

## MODELLING THE THERMODYNAMIC EQUILIBRIUM OF STRUVITE PRECIPITATION USING A HYBRID OPTIMIZATION TECHNIQUE

Claudia Santiviago Petzoldt<sup>(1),(2)</sup>, Iván López Moreda<sup>(2)</sup>

<sup>(1)</sup>Department of Industrial Applications, Chemistry Faculty, Universidad Nacional de Asunción, <sup>(2)</sup>Department of Reactor Engineering, Engineering Faculty, Universidad de la República  
<sup>(1)</sup>San Lorenzo/Paraguay, <sup>(2)</sup>Montevideo/Uruguay  
<sup>(1)</sup>csantiviago@qui.una.py

### ABSTRACT

Precipitation of struvite can be conceived as one of the main processes for recovering P and N from wastewater. This paper developed a thermodynamic model of struvite precipitation to predict the potential P recovery (PR) from wastewater streams by NaOH or HCl and  $MgCl_2 \cdot 6H_2O$  addition using the Gibbs free energy as objective function, by implementation of a hybrid optimization technique based on successive use of pattern search algorithm (PS) and classical sequential quadratic programming (SQP) method. The simulated PR, and equilibrium pH data were validated using synthetic wastewater in batch process; showing good correlations with the experimental data in both cases:  $R^2=99.4\%$  and  $R^2=99.3\%$  respectively. The validated model was used to evaluate the influence of molar ratios Mg/P (1.0, 1.2, 1.5, 2.0) and N/P (1.0, 2.0) for a orthophosphate phosphorus concentration (P-OP) of 200 ppm. The maximum PR reached for each combination of concentrations tested were evaluated, resulting the molar ratios N/P=2.0 and Mg/P=1.20 (pH=8.94) as a good industrial operation candidate, because achieves high PR (97.6%) at reasonable lower Mg concentration. For this condition, the effect of ionic strength produced by nonreactive ions ( $I^*$ ) was studied, showing that increases in  $I^*$  reduces the optimum PR achieved.

### KEY WORDS

Struvite. Mathematical modelling. Pattern search. Sequential quadratic programming.

### 1. Introduction

Agro-industrial wastewater streams, such as concentrated slaughterhouse wastewater, presents high concentrations of nutrients (N and P) that generally exceed those accepted for the discharge standards. Nutrients may cause eutrophication of the aquatic systems, difficulties for water supply and crystalline deposits by uncontrolled deposition of phosphate salts in the treatment systems. The undesirable struvite deposition was first reported in the seventies [1], and later other researchers reported the same problem [2], [3]. Furthermore, since P becomes a

limited resource, the technologies used to recover P from the waste stream are significantly appreciated [4]. Thus it is necessary to consider appropriate treatments that reduce the concentration of nutrients, seeking to ensure economic, social and environmental sustainability of these activities. The most common and economical method to remove nutrients from wastewater is through the biological process [5], which reduces the concentration of N compounds to  $N_2$  gas; incorporates the P to biomass and removes o discharges it with the sludges. The main drawbacks of this alternative are the large volume of sludge generated and that it removes part of P but does not recover it.

An alternative solution that allows the recovery of nutrients in wastewater is the crystallization as struvite (magnesium ammonium phosphate hexahydrate). The recovery of nutrient using this crystallization technique may provide an added value product: the struvite, which can be used as slow-release fertilizer, applicable to relatively low soil pH [6]; it contains a significant amount of nitrogen and magnesium, and is an effective alternative source of rock phosphate to maintain the agricultural production system. Also, struvite can be used as raw material in the phosphate industry, for making fire-resistant panels, and as a binding material in cements [7], [8].

Predicting potential nutrient removal from a wastewater stream of known chemical composition and under defined operating precipitation conditions constitutes an essential tool for the design of crystallization reactors, definition of the optimum operating conditions for each influent and to evaluate the operational efficiency. In biological wastewater nutrient removal it is also essential to know the conditions under which struvite precipitation is likely to occur to avoid its uncontrolled deposition.

Several thermodynamic models based on chemical equilibrium have been developed to predict with reasonable accuracy the potential P removal as struvite by precipitation [9-17]. In particular, the use of computer models, such as PHREEQC [17-19], MINTEQA2/ Visual Minteq [10], [16], [19-22], and MINEQL+ [11], [23] have

been used to determine the equilibrium speciation of struvite species constituents and therefore to predict struvite formation potential and PR. Since struvite is generally not provided in these internal databases, its thermodynamic data need to be defined by the user as well. The packages are typically complex, and solve most reactions using an algebraic approach.

MINEQL+ is an Environmental Research Software [24] that performs iterative analyses using an internal thermodynamic database and user specified constituent concentrations values to calculate equilibrium concentrations of all considered complexes [25]. PHREEQC is a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations [26]. Visual Minteq [27] is a chemical equilibrium computer program that has an extensive thermodynamic database that allows the calculation of speciation, solubility, and equilibrium of solid and dissolved phases of minerals in an aqueous solution [28]. This program is the Windows version of MINTEQA2 that was originally developed by the US EPA. STRUVITE, developed by the Water Research Commission, South Africa, is another program used for this propose, but it is specifically developed to predict the PR as struvite in wastewaters streams [29], and is used for research by some authors [30], [31].

The model developed by [13] uses an iterative residual procedure in MAPLE, the total phosphate concentration is obtained within a given tolerance, as well as the concentration of different precipitates; [9] uses Newton's method to find the approximate values of species concentration in urine; [15] express the struvite species concentration in terms of the known values and solves it numerically with iterative methods using MATLAB; [14] combine a genetic algorithm for initialization purpose with a standard Newton–Raphson method implemented in MATLAB environment to describe the chemical equilibria at different temperatures.

This paper presents the development of a simple thermochemical model, representative of struvite precipitation when the concentrations of ammonium is low enough to neglect the presence of  $\text{NH}_3$  (g) in the system and the pH is less than 10.0 to avoid the presence of  $\text{Mg}(\text{OH})_2$  in the solid phase [32], [33], since it reduces the P removal (PR) which is defined at Eq. (1).

$$\text{PR} = \frac{P_0 - P_f}{P_0} \quad (1)$$

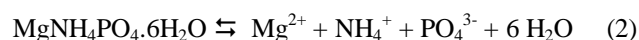
where  $P_0$ : P-OP before treatment ( $\text{mg}\cdot\text{L}^{-1}$ );  $P_f$ : remaining soluble P-OP after treatment ( $\text{mg}\cdot\text{L}^{-1}$ ).

