Assessing Nutrient Recovery from Piggery Effluents

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Abstract: The past few decades has seen an increase in livestock intensification within the Australian pig industry, which has lead to a waste management problem due to increased volumes of nutrient rich effluent leaving these facilities. Land application of these nutrient-rich effluents is economically and environmentally unsustainable in some circumstances. One promising alternative is to remove the nitrogen and phosphorus compounds by co-crystallising these compounds with magnesium, producing magnesium ammonium phosphate, commonly called struvite. Rigorous design of a struvite crystalliser requires detailed knowledge of crystallisation thermodynamics and kinetics, which depend on factors such as temperature, solution oversaturation and pH. The present study aims to evaluate struvite precipitation potential, using the Visual MINTEQ modelling package. A solution speciation model of struvite precipitation in different phases has been developed. This model indicates that across a wide range of pH (6-14) various other crystals form along with struvite, whereas struvite formation is dominant in the pH range of 7.75-9.27. Solution speciation modelling indicates that a Magnesium Ion Selective Electrode can be used to infer struvite supersaturation, enabling better modelling and control of crystal growth kinetics. A brief thermodynamic investigation on piggery wastewater collection pond will be performed using this model.

Keywords: *Struvite, Visual MINTEQ, Ion Selective Electrode, Supersaturation, Solid phases.*

1. INTRODUCTION

High nutrient loads from piggery effluents have implications for several environmental concerns, including soil acidification, eutrophication in water bodies, and burning of tree roots due to the over application of nitrogen. It is well known that struvite forms in wastewater streams that are supersaturated, leading to significant maintenance costs. The main forms of nutrients are Magnesium, Ammonium and Phosphate. Von Munch and Barr (2001) report that it is possible to recover nutrients from nutrient-rich wastewater streams. The key feature of this technique is the combined removal of ammonium and phosphate instigated by the addition of magnesium ions. The synthetic formation of struvite is expressed by below (Durrant *et al*. 1999).

$$Mg^+ + NH_2H_2PO_4 + 6H_2O \rightarrow MgNH_4PO_4.6H_2O + H^+ \qquad (1)$$

Performing batch kinetics experiments requires maintenance of constant supersaturation, in order to determine its effect on crystal growth rates. A solution speciation model, using Visual MINTEQ (version 2.11) for example, enables detailed assessment of struvite crystallization potential. This program is based on the MINTEQA2 version 4.0. The original version of MINTEQ was developed at Battelle Pacific North Western Laboratory (PNL) by combining the fundamental mathematical configuration of MINEQL with WATEQ3 (Allison *et al*. 1991).

This paper reports on the use of solution speciation modelling, using Visual MINTEQ in order to further improve our understanding of struvite solution thermodynamics. This is an important first step in developing process models for nutrient recovery systems design and control.

2. DATABASE MANAGEMENT IN Visual MINTEQ

The default database of Visual MINTEQ does not contain struvite as a supersaturated solid phase. The initial task therefore is to add struvite into the Visual MINTEQ database. The basic assumption of this model is the insignificant effect of infinite solid phases, finite solid phases and possible solid phases. To include the struvite in the database, Mg^{+2}, NH_4^+ and PO_4^{-3} ions were added to the input data file at constant pH (8.5), along with ionic strength, which is calculated via mass balance. The concentration of the incorporated solution composition was recorded in mg/L. The required values for augmenting the default solid phase list in Visual MINTEQ, are *Log K*, preferred species name, rate of change of enthalpy, charge of species, number of component and their name, along with stoichiometric composition ratios. The suggested ID and gram molecular weight of anhydrous struvite are 2000021 and 137, respectively. This database modification was compiled using the change of enthalpy, dH_r, at zero. The value of a change in enthalpy is used to adjust the equilibrium constant for temperatures other than 25°C. The values supplied in Visual MINTEQ's thermodynamic database are referenced to a temperature of 25°C. A new set of equilibrium constants is calculated before solving the equations. If the standard enthalpy change is not available in the database, MINTEQ uses the uncorrected *Log K* (25°C). However, no change of enthalpy was put into practice considering the temperature of the effluent collection pond in an open environment would be close to this point.

