Towards a generalized physicochemical framework

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ABSTRACT

Process models used for activated sludge, anaerobic digestion and in general wastewater treatment plant process design and optimization have traditionally focused on important biokinetic conversions. There is a growing realization that abiotic processes occurring in the wastewater (i.e. 'solvent') have a fundamental effect on plant performance. These processes include weak acid–base reactions (ionization), spontaneous or chemical dose-induced precipitate formation and chemical redox conversions, which influence pH, gas transfer, and directly or indirectly the biokinetic processes themselves. There is a large amount of fundamental information available (from chemical and other disciplines), which, due to its complexity and its diverse sources (originating from many different water and process environments), cannot be readily used in wastewater process design as yet. This position paper outlines the need, the methods, available knowledge and the fundamental approaches that would help to focus the effort of research groups to develop a physicochemical framework specifically in support of whole-plant process modeling. The findings are that, in general, existing models such as produced by the International Water Association for biological processes are limited by omission of key corrections such as non-ideal acid–base behavior, as well as major processes (e.g., ion precipitation). While the underlying chemistry is well understood, its applicability to wastewater applications is less well known. This justifies important further research, with both experimental and model development activities to clarify an approach to modeling of physicochemical processes.

Key words | chemical equilibrium, physicochemical framework, pH calculation, precipitation

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INTRODUCTION AND PROBLEM STATEMENT

This is a position paper that identifies key limitations in the popular International Water Association (IWA) biochemical models. It is based on discussions and subsequent research at the Physico-chemical Workshop at the Water Environment Federation and IWA-sponsored WWTmod2010 seminar at Mt St. Anne, in Quebec, Canada. The objective of the workshop and the present position paper is to identify the scope, need, and current capacity to develop and disseminate a common basis for implementation and solution of

physicochemical models within the current IWA modeling framework.

Physicochemical processes are those which commonly occur in biochemical systems, but which are not directly mediated by microbes. Such processes can act as stand-alone treatment (e.g., coagulation), have an impact on biochemical processes (e.g., pH, gas transfer), or be intimately linked to the underlying biochemical process (e.g., anaerobic digestion (AD) hydrogen transfer or bioelectrochemical systems). The fundamentals of physicochemical reactions are very well understood on a fundamental level (Stumm & Morgan 1996), and there are complex and accurate models that utilize the basic principles (Parkhurst & Appelo 1999). However, physicochemical sub-models in existing standardized biochemical models are often rudimentary, empirical, or both. The activated sludge model (ASM) series contains only the alkalinity state and a single film gas transfer model, while more complex models such as the pH system in the Anaerobic Digestion Model 1 (ADM1) are only valid for dilute systems, and do not include mechanistic (pH-based) precipitation. Specific limitations in these models are further addressed later in this position paper. Issues around modeling of physicochemical processes in wastewater systems were originally raised in a two-page position paper (Batstone 2009), which mainly identified technical issues across the range of wastewater treatment systems. This also identified that different models take different approaches, even though the underlying physicochemical processes are the same. This issue has become of even higher importance with a move towards plant-wide models, where a common physicochemical system across the whole model is very important.

Current wastewater models

The focus of this analysis is on standardized IWA models, and it is noted that other models (published or commercially available) may be more complete and/or address specific requirements (Fairlamb *et al.* 2003). For example, Sötemann *et al.* (2005) included two-phase (aqueous-gas) mixed weak acid–base chemical and physical processes for non-ideal conditions in ASM1 to predict reactor pH. Also, the focus of this discussion is wastewater treatment process models (e.g., ASM series, ADM1) and excludes other environmental models. The reasons for focusing on these models are: (a) the limitations can be readily identified, (b) the IWA model library addresses a diverse range of situations, (c) they are the most widely applied standardized models, and (d) they are broadly comparable in basis and nomenclature.

While this position paper is focused on wastewater treatment processes, it is also applicable to other, more complete models. For example, the RWQM No. 1 (Reichert *et al.* 2001) uses the same structured modeling approach as the ASM series, and includes chemical reactions (calcium carbonate precipitation as well as phosphate sorption and desorption on organics). This can be a useful source of information for the wastewater process modeling industry.

Existing IWA models contain a targeted but limited approach with regard to inclusion of the three major classes of physicochemical reactions: acid–base, gas transfer, and precipitation. No models include chemical oxidation/reduction. The approaches of the major models are given in Table 1.

Acid–base

The ASM models utilize a global alkalinity state (S_{ALK}), which is impacted by acid- or base-producing (or consuming) dynamic processes. Processes such as nitrification (acid producing) will decrease alkalinity, while processes such as ammonia release (base producing) will increase it. Thus, the alkalinity state provides an approximation that indicates whether pH is near neutrality, or well below it (Henze *et al.* 2000). It is assumed that, when alkalinity is depleted, pH will drop dramatically. A switch may be used to stop processes when alkalinity is low (e.g., alkalinity limitation on biological

Table 1 | Current approaches to physicochemical systems in IWA models

Model	Acid–Base	Gas–Liquid	Solid–Liquid
ASM1/ASM3[a]	Alkalinity state	Liq film controlled (k_La)[d]	None
ASM2/ASM2D[a]	Alkalinity state	Liq film controlled (k_La)[d]	Empirical P complex
ADM1[b]	pH calculated	Liq film controlled (k_La)	None
RWQM1[c]	pH calculated	Liq film controlled (k_La)	Empirical

[a]Henze *et al.* (2000).
[b]Batstone *et al.* (2002).
[c]Reichert *et al.* (2001).
[d]Not explicitly advocated, but typically used with implementations.

processes in ASM2-3). Alkalinity has long been used effectively with activated sludge modeling to flag pH problems. The approach is simple and computationally efficient. However, fundamental limitations include: (a) it is not generally possible to correlate alkalinity and pH, and (b) the alkalinity state is not related to a single underlying chemical component. While the additional complexity of implementing a carbon balance and pH calculations may offer small additional benefit when activated sludge processes are modeled in isolation, a carbon balance and pH calculations are essential for AD models. For this reason, plant-wide models will likely require carbon mass balances and physicochemical processes for both activated sludge and AD processes, to seamlessly integrate these processes.

