

A thermochemical model approach for struvite precipitation in anaerobically digested sludge dewatering liquid

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Abstract

Struvite precipitation is a promising alternative to remove and recover phosphorous from nutrient rich wastewater. Particularly, the liquid phase exiting anaerobic digestion reactors is an excellent stream to recover nutrients by this process. 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 this work, a thermochemical model for struvite precipitation is presented. Afterwards it is used to study the influence of combined operational conditions: Mg/P molar ratios (1.0, 1.5 and 2.0), N/P molar ratios (8.3 and 2.0), pH (7.0-10.0) and ionic strength produced by nonreactive ions I^* (0.00 M and 0.15 M) on the phosphorus removal efficiency (PR) with similar nutrient concentration to those found on the output of anaerobic reactors. For the conditions considered typical of anaerobically digested sludge dewatering liquid ($N-NH_4^+=750$ ppm and $P-OP=200$ ppm with $I^*=0.15$ M) the highest relative improve in PR respect to Mg/P stoichiometric relations is achieved at a molar ratio Mg/P=1.5, with a maximum PR obtained equal to 99.46% at pH=8.56.

Keywords

Struvite precipitation; ionic strength; anaerobically digested sludge dewatering liquid.

1. INTRODUCTION

Anaerobic digestion is the main technology used for the stabilization of organic solid residues, including (agro)industrial wastes and excess aerobic sludge from treatment of sewage (Mata-Alvarez et al., 2000; Appels et al., 2008; Khalid et al., 2011). However, the main drawback of anaerobic digestion is the low nutrient (nitrogen and phosphorous) removal that it can achieve (van Lier et al., 2008). Therefore, in the anaerobic digestion of solid wastes the concentration of nutrients in the liquid phase that exits the reactor is usually high.

Excess of 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. Furthermore, nutrient recovery has become more and more important in recent years as demand increases. This necessity for recovery is particularly important for phosphorous, as it is becoming an increasingly limited resource (Wang et al., 2006).

The traditional way for removing the nutrients in wastewater treatment is through biological processes: enhanced biological phosphorous removal (EBPR) for phosphorous and nitrification/denitrification for nitrogen (Cooper et al., 1994). However, these solutions have some drawbacks: the large amount of sludge generated and mainly that they remove nutrients but do not recover them.

The fate of the liquid phase that exits an anaerobic reactor varies depending on the type of residue treated. In the case of sewage sludge stabilization the liquid originated from the dewatering of the stabilized sludge (dewatering water) is a sidestream that is usually returned to the head of the plant,

therefore increasing the load in the main line nutrient removal processes. Removal, and if possible recovery of nutrients in this sidestream is an efficient and usually economic way of reducing nutrient load in the main line. In industrial waste treatment, on the other hand, the liquid phase exiting the reactor should be treated before it is discharged. In both cases, the application of novel processes for nutrient removal has been studied. Several novel processes have been developed for the removal of nitrogen in these nutrient rich wastewaters: SHARON, BABE, ANNAMOX (van Loosdrecht, 2008). For phosphorous removal, an alternative has been developed: the controlled crystallization of struvite (magnesium ammonium phosphate hexahydrate).

Controlled struvite crystallization is a chemical process that allows for the recovery of nutrients and provides an added value product: the struvite, which can be used as a slow-release fertilizer that contains phosphorous, nitrogen and magnesium (Uysal et al., 2010). The use of struvite is an effective and sustainable alternative to rock phosphate as a source of phosphorous as a fertilizer in the agricultural production system. Furthermore, struvite can be used 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).

It should also be noticed that anaerobic digestion increases the potential for struvite precipitation, due to the transformations that take place during the degradation of organic matter. Anaerobic digestion increases the ammonia concentration due to degradation of proteins, and the magnesium and phosphate concentrations increase as a consequence of cell lysis. Since only dissolved fraction of these components is able to form precipitates, the precipitation potential is greater after the anaerobic digestion process (Bhuiyan et al., 2007).

Münch and Barr (2001) present a study about controlled struvite crystallization in anaerobic digester sidestreams in an EBPR wastewater treatment plant. The proposed system, shown in Figure 1, is presented as a way of decreasing nutrient load into the main line of the wastewater treatment plant while recovering nutrients, and is a good example of the advantages of focusing on the sidestreams for the removal of nutrients. It can be seen that besides removing and recovering most of the phosphorous on the sidestream, some nitrogen is also recovered from this stream. The results were promising and they concluded that struvite precipitation is a suitable technology to recover phosphorous from sidestreams, particularly on EBPR treatment plants.