The validated model is used to evaluate the influence of molar ratios Mg/P and N/P for a P-OP concentration of 200 ppm. The maximum PR reached for each tested combination is evaluated. The effect of ionic strength

produced by nonreactive ions ( $I^*$ ) presents in the system is also studied for selected operating conditions.

## 2. Struvite precipitation thermodynamic. Background

Struvite precipitation involves various parameters: ammonium, magnesium and phosphate ion concentrations, supersaturation ratio, ionic strength, temperature, pH and also reaction time. The crystallization occurs in a supersaturated solution, as a result of the chemical reaction of the free  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  ions and the incorporation of six molecules of water, as hydration water (Eq. (2)) at slightly alkaline conditions.



The precipitation reaction is represented by an equilibrium constant, the struvite solubility product,  $K_{sp}$  which can be computed from the product of the involved reactant activities ( $a$ ) according to Eq. (3).

$$K_{SP} = a_{\text{Mg}^{2+}} \cdot a_{\text{NH}_4^+} \cdot a_{\text{PO}_4^{3-}} \quad (3)$$

As consequence of the existence of molecular interactions of ions in solution, a heterogeneous distribution of charges occurs in the system, which causes the appearance of an electric potential. This stabilization of solution causes the ions have less tendency to escape from solution (or precipitate in this case), so chemical activities are lower than the molar concentrations, and are defined by the product of the concentrations  $C_i$  in  $\text{mol}\cdot\text{L}^{-1}$  and activity coefficients  $\lambda_i$  of the corresponding ion  $i$  (Eq. (4)).

$$a_i = \lambda_i \cdot C_i \quad (4)$$

A measure of the intensity of the electric potential created by the ions in the solution can be obtained by the calculus of the ionic strength  $I$ , according to Eq. (5) devised by Lewis and Randall, based on each species of ionic concentration and its respective charge,  $Z_i$ .

$$I = 0.5 \sum C_i \cdot Z_i^2 \quad (5)$$

Activity coefficients can be calculated from several empirical relations such as: Debye-Hückel equation, Güntelberg approximation, Davies, Pitzer or Bromley equations [34]. Since the accuracy of each equation is determined by the ionic strength of the solution, the appropriate equation should be selected based on this parameter. This research uses the Davies equation (Eq. (6)) to calculate the activity coefficient. The Davies equation, an approximation of the Debye-Hückel equation, is capable of performing activity calculations for  $I < 0.2 \text{ M}$  [35].

$$\lambda_i = 10^{-A_{DH}Z_i\left[\frac{\sqrt{I}}{1+\sqrt{I}}-0.3I\right]} \quad (6)$$

$$A_{DH} = 1.82 \cdot 10^6 (\epsilon T)^{-3/2} \quad (7)$$

where  $A_{DH}$  is the Debye-Hückel constant determined by Eq. (7),  $\epsilon$  is the dielectric water constant, and  $T$  the absolute temperature.  $A_{DH}$  value is 0.499 at 25 °C.

In this work, the ionic strength was lower than 0.2 M in all cases, reaching at maximum of 0.04 M for the molar ratios N/P=1, Mg/P=1.2 at pH=7.0; this confirms the validity of the model choice. An additional term  $I^*$  is considered to take into account the ionic strength influence on the PR produced by other ionic salts in the system that affects the performance of the process. This model includes NaCl concentration, which represents these nonreactive ions.

The equilibrium conditional solubility product ( $P_{CS}$ ) is the product of molar concentrations of total dissolved magnesium, ammonia and orthophosphate species respectively calculated through the  $K_{sp}$  in a system at equilibrium (Eq. (8)). On the other hand, the product of the measured molar concentration of total dissolved magnesium, ammonia, and orthophosphate species, respectively it is called product of the analytical molar concentration ( $P_{SO}$ ) (Eq. (9)).

$$P_{CS} = \frac{K_{sp}}{\alpha_{Mg^{2+}} \cdot \alpha_{NH_4^+} \cdot \alpha_{PO_4^{3-}} \cdot \lambda_{Mg^{2+}} \cdot \lambda_{NH_4^+} \cdot \lambda_{PO_4^{3-}}} \quad (8)$$

$$P_{SO} = C_{T,Mg} \cdot C_{T,NH_4} \cdot C_{T,OP} \quad (9)$$

where  $C_{T,Mg}$ ,  $C_{T,NH_4}$  and  $C_{T,OP}$  are the total analytical concentrations of magnesium, ammonia, and P-OP, respectively; and  $\alpha_{Mg^{2+}}$ ,  $\alpha_{NH_4^+}$  and  $\alpha_{PO_4^{3-}}$  are respectively the ionization fractions, defined as:

$$\alpha_{Mg^{2+}} = \frac{C_{Mg^{2+}}}{C_{T,Mg}} \quad (10)$$

$$\alpha_{PO_4^{3-}} = \frac{C_{PO_4^{3-}}}{C_{T,OP}} \quad (11)$$

$$\alpha_{NH_4^+} = \frac{C_{NH_4^+}}{C_{T,NH_4}} \quad (12)$$

Supersaturation of the solution is the key parameter leading to crystallization. The supersaturation ratio ( $S_C$ ) is calculated using Eq. (13):

$$S_C = \left(\frac{P_{SO}}{P_{CS}}\right)^{1/\nu_r} \quad (13)$$

where  $\nu_r = 3$ ; is the number of reactants in anhydrous struvite. The supersaturation ratio can also be expressed in terms of  $K_{SP}$  (Eq. (14)).

$$S_C = \left(\frac{a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}}{K_{SP}}\right)^{1/\nu} \quad (14)$$

Values of  $S_C > 1.0$  indicate that supersaturated conditions exist and that precipitation is possible;  $S_C = 1$  characterizes the saturated condition, and  $S_C < 1$  indicates an undersaturated solution.