The value of *Log K*, used in Visual MINTEQ, refers to the logarithmic value of the equilibrium constant of reaction. For solids, the equilibrium constant of reaction, *K*, is reciprocal to the solubility product value (K_{sp}), and hence the value recommended in the Visual MINTEQ database management is the negative logarithmic value of the solubility product i.e., $-Log\ K_{sp}$ (Allison et al. 1991). Proposed values of $-Log\ K_{sp}$ from previous researchers are found in Table 1.

Table 1 Suggested value of $-Log\ K_{sp}$ by previous researchers

Recommended by	**$-$Log K_{sp}**
Bube (1910); Snoeyink and Jenkins (1980)	12.6
Taylor *et al.* (1963); Nelson (2000); Abbona (1979)	13.15
Burns and Finlayson (1982)	13.12
Ohlinger (1999)	13.27

It is felt that Ohlinger's work represents the most comprehensive treatment of this system. For this reason we employed a value of 13.27 for $-Log\ K_{sp}$ in our Visual MINTEQ input file. A priority order for thermodynamic stabilities of each solid is established by comparing the appropriate ion activity products *(IAP)* with the corresponding formation constant, after the aqueous phase has been equilibrated (Allison et al. 1991). The saturation index *(SI)* for each solid is defined as

$$SI = Log(IAP) - LogK_s \qquad (2)$$

where

K_s = Temperature corrected solubility constant.

The database system allows the solid phase to be formed when the solution is supersaturated indicating that the value of Saturation Index *(SI)* is greater than zero. For the equilibrium phase and undersaturated solution, the value of *SI* remains zero or less than zero.

3. FORMATION OTHER CRYSTALS

To investigate the influence of pH on struvite precipitation, the constituents of struvite, (i.e., Mg^{+2}, NH_4^+, PO_4^{3-}) were introduced into a Visual MINTEQ input file at pH values ranging from 6 to 14. The input concentrations of Mg^{+2}, NH_4^+, and PO_4^{3-} were 348, 261 and 1790.75 mg/L, respectively. This approach allows struvite or other crystals to form, either in undersaturated or supersaturated form. When the model is allowed to precipitate the supersaturated solids form in the solution. Table 2 highlights the potential solid phases that can result. It should be noted that struvite had to be added to the database as a solid, since it was not in the default database. Along these lines, it is possible that other solid phases might appear, but will not, since they are not defined in the database.

Figure 1 shows different types of solids formed in solution, predicted by Visual MINTEQ. Struvite formation dominates through the range of pH 7 to 10.5, and in the pH range of 7.75 to 9.27 struvite should be the only crystal that forms, based on the chemical species assumed to be present. Below pH 6.75 or above 9.27 other crystals such as Newberyite, Brucite, and Farringtonite form, which reduces the amount of struvite formed. Therefore, possible solids formed depend on the pH of the solution, which in turn alters the supersaturation of the solution. Based on ionic activity product, generated by the degree of supersaturation, different types of crystals will form. The formations of different types of crystal depend solely on the equilibrium constants, which are described in Table 1. As soon as the ion activity product *(IAP)* exceeds the minimum equilibrium constant of solubility, crystals appear in the solution. When the solution's Log *(IAP)* exceeds 13.27, struvite formation is precipitated, which is signified in the pH range 7-11 (Figure 1).

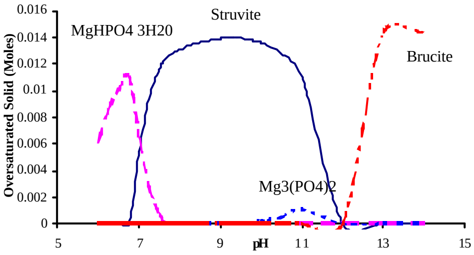

Figure 1. Solids in supersaturated solution

In the literature, the apparent pH for minimum solubility has been documented as between 9.0 to 11.0 (Snoeyink and Jenkins, 1980; Buchanan *et al.* 1994; Stumm and Morgan, 1996; Ohlinger, 1999;