Processes such as AD or nitrification–denitrification of high-strength wastewater streams also require explicit pH calculation using a charge balance, with either differential or algebraic calculation of speciation between the different forms of the acids and bases.

None of the IWA models include non-ideal behavior (i.e. activity, ion pairing etc.). Examples of nitrification–denitrification models with pH calculation using the charge balance approach (but not taking into account non-ideal behavior) are: Hellinga *et al.* (1999); Volcke (2006); Ganigue *et al.* (2010).

Solid–liquid

The ASM2D contains empirical relationships for precipitation or redissolution of metal phosphate complexes. The metal is nominally ferric ions ($Fe(OH)_3$), but the basic process can also be used for alum or calcium, with appropriate stoichiometry. Because pH is not calculated, the metal hydroxide is used as a driver for the forward (precipitation) process. The ADM1 does not consider metal ion precipitation, due to its complexity, though a potential approach is provided, based on calcium precipitation (Batstone *et al.* 2002)

Gas–liquid

The ASM series does not specify transport processes or consider mixing. The emphasis is on definition of the biological reactions (and for ASM2d a precipitation/dissolution reaction), so that the biokinetics can be implemented with any transport model, e.g., biofilms, reactive settlers, computational fluid dynamic (CFD) model, etc. Liquid-film controlled mass transfer is typically used for oxygen transfer when modelers implement the ASM series. Stripping of CO_2

or NH_3 is also not considered by the ASM series, but can be handled similarly with the appropriate effects on alkalinity.

The ADM1 advocates the use of liquid film controlled mass transfer to the headspace. The impact of pH on CO_2 speciation is considered.

None of the IWA models consider impact of non-ideality on gas dynamics or equilibrium. None of the models consider all the important greenhouses gases (i.e. N_2O).

Conclusions

The limitations of existing models are important. In particular, pH prediction is a key limitation in the ASM series, while the lack of ion activity correction (at low conductivity), ion pairing (at high conductivity), precipitation and phosphorus modeling are a limitation of the ADM1. Implementation in commercial packages has already started to address this issue in response to engineering demand.

Case studies demonstrating how standardized models can fail to predict specific situations, are highly important and has not been addressed in the literature. While beyond the scope of this report, examples where standardized models would fail include:

(a) failure of ASM1 to predict free acid inhibition during activated sludge nutrient removal (impact on nitrification and/or phosphorus removal). Calculation of pH is required;

(b) failure of ADM1 or nitrification models to predict pH correctly due to lack of activity corrections. Ganigue *et al.* (2010) noted an underprediction of the pH value during nitrification of landfill leachate and mentioned the effect of salinity as a possible cause for this deviation;

(c) failure of ASM2D to predict phosphorus precipitation kinetics driven by pH dependence.

PROCESSES

This section outlines the various physicochemical reactions that may be included. As is inherent in the name, physicochemical reactions are spontaneous (not biochemically mediated). Table 2 outlines the basic classes of physicochemical reactions with approximate general rates of reaction.

Acid–base reactions

Acid–base reactions are extremely rapid reactions, occurring in the liquid phase between a weak acid and its conjugate

Table 2 | Classes of physicochemical reactions, provided with typical reaction time constants

Type	Reaction speed	References
Acid–base	Very fast: time constants <0.1 s	Stumm & Morgan (1996)
Gas–liquid	Medium: time constants <1 min	Pauss *et al.* (1990)
Amorphous precipitation	Fast or medium: time constants <1 min	Szabo *et al.* (2008)
Crystalline precipitation	Slow: time constants >0.2 d	Musvoto *et al.* (2000a, b); Tait *et al.* (2009)
Chemical oxidation – reduction	Not well characterized, variable	

base. Examples include the carbonate, bicarbonate, and carbonic acid/carbon dioxide species within the inorganic carbon system, the ammonium/ammonia system, sulfide species within the inorganic sulfur system, the various phosphate species within the inorganic phosphorus system, and the acidic analogues for nitrite. Weak organic acids (acetate, etc.) also play a role. The reactions for the inorganic carbon system, where each reaction is governed by equilibrium, are as follows (with equilibrium constant K_A):

$$CO_3^{2-} \overset{K_{A,HCO_3^-}}{\longleftrightarrow} HCO_3^- \overset{K_{A,CO_2}}{\longleftrightarrow} CO_{2,L}* \tag{1}$$

where CO_3^{2-} is the weak base carbonate, HCO_3^- is the weaker base/weaker acid bicarbonate, and $CO_{2,L}$ is the liquid phase concentration of the weak acid carbon–dioxide. $CO_{2,L}$ represents the combined concentration of $CO_{2,L}$ and H_2CO_3, as the reaction between these is rapid, and equilibrium strongly favors $CO_{2,L}$ (Stumm & Morgan 1996). The reaction from H_2CO_3 to $CO_{2,L}$ is fast with a time constant of 0.05–0.1 s (Stumm & Morgan 1996). The forward reaction from $CO_{2,L}$ to H_2CO_3 is relatively slow, with a time constant on the order of 40 s (Stumm & Morgan 1996), but this is only

important where CO_2 is being transferred from gas to liquid, which seldom governs environmental processes.

