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Modelling of Struvite Chemistry

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Abstract

This paper shows the simulation results of struvite thermodynamics. The thermodynamic simulation shows the complex solution chemistry of struvite. Based on the thermodynamic simulation results, the complexes and ions present in struvite solution system are $MgOH^+$, $MgH_2PO_4^+$, $MgHPO_4$, $MgPO_4^-$, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, NH_3, NH_4^+, Mg^{2+} and PO_4^{3-}. The thermodynamic simulation results also show that the supersaturation of struvite system is a function of reactant concentration (concentration of total magnesium, ammonium and phosphate) and solution pH. The paper also includes the validation the developed thermodynamic model using Minteq (a specialized thermodynamic modeling package).

Keywords: Struvite, Thermodynamics, Simulation, Validation

1.0 Introduction

Livestock intensification is becoming an effluent discharge issue for the last couple of decades. Occasionally, strong nutrient loading in wastewater stream forms solid deposits and causes clogging of the wastewater distribution systems [1-5]. This situation of solid encrustation occurs when the solubility limit of nutrients exceeds the saturation limit [6], leading to the occurrence of supersaturated solution [1]. Solution supersaturation and pH value are the predominant parameters of struvite crystallization. The apparent pH for struvite crystallization is documented 7.5- 11.0 [1, 7-10] depending on solution concentrations. Study on struvite thermodynamics explored better understanding on struvite solution chemistry and resultant precipitation. Solution chemistry plays the key role in struvite crystal formation. In supersaturated solution, struvite forms by the chemical reaction of the free Mg^{2+}, NH_4^+ and PO_4^{3-} ions (equation 1). Additionally, the formation of struvite crystal incorporates six molecules of water, as the water of hydration: therefore struvite is known as magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$).

$$Mg^{2+} + NH_4^{+} + PO_4^{3-} \Leftrightarrow MgNH_4PO_4 \qquad (1)$$

2.0 Materials and Methods

2.1 Mathematical Modelling and Formulation

Supersaturation of the solution is the key parameter leading to crystallization, which in turn depends on solution pH and reactive solution concentration. Solutions consisting of Mg, NH_4 and PO_4 form complexes including Mg^{2+}, $MgOH^+$, $MgH_2PO_4^+$, $MgHPO_4$, $MgPO_4^-$, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, NH_3 and NH_4^+ [11, 12]. Thermodynamic equilibria for different

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complexes and relevant equilibrium constants are presented in Table 1, provided that $\{i\}$ the activity based concentrations and K_i is the equilibrium constant of the ***ith*** ion complexes (as demonstrated above).

The total constituent concentrations for Mg^{2+}, NH_4^+ and PO_4^{3-}, denoting C_{T_Mg}, C_{T_NH4}, C_{T_PO4}, are the sum of the ionic concentration of their complexes and free ions, which are illustrated in equations (2)-(4).

$$C_{T\_PO_4} = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] + [MgH_2PO_4^+] + [MgHPO_4] + [MgPO_4^-] \tag{2}$$

$$C_{T\_Mg} = [Mg^{2+}] + [MgOH^+] + [MgH_2PO_4^+] + [MgHPO_4] + [MgPO_4^-] \tag{3}$$

$$C_{T\_NH_4} = NH_3 + [NH_4^+] \tag{4}$$

Table 1 Value of Equilibrium Constants for Complexes

Equilibrium Equation	K_i	References
$K_{MgOH^+} = \frac{\{Mg^{2+}\}\{OH^-\}}{\{MgOH^+\}}$	$10^{-2.56}$	[13]
$K_{NH_4^+} = \frac{\{H^+\}\{NH_3\}}{\{NH_4^+\}}$	$10^{-9.25}$	[14]
$K_{HPO_4^{2-}} = \frac{\{H^+\}\{PO_4^{3-}\}}{\{HPO_4^{2-}\}}$	$10^{-12.35}$	[15]
$K_{H_2PO_4^-} = \frac{\{H^+\}\{HPO_4^{2-}\}}{\{H_2PO_4^-\}}$	$10^{-7.20}$	[15]
$K_{H_3PO_4} = \frac{\{H^+\}\{H_2PO_4^-\}}{\{H_3PO_4\}}$	$10^{-2.15}$	[16]
$K_{MgH_2PO_4^+} = \frac{\{Mg^{2+}\}\{H_2PO_4^-\}}{\{MgH_2PO_4^+\}}$	$10^{-0.45}$	[16]
$K_{MgHPO_4} = \frac{\{Mg^{2+}\}\{HPO_4^{2-}\}}{\{MgHPO_4\}}$	$10^{-2.91}$	[16]
$K_{MgPO_4^-} = \frac{\{Mg^{2+}\}\{PO_4^{3-}\}}{\{MgPO_4^-\}}$	$10^{-4.80}$	[16]
$K_w = [H^+][OH^-]$	10^{-14}	[1]

