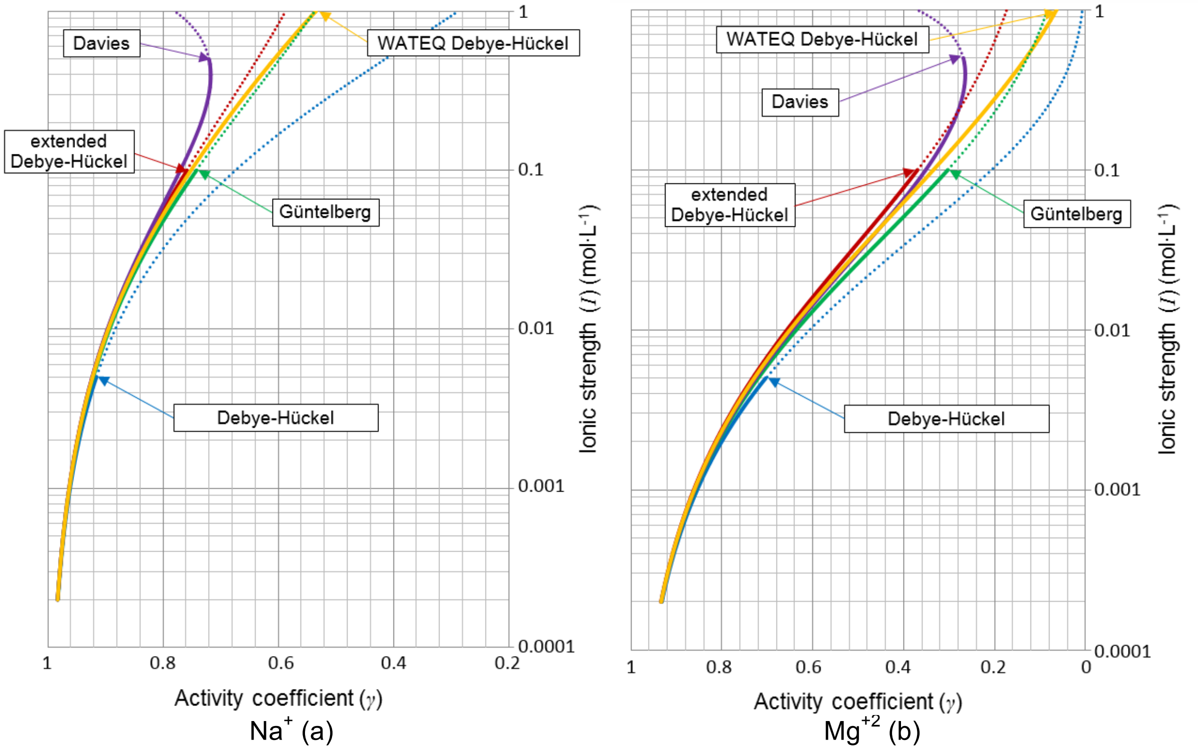

Figure 2.3.1. Activity coefficients of (a) sodium and (b) magnesium ions as calculated from five activity coefficient correlations.

LIQUID-SOLID PROCESSES

2.4. Precipitation and re-dissolution

Opposite to liquid-liquid processes, liquid-solid processes are assumed to occur slowly to reach equilibrium. In order to model precipitation reactions, the possibility of precipitation is calculated first by testing if the solution is supersaturated or not. The Saturation Index (SI) indicates if a solution is in equilibrium, undersaturated or supersaturated with respect to a mineral (i.e. whether a mineral precipitation might occur or not) (Merkel and Planer-Friedrich, 2008; Stumm and Morgan, 1996; Alley, 1993). If SI < 0, the liquid phase is undersaturated, thus a mineral might dissolve into the liquid phase. If SI = 0, the liquid phase is saturated or at equilibrium. While if SI > 0, the liquid phase is supersaturated and mineral precipitation might occur. It is calculated by:

$$\mathrm{SI} = \log\left(\frac{\mathrm{IAP}}{\mathrm{K_{SP}}}\right) \qquad \text{Eq. 2.4.1}$$

where:

IAP	Ion-activity product, the product of the activities of the elements comprising the mineral precipitate;
$\mathrm{K_{SP}}$	Solubility product constant of the mineral.

Considering an equilibrium reaction:

$$\mathrm{xM^{v+} + yA^{v-} \leftrightarrow M_xA_y} \qquad \text{Eq. 2.4.2}$$

The IAP is: $\mathrm{IAP = \{M^{v+}\}^x \cdot \{A^{v-}\}^y}$
while the $\mathrm{K_{SP}}$ is: $\mathrm{K_{SP} = \{M^{v+}\}_0{}^x \cdot \{A^{v-}\}_0{}^y}$.