Another example is the nitrite reaction to nitrous acid:

$$NO_2^- \overset{K_{A,HNO_2}}{\longleftrightarrow} HNO_2 \tag{2}$$

The concentration of the acid can be related to the concentration (or, more correctly, the activity) of the base from the equilibrium relationship (as an example, for free nitrous acid):

$$K_{A,HNO_2} = \frac{[NO_2^-][H^+]}{[HNO_2]} \tag{3}$$

If the total (acid + base) concentration is known for each component present, the concentration of each acid and base can be solved. An example for the nitrous acid and nitrite ion pair can be seen in Figure 1. The equations can be formulated either as: (a) the equilibrium equations + mass balance equations + the electroneutrality condition, known as the charge balance (Stumm &
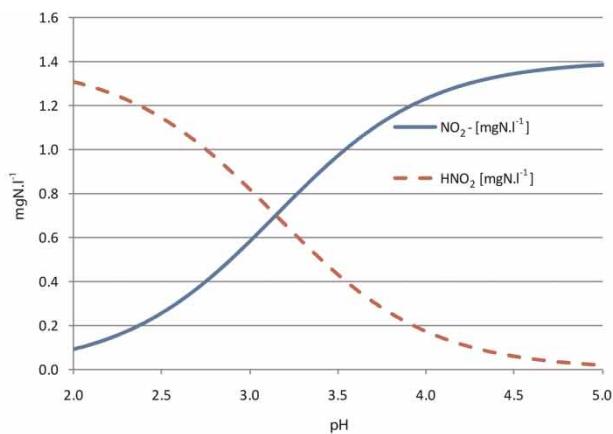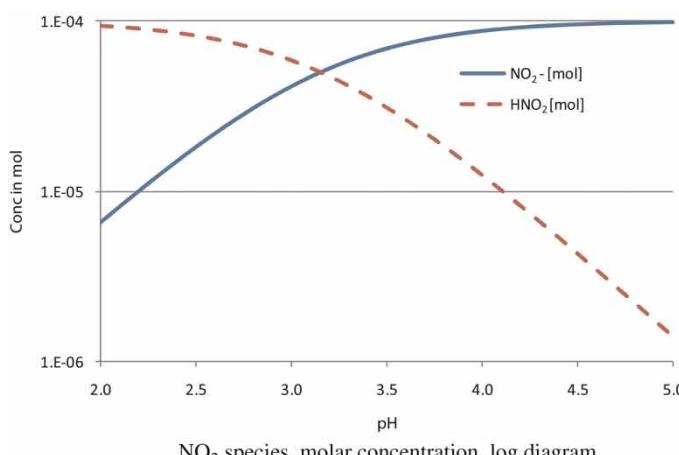
Figure 1 | $HNO_2 - NO_2^-$ concentrations of a solution containing 1.4 mgN L^{-1} (0.0001 mol) total NO_2 (log $K = -3.15$).

Morgan 1996), or (b) as a set of allocated mass balances, known as the Tableau method (Morel & Hering 1993). This provides a solvable set of non-linear implicit algebraic equations. These equations can then be solved as a set of stiff differential equations (DE approach), or as a set of algebraic equations to be solved in a non-linear algebraic equation solver (differential algebraic equation (DAE) approach) (Batstone *et al.* 2002). The equations can also be solved simultaneously with other differential equations in a DAE solver.

Conclusions

While understood on a fundamental level, any generalized approach needs to consider the acid–base system, as it so heavily impacts the remainder of the model framework. Solving the acid–base system is required to calculate pH, and this is a minimum requirement for a generalized physico-chemical model. Equation formulation is more important for communication than solution, with the charge balance approach being more readily understood by non-experts. A DAE solution approach is likely required for more complex models (Stumm & Morgan 1996). This is: (a) so that non-stiff solvers can be used to solve the biochemical system (with the algebraic system solved algebraically), and (b) because adding complex ion activity and precipitation behavior in the DE approach causes an exponential increase in the number of state variables. This can be controlled in the DAE approach by calculating many elements as algebraic variables.

Gas–liquid transfer

Gas–liquid transfer is important across the whole waste-water collection, treatment, and discharge process. Some important gas transfer mechanisms are (least soluble to most soluble gases):

- H_2 transfer.
- Aeration during aerobic stages.
- Nitrogen gas. Most of 'air' is nitrogen gas and most liquids in the plant are saturated with it. Its supersaturation status may play an important role in phase separation processes.
- Methane and N_2O supersaturation and environmental stripping causing greenhouse gas impacts.
- Carbon–dioxide and methane transfer during AD (carbon–dioxide is a weak acid).

- Transfer and odors, and occupational health and safety (OH&S) concerns caused by sulfide stripping (H_2S is a weak acid).
- Loss, odors, and OH&S concerns caused by ammonia stripping (NH_3 is a weak base).
- Detection and odors caused by organic acid and volatile organics stripping.

Note that many of the dissolved gases are also acids or bases, and hence the acid–base subsystem is vitally important to calculate gas transfer, while gas transfer has a significant impact on the acid–base subsystem through its effect on pH.

Transfer of material from the liquid to the gas phase (and vice versa) is described by dynamic mass transfer:

$$r_{gas,t} = K_{L^a}\left([S_{gas}]_L - \frac{[S_{gas}]_G}{H}\right) \tag{4}$$

where $r_{gas,t}$ is the gas transfer rate, $[S_{gas}]_L$ and $[S_{gas}]_G$ are the gas and liquid concentrations, H is Henry's Law coefficient (inverse of gas solubility) and a is the volume specific gas transfer area. The parameter K_L is a combination of resistance in the gas phase and resistance in the liquid phase:

$$\frac{1}{K_L} = \frac{1}{K_L} + \frac{1}{H \cdot K_G} \tag{5}$$

Depending on the relative ratio of k_G/k_L and the value of H, the relative contribution of gas and liquid phase resistance can be estimated. The ratio of k_G/k_L depends on the type of gas–liquid transfer apparatus, the specific compound under consideration and temperature (Munz & Roberts 1989). The typical reported values of k_G/k_L are in the range of 100–150. Munz & Roberts (1989) also suggest that liquid phase resistance is controlling when it accounts for more than 95% of the total resistance. Thus, assuming a k_G/k_L ratio of 100, it can be estimated that the H value has to be higher than 0.19 for liquid phase resistance to be governing. The value of Henry's constant for H_2S is 0.36. Munz & Roberts (1989) estimated an H value of 0.55, assuming a k_G/k_L value of 30–40, and place it in a range where both liquid and gas phase resistance may be required in the overall transfer resistance calculation depending on the ratio of k_G/k_L. On the other hand, for ammonia, Henry's constant being of the order of 5×10^{-4} makes the gas film resistance limiting.