### 3. Thermodynamic model

#### 3.1 Model formulation

A struvite precipitation model at least requires the incorporation of concentrations of the ionic species:  $NH_4^+$ ,  $PO_4^{3-}$ ,  $Mg^{2+}$ ,  $H^+$ ,  $OH^-$ , the dissolved species:  $NH_3$  and  $H_3PO_4$ , and the solid compound:  $MgNH_4PO_4 \cdot 6H_2O$ . However, others aqueous ions and dissolved species such as:  $H_3PO_4$ ,  $MgHPO_4$ ,  $NH_3(aq)$ ,  $H_2PO_4^-$ ,  $HPO_4^{2-}$ ,  $MgH_2PO_4^+$ ,  $MgOH^+$ ,  $MgPO_4^-$  and solids species such as:  $Mg(OH)_2$ ,  $Mg_3(PO_4)_2 \cdot 8H_2O$ ,  $Mg_3(PO_4)_2 \cdot 22H_2O$  or  $MgHPO_4 \cdot 3H_2O$  may interfere in the equilibrium system. The complexity of the models depends on the number of soluble and solid species considered.

This research considers the equations for ions, dissolved and solids species given in Table 1 and the struvite precipitation (Eq (2)). The  $pK_j$  values are calculated from the  $K_j$  values, according to Eqs. (24), (25).

Table 1  
pK values for considered reactions with involved species in the model at 25°C

Reaction $j$	$pK_j$
(15) $H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$	2.15
(16) $H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$	7.21
(17) $HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$	12.34
(18) $MgH_2PO_4^+ \rightleftharpoons H_2PO_4^- + Mg^{2+}$	1.51
(19) $MgHPO_4 \rightleftharpoons HPO_4^{2-} + Mg^{2+}$	2.91
(20) $MgPO_4^- \rightleftharpoons PO_4^{3-} + Mg^{2+}$	6.59
(21) $MgOH^+ \rightleftharpoons Mg^{2+} + OH^-$	2.56
(22) $NH_4^+ \rightleftharpoons NH_3(aq) + H^+$	9.25
(23) $H_2O \rightleftharpoons OH^- + H^+$	14.00

$$pK_j = -\log K_j \quad (24)$$

$$K_j = e^{-\frac{\Delta G_R^\circ}{RT}} \quad (25)$$

where  $R$  is the gas constant, and  $\Delta G_R^\circ$  is the free energy of reaction at 25°C given by:

$$\Delta G_R^\circ = \sum_p \nu_p \Delta G_{f,p}^\circ - \sum_r \nu_r \Delta G_{f,r}^\circ \quad (26)$$

$\Delta G_{f,p}^\circ$  and  $\Delta G_{f,r}^\circ$  are the free energies of formation or chemical potential values  $\mu_i$  for products and reactants respectively,  $\nu_p$  and  $\nu_r$  are the stoichiometric coefficients of products and reactants. The  $K_{SP}$  for struvite using in

this work is 13.26 [10]. The chemical potential values considered in this paper are shown in Table 2.

In one hand, precipitates such as  $Mg_3(PO_4)_2 \cdot 22H_2O$  and  $MgHPO_4 \cdot 3H_2O$  were not taken into account, because struvite precipitates at neutral and higher pH;  $MgHPO_4 \cdot 3H_2O$  precipitates significantly at lower pH (pH < 6) and  $Mg_3(PO_4)_2 \cdot 22H_2O$  has never been observed in the pH range of 6-9 and is reported to have a low precipitation rate [36]. In the other hand, the relative low molar ratio Mg/P required to achieve a high P removal as struvite, compared to the stoichiometric relation Mg/P in  $Mg_3(PO_4)_2 \cdot 8H_2O$  would not favour to the formation of this compound; therefore, it is also removed from the model. Furthermore, the presence of  $Mg(OH)_2$  in the system, which compete with struvite formation at pH > 10 [33] is neglected, to study the range of pH in which it is possible to maximize the P removal.

Table 2  
Chemical potential values at 25°C

Species <i>i</i>	$\mu_i$ (kJ·mol <sup>-1</sup> )	References
H <sub>3</sub> PO <sub>4</sub>	-1142.65	[37]
MgHPO <sub>4</sub>	-1560.67	[37]
NH <sub>3(aq)</sub>	-26.50	[38]
NH <sub>4</sub> <sup>+</sup>	-79.37	[37]
PO <sub>4</sub> <sup>3-</sup>	-1018.80	[37]
HPO <sub>4</sub> <sup>2-</sup>	-1089.26	[37]
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	-1130.40	[38]
Mg <sup>2+</sup>	-454.80	[37]
MgH <sub>2</sub> PO <sub>4</sub> <sup>+</sup>	-1593.84	[37]
MgOH <sup>+</sup>	-626.7	[38]
MgPO <sub>4</sub> <sup>-</sup>	-1511.21	[37]
H <sup>+</sup>	0	[37]
OH <sup>-</sup>	-157.29	[37]
H <sub>2</sub> O	-237.18	[37]
MgNH <sub>4</sub> PO <sub>4</sub> ·6H <sub>2</sub> O	-3051.1	[37]

In a reaction system the equilibrium condition at constant temperature and pressure occurs when the Gibbs free energy (G) reaches a minimum. The relation between G and  $\mu_i$  is showed in Eq. (27).

$$G = \sum_{i=1}^N \sum_{k=1}^{\pi} C_{ik} \mu_{ik} \quad (27)$$

$$\mu_{iL} = \mu_{iL}^{\circ}(T) + RT \ln(C_i \lambda_i) \quad (28)$$

$$\mu_{iS} = \mu_{iS}^{\circ}(T) \quad (29)$$

where all the components *i* must take into account in the two considered phases: solid (struvite) and liquid (the aqueous solution). To determine the equilibrium concentration of ions and dissolved species at equilibrium it is therefore necessary to minimize G. It is also mandatory that the mass and electroneutrality balances are met (Eqs. (30)-(33)).

Mass balance for Mg:

$$C_{T,Mg} = C_{MgH_2PO_4^+} + C_{Mg^{2+}} + C_{MgHPO_4} + C_{MgPO_4^-} + C_{MgOH^+} + PR \cdot C_{T,OP} \quad (30)$$

Mass balance for orthophosphate phosphorous:

$$C_{T,OP} = C_{H_3PO_4} + C_{H_2PO_4^-} + C_{HPO_4^{2-}} + C_{PO_4^{3-}} + C_{MgPO_4^-} + C_{MgH_2PO_4^+} + C_{MgHPO_4} + PR \cdot C_{T,OP} \quad (31)$$

Mass balance for ammonium:

$$C_{T,NH_4} = C_{NH_4^+} + C_{NH_3} + PR \cdot C_{T,OP} \quad (32)$$

Electroneutrality:

$$C_{Na^+} + C_{MgH_2PO_4^+} + 2 C_{Mg^{2+}} + C_{MgOH^+} + C_{H^+} + C_{NH_4^+} - C_{MgPO_4^-} - 3 C_{PO_4^{3-}} - C_{H_2PO_4^-} - C_{OH^-} - 2 C_{HPO_4^{2-}} - C_{Cl^-} = 0 \quad (33)$$

where  $C_{Na^+}$  and  $C_{Cl^-}$  are the molar concentration of sodium and chloride which comes from the representation of other ionic salts to study the effect of ionic strength in the system, and from the aggregation of NaOH or HCl and MgCl<sub>2</sub> to adjust the pH and ions molar ratio respectively.

