Development of a Process Model for Recovery of Nutrients from Wastewater by Precipitation as Struvite

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Nutrient removal from wastewater is becoming an increasing challenge for operators as regulatory authorities tighten discharge standards to avoid eutrophication problems in receiving waters (UWWTD, 1991). Nutrients like nitrogen and phosphorus can be removed from wastewater by precipitating these as the mineral struvite ($NH_4MgPO_4.6H_2O$). Struvite recovery helps utilities meet legal requirements imposed on wastewater disposal and reduce the area needed for wastewater application.

Struvite is a magnesium ammonium phosphate mineral known to be a "problem" material by wastewater operators. Frequently it is formed in sewage sludge digesters and liquid manure handling systems, where it causes blockages (Buchanan, 1994; Doyle and Parson,

2002). For that reason, struvite was considered a problem to eliminate and not a product that could be of economic interest until the 1960s, when Bridger et al. (1962) reported the excellent agronomic properties of struvite.

Now struvite is used as a premium-grade, slow-releasing fertilizer because it is sparingly soluble in water. It also finds use as a raw material in the phosphate industry for making fire-resistant panels and as a binding material in cements (Sarkar, 1990; Schuiling and Andrade, 1999). Recently there has been much attention on struvite production in wastewater treatment plants because of its ability to serve as a means for recovery and reuse of nutrients like nitrogen and phosphorus (Munch and Barr, 2001).

Significant costs are associated with the additional treatment processes required to

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meet the tighter discharge standards facing wastewater utilities (Wang et al., 2006). Existing techniques to remove nitrogen and phosphorous rely on biological methods like nitrification/denitrification and biological

Table 1. List of solids in the model

Number	Chemical name/Commercial name/Abbreviation	Chemical formula
1	Magnesium ammonium phosphate / Struvite	$MgNH_4PO_4 \cdot 6H_2O$
2	Magnesium hydrogen phosphate / Newberyite / MHP	$MgHPO_4$
3	Magnesium phosphate / Bobierrite / MP8	$Mg_3(PO_4)_2 \cdot 8H_2O$
4	Magnesium phosphate/ Cattiite / MP22	$Mg_3(PO_4)_2 \cdot 22H_2O$
5	Hydroxyapatite / HAP	$Ca_5(PO_4)_3OH$
6	Tricalcium phosphate / Whitlockite / TCP	$Ca_3(PO_4)_2$
7	Monenite / DCP	$CaHPO_4$
8	Octacalcium phosphate / OCP	$Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$
9	Dicalcium phosphate dehydrate / Brushite / DCPD	$CaHPO_4 \cdot 2H_2O$
10	Calcium carbonate / Calcite	$CaCO_3$
11	Magnesium carbonate / Magnesite	$MgCO_3$
12	Nesquehonite	$MgCO_3 \cdot 3H_2O$
13	Dolomite	$CaMg(CO_3)_2$
14	Huntite	$CaMg_3(CO_3)_4$
15	Magnesium hydroxide / Brucite	$Mg(OH)_2$

phosphorous removal that depend on the action of microorganisms on the wastewater, resulting in the transformation of these nutrients into a non-reusable and unrecoverable form. Chemical conversion to struvite may be seen as a better alternative to these conventional technologies because it would involve removing both ammonia- nitrogen and phosphate-phosphorus in the form of a precipitate that can be recovered as valuable byproduct.

The ability to predict struvite precipitation potential from a wastewater is an important consideration for designers and operators to determine the feasibility and economics of nutrient recovery as struvite, and for the subsequent design and operation of reactors for struvite precipitation. For good quality control, it is essential to know the best conditions under which struvite precipitation is likely to occur.

Upon mixing salts of magnesium, ammonium, and phosphate, several ionic and dissolved species and precipitates are formed, including struvite. A struvite precipitation model requires the incorporation of concentrations of at least the following:

- ionic species NH_4^+, PO_4^{3-}, and Mg^{2+}
- dissolved species NH_3 and H_3PO_4
- solid species $MgNH_4PO_4$

A number of other ionic species exist in equilibrium, however, including:

- HPO_4^{2-}
- $H_2PO_4^-$
- $MgOH^+$
- $MgPO_4^-$
- $MgH_2PO_4^+$

Also existing in equilibrium are these dissolved species:

- H_3PO_4
- $MgHPO_4$(dissolved)

Solid species existing in equilibrium include:

- $Mg_3(PO_4)_2 \cdot 8H_2O$
- $Mg_3(PO_4)_2 \cdot 22H_2O$
- $Mg(OH)_2$
- $MgHPO_4$(solid)

The complexity of models depends on the number of soluble and solid species considered. In this article, a comprehensive model is used to determine the concentrations of all species (dissolved, ionic and solid) to enable investigation of the purity and yield of struvite. It uses mass and charge balances in addition to the physico-chemical equilibrium equations.