When the gas transfer coefficient has been determined for one gas, the gas transfer for another can be

estimated based on the ratio of the diffusion coefficients in water for both gases (Matter-Mueller *et al.* 1981; Sperandio *et al.* 1999):

$$\frac{k_L, y}{k_L, z} = \left(\frac{D_y}{D_z}\right)^p \tag{6}$$

with k_L,y and k_L,z the overall mass transfer coefficients of the two gases, D_y and D_z the molecular diffusion coefficients of the two gases and p an empirical parameter usually equal to 0.5 (Sperandio *et al.* 1999) or 1 (Matter-Mueller *et al.* 1981).

Environmental factors or contamination (salt concentrations, surfactants) has an impact on gas transfer. They influence either the driving force (i.e. caused by changes in the saturation concentration), the resistance factors (i.e. k_L or k_G) or the interfacial area a. The impact on the saturation concentrations is usually lumped in a β-factor (Stenstrom & Gilbert 1981). The impact of contamination on the mass transfer coefficient is usually quantified by the α-factor (ratio of process water to clean water mass transfer coefficients, or $k_L a_{pw}/k_L a_{cw}$) (Stenstrom & Gilbert 1981). This α-factor lumps together several conditions having an impact on the gas–liquid transfer. The type of aerator is one such condition, i.e. lower flow regime gas–liquid interfaces (such as the ones produced by fine-pore diffusers) generally have lower α values than higher flow regime interfaces (such as the ones produced by coarse-bubble diffusers or surface aerators) for similar conditions (Stenstrom & Gilbert 1981). Also the mixed liquor suspended solids (MLSS) concentrations (or sludge age) and the presence of surfactants (Puigdomenech *et al.* 1997; Rosso & Stenstrom 2006; Cierkens *et al.* 2012) have been documented to impact gas transfer and are lumped into the α-factor. However, for higher MLSS concentrations (higher than 5 g/L), as observed in membrane bioreactor systems, an inverse trend in the α-factor has been observed, i.e. at these higher MLSS concentrations the α-factor decreases with increasing MLSS (Judd 2011).

Conclusions

Gas–liquid transfer has wide applicability, with good suitability to be addressed in a generalized model. The current approaches are quite standardized and effective, with the similar basic relationship across all models. In diffused aeration, separate models of aerators are used to determine $k_L a$. One of the key issues raised is the determination of the transfer area of different gaseous phases in contact with water. These could be the free liquid surface in contact with the atmosphere, air supply in aerated reactors, and gas generated by biochemical processes (e.g., anaerobic digesters and anoxic systems, where the gas composition can be atmospheric or enriched with oxygen, etc.). The calculation of the gas composition and the contact area a for each one of these phases (several gas phases are typically in contact with the liquid in the reactor) will have an important effect in the acid–base and biochemical processes, particularly in systems where gas is generated (e.g., anaerobic digesters and anoxic systems). The impact of activity on gas solubility can be independently addressed by ion activity corrections, but specific corrections are required to determine the impact of non-ideal behavior and contamination on k_L. In summary, the current $k_L a$ approach is effective (first order equilibrium driven transfer), particularly if general activity corrections are applied to solubility. However, work should be done to better assess the impact of non-ideality on dynamics.

Precipitation

Metal ion precipitation and coagulation are similar processes, resulting in transfer of metal ions and associated anions from the liquid to the solid phase. The first term generally refers to formation of hard metal precipitates such as calcium carbonate and calcium phosphate (e.g., (Musvoto *et al.* 2000b), while the second generally refers to formation of soft flocs from primary precipitates, commonly by ferrous or alum phosphate coagulation for wastewater treatment (e.g., Takacs *et al.* 2006). Common precipitants include:

(a) Metal (Ca, Mg, Fe, Al) ion phosphates and related compounds (e.g., struvite).
(b) Metal (All) ion hydroxides.
(c) Metal (Ca, Mg) carbonates (CO_3^{2-}).
(d) Metal (Fe, heavy metal) sulfides.

Precipitation processes are critical in modern wastewater treatment. They describe the behavior of phosphorus in all stages, as well as calcium and magnesium scaling. The presence of precipitates provides a slow buffer to changes in pH, and emerging processes (e.g., phosphorus recovery (Kim *et al.* 2007)) are highly dependent on metal ion precipitation.

Of the IWA wastewater treatment models, only ASM2/2D contains precipitation, and in this case, it is an empirical first order pseudo-equilibrium process (Henze *et al.* 2000).

Approach 1

A common method of modeling precipitation is a pseudo-equilibrium approach, with a first-order coefficient (van Langerak & Hamelers 1997; Henze *et al.* 2000; Batstone & Keller 2003; Takacs *et al.* 2006). As an example, the formation of struvite ($MgNH_4PO_4.6H_2O$) is modeled as:

$$r_{stru} = k_{emp}\left([Mg^{2+}][NH_4^+][PO_4^{3-}] - K_{SP}\right) \tag{7}$$

where r_{stru} is the crystallization rate, k_{emp} is a kinetic coefficient, K_{SP} is the solubility product, and is approximately $10^{-12.6}$. A continuous or discrete switch is needed to prevent negative struvite concentrations. This is a simple method to model precipitation processes, but is almost entirely empirical.

Approach 2

An alternative is the approach followed by the University of Cape Town (Musvoto *et al.* 2000b), which is also equilibrium driven, but is closer to fundamental relationships used for crystallization (Tait *et al.* 2009). A modified (more generalized) form of this for struvite is:

$$r_{stru} = k\left(\left(\frac{[Mg^{2+}][NH_4^+][PO_4^{3-}]}{K_{SP}}\right)^{1/3} - 1\right)^3 \tag{8}$$

where the exponent is known from prior empirical studies on precipitation (Musvoto *et al.* 2000a).

The actual process of crystallization is complicated by several issues:

(a) Impact of non-ideal behavior; ions engaged in precipitation are divalent and trivalent. These are most influenced by non-ideal behavior, and ions form soluble ion pairs at elevated concentrations prior to precipitation.