Mass balances are then 4 linear equality constraints in the proposed optimization problem. Additionally, it is required that the chemical equilibria showed in Table 3 are satisfied. Consequently, the optimization problem presents 10 nonlinear equality constraints.

Table 3  
Nonlinear equality constraints: Chemical equilibria to be satisfied by the model

Reaction <i>j</i>	Nonlinear equality constraints	Eq.
(15)	$pK_{15} + \log\left(\frac{\alpha_{H_2PO_4^-} \cdot \alpha_{H^+}}{\alpha_{H_3PO_4}}\right) = 0$	(34)
(16)	$pK_{16} + \log\left(\frac{\alpha_{HPO_4^{2-}} \cdot \alpha_{H^+}}{\alpha_{H_2PO_4^-}}\right) = 0$	(35)
(17)	$pK_{17} + \log\left(\frac{\alpha_{PO_4^{3-}} \cdot \alpha_{H^+}}{\alpha_{HPO_4^{2-}}}\right) = 0$	(36)
(18)	$pK_{18} + \log\left(\frac{\alpha_{H_2PO_4^-} \cdot \alpha_{Mg^{2+}}}{\alpha_{MgH_2PO_4^+}}\right) = 0$	(37)
(19)	$pK_{19} + \log\left(\frac{\alpha_{HPO_4^{2-}} \cdot \alpha_{Mg^{2+}}}{\alpha_{MgHPO_4}}\right) = 0$	(38)
(20)	$pK_{20} + \log\left(\frac{\alpha_{PO_4^{3-}} \cdot \alpha_{Mg^{2+}}}{\alpha_{MgPO_4^-}}\right) = 0$	(39)
(21)	$pK_{21} + \log\left(\frac{\alpha_{OH^-} \cdot \alpha_{Mg^{2+}}}{\alpha_{MgOH^+}}\right) = 0$	(40)
(22)	$pK_{22} + \log\left(\frac{\alpha_{NH_3} \cdot \alpha_{H^+}}{\alpha_{NH_4^+}}\right) = 0$	(41)
(23)	$pK_{23} + \log\left(\frac{\alpha_{OH^-} \cdot \alpha_{H^+}}{\alpha_{H_2O}}\right) = 0$	(42)
(2)	$pK_{SP} + \log(a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}) = 0$	(43) <sup>(*)</sup>

<sup>(\*)</sup> Eq. (43) is a different expression of Eq. (14) applied to a saturated solution.

The 14 variables (13 concentrations  $C_i$  + 1 fractional P removal PR) are bounded. The lower bounds for  $C_{H^+}$  and

$C_{OH^-}$  are  $10^{-pH_0}$  and  $10^{-6}$  respectively; for the remaining variables the lower bounds are equal to 0. The upper bounds for the  $C_i$  are represented by the maximal concentrations of the limiting Mg, N or P element in the influent and present in the compound;  $10^{-6}$  for  $C_{H^+}$  (at  $pH < 6$  the struvite not precipitate);  $10^{-pOH_0}$  for  $C_{OH^-}$  and 1 for the PR.  $pH_0$  and  $pOH_0$  are the pH and pOH values adjusted by addition of NaOH and HCl as appropriate.

The thermodynamic model is formulated with the following assumptions:

- (a) Ionic and dissolved species in the system are the indicated in Table 2. Precipitate which may be formed in assay recovery conditions is only struvite.
- (b) All reactions are in an equilibrium state. In the struvite crystallization process, the reactions are rapid; therefore, the dynamics of the reactions are ignored and equilibrium relationships are used to determine the species concentrations.
- (c) The system is run at isothermal and isobaric conditions: 25°C and 101.325 kPa.
- (d) Non reaction ionic species are represented by NaCl.
- (e) pH is kept constant (6.9 - 10.0) by addition of NaOH or HCl, which meant that  $C_{H^+}$  and  $C_{OH^-}$  are known.
- (f) The formation of complexes with  $Cl^-$  or  $Na^+$  is neglected, based on [39], just like complexes created since more than two ions.

### 3.2 Solving the thermodynamic model

This is a constraint nonlinear optimization problem, with 4 additional linear equality constraints. The SQP is one of the most successful methods for the numerical solution of constrained nonlinear optimization problems, nevertheless is very sensitive to the choice of the initial guess and may often lead to a convergence failure; the only way to achieve the convergence is select an initial value close enough to the desired root.

Motivated by this inconvenient and to guarantee the success of the optimization procedure this work proposes an automatic generation of good starting points; those are used to perform the search with optimization method SQP in MATLAB environment (*fmincon* function with *SQP Algorithm*). To perform a preliminary search in the solution space with  $56 \cdot 10^3$  evaluations to locate the neighborhood of the solution a pattern search algorithm (PS) is used. Then, using the solution found with the PS as initial guess, the gradient-based algorithm SQP is applied. The technique avoids the drawbacks of both methods: the long times required by the PS to achieve a solution and the often failures convergence by the SQP as product of a bad choice of the initial values.

Figure 1 shows the calculus steps of the equilibrium conditions contemplated by the model for each characteristic influent.