The activity coefficient is calculated using Davis equation, as shown in equation (5). The ionization fractions of Mg^{2+}, NH_4^+ and PO_4^{3-} ($\alpha_{Mg^{2+}}, \alpha_{PO_4^{3-}}, \alpha_{NH_4^+}$) can be defined by the quotient of free ion concentration and the total concentration of each chemical species.

$$-Log\gamma_i = AZ_i^2\left[\frac{I^{1/2}}{1+I^{1/2}}\right] - 0.3I \tag{5}$$

Where
γ_i = Activity of solution

I = Ionic strength in mol/l
Z_i = Valency of the corresponding elements
A = DeBye-Hückel constant, has a value of 0.493, 0.499, 0.509 and 0.519 at 5, 15, 25 and 35°C, respectively [17].

Two types of solubility products describe the solubility status, which include the Conditional Solubility Product (P_{cs}) and the Product of Analytical Molar Concentration (P_{so}) [1]. The conditional Solubility Product (P_{cs}) relates to the solution properties, including ionization fraction (α_i), activity coefficients (γ_i) and the minimum struvite solubility product (K_{so}) [7]. The Product of the Analytical Molar Concentration relates to the total concentrations of reactive constituents ($C_{T,i}$), where ***i*** represents the concentration of magnesium, ammonium, and phosphate, as required [1]. The mathematical definition of the minimum solubility product of struvite is shown in equation (6). The mathematical formula of the Conditional Solubility Product (P_{cs}) and the Product of the Analytical Molar Concentration (P_{so}) are demonstrated in equations (7) and (8), respectively.

$$K_{so} = C_{T\_Mg}\alpha_{Mg^{2+}}\gamma_{Mg^{2+}}.C_{T\_PO4}\alpha_{PO_4^{3-}}\gamma_{PO_4^{3-}}.C_{T\_NH4}\alpha_{NH_4^+}\gamma_{NH_4^+} \tag{6}$$

$$P_{cs} = \frac{K_{so}}{\alpha_{Mg^{2+}}\gamma_{Mg^{2+}}\alpha_{NH_4^+}\gamma_{NH_4^+}\alpha_{PO_4^{3-}}\gamma_{PO_4^{3-}}} \tag{7}$$

$$P_{so} = C_{T\_Mg}.C_{T\_PO4}.C_{T\_NH4} \tag{8}$$

Solutions with a higher value of the Concentration Product than the Conditional Solubility Product ($P_{so} > P_{cs}$) refers to a supersaturated solution. Equal numerical values of P_{cs} and P_{so} characterize the saturated condition of solution, where as $P_{so} < P_{cs}$ demonstrates the undersaturated condition of a solution [1]. The negative logarithmic value of the minimum struvite solubility product (pK_{so}) value applied in this thermodynamic modeling is 13.26 [7].