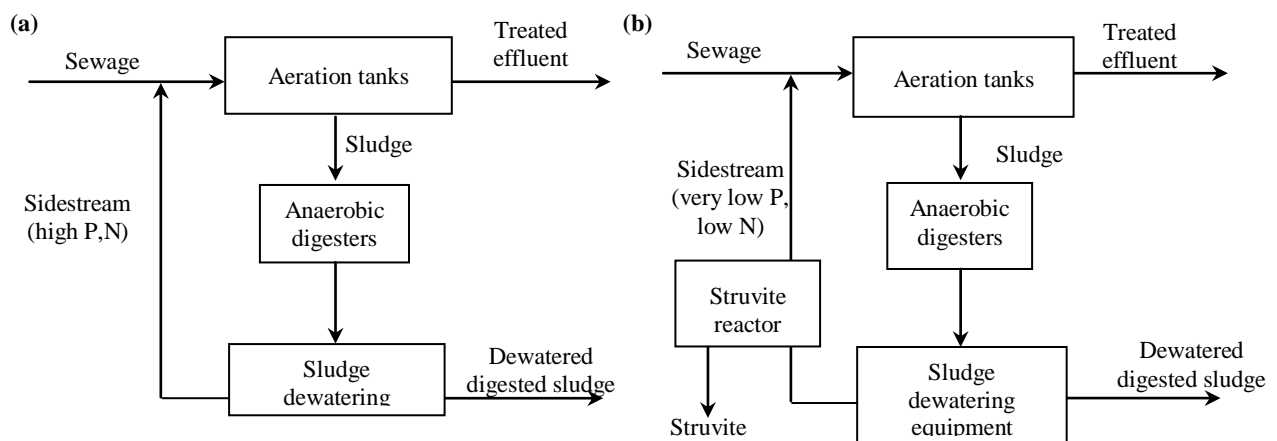


Figure 1. Process flowsheet of EBPR wastewater treatment plant (a) without sidestream treatment and (b) with sidestream treatment by struvite precipitation. Source: adapted from Munch and Barr (2001).

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. Some of these models have been developed for or used to predict this potential in nutrient rich wastewaters, conditions similar to those found after anaerobic digestion of solid residues. Celen et al. (2007) used a chemical equilibrium model (Visual Minteq) to predict the removal of phosphorous in swine wastewater and to propose amendments in order to maximize struvite precipitation. Wang et al. (2005) developed a model to take into account component ion molar ratios and pH in struvite precipitation in the effluent of anaerobic lagoons treating concentrated animal feeding operations wastewater. Gadekar and Pullammanappallil (2010) presented a chemical equilibrium model for struvite precipitation that was validated using several literature experimental data sources, including various nutrient rich wastewaters, both anaerobically digested and fresh.

This paper presents the development of a simple thermochemical model, representative of struvite precipitation when the pH is less than 10.0 to avoid the presence of $Mg(OH)_2$ in the solid phase (Bouropoulos and Koutsoukos, 2000; Su et al., 2014), since it reduces the phosphorous removal (PR) which is defined at Eq. (1).

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

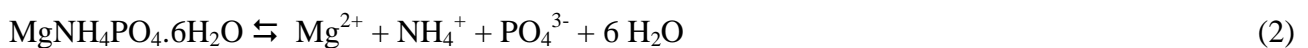
where P_o : orthophosphate phosphorous (P-OP) before treatment ($mg \cdot L^{-1}$); P_f : remaining soluble P-OP after treatment ($mg \cdot L^{-1}$).

The validated model is used to evaluate the influence of pH (7.0–10.0), molar ratios Mg/P (1.0, 1.5 and 2.0), and ionic strength produced by nonreactive ions ($I^*=0.15$ M) presents in the system for a P-OP concentration of 200 ppm and a $N-NH_4^+$ concentration of 750 ppm (molar ratio N/P=8.3), which represents the nutrients concentrations levels of anaerobically digested sludge dewatering liquid for a sewage treatment plant (Fujimoto et al., 1991). Also is study the impact produced by the reduction of $N-NH_4^+$ concentration at 180 ppm (molar ratio N/P=2.0) by simulation with the respective validated model. The maximum PR reached for each tested combination is evaluated.

