FORMULATION OF A GENERAL MODEL FOR SIMULATION OF pH IN WASTEWATER TREATMENT PROCESSES

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ABSTRACT

A general pH model was formulated to include all of the major acid-base systems and strong ions typically found in municipal wastewaters. The objective of the model is to provide a method to calculate the pH throughout the activated sludge plant, including the liquid and solids lines. This is necessary to support accurate modeling of biological and physico-chemical processes. The model was incorporated into the BioWinV2.1 wastewater treatment plant simulator and tested on several clean-water acid-base titrations. The model also was shown to predict the response of a nitrification rate test in which ammonia and carbon dioxide stripping were significant factors.

KEYWORDS

pH, modeling, simulation, nitrification, weak acid/base systems

INTRODUCTION

It has been recognized from the early stages of wastewater process modeling that pH is an important factor in simulating the performance of biological wastewater treatment processes, including activated sludge and anaerobic digestion. The pH impacts the species distribution of the weak acid systems (carbonate, ammonia, phosphate, acetate, propionate, etc.) present in the process. This in turn dictates the rate of many of the biological and physico-chemical phenomena occurring in these systems. For example, (1) biological activity, that can be severely limited outside an optimal pH range, (2) chemical precipitation reactions when metal salts such as alum or ferric chloride are added for chemical P removal, (3) spontaneous precipitation of magnesium and calcium phosphates (struvite, HDP, HAP), and (4) stripping of ammonia at high pH. It is difficult to model pH because the underlying components and reactions are so fast and complex. The approach to date in activated sludge models has been to track alkalinity changes instead, and
use that as a pseudo indicator of potential pH instability problems. This approach assumes that the pH remains approximately constant and is in a region where it does not impact biological activity. Another disadvantage of using alkalinity is that it offers no means for modelling physico-chemical phenomena such as precipitation. In systems with significant volatile fatty acid concentrations, such as acid fermenters or digesters or in systems where significant gas transfer may occur, the predicted alkalinity may not be a good indicator of steady pH conditions. Calculation of the pH must consider the concentrations of strong acids and bases, the dissociation states of the weak acid, carbonate and phosphate systems, chemical precipitation reactions, and potential stripping of components involved in the acid-base systems such as ammonia and carbon dioxide. All of these processes can be described using a kinetic approach (Musvoto et al., 2000), but the rates of many of the reactions involved typically are four to twenty orders of magnitude larger than typical biological rates. As a result, calculation of the pH using a kinetic-based model will significantly reduce simulation speed. Batstone et al. (2002) describe a mixed kinetic/equilibrium based approach specifically for anaerobic digestion. However, there is a need for a method that is general enough to apply for all the major environments in the wastewater treatment plant. The formulation of the pH model described in this paper is applicable across a wide range of biological treatment process models (i.e. ASM-series for activated sludge, ADM1 for anaerobic digesters, etc.). The model is applied to a number of simple systems in this paper.

MODEL DESCRIPTION

The pH model is based on the following elements:

1. Equilibrium modeling of the phosphate, carbonate, ammonium, volatile fatty acid systems and typical strong ions in wastewater (Mg$^{2+}$, Ca$^{2+}$, NO$_3^-$, etc.).
2. Incorporation of activity coefficients based on the ionic strength of the solution.
4. Biological activity affecting compounds included in the model (e.g. CO$_2$ and many others)

Equilibrium expressions for the acid-base systems included in the model are shown in Table 1. These equilibria represent the predominant acid-base systems occurring in wastewater treatment systems.

All of the equilibrium expressions in Table 1 are expressed in terms of active concentrations rather than molar concentrations. The interaction of ions in solution causes a deviation from ideal behaviour whereby the activity of the ions in equilibrium reactions is less than expected from the molar concentrations. To account for this behaviour, the molar concentration of the ions is reduced by a
factor known as the activity coefficient. The reduced ionic concentration is called the active concentration, as determined in the following expression:

\[(X_i) = f_i \left[ X_i \right] \]

where
\[(X_i) = \text{active concentration of } X_i \]
\[[X_i] = \text{molar concentration of ion } X_i \]
\[f_i = \text{activity coefficient of ion } X_i \]