(b) Crystallization is a two-step process. Before crystals can develop, nuclei must be in the wastewater first to act as centers for crystallization. Thus, crystal growth must be preceded by nucleation (Mullin 2001). Either nucleation or the subsequent crystal growth can be rate limiting. This can be adjusted for by including the existing solid product in the crystallization reaction, but adds another layer of complexity to the model.

(c) Specific compounds can both promote and inhibit reactions. This can be general (through ion pairing, activity etc.) or specific (poisoning or promotion).

Multiple precipitates

Equilibrium or dynamic conditions in concentrated liquid solutions such as digester centrate may lead to multiple precipitates forming. Finding the right combination of precipitates forming, particularly if the precipitation potential needs to be determined directly from solubilities for each combination of solids, is not trivial. The supersaturation index (SSI) for each potential precipitate can provide guidance. If the product of the activities of ions participating in a precipitate is larger than the solubility constant, the solution is supersaturated for the specific precipitate. However, for 'n' precipitates, 2^n solutions must be considered. In reality some of these solutions may not be physically feasible. From chemical equilibrium tables (NIST 2001) about 30 potential precipitates can be identified; 2^{30} large equation systems are beyond the scope of practical applicability. A mixture of kinetic and equilibrium expressions can significantly simplify the computational demand. Slow precipitating reactions can be implemented together with faster precipitating reactions as competitive parallel kinetic processes, with the equilibrium scenario (as would be obtained with long retention times) represented by the most stable combination of precipitates (Musvoto *et al.* 2000b).

Conclusions

Precipitation is critical to include in most modern wastewater treatment processes and a generalized approach to its modeling is important. With the exception of the work of the University of Cape Town group, and specific precipitates, a generalized approach to precipitation has not been widely utilized by wastewater researchers. The effective simulation of precipitation kinetics depends on a good overall framework, including acid–base description, as the pH dependency is vital to proper precipitation prediction. We believe that, while some precipitation processes may be represented by algebraic formulations (e.g., FeS), dynamic equations are generally required, as time constants for certain process rates are similar to biological rates. Experimental validation is also highly important to improve confidence in the models used and to address common examples. This can be done by relatively

simple batch precipitation experiments in different matrices and there are good examples in the literature (Musvoto *et al.* 2000b). Some phenomena (e.g., scaling) are likely very difficult to predict, but, in general, describing precipitation is a highly important component of a generalized model.

Chemical oxidation–reduction

Spontaneous chemical reactions apart from those involving ions or gases are also relevant to wastewater processes. They involve oxidation or reduction of specific chemicals, which can have an impact on the biochemical and physicochemical system. Important redox systems in the wastewater environment that act as spontaneous mediators include:

(a) S^{2-}/S^0
(b) Fe^{2+}/Fe^{3+}
(c) O_3, ClO^-

These chemicals will react spontaneously with each other as well as with other normally non-reactive chemicals (e.g., O_2, NO_3^-, organics). The importance in an overall model is: (a) accounting for the oxidation and reduction in the overall chemical oxygen demand balance, and (b) accounting for the modified state of the reactive chemicals during other physicochemical and biochemical reactions.

Conclusion

Oxidation/reduction processes are a lower priority compared with other reactions, as, even though these chemicals are widespread in wastewater treatment, the impact of spontaneous redox reactions is low compared with the impact of other biochemical reactions. The key compound which may be important is iron (Fe^{2+}/Fe^{3+}) as this will reduce under anaerobic conditions and oxidize under aerobic conditions consuming oxygen. Both reactions will alter its behavior towards anions, particularly OH^-, PO_4^{3-} and S^{2-}. This may make it difficult to simulate phosphate and sulfide. There are two approaches. The specific approach is to assume that all Fe is as Fe^{2+} under anaerobic conditions and Fe^{3+} under aerobic conditions. This would describe transformation of precipitates. The generalized approach is to fully model redox reactions, with an overall 'redox' output, analogous to pH. However, with respect to comparing model outputs with measured data, it is noted that redox probes are generally relative in their measure of redox, even when recently calibrated.

CORRECTIONS

The chemical processes themselves are influenced by a number of factors such as non-ideality, temperature and atmospheric and hydraulic pressure. Corrections to the physicochemical system have been largely neglected in standardized models, though the principles are generally well understood. While there are additional case-specific corrections (e.g., gas non-ideality) the major impacts are solution non-ideality and temperature, as discussed further below. The impact of complex organic buffers is really related to acid–base processes, but it has been included as a correction here.

Non-ideality

Solutions begin to behave non-ideally when not infinitely dilute. Under non-ideality, the activity of a component is lower than its concentration. Solution non-ideality is often referred to (but not fully defined as) ionic strength, or ion activity. Non-ideality has an impact on both ionic and non-ionic species within the solution. The deviation is caused by changes in hydration of molecules, changes in surface properties of solid and gas boundary layers, and chemical interactions in the solution as a whole. Specific chemical interactions (ion pairing) need to be handled separately. None of the IWA models represent non-ideal ion behavior, while commercial software is ahead of standardized models by inclusion of simple ion activity. Simplified ion activity correction is included in the University of Cape Town models (Musvoto *et al.* 2000a), together with some ion pairing behavior.