Note that SI only indicates what could happen thermodynamically. However, it does not indicate the rate by which the process will proceed. This means that a solution may be super-saturated for a very long time (i.e. it will take a long time for the mineral to precipitate). There are several equations available for kinetic rates describing crystallization.

The general form of the crystallization rate given by Koutsoukos et al. (1980) and first proposed by Davies and Jones (1955) as applied to silver chloride precipitation is:

$$\mathrm{r_i = k_{cryst} s\left[\left(\{M^{v+}\}^x \cdot \{A^{v-}\}^y\right)^{\frac{1}{v}} - \left(\{M^{v+}\}_0{}^x \cdot \{A^{v-}\}_0{}^y\right)^{\frac{1}{v}}\right]^n} \qquad \text{Eq. 2.4.3}$$

where:

$\mathrm{r_i}$	Precipitation kinetic rate;
$\mathrm{k_{cryst}}$	Precipitation rate constant;
s	Proportional to the total number of available growth sites on the added seed material;
$\mathrm{\{M^{v+}\}^x, \{A^{v-}\}^y}$	activities of lattice ions at time *t*;
$\mathrm{\{M^{v+}\}_0{}^x, \{A^{v-}\}_0{}^y}$	activities of lattice ions at equilibrium;
v	v+ + v-;
n	A constant, typically 2.

This rate equation has been used for kinetic studies (Koutsopoulos, 2002; Koutsoukos, 1980; Nancollas and Reddy, 1971) as well as in modelling of precipitation reactions as applied to wastewater treatment (Barat et al., 2011; Musvoto et al., 2000a; 2000b, 2000c). The equation describes how the difference between the concentration of contributing ions in a solution and their equilibrium concentrations is the thermodynamic driving force that dictates the occurrence of precipitation.

Kazadi Mbamba et al. (2015a; 2015b) have adapted the crystallization rate presented by Nielsen (1984):

$$r_i = k_{cryst}\, X_{crsyt} \left[\left(\frac{\{M^{v+}\}^x \cdot \{A^{v-}\}^y}{K_{SP}} \right)^{\frac{1}{v}} - 1 \right]^n \qquad \text{Eq. 2.4.4}$$

Lizarralde et al. (2015) have presented the kinetic rate for precipitation reactions based on the work by Koutsoukos et al. (1980) and improved it with a consideration of the effect of crystal seeding, TSS concentration, and delay of nucleation (spontaneous nucleation).

$$r_i = k_{cryst} s \left[(\{M^{v+}\}^x \cdot \{A^{v-}\}^y)^{\frac{1}{v}} - \left(\{M^{v+}\}_0{}^x \cdot \{A^{v-}\}_0{}^y \right)^{\frac{1}{v}} \right]^n \cdot (A_{SO} + A_{XTSS} + A_{SN}) \qquad \text{Eq. 2.4.5}$$

where:

A_{SO}	$s_0 \dfrac{[M_xA_y]}{[M_xA_y]_0 + K_2}$
A_{XTSS}	$\dfrac{X_{TSS}}{X_{TSS} + K_3}$
A_{SN}	$\dfrac{[M^{v+}]^x \cdot [A^{v-}]^y}{[M^{v+}]^x \cdot [A^{v-}]^y + K_1}$
K_1, K_2, K_3	Constants with very small values to guarantee numerical stability.

s_0 is an adimensional parameter representing the growth of interfacial area concentration assuming a constant size distribution.

The first two added terms (A_{SO}, A_{XTSS}) represent crystal growth when support material is added and the last term (A_{SN}) is added to describe crystal growth when no seed material is added.

Building the model also requires identification of the possible precipitates or else there might be missed components or the model will be overly complex. This is the advantage of using an external software tool because all possible precipitates could be reflected. That is also the reason why it is advantageous to have prior knowledge and process understanding. Musvoto et al. (2000a; 2000b; 2000c) have identified precipitates (see Table) that are likely to occur in wastewater treatment plants. The types of precipitates are also highly dependent on the influent and the use of metals for chemical precipitation.

Some examples of minerals which are identified to precipitate during wastewater treatment are listed in Table 2.4.1.

Table 2.4.1. Common mineral precipitates formed during wastewater treatment.