**Table 1: Acid-base equilibrium expressions included in the general pH model**

<table>
<thead>
<tr>
<th>System</th>
<th>Equilibrium Expression</th>
<th>Equilibrium Constant @20°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>((H^+)(OH^-) = K_w)</td>
<td>(6.867 \times 10^{-15})</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>((H^+)(HCO_3^-) = K_{iCO_3} 1)</td>
<td>(4.14 \times 10^{-7})</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>((H^+)(CO_3^{2-}) = K_{iCO_3} 2)</td>
<td>(4.201 \times 10^{-11})</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>((H^+)(CH_3COO^-) = K_{iAc})</td>
<td>(1.754 \times 10^{-5})</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>((H^+)(CH_3CH_2COO^-) = K_{iPr})</td>
<td>(1.318 \times 10^{-5})</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>((H^+)(H_2PO_4^-) = K_{iPO_4} 1)</td>
<td>(7.452 \times 10^{-3})</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>((H^+)(HPO_4^{2-}) = K_{iPO_4} 2)</td>
<td>(6.103 \times 10^{-8})</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>((H^+)(PO_4^{3-}) = K_{iPO_4} 3)</td>
<td>(9.484 \times 10^{-13})</td>
</tr>
<tr>
<td>Ammonium</td>
<td>((H^+)(NH_3) = K_{iNH_3})</td>
<td>(3.966 \times 10^{-10})</td>
</tr>
</tbody>
</table>
Activity coefficients are estimated in the general pH model using the Davies equation, which is a simplification of the extended Debye-Hückel law. The activity coefficient \( f_i \) for each ion \( i \) in solution is determined as follows (Loewenthal and Marais, 1976):

\[
\log f_i = -0.5 \cdot Z_i^2 \left( \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.2 \mu \right) \tag{2}
\]

where,

\( Z_i = \) ionic charge of ion \( X_i \)
\( \mu = \) ionic strength of solution

Note that because the deviation from ideal solution behaviour is caused by electrostatic attraction between ions, the activity coefficient of a neutral species in solution (i.e. \( \text{H}_2\text{CO}_3^+ \)) is 1.

The expression for ionic strength is as follows:

\[
\mu = 0.5 \sum_{i=1}^{n} [X_i]Z_i^2 \tag{3}
\]

where,

\( n = \) the number of ionic species in solution

Since the overall charge of the solution must be neutral, the sum of the concentrations of the positively charged ions in solution must equal the sum of the negatively charged ion concentrations. This charge balance relationship is expressed for the pH model as follows:

\[
[H^+] + [\text{NH}_4^+] + 2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] + [\text{Cations}] + V_{\text{Me}} \cdot [\text{Me}] \\
= [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + \\
3[PO_4^{3-}] + [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + \\
[\text{CH}_3\text{COO}^-] + [\text{CH}_3\text{CH}_2\text{COO}^-] + \\
[\text{NO}_3^-] + [\text{Anions}^-] \tag{4}
\]

In addition to the ionic species shown in Table 1, there are a number of other ions likely to occur in significant concentrations in wastewater treatment systems, and these have been included in the charge balance. Calcium (\( \text{Ca}^{2+} \)) and Magnesium (\( \text{Mg}^{2+} \)) will be present in the natural source waters. Although modeling of phosphorus precipitation is not discussed in this paper, a general term for metal
species (Me) with charge VMe has been added to the charge balance to allow for chemical phosphorus removal. General variables have also been added for cations (Cations+) and anions (Anions-) to account for additional species not included separately (i.e. Na+, Cl-, etc.). These variables also allow for addition of strong acids and bases (see the examples below).

Material balances are written for each of the total species concentrations in the charge balance. For example, a material balance for total dissolved inorganic carbon in a reaction vessel is written as follows:

\[
\frac{dM_{CO2\text{t},L}}{dt} = Q_{L,i} S_{CO2\text{t},i} - Q_{L,o} S_{CO2\text{t},o} - (CO_2 \text{Stripping}) + (\text{Net Reaction})
\]

where,

- Subscript \(i\) = influent
- Subscript \(o\) = effluent
- \(M_{CO2\text{t},L}\) = mass of dissolved total inorganic carbon
- \(S_{CO2\text{t}}\) = total dissolved inorganic carbon concentration
- \(Q_L\) = liquid flowrate
- Net Reaction = biological reaction rate

\[
CO_2 \text{Stripping} = -k_{L,CO2} \cdot A_{GT} \cdot (S_{CO2,\text{sat}} - [H_2CO_3^-]) \cdot V_L
\]

where,

- \(k_L\) = liquid phase mass transfer coefficient
- \(A_{GT}\) = specific interfacial area for gas transfer
- \(S_{CO2,\text{sat}}\) = saturation dissolved CO2 concentration
- \([H_2CO_3^-]\) = undissociated carbonic acid concentration