The model described here considers all the 15 different solid species reported in the literature that are produced when magnesium, calcium, phosphate, ammonium, carbonate, and bicarbonate ions are present in solution

(Çelen et al., 2007). These ions, except for magnesium, typically are contained in many types of wastewater.

The applicability of the model to predict struvite precipitation potential was tested on various wastewaters, such as centrate from a sewage sludge digester, flushed dairy manure, and stillage from a cellulosic ethanol plant, and was validated by comparing it to experimental data.

Methods

The methods are presented in three parts: 1) model formulation, 2) model simulation, and 3) experiments performed in our laboratory to validate the model.

Model Formulation:

The model describes the chemical equilibrium in a system in the presence of ionic species like ammonium (ammonium chloride), magnesium (magnesium chloride), phosphate (potassium phosphate), calcium and carbonate (calcium carbonate). It was formulated based on the following assumptions:

- Dissolved and ionic species present in the system are NH_3, NH_4^+, PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, H_3PO_4, $MgOH^+$, $MgH_2PO_4^+$, $MgPO_4^-$, $MgHPO_4$(dissolved), CO_3^{2-}, HCO_3^-, H_2CO_3, CH_3COOH (representing organic acids), CH_3COO^-, Ca^{2+}, Na^+, K^+, Mg^{2+}, H^+, Cl^- and OH^-
- Other cations and anions were lumped together as a variable 'exions', which was set equal to Σ[cations modeled] - Σ[anions modeled].
- Fifteen different precipitates may be produced (listed in Table 1).
- pH was kept constant by addition of NaOH or HCl.
- Reactions are at equilibrium.
- Reactions proceed in a batch reactor.
- Reactions occur at room temperature (25°C).
- Activity coefficients were assumed to be unity.
- Effect of ionic strength on activity was neglected.

The model considers overall mass balance for magnesium, nitrogen, phosphorus, calcium, and inorganic carbon, electro-neutrality, and chemical and solubility equilibrium equations to describe the system. Values of equilibrium constants and solubility products at 25°C were taken from Scott (2001), Harada et al. (2006) and Moon et al. (2007). Particularly important is the solubility product for struvite. Values ranging between 12.6 and 13.26 have been reported (Ohlinger et al., 1998). In the present model, a value of 12.7 was used.

Model simulation:

Polymath Educational Version 6.1 was used to solve the model equations. The procedure that was followed for simulating, validat-

ing, and applying the model is described in a flow chart in Figure 1.

After the concentrations of total ammonia, orthophosphate, calcium, and potassium are measured, the mass of sodium hydroxide required (Na_{expt}) to raise the pH of sample to a preset pH value (pH_{sp}) is determined experimentally. pH_{sp} is chosen as the pH at which the precipitation reaction is carried out. These values are input into the model. Initial guesses for residual Mg^{2+}, NH_4^+, PO_4^{3-}, CO_3^{2-} and Ca^{2+} are needed. Polymath program solves the expressions and gives concentrations of dissolved and ionic species and concentrations of solid components.

Using the charge balance equation, the appropriate "exion" concentration was determined by trial and error so that the sodium requirement determined in the model (Na_{model}) matches Na_{expt}. Then the model is used to determine the amount of magnesium (Mg_t) required to lower the soluble phosphate or total ammonia to below minimum threshold values P_{min} and N_{min} respectively. The Mg_t value is guessed and the model is run.

The model output for residual phosphate or ammonia is compared to P_{min} or N_{min}. If the desired residual values are obtained within a tolerance limit, then that particular Mg_t used in the simulation is the magnesium requirement per liter of sample and the amount of magnesium chloride required is calculated.

Experiments:

Struvite precipitation experiments were carried out with synthetic solution, centrate from a sewage sludge digester, dairy flushwater, and cellulosic ethanol stillage.

A synthetic solution was prepared by dissolving 544 mg of potassium dihydrogen phosphate (KH_2PO_4), 1872.5 mg of ammonium chloride (NH_4Cl), and 812 mg magnesium chloride ($MgCl_2.6H_2O$) in one liter of distilled water. This yielded a solution containing 4 mM PO_4^{3-} (P_t), 35 mM of total ammonia (N_t), and 4 mM of magnesium (Mg_t).