Even though this work presents results of a simulation at the conditions detailed above, it should be noticed that it can be applied to every condition that can normally be found on the output of an anaerobic system, be it solid digester or wastewater treatment anaerobic reactors.

2. STRUVITE PRECIPITATION

Determining potential PR as struvite implicates first determining struvite equilibrium under the conditions of the process stream: ammonium, magnesium and phosphate ion concentrations, supersaturation ratio, ionic strength, temperature, pH and also reaction time. Crystallization occurs in a supersaturated solution, as a result of the chemical reaction of the free Mg^{2+} , NH_4^+ , and PO_4^{3-} ions and the incorporation of six molecules of water (Eq. (2)) at slightly alkaline conditions.



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

$$K_{SP} = a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{2-}} \quad (3)$$

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 λ_i of the corresponding ion i (Eq. (4)).

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

A measure 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 .

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

The Davies equation (Eq. (6)), an approximation of the Debye-Hückel equation, is capable of performing activity calculations for $I < 0.2$ M (Mullin, 1993); in this work, ionic strength was lower than 0.2 M in all studied cases and therefore it is used to calculate the activity coefficients.

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

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

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

This model includes NaCl concentration to represent the nonreactive ions presents in the system, which provides an additional ionic strength contribution I^* .

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)). 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:

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

$$\alpha_{PO_4^{2-}} = \frac{C_{PO_4^{2-}}}{C_{T,OP}} \quad (11)$$

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

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

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

where $|v_r|=3$; is the number of reactants in anhydrous struvite.

The supersaturation ratio can also be expressed in terms of K_{SP} :

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

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. CHEMICAL EQUILIBRIUM MODEL

3.1 Model formulation

The complexity of the models depends on the number of soluble and solid species considered. This research considers the equations for ionic, dissolved and solid species given in Table 1 and struvite precipitation (Eq (2)). The pK_j values are calculated from K_j values, according to Eqs. (24)-(25).

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

Eq.	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

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

$$K_j = e^{-\frac{\Delta G_R^0}{RT}} \quad (25)$$

where R is the gas constant, and ΔG_R° is the free energy of reaction at 25°C given by:

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

$\Delta G_{f,p}^\circ$ and $\Delta G_{f,r}^\circ$ are the free energies of formation or chemical potential values μ_i for products and reactants respectively, v_p and v_r are the stoichiometric coefficients of products and reactants.

The K_{SP} for struvite used in this work is 13.26 (Ohlinger et al., 1998) and the chemical potential values at 25°C considered were taken from Vieillard and Tardy (2012) and Wagman et al. (1982).

On 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 6.0-9.0 and is reported to have a low precipitation rate (Mamais et al., 1994). On 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 (Su et al., 2014) is neglected, to study the range of pH in which it is possible to maximize PR.

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 μ_j 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 be taken into account in the two considered phases k : solid S (struvite) and liquid L (the aqueous solution).

To determine the equilibrium concentration species at equilibrium it is therefore necessary to minimize G . It is also mandatory that the mass and electroneutrality balances are satisfied (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:

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

Mass balance for ammonium:

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

Electroneutrality:

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

(33)

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 (as appropriate) and $MgCl_2$ 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 for the 10 reactions involved in the model are satisfied (10 nonlinear equality constraints). Eq. (34) represents those equilibria.

$$pK_j + \log \prod_{i=1}^n (a_i)^{v_i} = 0 \quad (34)$$

The formation of complexes with Cl^- or Na^+ are neglected, based on Garrels and Thompson (1962), just like complexes created by more than two ions.

3.2 Solving the thermodynamic model

This is a constraint nonlinear optimization problem, with 10 nonlinear equality constraints and 4 linear equality constraints. To guarantee the success of the optimization procedure this work proposes the generation of good starting points which are used to perform the optimization with SQP method in MATLAB environment. A preliminary search in the solution space with $28 \cdot 10^3$ evaluations to locate the neighborhood of the solution is performed with a pattern search algorithm (PS). Then, using the solution found with the PS as initial guess, the gradient-based algorithm SQP is applied.

The input data to calculate the equilibrium conditions includes characteristics of a particular influent: $C_{T,OP}$, C_{T,NH_4} , $C_{T,Mg}$, C_{NaOH} or C_{HCl} (added to adjust pH), I^* (in this work equal to 0.15 M or 0.00 M), and thermodynamic data at 25°C (μ_{iL}° , μ_{iS}° , pK_{SP}).