The “Net Production by Reaction” term accounts for biological generation (e.g. from oxidation of organics by heterotrophs) and consumption (e.g. by autotrophs). The saturation concentration (\(S_{CO2,\text{sat}}\)) in the “Gas Stripping” term is calculated from a Henry’s law relationship at the system temperature and pressure. A simplification of the model assumes that the gas phase concentration of the component is constant (i.e. atmospheric concentration for CO2, zero for ammonia), and therefore the saturation concentration of the dissolved component is constant for a given temperature. However, for many systems (e.g., anaerobic digesters), a material balance is also required for the gas phase. For the carbon dioxide component, the gas phase material balance is written as follows:
\[
\frac{dM_{CO2,G}}{dt} = Q_G G_{CO2,G} - Q_{G,0} G_{CO2,0} + (CO_2 \text{ Stripping})
\]

where

\[
\begin{align*}
M_{CO2,G} & = \text{mass of CO}_2 \text{ in the gas phase} \\
Q_G & = \text{gas flowrate} \\
G_{CO2} & = \text{gas phase carbon dioxide concentration}
\end{align*}
\]

Similar material balances (gas and liquid phase) are required for the total ammonia concentration. For the other ionic species in solution (i.e. volatile acids, phosphate, etc.), there is no stripping and thus material balances for these components are written only for the liquid phase.

To simulate the pH response of a system, the following stepwise procedure is followed:

1. Material balances are solved to find a steady state, or used to compute the derivatives for the next time step in a dynamic simulation. This determines the total species concentrations.
2. An initial estimate of pH and ionic strength (\(\mu\)) is obtained (typically from the last solution of the system state).
3. Equations (3) and (4) are solved simultaneously for a new pH and \(\mu\) using an iterative non-linear equation solver such as the Newton-Raphson method.

**MODEL DISCUSSION**

**Alkalinity and species ionization**

Figure 1 shows a logarithmic-concentration versus pH diagram for the carbonate system. This diagram was generated with the pH model by simulating a system with a total dissolved inorganic carbon concentration of 10 mmol/L, and successively adding an increasing amount of anion to the system to change the pH. The model determines alkalinity by noting that at the H\(_2\)CO\(_3^*\) equivalence point \([H^+] = [HCO_3^-]\). This additional equation can then be used to solve the carbonate equilibrium explicitly to determine the [HCO\(_3^-\)] concentration (and consequently the pH). From this the charge balance can be used to calculate the amount of strong acid that would be required to move the solution to the H\(_2\)CO\(_3^*\) equivalence point. As a result, the impact of all of the ionic species included in the general pH model is considered in the calculation of alkalinity. Note that the alkalinity is not explicitly related to the stoichiometry of the biological processes in the system when estimated with the pH model. Instead, it is related to concentrations of ionic species at the current system state.
Figure 1: Logarithmic concentration versus pH diagram for the carbonate system as generated by the general pH model.

Titration of Acids and Bases

Verification of the general pH model included the simulation of various titrations of acids and bases in clean water. The simulations were conducted in BioWinV2.1 which incorporates the pH model. The simulation configuration (Figure 2) consisted of a variable volume reactor to represent a titration vessel, and an influent stream with a constant flow to represent the standard solution. The initial volume of the reactor was 50 L. The flowrate of the standard solution was 1 L/min. Table 2 summarizes simulated experimental conditions that represent the following types of titrations:

- Strong acid titrated with a strong base standard solution;
- Weak acid titrated with a strong base standard;
- Weak base titrated with a strong acid standard;
- Weak acid titrated with a weak base standard.

The table shows the concentrations of the reagents, and the components and concentrations used in the model to reflect those conditions. Note that in BioWin, the concentrations of reagents that are involved in the biological processes of the model (i.e. acetic acid and ammonia) are expressed in mg/L units. The concentrations of reagents that are primarily part of the acid base system (i.e. cations and anions), are expressed in units of meq/L.
Figures 3 to 6 show the results of the titration simulations compared to data from a standard chemistry text (Mortimer, 1975). These results verify that the acid-base equilibrium chemistry is correctly formulated in the pH model. The slight discrepancies between the actual and observed titration curves (for example, the equivalence point in Figure 4) are due to the incorporation of activity coefficients and the use of slightly different equilibrium constants in the general pH model.