Doyle *et al*., 2001). Ohlinger *et al*. (1999) acknowledge that the pH for minimum solubility of struvite as 10.3, whereas it has previously been suggested as 10.7 (Snoeyink and Jenkins, 1980; Stumm and Morgan, 1996). Buchanan et al. (1994) reported the minimum value of pH for struvite solubility was 9.0. Doyle et al. (2001) demonstrated that the minimum solubility of struvite occurred at pH 9.0 to 10.0, with the struvite precipitation commencing at 7.5. Buchanan et al. (1994) observed the range of pH at which struvite forms was 7.0 to 11.0. Doyle et al. (2001) documented that struvite precipitation was highly unlikely below pH 7.88 although pH 7.5 resulted in the definite reduction of nutrient composition. It is therefore recommended by Doyle et al. (2001) to use pH 8.0 for favourable precipitation and 8.83 for rapid struvite precipitation.

Table 2. Logarithmic activity product of different solid phase

Product name	**Chemical Composition**	**Log (IAP)**
Brucite	$Mg(OH)_2$	-16.84399
Active Mg $(OH)_2$	$Mg(OH)_2$	-21.58409
Periclase	MgO	-18.794
Farringtonite	$Mg_3\,(PO4)_2$	23.28
Newberyite	$MgHPO_4.3H_2O$	18.175
Struvite	$MgNH_4PO_4$	13.27

4. INFLUENCE OF COMPOSITION ON STRUVITE FORMATION

The main purpose of this modelling is to determine the optimum conditions for struvite formation. The presumed optimum pH is deemed to be 8.5 from previous section in this paper. The input data in the Visual MINTEQ input file is 1 : x : y, which expresses the ratio of NH_4^+, Mg^{+2}, PO_4^{-3} by means of a fixed NH_4^+ concentration of 261 mg/L and variable amounts of Mg^{+2} and PO_4^{-3}. A constant level of NH_4^+ ion is used, due to its disinclination to form complexes, which in turn maintains the fairly stable ionic activity. The precise forms of complexes of different components are presented in Table 3.

Due to the presence of different complexes of Mg^{+2} and PO_4^{-3}, solution ionic activity depends solely on their composition at constant pH. Figure 2 represents the trend of struvite formation at variable Mg^{+2} and PO_4^{-3} compositions, at pH of 8.5.

Figure 2, below, shows that a suitable composition ratio of ammonium, magnesium and phosphate ion is

$$NH_4^+ : Mg^{2+} : PO_4^{3-} = 1:1.1:1.3. \qquad (3)$$

Table 3. Percentage distribution among dissolved and adsorbed species

Component	**Complexes**
PO_4^{-3}	PO_4^{-3}, $MgHPO_4$ (aq), HPO_4^{-2}, $H_2PO_4^-$, $MgPO_4^-$
NH_4^{+1}	NH_4^+, NH_3 (aq)
Mg^{+2}	Mg^{+2}, $MgH_2PO_4^+$, $MgHPO_4$ (aq), $MgOH^+$, $MgPO_4^-$

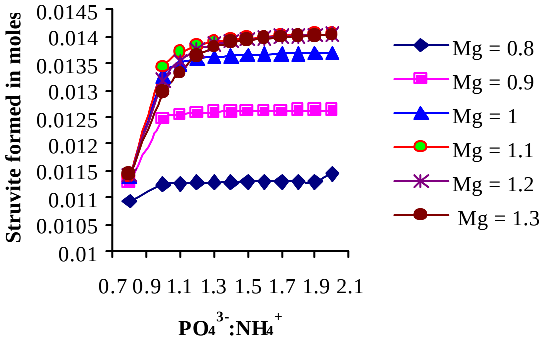

Figure 2. Influence of relative composition on struvite formation.

5. ION SELECTIVE ELECTRODE

Two types of experimental configuration, either constant pH or constant supersaturation, would usually be implemented for struvite reactor design purposes (Söhnel and Garside, 1992). It has been proposed that semi-batch precipitation with constant supersaturation is more efficient than the constant pH case (Söhnel and Garside, 1992).