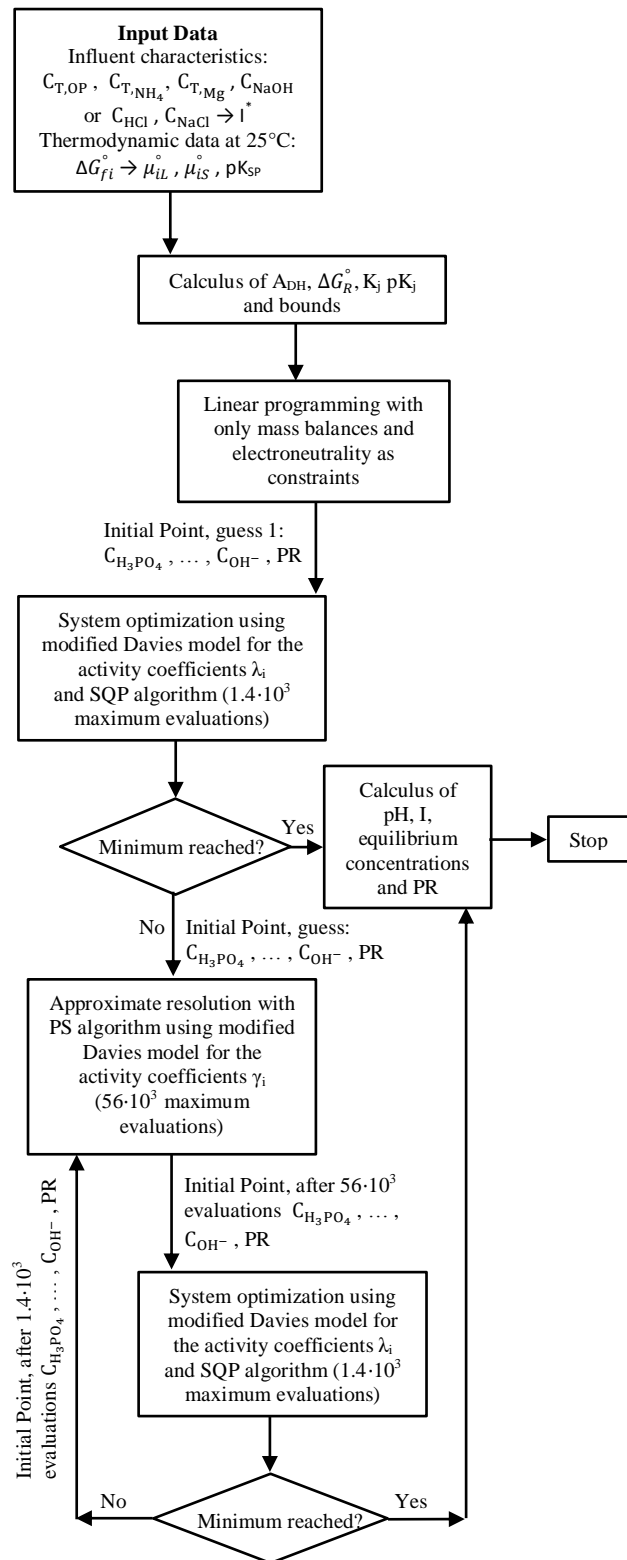


Figure 1. Chemical equilibrium concentrations and PR by struvite precipitation.

From some initial influent conditions, it is possible that a good initial guess from the SQP algorithm is the solution of a linear optimization of the problem, excluding nonlinear constraints. Therefore initially it is posed a linear programming, with Eq. (27) as the objective

function and with the mass balances and electroneutrality as the only constraints (Eqs. (30)-(33)), reducing the computer time for those cases where this strategy it is successful. The SQP algorithm runs for 1400 evaluations; if in this number of runs convergence is not achieved (constraint tolerance =  $10^{-6}$ ) the hybrid optimization PS+SQP runs. The solution of the linear programming is used in the first run of the PS algorithm. When the SQP algorithm does not converge, the last point achieved is used to initialize the PS algorithm until the solution is reached.

### 3.3 Model validation. Experimental procedure

The model was validated with experimental data using synthetic wastewater solutions. The experiments were performed at 25°C, in batch process using a Jar tester (Phipps and Bird PB-900) of 6 containers of 1 L each, with shaking at 150 rpm for 3 h for which the reactions were assumed to reach equilibrium, that is confirmed because the pH was stabilized (pH measures every 30 min). NaOH (1 N) or HCl (1 N) were used to adjust initial pH as appropriate in the range 6.9-10.0. Synthetic feeds were prepared with concentrations of 200 ppm P-OP and 180 ppm N-NH<sub>4</sub>, by (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> dissolution in distilled water. The source of Mg (4000 ppm) was a water solution of MgCl<sub>2</sub>·6H<sub>2</sub>O added at 155 ppm in all the assays. Therefore, the molar ratios Mg/P and N/P were 1.0 and 2.0 in the validate experiences.

In one hand, samples of 50 mL were taken from each treatment and centrifuged for 15 minutes in a centrifuge (Sigma 3-16KL) at 4500 rpm to separate the precipitated struvite before measuring the residual dissolved P-OP. The final concentration of P dissolved in the samples was measured using the method of ammonium vanadomolybdate [40] using a UV-Vis spectrophotometer (Spectronic 21 - Bausch & Lomb). On the other hand, 500 mL of the assays when the equilibrium pH was 7.3, 7.6, 8.5 and 10.0 were filtrated with 0.45 μm filter paper, and the crystals were dried at room temperature, and then analyzed with X-ray diffraction (XRD) that confirm the presence of pure struvite in all cases.

To determinate the experimental error, some analyses were performed in triplicate. Statistical analysis of experimental data was performed by using the ACTION STAT software.

## 4. Results and discussion

### 4.1 Verification of the proposed model

The Figure 2 shows model and measured PR (%) for the range of pH 6.9-10.0 when the P-OP was 200 ppm, the molar ratios Mg/P=1 and N/P=2.

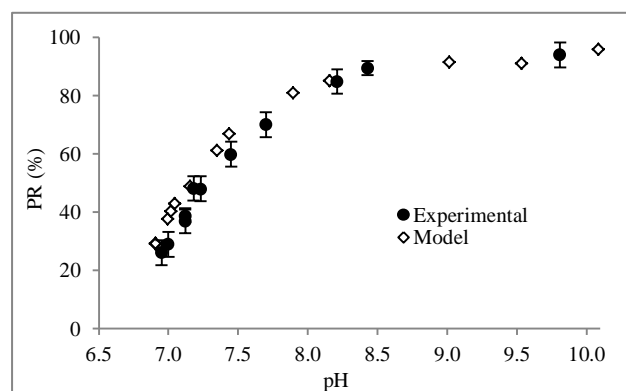


Figure 2. Predicting and measured PR (%) as struvite for P-OP=200 ppm at the molar ratios Mg/P=1 and N/P=2, T=25°C.