The active mass of each reactant (free ion concentration) and the rate of chemical reaction for struvite precipitation are proportional to the degree of supersaturation [7, 17]. Often, the degree of supersaturation is expressed by the critical supersaturation ratio (S_c) relating to the Thermodynamic Conditional Solubility Product (P_{cs}) and the Concentration Product of reactants (P_{so}), as shown in the equation (10) [1, 7]. Based on the chemical formation of struvite, the number of species in anhydrous struvite is $\nu = 3$.

$$S_c = \left(\frac{P_{so}}{P_{cs}}\right)^{1/\nu} \tag{9}$$

$$S_c = \left(\frac{C_{T\_Mg}C_{T\_NH4}C_{T\_PO4}}{\left(K_{so}/\gamma_{Mg^{2+}}\gamma_{NH_4^+}\gamma_{PO_4^{3-}}\alpha_{Mg^{2+}}\alpha_{NH_4^+}\alpha_{PO_4^{3-}}\right)}\right)^{1/3} \tag{10}$$

The solution thermodynamic properties specify the state of saturation, free ion concentrations, molar concentration of ion complexes and the state of precipitation. The precipitation of struvite occurs in supersaturated solutions, which is particularly influenced by solution pH and reactant concentration [17, 18].

3.0 Result and Discussion

3.1 Struvite Chemistry

The thermodynamic modeling was derived using Cabarlah Park primary pond data, investigated by Queensland DPI. The respective concentration of magnesium, ammonium and phosphate of the Cabarlah Park primary pond effluent are 26, 199.7 and 34.1 mg/l.

The ionic interactions between Mg^{2+} and the different PO_4^{3-} ions (PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$) cause the formation of magnesium phosphate ion ($MgPO_4^-$), aqueous magnesium mono-hydrogen phosphate ($MgHPO_4$) and magnesium di-hydrogen phosphate ($MgH_2PO_4^+$). The rest of the total magnesium remains as free Mg^{2+} ion.

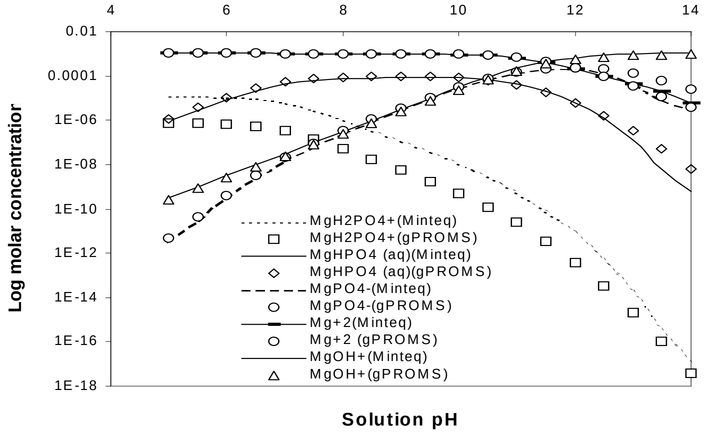

Figure 1 Presence of different Magnesium complexes in Struvite system

Figures 1 and 2 show the log concentration of different magnesium, phosphate and magnesium-phosphate complexes over the pH range 5 to 14. It is observed from the simulation response that in compare to free Mg^{2+} ion, small amount of magnesium remains as magnesium-phosphate complexes. At higher pH (above 10.5) most of the total magnesium forms $MgOH^+$ complex. A validation of the model response for magnesium/ magnesium-phosphate complexes is made using vMinteq (a specialized thermodynamic modeling package). Very close similarities have been observed of the thermodynamic responses between gPROMS output and vMinteq output, which shows the acceptability of the thermodynamic modeling using gPROMS process simulation software.

Over the range of pH<10, the free PO_4^{3-} ion concentration is reasonably small when compared to Mg^{2+} ion (Figure 2), since the major portion of phosphate remains as $MgPO_4^-$, $MgHPO_4$ (aq), $MgH_2PO_4^{2-}$, $H_2PO_4^-$, H_3PO_4 and HPO_4^{2-}. However, above pH 10.5, the concentration of free PO_4^{3-} increases considerably due to the de-protonation of HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4.