Bouropoulos and Koutsoukos (2000) dealt with this scheme using mechanically coupled burettes from an automatic titrator to maintain constant pH, as well as constant composition, which in turn maintained constant supersaturation conditions. The approach of the present investigation will use magnesium Ion Selective Elective (ISE) along with a pH controller to maintain constant level of supersaturation. Two types of ion selective electrodes, magnesium ion selective electrode and ammonium ion selective electrode, are considered in this investigation. Based on the Visual MINTEQ modelling, the following two difficulties have been identified in selecting the more suitable ISE:

1. Percentage of available free ions and
2. Interference from other ions.

5.1. PERCENTAGE OF AVAILABLE FREE IONS

The sensitivity of a particular ISE depends on the level of free ions present in the solution. Ionic concentrations of Mg^{+2}, NH_4^+ and PO_4^{-3} at 348, 257 and 304 mg/L were introduced in the Visual MINTEQ input file at different pH and temperature levels. It is worth pointing out that $MgCl_2$ and $NH_4H_2PO_4$ were used in batch experiments as the source of Mg^{+2} and NH_4^+, respectively. Figures 3 and 4 are developed from Visual MINTEQ output data, showing the levels of free ionic concentrations for ammonium and magnesium. Clearly the percentage of free Mg^{+2} is much greater than that of NH_4^+, which varies strongly with varying pH and temperature levels.

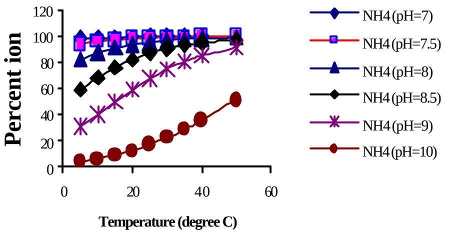

Figure 3. Free NH_4^+ in various conditions

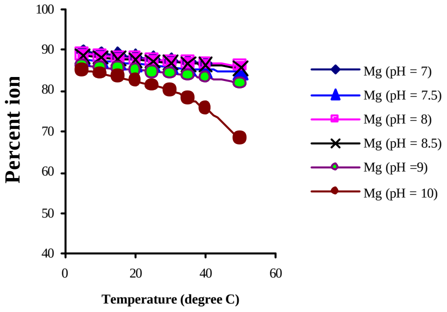

Figure 4. Free Mg^{+2} in various conditions

Interferent (mg/L)	Interferent / Mg^{+2}	% Mg^{+2}_{Ca+2}	% Mg^{+2}_{Na+}	% Mg^{+2}_{Fe+2}
0	0	85.145	85.145	85.145
30	0.0862	85.893	85.232	86.319
100	0.287	87.319	85.431	88.653
500	1.437	92.137	86.471	94.971

Table 4. Influence of Interferent on Mg Ion

5.2. INTERFERENCE FROM OTHER IONS

Another problem of the ISE measurement is the effect of interference from other ions, since many ISEs are non-specific and sensitive to other ions to some extent. This effect could be adverse for real effluent where various types of chemicals exist in the mother liquor. The interference of wide varieties of ions with the mother constituents of struvite could reduce ionic strength and activity of the solution relative to its true values, particularly at high concentrations. In very dilute solutions these interferences are ineffective in influencing the efficiency of the Magnesium ISE. The key interferences on Magnesium ISEs are considered in this modelling include Cu^{+2}, Zn^{+2}, Ni^{+2}, Fe^{+2}, Na^+, K^+, and Ca^{+2}. The consequence of interference is defined by equation 4:

$$IA = \frac{C}{C'}, \qquad (4)$$

where

IA = Interference ratio

C = Concentration of interfering ion in molarity

C' = Concentration of measured ion in molarity.

To identify the interference of Mg^{+2} with other ions, such as Cu^{+2}, Zn^{+2}, Ni^{+2}, Fe^{+2}, Na^+, K^+, Ca^{+2}, the main component of struvite was inserted in Visual MINTEQ input file along with the interference ion with variable concentrations. The concentration of Mg^{+2}, NH_4^+ and PO_4^{-3} are 348, 257 and 304 mg/L, respectively at a temperature of 25° C. The model was simulated at pH 8.5. The selected output of the model, describing the effect of various ions on Mg^{+2} more precisely, is represented in Table 4. Significant interference between Mg^{+2} and other ions is observed when the interference ratio is 1.437 or greater, particularly for Ca^{+2} and Fe^{+2}. The interference of other ions is less significant. However, the concentration of Ca^{+2} and Fe^{+2} is unlikely to exceed the concentration of Mg^{+2}. The complexes of PO_4^{-3}, NH_4^+ and Ca^{+2} are $CaPO_4$, $CaNH_3^{+2}$, $CaHPO_4$ (aq), $CaNH_3^{+2}$, $CaPO_4^-$, $CaH_2PO_4^+$, $CaHPO_4$ (aq), which increase the free ion concentration of magnesium. This setback affects the ionic strength of the solution, reducing the measured activity relative to the true concentration of magnesium, and corrupts measurements of the true readings. However, for the solution of diluted interfering ions, this complexity is rather insignificant and can be ignored (Table 4).