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 a linear programming is proposed, with the 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 representative of anaerobically digested sludge dewatering liquid concentration: 200 ppm P-OP and 750 N- NH_4^+ (molar ratio N/P=8.3). To study the impact of reducing the NH_4^+ concentrations (or N/P molar ratio), the model was also validated using the same representative P-OP concentration with lower N- NH_4^+ concentration: 180 ppm (N/P=2.0).

The experiments were performed at 25°C at atmospheric pressure, 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. The equilibrium state is confirmed by the pH stabilization (equilibrium pH: pH). The pH was measured initially (initial pH: pH₀) and every 30 min. NaOH (1 N) or HCl (1 N) were used to adjust pH₀ as appropriate in the range 7.5-10.0. The synthetic feed with N/P=2.0 were prepared by (NH₄)₂HPO₄ dissolution in distilled water. For N/P=8.3, NH₄Cl is also added as required to achieve the desired N-NH₄⁺ concentration. The source of Mg (4000 ppm) was a water solution of MgCl₂.6H₂O added at 155 ppm in all the assays; for achieve a molar ratio Mg/P=1.0 in both validation experiences.

Samples of 50 mL were taken from each treatment and centrifuged for 15 minutes (Sigma 3-16KL) at 4500 rpm to separate the precipitated struvite before measuring the residual dissolved P-OP. The concentration of P-OP dissolved in the samples was measured using the method of ammonium vanadomolybdate (APHA, 2005) using a UV-Vis spectrophotometer (Spectronic 21 - Bausch & Lomb). Additionally, 500 mL were taken from the assays when the equilibrium pH was 7.3, 8.5 and 10.0 for the test with N/P=2.0 and 7.6 and 10.0 for N/P=8.3 and filtrated with 0.45 µm filter paper. The crystals were dried at room temperature and analysed with X-ray diffraction that confirmed the presence of pure struvite in all cases.

To determinate the experimental error some tests were performed in triplicate: for N/P=8.3 analyses with pH₀ 7.5, 8.3 and 10.0, and treatments with pH₀ 8.52 and 9.50 for N/P=2.0.

4. RESULTS AND DISCUSSION

4.1 Testing the validity of the model

Figure 2 shows simulated and measured PR (%) for the range of equilibrium pH 6.9-10.0 for N/P=2.0, and pH 6.6-10.0 for N/P=8.3; with P-OP=200 ppm at Mg/P=1 and T=25°C.

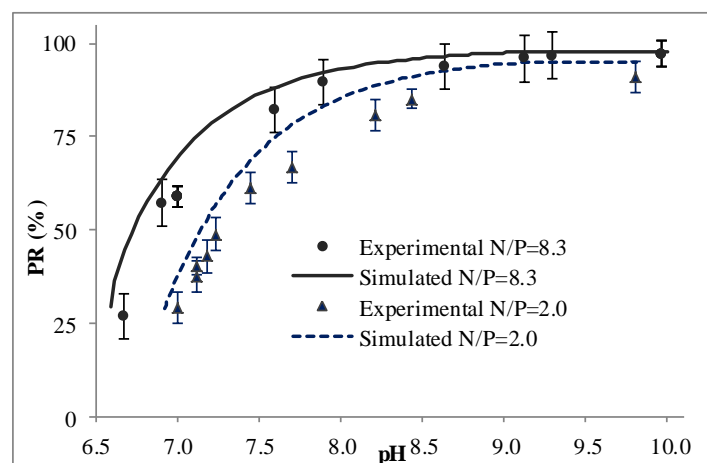


Figure 2. Predicting and measured PR (%) as struvite for P-OP=200 ppm, Mg/P=1 for N/P=2.0 and N/P=8.3 at T=25°C.

The validation can be assessed by comparing the simulated (y) and experimental data (x) for PR and equilibrium pH. Figure 3(a) exhibits a high correspondence between the experimental and simulated data sets for PR at both N/P molar ratios evaluated ($R^2=98.7\%$ and $R^2=98.3\%$ for N/P=8.3 and N/P=2.0 respectively). Figure 3(b) exhibits a high correspondence between the experimental and simulated data sets for equilibrium pH ($R^2=99.7\%$ and $R^2=98.9\%$ for N/P=8.3 and N/P=2.0 respectively). The high correspondences ($y=x$) and slopes close to 1.0 reflect the successful validation of the proposed model for both N/P molar ratios evaluated.