In non-ideal solutions, calculations relating to an ion (e.g., pH, acid–base equilibrium etc.) are done using the ion's activity (a_i), rather than molal concentration. Activity is analogous to molal concentration in an ideal solution. Activity can be calculated as shown below:

$$a_i = \gamma_i C_i^{z\pm} \tag{9}$$

where a_i is the activity of the ion, γ_i is the activity coefficient for ion i, and $C_i^{z\pm}$ is the molar concentration for ion i. In simple cases relevant equations can be corrected directly and the molal concentration used in place of the activity. The level of non-ideality can be estimated by calculation of

ionic strength (Stumm and Morgan 1996; Hamann *et al.* 2007):

$$I = \frac{1}{2} \sum_{i=1} C_i z_i^2 \qquad (10)$$

where I is the ionic strength, C_i is the molar concentration of ion i, and z_i is the valence of ion i. There are then a number of corrections to calculate activity coefficients for ions of different valencies. The simplest is the Debye–Hückel equation (Hamann *et al.* 2007):

$$\log(\gamma_i) = -A z_i^2 \sqrt{I} \qquad (11)$$

where A is a solvent-specific constant. Therefore, for this simple equation, there will be common γ_i values for monovalent, divalent, and trivalent ions. Obviously higher valency ions will be more influenced. There are many more complex corrections available (Morel & Hering 1993; Stumm & Morgan 1996; Langmuir 1997; Hamann *et al.* 2007), but one to highlight in particular is the extended Debye–Hückel equation (Langmuir 1997) as used in PhreeqC (Parkhurst & Appelo 1999), which allows correction of non-valent compounds:

$$\log(\gamma_i) = \frac{-A z_i^2 \sqrt{I}}{1 + B \alpha_i^0 \sqrt{I}} + b_i I \qquad (12)$$

where A and B are solute and temperature specific, while α_i^0 and b_i are ion specific. For non-valent compounds (z_i being zero), activity correction becomes linear with ionic strength (Setchenow equation (Langmuir 1997)). In principle, the whole process of calculation should be iterative as the concentration of ions depends on activity, which depends on strength, which depends on concentration in an implicit loop. This becomes more complex with higher levels of correction.

The correction required depends on ionic strength. Ionic strength and the necessary components in the model to control errors in pH to <5% are summarized in Table 3 (this is based on initial calculations by the authors and needs to be further tested).

At an ionic strength of 1–5 M in landfill leachate, approximately 50% of non-ideality can be explained by inclusion of non-specific activity (levels 3–4), while the other 50% can be explained by specific ion pairing (level 5) (Tait *et al.* 2009).

Conclusions

While adding ion activity does add some complexity to the model, coefficients associated with all models have been well established in the literature, hence preventing the need for calibration and extra data collection. Level 2 activity correction should be regarded as the minimum for low strength and/or non-precipitating systems. The main barrier to implementation of level 3 and above is that it generates an algebraic loop, and practical implementation requires a DAE approach to solution of the weak acid–base system. In general, however, to properly correct for the impact of activity on precipitation equilibrium, a level 3 or higher approach is required. Level 4 could also enable replacement of the current empirical approach to gas–liquid transfer corrections for salinity in aeration systems.

Temperature

Temperature has a strong impact on all physicochemical processes. The largest impact is change in equilibrium, due to a change in free energy of reaction. This will generally cause gas solubility to decrease and acidity coefficients to decrease,

Table 3 | Required non-ideality corrections to achieve pH error of <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 treatment plants	Non-iterative simple correction $K_{a,\text{corr}} \approx \gamma K_a$[a]
3	<1 (only ion activity)	Sea water, anaerobic digesters	Full iterative calculation of ion activity using appropriate activity calculation
4	<1 (activity with non-valents)	As above, with gas transfer	As above, with use of the non-valent form of Equation (12).
5	<5	Strong industrial, landfill leachate, reverse osmosis brine	As for level 4, but inclusion of specific ion pairs

[a] γ is the activity correction for single valency ions suitable for K_a (generally monovalent for simple corrections).

and may cause solid solubility to increase or decrease. The IWA ASM series does not put an emphasis on the effect of temperature except for oxygen solubility and mass transfer kinetics, and the priority in that case has been on biochemical processes. The ADM1 contains correction of gas solubility and acidity coefficients. Basic correction is described by the van't Hoff equation, which describes the change in free energy with temperature, based on enthalpy of reaction (Stumm & Morgan 1996; Puigdomenech *et al.* 1997). In the ADM1 scientific and technical report (Batstone *et al.* 2002), the use of the constant enthalpy form of the van't Hoff equation is recommended:

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{13}$$

where K_1 and K_2 are equilibrium coefficients at temperatures T_1 and T_2 (K) respectively, ΔH^0 is the enthalpy of reaction, and R is the universal gas law constant. This relationship holds true for most acidity coefficients and gas solubilities in wastewater treatment. It needs to be assessed for its applicability to solids.

Reaction rates will generally increase with temperature according to the Arrhenius equation, but values of activation energies are generally not available due to difficulty in measurement and calculation.

Conclusions

Impact of temperature needs to be included in any generalized model. The authors believe that a single, fundamental relationship is preferable to empirical relationships. Analysis is required to validate application of the van't Hoff law against the wide range of coefficients to be used. This should be done against: (a) acidity coefficients, (b) gas solubilities, (c) solids solubilities, (d) activity coefficients, and (e) ion pairing coefficients. A wide temperature range for consideration could be 0–60 °C. Constants will be classified either as (i) not varying substantially with temperature; (ii) following van't Hoff constant enthalpy equation; (iii) following van't Hoff with variable enthalpy; or (iv) must be represented empirically. A review should also be done to assess applicability of the van't Hoff equation, as well as parameters for temperature dependency of kinetics.

Reactions with organic solids

While it is well known that organic solids (particularly microbes) are reactive (Madigan *et al.* 2000), their impact

on the physicochemical system has not been considered in models that the authors are aware of. A search in the literature returns a few results (Van Vooren *et al.* 1999; Szabo *et al.* 2008). Microbes and organic solids may act as acidity buffers, with negatively charged sites at high pH, and neutrally charged sites at neutral and low pH. They may also act as complexing agents for cations. It is not known whether anaerobically digested solids behave differently from activated sludge or primary sludge, but given the different nature of the solids it is likely. The preliminary results obtained by the authors indicate that the impact is quite strong at high solids (>3% anaerobic digestate), with an error of 2 pH units after titration with 7 mL of 0.2 M HCl (Figure 2).

To highlight the impact of solids, Figure 3 provides a comparison between experimental and simulation results for a titration of a pure solution of sodium bicarbonate and sodium hydroxide without organics or suspended solids, titrated with 0.45 M hydrochloric acid. The model is an equilibrium model with activity correction (Westergreen *et al.* 2012). In this case simulated and experimental pH shows a good agreement.