**Figure 2:** BioWin configuration for the simulation of various acid and base titration experiments

![BioWin configuration for the simulation of various acid and base titration experiments](image)

**Table 2:** Summary of simulated titration experiments

<table>
<thead>
<tr>
<th>Titration Vessel Reagent</th>
<th>Standard Reagent</th>
<th>Titration Vessel Initial Concentrations</th>
<th>Standard Solution Concentrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.10 N HCl</td>
<td>0.10 N NaOH</td>
<td>[Anions] = 100 meq/L</td>
<td>[Cations] = 100 meq/L</td>
</tr>
<tr>
<td>0.10 N CH₃COOH</td>
<td>0.10 N NaOH</td>
<td>[CH₃COOH] = 6000 mg/L</td>
<td>[Cations] = 100 meq/L</td>
</tr>
<tr>
<td>0.10 N NH₃</td>
<td>0.10 N HCl</td>
<td>[NH₃] = 1400 mg/L</td>
<td>[Anions] = 100 meq/L</td>
</tr>
<tr>
<td>0.10 N CH₃COOH</td>
<td>0.10 N NH₃</td>
<td>[CH₃COOH] = 6000 mg/L</td>
<td>[NH₃] = 1400 mg/L</td>
</tr>
</tbody>
</table>
Figure 3: Results from simulation of 0.10 N HCL titrated with 0.10 N NaOH.

Figure 4: Results from simulation of 0.10 N CH₃COOH titrated with 0.10 N NaOH.
Figure 5: Results from simulation of 0.10 N NH$_3$ titrated with 0.10 N HCL.

Figure 6: Results from simulation of 0.10 N CH$_3$COOH titrated with 0.10 N NH$_3$.

Simulation of a Nitrification Rate Test
The pH model was tested for a domestic wastewater system by simulating a batch “High F/M” nitrification rate test (Melcer et al., 2002). In the experiment, 75 mL of nitrifying mixed liquor with a total suspended solids concentration of 2078 mg/L was added to secondary effluent for a combined total volume of 3 L. The test was spiked with ammonium chloride to achieve an initial total ammonia-N concentration of 120 mg/L. At the start of the test 1.0 g of NaHCO₃ was added, and 1.0 g was added three more times over the course of the test. The liquid was mixed with a magnetic stir bar and aerated continuously with an aquarium air pump and a ceramic aeration stone. Samples were extracted intermittently for analysis of NO₃-N, NO₂-N, and total ammonia-N. The pH was measured continuously throughout the test.

Similar nitrification rate tests had been conducted with intermittent aeration controlled by a dissolved oxygen controller. One of the objectives of this test was to determine the impact of continuous aeration on the response.

Figure 7 shows the simulated and measured nitrogen response. Two cases are shown for the simulated ammonia response. In the first case, the kₗ for ammonia stripping was set equal to zero. In this case, the decrease in the ammonia concentration is due primarily to nitrification. In the second case, the kₗ was set to 0.05 m/d. In this case, the simulation results closely followed the measured ammonia concentration, indicating that significant ammonia stripping was occurring during the test.

Figure 8 is a plot of the simulated and measured pH. The initial response indicates a rapid increase in the pH due to the stripping of dissolved carbon dioxide. The pH throughout the test is significantly higher than previous tests conducted with intermittent aeration.

To understand the response in this experiment, it is informative to examine the logarithmic-concentration versus pH diagram for ammonia shown in Figure 9. The pH region of the experiment is shown on the diagram, and it is clear that a significant amount of the ammonia is in the unionized NH₃ form. Because this is the form that is stripped, the higher pH in this experiment resulted in significant ammonia stripping.
Figure 7: Simulated and measured nitrogen response during the batch “High F/M” nitrification rate test.

Figure 8: Simulated and observed pH response during the batch “High F/M” nitrification rate test.
Figure 9: Logarithmic concentration versus pH diagram for ammonia as generated by the general pH model. The pH range during the test is shown by the shaded band.