Mineral	Chemical formula
Amorphous calcium phosphate (ACP)	$Ca_3(PO_4)_2$
Calcite (CCM)	$CaCO_3$
Struvite	$MgNH_4PO_4$
Newberryite	$MgHPO_4{:}3H_2O$
Hydroxyapatite (HAP)	$Ca_5(PO4)_3OH$
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4{:}2H_2O$
Octacalcium phosphate (OCP)	$Ca_4H(PO_4)_3{:}3H_2O$
Aragonite (ACC)	$CaCO_3$
Magnesite	$MgCO_3$
K-struvite	$KMgPO_4$
Iron sulfide	FeS
Iron phosphate	$FePO_4$
Aluminium phosphate	$AlPO_4$
Vivianite	$Fe_3(PO_4)_2{:}8H_2O$

Lettinga et al. (1997); Musvoto et al. (2000a, 2000b, 2000c); Maurer and Boller (1999); Carlsson et al. (1997); Clark et al. (1997); Wang et al. (2016)

Unlike the equilibrium constants used in aqueous phase chemistry, the constants used to model precipitation reactions usually vary between databases and literature references. Because of this, one should take caution when using the solubility product constants for certain minerals. In addition, not all information can be found in one database. For example, the K_{SP} value for K-struvite and Iron phosphate cannot be found in the database of MINTEQ (Gustafsson, 2010). One reason is that this database is mostly used for geochemical studies and such precipitates are not common in groundwater. One could add manually the values found elsewhere (e.g. literature) for these minerals in the database.

Dissolution can be considered as the inverse of the precipitation kinetics. In line with this, the dissolution rate equation could be expressed in the general form as:

$$r_i = -k_{diss}s\left(\left(\{M^{v+}\}^x \cdot \{A^{v-}\}^y\right)^{\frac{1}{v}} - \left(\{M^{v+}\}_0{}^x \cdot \{A^{v-}\}_0{}^y\right)^{\frac{1}{v}}\right)^n \qquad \text{Eq. 2.4.6}$$

Lizarralde et al. (2015) mathematically expressed the dissolution rate similar to Eq. 2.4.5 with the exception of activation terms A_{XTSS} and A_{SN}, which do not affect the re-dissolution

$$r_i = -k_{diss}s\left(\left(\{M^{v+}\}^x \cdot \{A^{v-}\}^y\right)^{\frac{1}{v}} - \left(\{M^{v+}\}_0{}^x \cdot \{A^{v-}\}_0{}^y\right)^{\frac{1}{v}}\right)^n \cdot (A_{SO}) \qquad \text{Eq. 2.4.7}$$

LIQUID-GAS PROCESSES

2.5. Stripping/volatilization and absorption

Mass transfer between the liquid phase and gas phase are modelled to describe the dissolution of the gaseous components formed during biological reactions into the aqueous phase (i.e. absorption) as well as the mass transfer of the dissolved form of these gaseous components into the gas phase (i.e. volatilization - due to natural phenomenon; stripping - due to a mechanical device). Derived from Fick's first law (Fick, 1855), the equation below is a very common form of the kinetic rate equation for the liquid-gas transfer:

$$r_{i,G/L} = k_L \cdot a \cdot \left(K_{H,i} \cdot P_i - C_i\right) \qquad \text{Eq. 2.5.1}$$

where:

$r_{i,G/L}$	Mass transfer rate between the gas and liquid phase;
$k_L a$	Gas transfer coefficient;
k_L	Mass transfer rate;
a	Contact area between the liquid and gas phase;
$K_{H,i}$	Henry's constant;
P_i	Partial pressure;
C_i	Dissolved concentration of the gaseous component.

The product of the Henry's constant and the partial pressure of the gas $\left(K_{H,i} \cdot P_i\right)$ gives the saturation concentration (C_S). The gas transfer coefficient $(k_L a)$ is dependent on the temperature. ASCE (1993) gives the widely-used relationship between $k_L a$ (in d^{-1}) and temperature (°C):

$$k_L a\ (T) = 1.024^{(T-15)} \cdot k_L a\ (15\ °C) \qquad \text{Eq. 2.5.2}$$

The most common gaseous components which can be considered during modelling of stripping processes in wastewater treatment are: O_2, CO_2, NH_3, N_2, H_2, CH_4, and H_2S (Lizarralde et al., 2015).