Conclusions

Given the lack of literature, it is important to quantify this issue, as its potential impact, particularly in high solids environments (clarifiers, digesters), is very high.
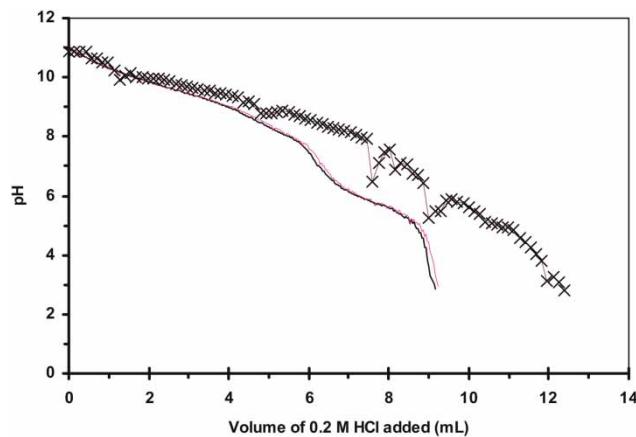

Figure 2 │ Titration in the presence of (x) and without organic solids (line). The sample was an anaerobic digestate with a solids concentration of approximately 3%. The solid grey line (blue in online version) is an automated on-line filtration and analysis, while the solid black line (purple in online version) is an off-line filtration and analysis. This indicates that CO_2 stripping during analysis has no impact.
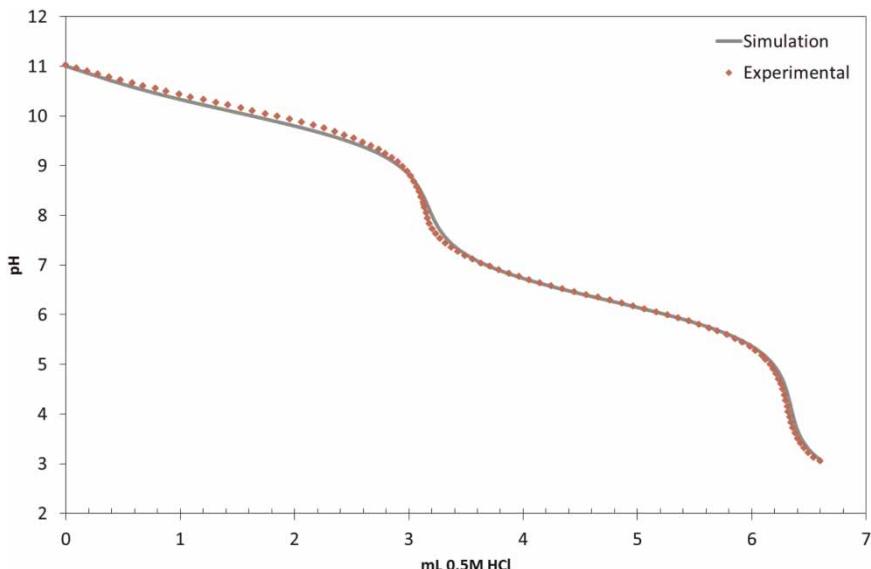
Figure 3 | Pure solution: 0.01 M NaHCO$_3^-$ with sodium hydroxide titrated with 0.5 M hydrochloric acid.

IMPLEMENTATION AND SOLUTION

Methods for solving the acid–base and physicochemical system have been well established. As discussed in the acid–base reaction section, equations can be formulated as fast dynamic equations, or it can be assumed that the equations are at equilibrium (Hellinga *et al.* 1999). These are addressed individually below. The ADM1 proposed equations to solve the pH according to both approaches (Batstone *et al.* 2002). Given the speed of acid–base reactions, if appropriately fast kinetic coefficients are chosen for the acid–base system (Stumm & Morgan 1996), the results should be the same (Musvoto *et al.* 2000a). Gas–liquid and solid–liquid reactions may be represented as differential or algebraic equations depending on the speed of the process. For very simple models an alternative is to simplify the acid–base reactions into the biochemical systems. This is the method used in the ASM models (via alkalinity), but it is also possible to extend this method to calculate pH (Siegrist *et al.* 2002). This method is inherently limited to very simple models, and still induces model stiffness.

The differential approach represents the mass balance of each acid and base as a differential equation, and requires a modification of the acid-base equations (Equation (3)) to represent them as rates (impacting the states of nitrite and free nitrous acid respectively in this case). These rates are naturally high (Stumm & Morgan 1996; Musvoto *et al.* 2000a), and must be maintained at a high level ($>10^8 \, d^{-1}$) to avoid model artifacts (errors), particularly in discretized systems such as biofilms. In particular, artifacts present as non-equilibrium concentrations of the acid and base pair at a given pH, which can cause errors in subsequent processes, including diffusion and gas transfer. However, when there are both fast and slow processes in a model, the model becomes more difficult to solve for explicit differential solvers. Essentially, the step length and numerical solution stability is controlled by the rapid process, whilst the dynamic behavior is determined by the slow process (Hangos & Cameron 2001). As such, implicit stiff solvers (backward Euler, DASSL, ODE15s, Gear' Stiff, CVODE) need to be used to solve such models. These inherently include a non-linear algebraic solver as part of the differential system, and providing the algebraic acid–base equations as differential equations is mainly for convenience on the part of the user. Essentially, almost all stiff solvers are also DAE solvers. Stiff solvers are excellent for stiff differential equations, but they are inherently slow or unstable when inputs or disturbances are dynamic or where the model is discontinuous (including derivatives), e.g., when using on/off controllers, timers, etc. This strongly limits application of the model. Finally, as an additional negative of the DE approach, an algebraic solver is still needed to represent complex activity, and where ion pairs are to be represented each pair must be represented by an additional differential state. Therefore, as physicochemical model complexity increases, the number of states increases dramatically.