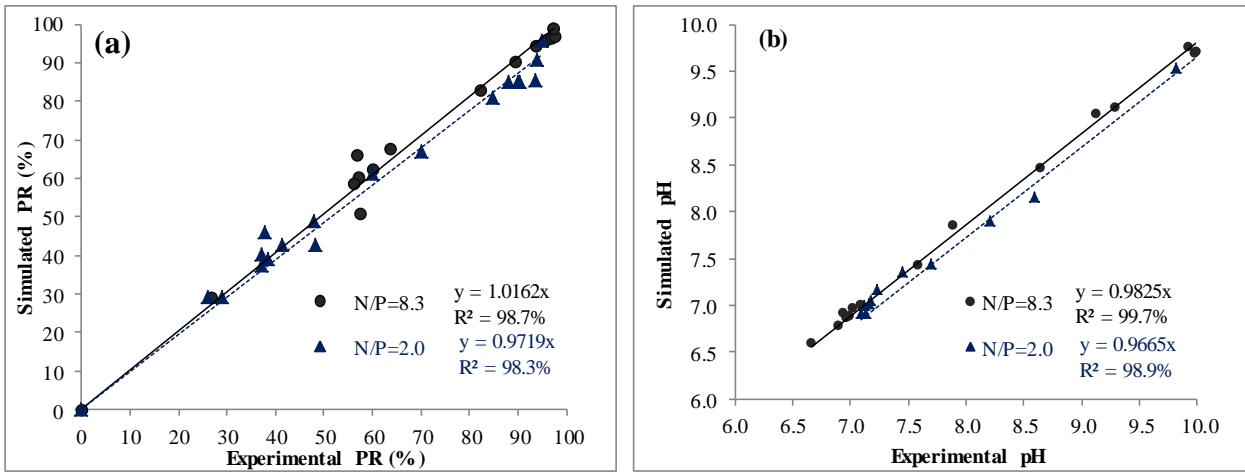


Figure 3. Linear correlations for simulated and experimental data: P-OP=200 ppm, Mg/P=1.0 and T=25°C at molar ratios N/P=8.3 and N/P=2.0 (a) PR (%); (b) pH.

4.2 Influence of combined operational conditions on the phosphorus removal with different ionic strength

Using the developed model, the PR as a pH function was simulated at molar ratios Mg/P: 1.0, 1.5 and 2.0 for two N/P molar ratios: 8.3 and 2.0, varying the ionic strength produced by the non-reactive ions (I^*) presents in the system. Results are shown in Figure 4. Figure 5 shows the maximum PR reached at optimum pH for simulated cases.