Figure 10 shows the simulated alkalinity during the experiment; the saw tooth shape clearly indicates the consumption and intermittent addition of alkalinity. It should also be noted that for the duration of the experiment the alkalinity was maintained above 5 meq/L as alkalinity. In considering the impact of low pH on biological activity Henze et al. (1987) suggest that “if total alkalinity falls below about 50 g / m³ as calcium carbonate (CaCO₃) (1 mole total alkalinity / m³), then the pH becomes unstable”. For this reason many models use alkalinity as an indicator of stable pH, however at high pH the alkalinity provides little information as to the impact that pH may have on biological activity. Figure 11 shows the observed nitrogen response and the simulated nitrogen response for two cases. In the first case the experiment was simulated using a pH inhibition function on biological activity, while in the second case the simulation was performed without considering inhibition. It is evident that the simulation which considers pH inhibition at high pH provides a more accurate estimate of the observed experimental response. The nitrification rate used for both simulations was 0.9 day⁻¹ which was independently measured by Jones et al. (2003) for the same sludge.
Figure 10: Batch test simulated alkalinity.

Figure 11: Effect of pH inhibition on predicted nitrification rate.

Simulation of Swine Wastewater Aeration

The pH model was tested for a piggery wastewater by simulating a batch aeration test. Suzuki et al. (2002) investigated the precipitation of calcium, magnesium
and phosphate in swine wastewater through aeration. A batch of 30L of screened piggery wastewater was continuously aerated for three hours. Measurements of the system pH, inorganic carbon concentration and the concentrations of soluble magnesium, calcium and PO₄-P were taken over the course of the experiment. The experiment was designed to determine if significant precipitation could be achieved without the addition of chemicals to raise the pH.

Figure 12 shows the simulated and observed pH and inorganic carbon concentrations for the batch experiment. Inorganic carbon (IC) is defined as follows:

\[ IC = [H_2CO_3^+] + [HCO_3^-] + [CO_3^{2-}] \]

The stripping of carbon dioxide and the effect of this on pH is accurately predicted by the combination of the gas transfer model and the pH model. The stripping of CO₂ will also be ineffective to raise the pH much above 9.0 as the carbonate equilibrium shifts almost completely towards the ionized forms (see Figure 1).

**Figure 12: Response of inorganic carbon and pH during aeration of piggery waste.**

![Graph showing pH and IC concentrations](image)

Figure 13 shows the observed and simulated responses of the concentrations of soluble calcium, magnesium and PO₄-P during the aeration experiment. The simulated responses for magnesium and calcium accurately reflect the observed responses over the entire course of the experiment. The simulated response of
calcium lags the observed response over the first hour and a half of the experiment, but provides reasonable estimates for the rest of the experiment. Although the precipitation model is not discussed in this paper these results are presented to illustrate the importance of accurate determination of the pH and ionized species concentrations on simulation of precipitation behaviour.

**Figure 13:** Observed and simulated soluble concentration responses during batch aeration of piggery waste for (a) calcium, (b) magnesium and (c) PO$_4$-P.
CONCLUSIONS

A general pH model was formulated to include all of the major acid-base systems and strong ions typically found in municipal wastewaters. The model was implemented in the BioWinV2.1 wastewater treatment plant simulator. The model has been tested and provided good predictions for pH on a number of systems including:

1. Several clean-water acid-base titrations.
2. Carbonate, ammonia and phosphate logarithmic-concentration versus pH diagrams.
3. A batch nitrification rate test in which pH inhibition of biological activity and gas phase transfer of ammonia and carbon dioxide were significant factors.
4. A batch swine wastewater aeration test in which chemical precipitation reactions and gas phase transfer of carbon dioxide were significant factors.

A robust pH model is essential for reliable simulation of many important wastewater treatment operations. Some developments made possible as a result of the ability to model pH are:

1. Gas phase modeling which is important for modeling anaerobic digestion and precipitation processes. Calculation of gas transfer rates requires knowledge of the species ionization states and consequently the pH of the system.
2. Inhibition of biological activity at low and high pH.
3. Kinetic-based, pH dependent modeling of aluminium and ferric dosing for phosphorus precipitation, including hydroxide sludge formation, integrated into the biological model matrix.
4. Kinetic-based, pH dependent modeling of the spontaneous precipitation of struvite and calcium phosphates, integrated into the biological model matrix. Accurate prediction of struvite precipitation also requires modeling of magnesium concentrations, both the soluble magnesium and that stored in organisms.

REFERENCES