In a DAE approach, the acid–base equations are represented as algebraic equations (Equation (3)), and formulated such that the left-hand side is zero, and individual acids and bases are calculated as implicit algebraic equations. For each acid–base pair there is a differential state representing the sum of the two (acid + base), as well as two algebraic variables to represent the concentration of the acid and base. Slow processes (e.g., biochemical, precipitation, gas–liquid transfer) only affect the differential state. The two algebraic equations are the acid–base equation (Equation (3)), as well as the mass balance. In addition to the acid–base couples of algebraic equations, there is also the charge balance equation (to calculate [H^+]). There are therefore generally a large number of non-linear implicit algebraic equations to be solved, using a capable algebraic solver.

For simple systems, it is possible to manually reformulate the equations such that they are explicit. For complex systems automated symbolic manipulation is also possible (Takács 2008). However, as model complexity increases, the complexity of the explicit solution increases dramatically such that it is generally faster to solve the implicit equations (normally two to three steps) than to calculate the right-hand side of a very complex explicit solution. This is especially true in the context of a differential model, where the initial estimate is taken from the previous time step, and is likely very close to the solution, asking for only a few iterations of the solver.

An algebraic approach also allows further analysis of the model and, if necessary, solution of other fast reactions (e.g., some gas transfer and precipitation, or even biochemical) within the algebraic subsystem (Rosen *et al.* 2006). This can be used to further optimize the model solution speed when used with a non-stiff solver.

Conclusions

The authors recommend that an algebraic approach be taken towards acid–base equations and a default approach of differential equations for gas transfer and precipitation owing to the relative values of the time constants. Acid–base systems should be formulated using algebraic equations because: (a) solving as differential equations requires the use of stiff solvers, which limits application and formulation of the model, and (b) it reduces the number of states with more complex models, by calculating many variables as algebraically dependent outputs. Algebraic solvers are widely used already – for example to calculate the impact of hydraulic recycles. Many solid–liquid and gas–liquid

processes can also be represented by algebraic equations if fast enough, and this may be required to avoid excessive model stiffness. Model analysis of algebraic equation non-linearity and/or differential equation stiffness is also an important part of the solution strategy.

Other software outside the wastewater field

There are a range of packages that predict speciation under different conditions. Most packages only consider equilibrium, and are orientated mainly towards prediction of speciation. Key examples are:

(a) PhreeqC–USGS. Orientated towards geology (Parkhurst & Appelo 1999).
(b) MINTEQA2– USEPA. Developed to describe environmental interactions (Allison *et al.* 1991, or the version Visual MINTEQ which is regularly kept up to date – Gustafsson 2012).
(c) ChemEQL, EAWAG, Switzerland.
(d) The Geochemist's Workbench® – Aqueous Solutions, Champaign, IL, USA.
(e) MINEQL + 4.6 (Environmental Research Software 2012).

This list is by no means exhaustive, and a maintained list is given in http://en.wikipedia.org/wiki/Chemical_equilibrium#Computer_programs (accessed 24/4/2012). The listed packages were designed to describe chemical equilibria within their specific application. This may have direct application to wastewater modeling. They are generally designed to be very expandable, having ion activity and other corrections applicable to most situations (e.g., up to level 5 non-ideality correction), and many are open source. Obviously if these packages are directly applicable or easily modified to wastewater applications, this would avoid much of the effort involved in developing a new framework. The packages are typically complex, and solve most reactions (including gas transfer and precipitation) using an algebraic approach, but some have the capability to integrate kinetics.

Conclusions

Aquatic chemistry packages focus on algebraic solutions with long time scales compared with wastewater systems. Even biological reactions are normally solved algebraically in such packages. While it is possible to define and solve biological equations, the models are built around

an algebraic approach. Hence, they are not ideally or directly applicable to wastewater systems. However, the databases associated with these models will be extremely valuable as a source of data, and the models may be used in virtual experiments to conduct sensitivity analysis and validate a wastewater physicochemical model, as they are very comprehensive, with excellent predictive capability within their area of application.

CONCLUSIONS AND FUTURE WORK

Important issues

The authors believe that the two critical issues (compared with the basic requirement of plant-wide pH prediction) are adding precipitation as a process and an integrated approach for handling non-ideal behavior. This can also be seen in prioritization by commercial developers. Properly handling non-ideal behavior will address other issues (such as the impact of salts on gas–liquid transfer).

Need for an IWA task group and technical report

Motivation and interest in physicochemical reactions and a common approach are relatively high. The fact that there have been a number of different approaches taken, despite the underlying reactions being the same, indicates that the field can benefit from a common approach. This can have a limited number of levels of complexity, depending on the application. While it is recognized that a generalized approach applicable to a wide range of situations will add complexity, many of the model parameters are known on a fundamental level, and specific mechanisms can be selectively disabled in-block to increase simulation speeds. However, a generalized approach should be scaleable and widely applicable. In general, the default would be capable of plant-wide domestic wastewater prediction, including correction of non-ideal behavior, and simple precipitation. This can be supported by reference implementations in common languages, including (if necessary) solvers.

Approach and future steps

The conclusion from this position paper and the related workshop is that a common approach should be developed, through establishing an IWA Task Group that would work towards a scientific and technical report. A key issue of

importance is to bring in aquatic chemistry expertise to provide objective capacity to the wastewater field.

Key tasks include:

(a) The basic elements of a generalized model need to be formed, mainly by literature review, discussion, and workshops.
(b) Some specific elements may need experimental analysis, requiring a mechanism to readily conduct, discuss, and disseminate experiments as required.
(c) The different generalized models need to be formulated, implemented, and verified.
(d) Models need validation against other complex models (e.g., those referenced in this paper) as well as experiments.
(e) Two types of batch experiments can be done as standard – automated titrations and crystallization experiments. Titrations if performed with care (such as shown in Figure 2) are relatively straightforward and require minimal equipment (see, for instance, Van Vooren *et al.* 1999). Crystallization experiments are more complex, and generally require access to ion chromatography.

While the experimental work adds minor complexity to the Task Group, it would provide an additional level of validation to the Task Group outcomes, specifically orientated towards the target application.

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