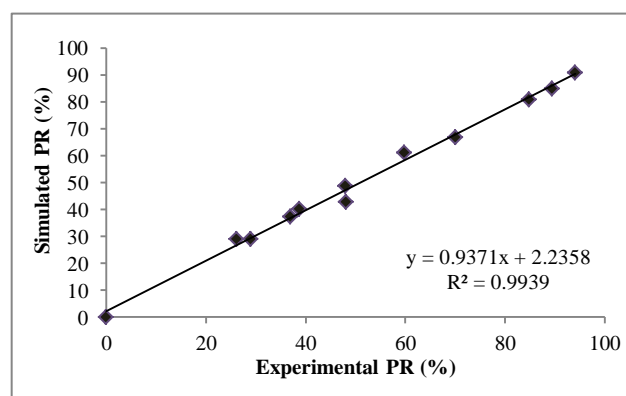


Figure 3. Linear correlations between PR (%) obtained by simulated and experimental data for P-OP=200 ppm at the molar ratios Mg/P=1 and N/P=2, T=25°C.

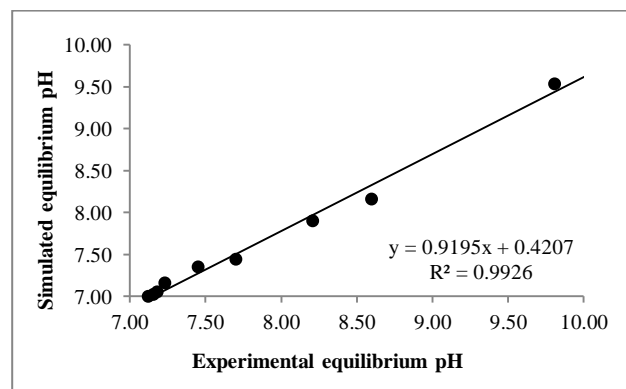


Figure 4. Linear correlations between pH obtained by the simulated data and experimental measurements for P-OP=200 ppm at the molar ratios Mg/P=1 and N/P=2, T=25°C.

The validation can be assessed by comparing the simulated (y) and experimental data (x): PR and equilibrium pH. Figures 3 and 4 exhibits a high correspondence between the experimental and simulated data sets ( $R^2=99.4\%$  for PR and  $R^2=98.9\%$  for

equilibrium pH). The high correspondences ( $y=x$ ) reflect the successful validation of the proposed model.

#### 4.2 Effect of molar ratio Mg/P and N/P at different pH on the phosphorus removal

Using the developed model, the PR as a pH function was simulated at molar ratios Mg/P: 1.0, 1.2, 1.5 and 2.0 for two N/P molar ratios: 2.0 and 1.0; the obtained results are shown in Figure 5.

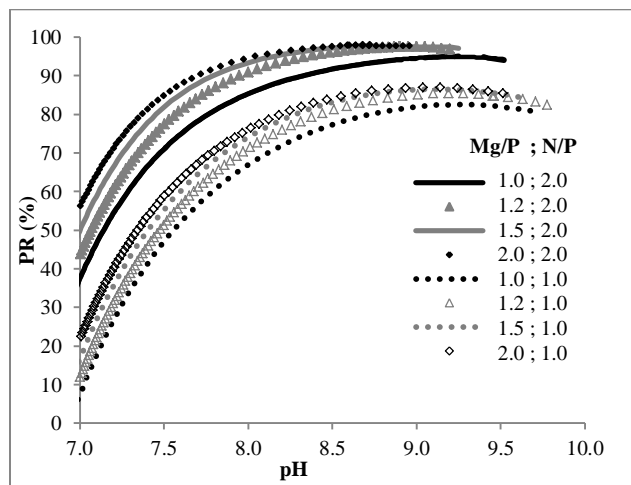


Figure 5. Influence of molar ratios Mg/P (1.0, 1.2, 1.5 and 2.0) and N/P (1.0, 2.0) at different pH on the PR for P-OP=200 ppm at T=25°C.

For the N/P molar ratios evaluated, initially the increases in pH produces a higher PR, likely due to an increase of free  $\text{PO}_4^{3-}$  as a consequence of the successive deprotonation of  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$  and  $\text{H}_3\text{PO}_4$  (Eqs. (15)-(17)). Consequently, the solution supersaturation increases and promotes struvite precipitation. However, this improvement in PR is counteracted by a decrease in the free  $\text{NH}_4^+$  concentration (transformed to  $\text{NH}_3$  (Eq. (22)), which becomes more and more relevant, finally exceeding the positive effect in the supersaturation ratio produced by the first one. Similarly, the reduction in initial concentration of N for the same effluent pH and Mg/P ratio leads to a lower PR, since the free  $\text{NH}_4^+$  is transformed to  $\text{NH}_3$ .

For the two N/P molar ratios evaluated, the increment in Mg/P relations improves the PR, due to a higher concentration of free  $\text{Mg}^{2+}$  in the system. However, at higher pH, the increase in PR is less sensitive to Mg/P, because the negative effect produced by the disappearance of  $\text{NH}_4^+$  in the supersaturation ratio prevails over the  $\alpha_{\text{Mg}^{2+}}$  rise.

Figure 6 shows the optimum pH and the respective maximum PR for each simulated process condition.

The higher relative improve  $\Delta\text{PR}/(\Delta\text{Mg}/\text{P})$  is obtained at molar ratio Mg/P=1.20 for both relations N/P evaluated. At this ratio, for N/P=1.0 the maximum PR of 85.7% is reached at pH=8.94. In practice, for P-OP concentration of 200 ppm the combination of molar ratios N/P=2.0 and Mg/P=1.20 is a good candidate as operational point, because achieves high PR at reasonably low Mg concentration. For this reason, in the following section the effect of ionic strength  $I^*$  in this condition is studied.

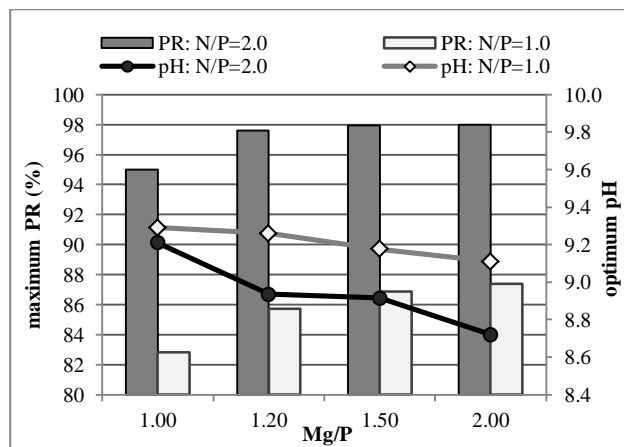


Figure 6. Optimal pH operating conditions and maximum PR (%) at molar ratio Mg/P (1.0, 1.2, 1.5 and 2.0) and N/P (1.0, 2.0) for P-OP=200 ppm at T=25°C.