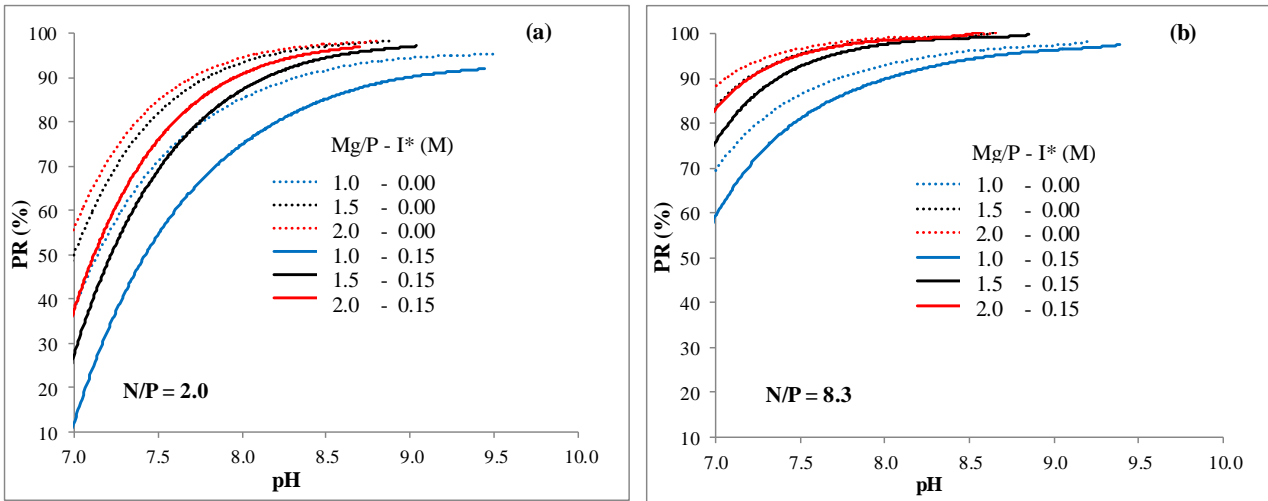


Figure 4. Influence of molar ratios Mg/P (1.0, 1.5 and 2.0), pH (7.0–10.0) and I^* (0.00 M, 0.15 M) on the PR for P-OP= 200 ppm at T=25°C for (a) N/P=2.0; (b) N/P=8.3.

Figures 4 and 5 demonstrate that phosphate removal efficiency increases with N/P molar ratio inside the reactor for same operational pH, Mg/P molar ratio and I^* . Previous research suggested the same results, and claimed that a stoichiometric excess of ammonium would favour struvite precipitation (Stratful et al., 2001).

In all simulated cases, the PR improvement produced by increment the N/P molar ratio is more significant at lower pH than at higher pH (Figure 4). The relative percentage reduction in PR produced by decrease N/P from 8.3 to 2.0 are shown in Table 2; the negative impact is more pronounced at low pH, low Mg/P and high I^* .

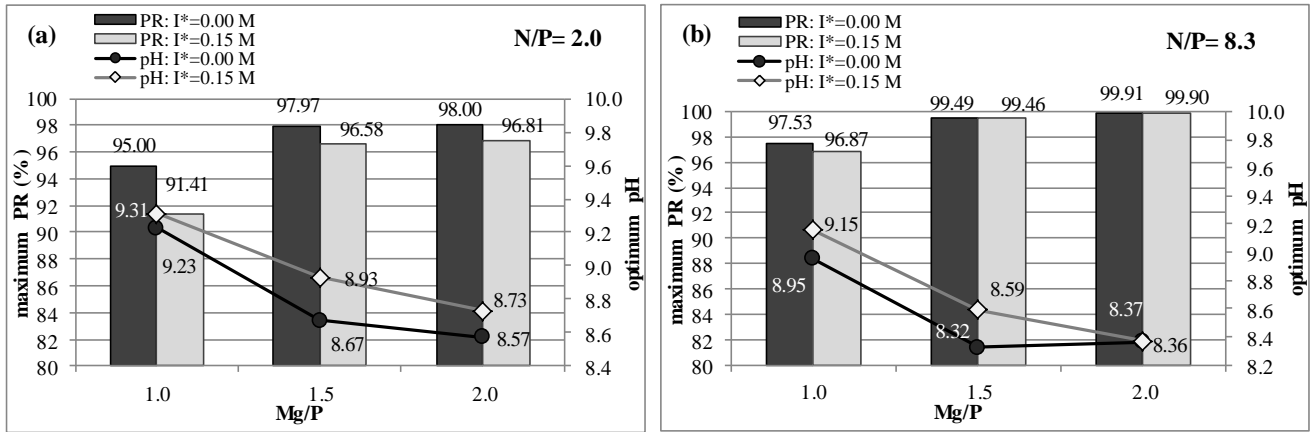


Figure 5. Optimal pH and maximum PR (%) for P-OP =200 ppm at T=25°C for two N/P molar ratios: (a) N/P=2.0; (b) N/P=8.3.

Table 2. Relative effects in PR (%) produced by influence of combined operational conditions on the phosphorus removal with P-OP=200 ppm at T=25°C.

Relative percentage reduction produced in maximum PR by decrease in N/P molar ratio					
	Mg/P	1.00	1.50	2.00	
Optimal condition	I* = 0.00 M	-2.59	-1.53	-1.92	
	I* = 0.15 M	-5.64	-2.90	-3.09	
At pH=7.0	I* = 0.00 M	-47.29	-42.33	-35.01	
	I* = 0.15 M	-81.25	-63.05	-53.82	
Sensibility and relative percentage improvement in maximum PR by increment in excess Mg/P stoichiometric ratio					
	I* (M)	0.00		0.15	
	Mg/P	1.50	2.00	1.50	2.00
N/P 2.0	Percentage relative improvement in maximum PR	3.12	3.15	5.65	5.91
	$\Delta PR/(\Delta Mg/P)$	5.92	2.99	10.33	5.40
N/P 8.3	Percentage relative improvement in maximum PR	2.01	2.45	2.67	3.13
	$\Delta PR/(\Delta Mg/P)$	3.92	2.39	5.17	3.03
Relative percentage reduction produced in PR by increment in I*					
	Mg/P	1.00	1.50	2.00	
Optimal condition	N/P = 2.0	-3.78	-1.42	-1.21	
	N/P = 8.3	-0.67	-0.03	-0.01	
At pH=7.0	N/P = 2.0	-70.35	-43.98	-33.55	
	N/P = 8.3	-16.63	-1.98	-1.04	