6. POND INVESTIGATIONS

The possibility of different solids formation in piggery wastewater is performed in a piggery wastewater pond. Sample was collected from primary pond (P), secondary pond (S) and final irrigation pond (F) at a pH 7.9, 8.0 and 7.8, respectively. The investigation was performed for major and minor nutrients. A solution speciation model using Visual MINTEQ was employed across a wide range of pH. The existing database in Visual MINTEQ modelling was modified for struvite and Magnesium Potassium Phosphate using the thermodynamic data presented in Table 5.

Table 5. Thermodynamic data for database management for evaluation of pond data

Name of Crystal	Delta_h	Log_K
$MgNH_4PO_4$	0	-13.27 (Ohlinger 1999)
MgKP	0	-10.6197 (Taylor et al. 1963)

The brief result of major solids formation is summarised in Table 6. The value of saturation index (SI) in Table 6 represents the solution's characteristics. It is worth pointing out that SI>0 and SI<0 express supersaturated solid and undersaturated solid situations, respectively, while a value of SI=0 represents chemical equilibrium. The wastewater of primary, secondary and final irrigation ponds in a pig farm remain in a saturated state for HAP (Hydroxyapatite: $Ca_5(PO_4)_3{:}2H_2O$) and $MnHPO_4$ in the wide range of pH, whereas Brucite ($Mg(OH)_2$) remain in saturated stage at higher pH. MKP (Magnesium Potassium Phosphate: $MgKPO_4{:}6H_2O$) and struvite (Magnesium Ammonium Phosphate: $MgNH_4PO_4{:}6H_2O$) remain undersaturated, owing to low concentrations of Magnesium. It is therefore necessary to maintain a higher optimum level of Magnesium in order to supersaturate the system to yield struvite crystals. Recovery of phosphorus using struvite crystallization has significance as it removes ammonium and phosphorus simultaneously.

Table 6. SI of different solids for the piggery pond under evaluation

	pH	Brucite	HAP	MKP	$MnHPO_4$	MAP
P	7.9	-4.4	0	-24.26	0	-27.11
P	8.5	-3.2	0	-23.63	0	-26.54
P	10.7	0	0	-22.58	0	-26.82
S	8.0	-4.3	0	-24.36	0	-26.93
S	8.5	-3.3	0	-23.85	0	-27.34
S	10.7	0	0	-22.57	0	-26.87
F	7.8	-4.6	0	-24.37	0	-27.35
F	8.5	-3.2	0	-23.64	0	-26.66
F	10.7	0	0	-22.57	0	-26.93

P = primary, S=secondary, F=final irrigation

7. CONCLUSIONS

1. The range of pH for experiments is proposed to be 7.75 to 9.27, although the suggested optimum pH is 8.5. Further experimental investigation is necessary.
2. A magnesium Ion Selective Electrode has been identified to be more effective than an ammonium Ion Selective Electrode to infer and control the composition, and therefore supersaturation, of the solution.
3. The effect of interfering ions is essentially insignificant, since the interfering ions remain in diluted form both in synthetic solution as well as in real piggery effluents.
4. The solid phases found in this struvite model are Struvite, Brucite, Periclase, Newberyite and Farringtonite. However in the proposed operating range struvite is the dominant solid phase. When struvite is the dominant solid phase in its characterized supersaturated solution, most of the excluded solid phases remain in undersaturated form unless their IAP exceeds the solubility product values, exist in Visual MINTEQ default databases.

Overall, the use of the solution thermodynamics package, Visual MINTEQ, has assisted greatly in the preliminary design and development of nutrient recovery systems for piggery effluent streams.

7. ACKNOWLEDGEMENT

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