#### 4.3 Effect of ionic strength

Figure 7 shows the effect of ionic strength produced by nonreactive ions at different pH on the PR.

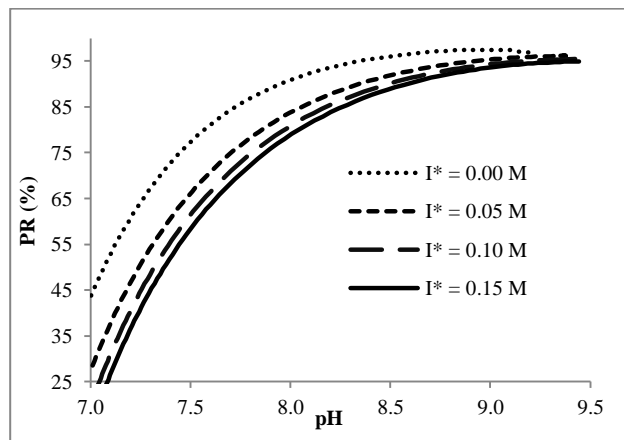


Figure 7. Effect of ionic strength produced by nonreactive ions at different pH on the P removal for P-OP=200 ppm, and the molar ratios Mg/P=1.2, N/P=2 at T=25°C.

An increase in  $I^*$  reduces the PR by solution stabilization and increases the optimum pH as shown in Figure 8.

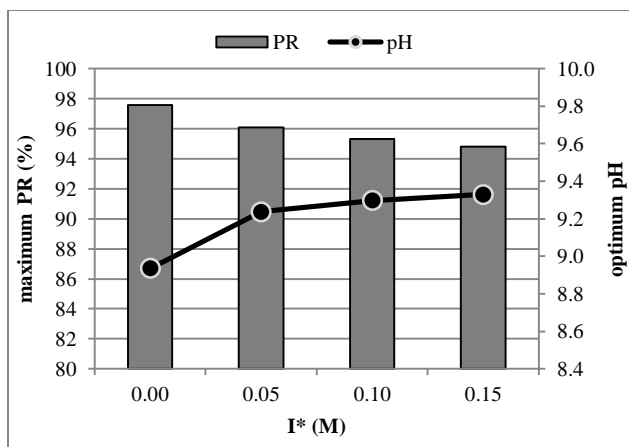


Figure 8. Effect of ionic strength in the optimal pH operating conditions and maximum PR (%) at molar ratios Mg/P = 1.2, N/P = 2, for P-OP= 200 ppm at T=25°C.

## 5. Conclusions

A hybrid optimization procedure combining a PS algorithm and SQP method has been developed to predict the potential P-OP removal as struvite from a wastewater stream with known chemical composition and defined operational precipitation conditions. The hybrid strategy leads to an efficient search: the PS provides good starting points for the subsequent facility local search by the SQP method.

The predicted values matched fairly well with the experimental results for PR and equilibrium pH (in range 7.0-10.0) and for the concentrations tested (P-OP: 200 ppm, Mg/P=1.0 and N/P=2.0).

For the P-OP concentration evaluated (200 ppm) the condition defined by molar ratios N/P=2.0 and Mg/P=1.20 result in a good industrial operation candidate: high PR (97.6%) is achieved at a reasonably lower Mg concentration, which means lower reagents cost.

An increment at ionic strength reduces the maximum PR reached. For P-OP=200 ppm and molar ratios N/P=2.0 and Mg/P=1.20, the maximum PR achieved at  $I^*=0.15$  M is reduced in 2.9% respect to the PR reached at  $I^*=0$  M.

## Acknowledgements

The project that gives rise to the results presented in this publication was funded by CONACYT through PROCENCIA Program Fund resources for Excellence in Education and Research - FEEI from FONACIDE, Paraguay; and from the National Agency for Research and Innovation under the POS\_NAC\_2014\_102893 code, Uruguay. The authors would like to thank two

undergraduate students: María José Matto and Juan Peralta from the Chemistry Faculty of Universidad Nacional de Asunción, for performing some experimental validation tests; and also Dr. Ricardo Faccio, of the Physics Department of the Chemistry Faculty from Universidad de la República, Uruguay for DRX analysis of samples.

## References

- [1] J. Borgerding, Phosphate deposits in digestion systems, *J. Water Pollu (1) C. Fed.* 44, 1972, 813–819.
- [2] P.W. Westerman, J.L.M. Safley & J.C. Barker, Crystalline build-up in swine and poultry flush systems, *Proc. Fifth International Symposium on Agricultural Wastes, American Society of Agricultural Engineers*, St. Joseph, MI, 1985, 613–623.
- [3] K. M. Webb & G.E Ho, Struvite solubility and its application to a piggery effluent problem, *Water Sci. Technol.* 26, 1992, 2229–2232.
- [4] J. Wang, Y. Song, P. Yuan, J. Peng & M. Fan, Modeling the crystallization of magnesium ammonium phosphate for phosphorus recovery, *Chemosphere* 65, 2006, 1182–1187.
- [5] P. Cooper, M. Day & V. Thomas, Process options for phosphorus and nitrogen removal from wastewater, *J. Inst. Water Environ. Manage.* 8, 1994, 84–92.
- [6] A. Uysal, Y.D. Yilmazel, & G.N. Demirer, The determination of fertilizer quality of the formed struvite from effluent of a sewage sludge anaerobic digester, *J. of Hazardous Materials* 181(1-3), 2010, 248-254.
- [7] R.D. Schuling, A. Andrade, Recovery of struvite from calf manure, *Environmental Technology*, 20, 1999, 765–768.
- [8] A.K. Sarkar, Phosphate cement-based fast setting binders, *J. of American Ceramic Society Bulletin*, 69, 1990, 234–238.
- [9] H. Harada, Y. Shimizu, Y. Miyagoshi, S. Matsui, T. Matsuda, & T. Nagasaka, Predicting struvite formation for phosphorus recovery from human urine using an equilibrium model, *Water Sci. Technol.* 54, 2006, 247–255.
- [10] K.N. Ohlinger, T.M. Young & E.D. Schroeder, Predicting struvite formation in digestion, *Water Research*, 32, 1998, 3607–3614.
- [11] J. Wang, J.G. Burken, X. Zhang, & R. Surampalli, Engineered struvite precipitation: Impacts of component-ion molar ratios, *J. Environ. Engng.* 131, 2005, 1433–1440.
- [12] M.I. Ali, P.A. Schneider, A fed-batch design approach of struvite system in controlled supersaturation, *Chem. Eng. Sci.* 61 (12), 2006, 3951-3961.
- [13] S. Gadekar., P. Pullammanappallil, Validation and applications of a chemical equilibrium model for struvite precipitation, *Environmental Modeling and Assessment* 15, 2010, 201–209.
- [14] M. Hanhoun, L. Montastruc, C. Azzaro-Pantel, B. Biscans, M. Freche & L. Pibouleau, Temperature impact assessment on struvite solubility product: a thermodynamic modeling approach, *Chem. Eng. J.* 167, 2011, 50–58.