For both assayed N/P molar ratios and independently of I*, a stoichiometric excess of Mg improve the achieved PR (Figures 4 and 5), although this improvement is least significant as Mg/P increases. This result coincides with the work of Demeestere et al. (2001) which reports that the phosphorus removal efficiency was not found to change significantly after a Mg/P ratio around 2. Table 2 demonstrates this increase in terms of sensibility $\Delta PR/(\Delta Mg/P)$; the positive impact in the PR produced by increase in Mg/P is more significant at lower N/P and higher I*.

The ionic strength impacts negatively in PR because the solution stabilization increases the conditional solubility product. This impact is more relevant at low pH, N/P and Mg/P molar ratios as shown in Table 2.

4.3 Chemical explanation

Figure 6 shows the ionization fraction of struvite components in equilibrium at the simulated conditions. Ionization fraction of Mg^{2+} at high pH values and ionization fraction of NH_4^+ presents negative trend with respect to pH, whereas ionization fraction of PO_4^{3-} showed a positive trend in all the evaluated range.

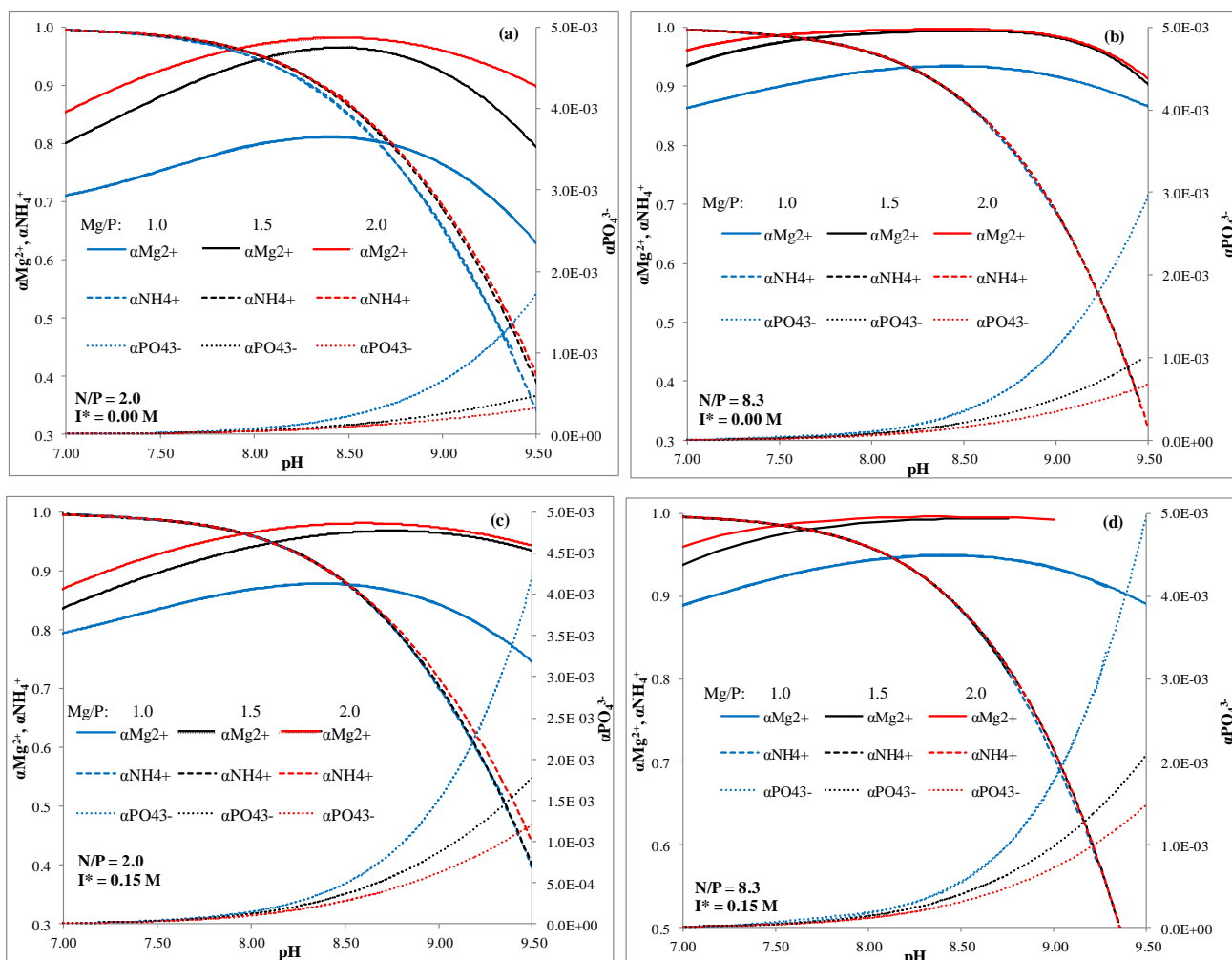


Figure 6. Ionization fraction of struvite components at different equilibrium pH and Mg/P molar ratios for P-OP=200 ppm and $T=25^\circ\text{C}$ with (a) $\text{N/P}=2.0$, $I^*=0.00\text{ M}$; (b) $\text{N/P}=8.3$, $I^*=0.00\text{ M}$; (c) $\text{N/P}=2.0$, $I^*=0.15\text{ M}$; (d) $\text{N/P}=8.3$, $I^*=0.15\text{ M}$.

Initially the increases in pH produces higher PR independently of I^* , Mg/P or N/P applied, likely due to an increase of free PO_4^{3-} (dotted lines), as a consequence of the successive deprotonation of HPO_4^{2-} , H_2PO_4^- and H_3PO_4 that promotes solution supersaturation and consequently struvite precipitation. However, this improvement in PR is counteracted by decrease in the free NH_4^+ concentration which is transformed to NH_3 (hatched lines) and 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 NH_4^+ is transformed to NH_3 .

The increment in Mg/P relations improves the PR, due to a higher concentration of free 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 NH_4^+ in the supersaturation ratio prevails over the free Mg^{2+} rise.