OTHER

2.6. Temperature correction

For most of the kinetic rate used, temperature is an important variable that affects the kinetic parameters such as presented in Eq. 2.5.2. The Arrhenius equation is widely used to quantify the effect of temperature on the kinetic rates of chemical and biochemical reactions (Fogler, 2005; Peleg et al., 2012). The relationship is given by:

$$\mathrm{k(T)} = \mathrm{A} \cdot \exp\left[\frac{-\mathrm{E}}{\mathrm{R} \cdot \mathrm{T}}\right] \qquad \text{Eq. 2.6.1}$$

where:

$\mathrm{k(T)}$	Rate constant as a function of temperature;
A	Pre-exponential factor;
E	Activation energy;
R	Gas constant;
T	Temperature (K).

In several processes occurring in biological systems, a variant of this equation has been widely used (Sheridan et al., 2012; Henze et al., 2000). The equation has been reformed into what is called the Modified Arrhenius Function (MAF), given by:

$$\mathrm{k(T)} = \mathrm{k}_{20} \cdot \theta^{(\mathrm{T}-20)} \qquad \text{Eq. 2.6.2}$$

where:

k_{20}	Rate constant at 20 °C;
θ	Temperature correction factor.

This equation has been easier to use since the temperature is given in degrees Celsius and the correction factor is fairly measureable (Kadlec and Knight, 1996; Kadlec et al., 2009; Nguyen et al., 2014). However, the main assumption is that the operating temperature should be close to or lower than 20 °C. Sheridan et al. (2012) has shown that an error as high as 25% is found if used at temperatures up to 50 °C.

Sheridan et al. (2012) thus suggested a further modified Arrhenius equation for use in biological systems and applicable for all temperature ranges:

$$\mathrm{k(T)} = \mathrm{k}_{293} \cdot \exp\left[\beta\left(\frac{\mathrm{T}-293}{293 \cdot \mathrm{T}}\right)\right] \qquad \text{Eq. 2.6.3}$$

where:

k_{293}	Rate constant at 293 K (20 °C);
β	$\frac{\mathrm{E}}{\mathrm{R}}$

On the other hand, the expanded square root equation of Ratkowsky (Ratkowsky et al., 1983) can also be used to describe the temperature effects during microbial growth:

$$\mu(\mathrm{T}) = \left[\mathrm{b}(\mathrm{T}-\mathrm{T_{min}})\left(1-\mathrm{e}^{\mathrm{c}(\mathrm{T}-\mathrm{T_{max}})}\right)\right]^2 \qquad \text{Eq. 2.6.4}$$

where:

$\mu(\mathrm{T})$	Growth constant as a function of temperature;
b, c	Empirical parameter;
$\mathrm{T_{min}}$	Minimum temperature at which growth is observed;
$\mathrm{T_{max}}$	Maximum temperature at which growth is observed.

Hiatt (2006) and Hiatt and Grady (2008) have used this Ratkowsky equation for describing the growth of heterotrophs and autotrophs. According to Ratkowsky et al. (1983), the equation eliminates the need for setting upper limits on the valid temperature range. Between the temperatures of 5 °C and 25 °C, the behaviour of the Arrhenius and Ratkowsky equations are similar. At temperatures higher than 25 °C the values are still increasing for Arrhenius. However, using the Ratkowsky equation at temperatures higher than 25 °C the values are slowly increasing until it reaches a maximum pre-defined temperature and will then start to decrease at further higher temperatures. Some models, such as SHARON (Single reactor system for High activity Ammonia Removal Over Nitrite) process, typically is operated at high temperatures (i.e. 30-40 °C) (Hellinga et al., 1999; Volcke et al., 2007) and the use of the Ratkowsky equation is preferable.

3. IMPLEMENTATION DETAILS AND NUMERICAL ISSUES

The implementation of the physico-chemical model within plant-wide frameworks leads to some numerical issue that need to be addressed. The aqueous phase chemistry reacts very quickly, while the biological processes (as well as precipitation) reacts very slowly giving rise to a stiff system (Solon et al., 2015; Flores-Alsina et al., 2015; Lizarralde et al., 2015). Implicit solvers could be used to solve these types of systems, but not very efficiently for dynamic inputs, noise and controller characteristics (if used for a control perspective). Rosen et al. (2006) have solved this type of issue in the past for ADM1 by solving pH and hydrogen states as independent algebraic equations and used an explicit Runge-Kutta solver for the other ordinary differential equations (ODE). However, this approach cannot be used due to the large interdependencies within the algebraic system. Solon et al. (2015) and Flores-Alsina et al. (2015) have used a multi-dimensional version of the Newton-Raphson method (Press et al., 2007) to solve the highly interdependent nonlinear algebraic system while the differential equations are solved separately with an ODE solver. Musvoto et al. (2000a; 2000b), Sötemann et al. (2005a; 2005b), and Poinapen and Ekama (2010) have used chemical species in their state vectors and thus have expressed all processes as ODEs. Lizarralde et al. (2015) have calculated fast reactions (e.g. aqueous phase chemistry) as differential algebraic equations (DAEs) at each time step similar to Batstone et al. (2002) and Rosen et al. (2006) for ADM1. Components are included in the state vector and are calculated using ODEs, but at each time step, the concentration of each species is calculated using algebraic equations (DAEs).