- [15] M.S. Rahaman, D.S. Mavinic, D.S., A. Meikleham & N. Ellis, Modeling phosphorus removal and recovery from anaerobic digester supernatant through struvite crystallization in a fluidized bed reactor, *Water Res.* 51, 2014, 1-10.
- [16] I. Celen, J.R. Buchanan, R.T. Burns, R.B. Robinson & D.R. Raman, Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure, *Water Res.* 41, 2007, 1689–1696.
- [17] M. Iqbal, M; H. Bhuiyan, & D.S Mavinic, Assessing struvite precipitation in a pilot-scale fluidized bed crystallizer, *Environmental technology*, 29, 2008, 1157-1167.
- [18] M.I.H. Bhuiyan, D.S. Mavinic, F. Koch, Phosphorus recovery from wastewater through struvite formation in fluidized bed reactors: a sustainable approach, *Water Sci. Technol.*, 57(2), 2008, 175-181.
- [19] J.S. Wang, Y.H. Song, P. Yuan, J.F. Peng & M.H. Fan, Modeling the crystallization of magnesium ammonium phosphate for phosphorus recovery, *Chemosphere* 65, 2006, 1182–1187.
- [20] W.G. Harris, A.C. Wilkie, X. Cao & R. Sirengo, Bench-scale recovery of phosphorus from flushed dairy manure wastewater, *Bioresource Technology*, 99, 2008, 3036-3043.
- [21] J.R. Buchanan, C.R. Mote & R.B. Robinson, Thermodynamic of struvite formation. *Am. Soc. Agric. Eng.* 37 (2), 1994, 617–621.
- [22] A. Miles, T.G. Ellis, Struvite precipitation potential for nutrient recovery from anaerobically treated wastes. *Water Sci. Technol.* 43, 2000, 259e266.
- [23] J.D. Doyle, R. Philp, J. Churchley & S.A. Parsons, Analysis of struvite precipitation in real and synthetic liquors, *Transactions of the Institute of Chemical Engineers* 78, 2000, 480-488.
- [24] Environmental Research Software 2012 MINEQL+4.6. Chemical Speciation Modelling for the Real World <http://www.mineql.com/index.html> (last accessed 16 April 2016).
- [25] J.C. Westall, J.L. Zachary & F.M.M Morel, MINEQL A computer program for the calculation of chemical equilibrium composition of aqueous systems. MIT Press, Cambridge, MA, 1976.
- [26] D.L. Parkhurst, C.A.J. Appelo. User's guide to PHREEQC (Version 2) - a computer program for speciation, reaction- path, advective-transport, and inverse geochemical calculations. *USGS water- Resources Investigation Report*, 1999, 99-4259.
- [27] J.D. Allison, D.S. Brown, & K.J.A. Novo-Gradac, 30605: EPA (USA). MINTEQA2/PRODEF2, A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual. EPA, Athens EPA/600/3-91/021, 1991.
- [28] J.P. Gustafsson, Visual MINTEQ, ver 2.32. Royal Institute of Technology, Stockholm, Sweden, Department of Land and Water Resources Engineering, 2005.
- [29] R. Loewenthal, U. Kornmuller, & E. van Heerden, Modelling struvite precipitation in anaerobic treatment systems, *Water Sci. Technol.*, 1994, 30 (12), 107-116.
- [30] S.A. Parsons et al., Assessing the potential for struvite recovery at sewage treatment works, *Environmental Technology*, 22, 2001, 1279-1286.
- [31] J.D. Doyle, S.A. Parsons, Struvite formation, control and recovery, *Water Res.* 36 (16), 2002, 3925-3940.
- [32] N.C. Bouropoulos, P.G. Koutsoukos, Spontaneous precipitation of struvite from aqueous solutions, *J. Cryst. Growth*, 213, 2000, 381–388.
- [33] C.C. Su, R.R.M. Abarca, M.D.G. de Luna, & M.C. Lu, Phosphate recovery from fluidized-bed wastewater by struvite crystallization technology, *J. of the Taiwan Institute of Chemical Engineers*, 45(5), 2014, 2395-2402.
- [34] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, 3rd Ed. (NY: John Wiley and Sons, 1996).
- [35] J.W. Mullin, *Crystallization* (UK: Butterworth-Heinemann Publications, Ipswich, 1993).
- [36] D. Mamais, P.A. Pitt, Y.W. Cheng, J. Loiacono & D. Jenkins, Determination of ferric chloride dose to control struvite precipitation in anaerobic sludge digesters, *Water Environ. Res.* 66(7), 1994, 912–918.
- [37] P. Vieillard, Y. Tardy, *Thermochemical Properties of Phosphates. Ch. Phosphate Mineral* (Springer, 2012).
- [38] National Bureau of Standards Tables of Chemical Thermodynamic Properties. 1982. D.D. Wagman, editor. American Chemical Society and American Institute of Physics for the National Bureau of Standards, Washington DC.
- [39] R.M. Garrels, M.E. Thompson, A chemical model for sea water at 25°C and 1 atmosphere total pressure, *Am. J. Sci.*, 260, 1962, 57-66.
- [40] A.E. Greenberg, L.S. Clesceri, & A.D. Eaton, *Standard Methods for the Examination of Water and Wastewater* (Washington, DC: American Public Health Association (APHA), 2002).