Precipitation experiments were carried out in a 250-mL Erlenmeyer flask, in which 100 mL of this solution was used. This gave an initial $NH_4^+/Mg^{2+}/PO_4^{3-}$ ratio of ~35:3:4. A magnetic stirrer was used for mixing. The pH of the solution was monitored continuously with a pH probe. pH of the solution was ad-

justed to 8.9 by adding 5 N NaOH. Precipitation was found to occur instantaneously.

After reaching a pH of 8.9, the solution was stirred for another 10 minutes. Then the whole 250 mL solution was filtered using 0.6-µm Whatman filter paper to recover the precipitate, which was dried overnight in oven at 104°C and weighed. The experiment was repeated three times.

Dairy flush water samples were obtained from the barns of the University of Florida's Dairy Research Unit. Centrate was obtained

from the Buckman Sewage Treatment Plant in Jacksonville. Cellulosic ethanol stillage samples were obtained from the Biofuels Pilot Plant of the University's Agricultural and Biological Engineering Department. Table 2 lists the characteristics of these wastewater samples.

The precipitation reaction was carried out in a closed 10-liter vessel containing nine liters of sample under well-controlled conditions and continuous pH monitoring by adding these quantities of magnesium chloride and

Table 2. Characteristics of Wastewater

Wastewater (treated to N_{min} = 50 ppm or P_{min} = 10 ppm)	pH	Total ammonia-nitrogen, N_t (mg/L)	Orthophosphate – phosphorus, P_t (mg/L)	Sodium hydroxide required for pH_{sp} (g/L)	Exions from model (mole/L)	Mg_t Required (mg/L)
Flushed dairy manure (P_{min})	7.25	740.8	50.66	0.44	0.00257	30.56
Anaerobically treated dairy manure (P_{min})	6.8	1586	40.93	-	0.00257	27.0
Aerobically treated dairy manure (P_{min})	7.55	497.7	30.51	-	0.00257	21.75
Centrate (P_{min})	7.4	710.0	103.0	0.432	0.003751	105.6
Anaerobically digested cellulosic ethanol stillage (N_{min})	6.2	284.9	590.9	1.06	0.00147	500.0
Cellulosic ethanol stillage (N_{min})	6.9	230.0	809.0	2.3	0.0247	350.0

Figure 1. Flow chart of model simulation steps

Flowchart text (left/center):

START

Characterize sample for total ammonia nitrogen (N_t), total soluble phosphate (P_t), calcium, potassium, alkalinity and pH

Titrate sample with known concentration of sodium hydroxide

Determine sodium hydroxide requirement to increase pH to specified value (pH_{sp})

Calculate sodium required (Na_{expt})

Update Exion value

Input N_t, P_t, Ca, K, pHsp

Initial guesses for residual NH4+, PO43-, Mg2+ and tolerance for convergence

Run model until numerical convergence. Model outputs values of all dissolved, ionic and solid species concentration Calculate Na from charge balance (Na_{model})

NO

Is $Na_{model} = Na_{expt}$?

YES

Guess Mgt

Input N_t, P_t, Ca, K, Exion, pH_{sp}

Run model until numerical convergence. Model outputs values of all dissolved, ionic and solid species concentration

NO

If P_t is limiting in sample: Check residual soluble $P \le P_{min}$?
If N_t is limiting in sample: Check residual soluble $N \le N_{min}$?

YES

Output-amount of total solids, all solids, % struvite, residual soluble P and N values

END

Continued from page 19

sodium hydroxide. The reaction was allowed to occur for 20 minutes. Air was sparged through the solution for mixing, followed by a settling time of three hours under quiescent conditions. After the procedure was completed, total solids, suspended solids, the residual soluble total ammonia-nitrogen, and orthophosphate-phosphorus were determined and compared with the results given by the model.

Results & Discussion

A previous version of the model that included only the magnesium precipitates (MHP, MP8, MP22, struvite, and $Mg(OH)_2$) was tested on struvite precipitation data using various types of wastewater (Gadekar and Pullammanappallil, 2009). These data were obtained from literature. It was found that the error in struvite prediction was below 10 percent for most data sets, except for two sets obtained from experiments that used synthetic solutions (Harada et al., 2006; Stratful et al., 2001). It was found that the present model simulated these literature data better.