Solon et al. (2015) and Flores-Alsina et al. (2015) have used external software (i.e. MINTEQ) in order to check the precision of their results in relation to the values obtained from MINTEQ, both results agreeing in values. Lizarralde et al. (2014) have further shown both the uses of an external software tool or a tailored code to solve the aqueous phase chemistry. Both have shown similar simulation results, however, it was with the tailored code that showed the fastest simulation times (Lizzaralde et al., 2014; 2015). It should be noted, however, that in their study species which are considered insignificant were removed from the tailored code in order to improve the simulation speed.

Nevertheless, it is still an on-going discussion whether using a tailored code or including a geochemical software as a sub-routine to the biochemical model. It could be that the geochemical software could be faster as long as the number of components is also decreased based on the needs of the biochemical model.

4. AVAILABLE SOFTWARE TOOLS

PHREEQC (Parkhurst and Appelo, 1999) is a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations published by the US Geological Survey (USGS). It is designed to perform a wide variety of aqueous geochemical calculations. It also includes the Pitzer aqueous model which can be used for high-salinity waters that are beyond the range of application for the Debye-Hückel theory. It is mentioned in their limitations the lack of internal consistency in the data in the databases. No systematic attempts have been made to determine the current consistency of the data with the original experimental data.

MINTEQ or Visual MINTEQ (Gustafsson, 2010) is also a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria, sorption, etc. for natural waters. Furthermore, it includes state-of-the-art complexation models to estimate binding of ions to hydroxide surfaces and organic matter. The code that is being used was originally built on USEPA's MINTEQA2 software and is maintained at the Royal Institute of Technology (KTH), Stockholm, Sweden. It runs on the Windows platform. It also interacts with Excel for data import and export.

MINTEQA2 (Allisson et al., 1991) is an equilibrium speciation model that can be used to calculate the equilibrium composition of dilute aqueous solutions in the laboratory or in natural aqueous systems. The model is useful for calculating the equilibrium mass distribution among dissolved species, adsorbed species, and multiple solid phases under a variety of conditions including a gas phase with constant partial pressures. A comprehensive database is included that is adequate for solving a broad range of problems without the need for additional user-supplied equilibrium constants.

CHEAQS Next (Verweij, 2008) is the next generation of the speciation program CHEQS Pro. CHEAQS Next is a computer program for calculating CHemical Equilibria in AQuatic Systems. You supply input data, the program calculates the chemical speciation for you. CHEAQS Next is freeware. You can calculate the concentration of complexes, but you can also calculate: redox equilibria, complexation by natural organic matter, solids that are formed due to oversaturation, adsorption (surface complexation model).

The Geochemist's Workbench® (Lee and Goldhaber, 2011) is an integrated geochemical modelling package for balancing chemical reactions, calculating stability diagrams and equilibrium states of natural waters, modelling reactive transport, plotting capabilities and data storage. It makes use of the thermodynamic datasets from other tools, such as PHREEQC, WATEQ4F, and Visual MINTEQ. It can also calculate flow fields dynamically, which makes it unique among the other tools.

Aside from these, there are still numerous geochemical modelling programs in use such as: MINEQL+, WHAM, WATEQ4F, SOLMINEQ, CrunchFlow, CHEPROO, ECOSAT, Aqion, CHESS, HSC Chemistry®, HYDROGEOCHEM, ChemPlugin, ChemEQL, TOUGHREACT.

5. CONCLUSIONS

The important aspects of a physico-chemical model are:

- Weak acid-base and wastewater solution chemistry (i.e. speciation and ion pairing);
- Solid-liquid mass transfer processes (i.e. precipitation and dissolution);
- Gas-liquid mass transfer processes (i.e. stripping/volatilization and absorption);
- Non-ideality corrections (i.e. ionic strength effects/activity correction).

This literature review could be part of a general framework that could be used for physico-chemical modelling as applied to wastewater treatment systems. It could serve as a list of recommendations for including the aspects listed above in a PCM that one wants to develop for his/her own system. It does not have to include everything that is written here, but rather the user should look at his/her own system on a case-to-case basis and use what is needed and suitable.

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