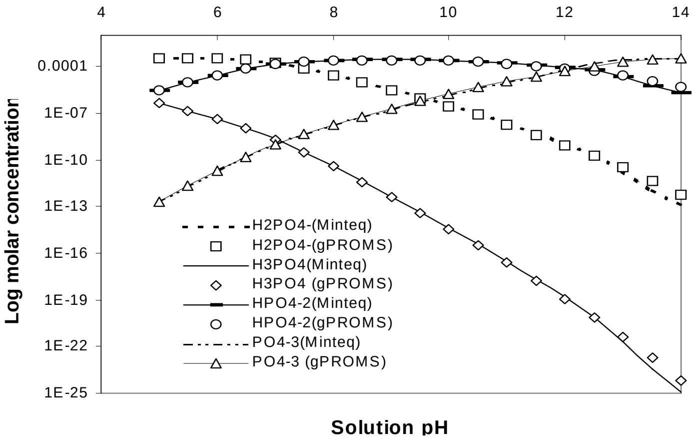

Figure 2 Presence of different Phosphate complexes in Struvite system

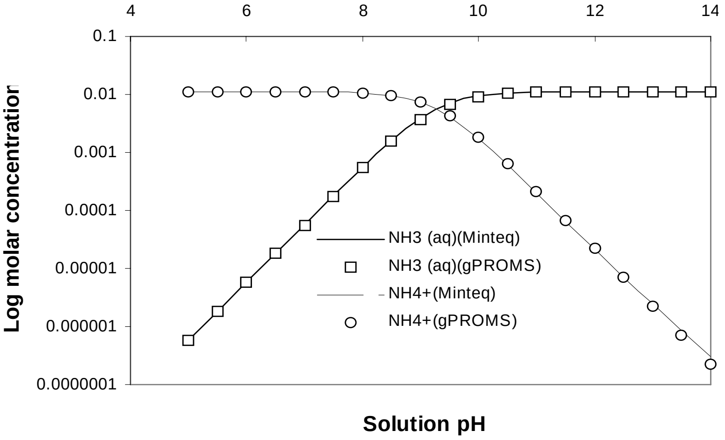

Figure 3 Presence Of different ammonium complexes in struvite system

With the given concentration (in the previous paragraph), the thermodynamic simulation results show that the major portion of total ammonium remain as free NH_4^+ ion below pH 8.5 (Figure 3), and decreases rapidly due to the transformation of NH_4^+ to NH_3 in alkaline phase.

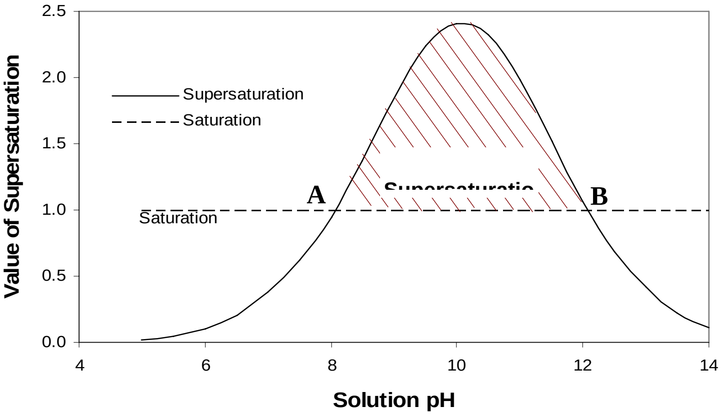

Figure 4 State of saturation at different pH value (based on the critical supersaturation ratio, S_c)

Figure 4 shows the computed response of the struvite supersaturation over the pH range 5 to 14 for a solution concentration of 26mg/l magnesium, 199.7mg/l ammonium and 34.1mg/l phosphate. As described in section 3, saturation of solution reflects that the value of conditional solubility product (P_{cs}) and analytical concentration product (P_{so}) is equal. At the supersaturation of solution, analytical concentration product (P_{so}) is higher than the conditional solubility product (P_{cs}). Based on Figure 4, model input solution remains in supersaturated state between pH ranges 7.8 to 12 (AB), with maximum supersaturation at pH 10.1.

It is worthwhile pointing out that the struvite thermodynamic and solution chemistry, described in the previous paragraphs, is based on the effluent pond data of magnesium, ammonium and phosphate along with the relevant chemical equilibria. For the additional chemical species of the pond data, an extension of the gPROMS coding and simulation must be included.

4.0 Conclusions

Solution chemistry plays an important role in struvite precipitation. Thermodynamic simulation result shows that both solution pH and free ion concentration of dissolved species (magnesium, ammonium and phosphate) plays most significant role in struvite crystallization.

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