Using the present model, the error between model predictions and data from Harada et al (2006) was only 0.4 percent. The experiments of Stratful., et al. (2001) yielded total solid precipitate of 909 mg/L. In compar-

ison, the model prediction using their experimental conditions was 893.2 mg/L—an error of only 1.7 percent. The present model was able to improve upon the predictions of the previous version of model.

The model predictions then were compared to experimental data that was conducted with synthetic solutions and real wastewater like centrate, dairy manure, and cellulosic ethanol stillage. Experimental results, model predictions, and error between these are given in Table 3.

When a synthetic solution was tested for struvite precipitation, it was found that residual soluble phosphate -P level was reduced to 25.47 ppm and residual total ammonia-N was reduced to 430 ppm. The model predicted a residual P of 29.06 ppm and residual N of 447.5 ppm.

The total solids determined experimentally also were compared with model predictions. Even though model predictions of N and P residuals agreed well with the experiment, the error in total solids prediction was found to be 30.41 percent. Total solids was overpredicted by the model, possibly because a portion of the solids was fine and therefore was not retained on 0.6-μm filter paper.

For the case of the centrate, a 99-percent phosphate recovery was witnessed as a result of struvite precipitation carried out at a pH of 8.4. The model predictions were very close to experimental data.

In the case of the dairy manure sample, the reaction was carried out in two steps. It was found that the P removal was higher for a two-step process than that for a single-step process. Phosphate-P level was reduced from 50.66 ppm to 5.3 ppm in two steps. The model predictions were close to experimental data.

The pH of anaerobically digested cellulosic ethanol stillage was found to have dropped to 6 upon storage for a long period at room temperature after digestion. Struvite precipitation was carried out at pH 9.0. The P level was reduced to 41.56 ppm from 590.9 ppm, which was close to 34.08 ppm predicted by the model. The model predicted the production of a variety of Mg precipitates in addition to struvite, such as MHP and $Mg(OH)_2$.

Similarly, model predictions agreed well with experimental results using untreated cellulosic stillage. In this case, only a small quantity of magnesium chloride was added, so the extent of removal of P was not high. The experiment resulted in a residual P of 566 ppm after Step 1 and 532 ppm after Step 2, which was close to the model prediction of 585 ppm and 537.24 ppm after Steps 1 and 2, respectively.

Conclusions

- A model was developed for predicting struvite precipitation in a batch reactor containing solutions of ammonium, magnesium, phosphate, calcium, and carbonate.
- The model incorporated 15 different precipitates and solved for precipitate, residual ion, and dissolved species concentrations using mass balance equations for magnesium, phosphorus, and nitrogen, along with chemical equilibrium and charge balance equations.
- The model was validated against experimental data using a variety of wastewater, including dairy manure, anaerobically and aerobically treated manure, centrate from a sludge digester, and treated and untreated cellulosic ethanol stillage.

Acknowledgement

Table 3. Model Validation

Wastewater		Experimental Data			Model Predictions				Error (%)	
		Residual Phosphate-P (mg/L)	Residual Total Ammonia-N (mg/L)	Total solids (g/L)	Residual Phosphate-P (mg/L)	Residual Total Ammonia-N (mg/L)	Total solids (g/L)	Struvite (g/L)	Phosphate-P removed	Total solids
Synthetic solution		25.47	430.0	0.291	29.06	447.5	0.419	0.415	3.64	30.55
Centrate		0.5	680.0	6.24	0.83	615.0	6.1	0.354	0.322	2.24
Untreated flushed dairy manure	Step 1	22.35	720.1	2.35	22.1	728.1	2.93	0.226	0.875	19.8
	Step 2	5.7	385.6	ND	2.75	388.2	6.4	0.942	15.06	-
Anerobically treated dairy manure	Step 1	15.7	1580.7	ND	15.67	1574.7	0.11	0.11	0.119	-
	Step 2	4.5	895.2	ND	5.83	891.6	0.043	0.043	11.875	-
Aerobically treated dairy manure	Step 1	9.74	475.8	ND	10.5	479.8	0.177	0.174	3.66	-
	Step 2	2.4	385.3	ND	2.38	382.2	0.032	0.032	0.271	-
Anaerobically digested cellulosic ethanol stillage		41.56	55.85	2.25	34.08	53.37	2.58	2.265	1.343	12.62
Cellulosic ethanol stillage	Step 1	566	130	1.2	585	130.6	1.3	0.96	7.82	8.91
	Step 2	532	95	0.2	537.2	117.2	0.163	0.072	15.4	18.5

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