The increase in I^* produces an increment in free Mg^{2+} , PO_4^{3-} and NH_4^+ . This increment is not sufficient to counteract the decrease in activity coefficients λ of struvite components produced by the high charges Z from these ions in solution (Eq. (6)). The net effect is a decrease in the achieved PR for the same operational conditions.

CONCLUSIONS

A hybrid optimization procedure combining a PS+SQP algorithm 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 model was validated using nutrient representative concentrations of anaerobically digested sludge dewatering liquid: 200 ppm P-OP with 750 N- NH_4^+ (molar ratio N/P=8.3) and 180 N- NH_4^+ (molar ratio N/P=2.0) showing good correlations with the experimental data in both cases: $R^2=98.7\%$ and $R^2=98.3\%$ for PR and $R^2=99.7\%$ and $R^2=98.9\%$ for equilibrium pH respectively.

Independently of I^* and N/P, a stoichiometric excess of Mg improve the achieved PR although this improvement is least significant as Mg/P increases. The positive impact in the PR produced by increase in Mg/P is more significant at lower N/P and higher I^* .

The phosphate removal efficiency decreases with the N- NH_4^+ concentration at all pH evaluated for same operational Mg/P molar ratio and I^* . The relative percentage reduction is more pronounced at low pH, low Mg/P and high I^* .

The increase in I^* produces a decrease in the achieved PR for the same operational conditions. This negative impact is more relevant at low pH, N/P and Mg/P molar ratios.

For the conditions considered typical of anaerobically digested sludge dewatering liquid (N- $NH_4^+=750$ ppm and P-OP=200 ppm with $I^*=0.15$ M) the highest relative improve in PR respect to Mg/P stoichiometric relations is achieved at a molar ratio Mg/P=1.5. The maximum PR obtained was 99.46% at pH=8.56. Even though this work presents results of a simulation at the conditions detailed above, it should be noticed that it can be applied to every condition that can normally be found on the output of an anaerobic system.

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