Modelling the thermodynamic equilibrium of struvite precipitation as an alternative to remove and recover P from nutrient rich wastewater

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PROBLEM STATEMENT

P: the limiting resource of agriculture

Eutrophication

Uncontrolled struvite deposition

INTRODUCTION

Anaerobic treatment of agroindustrial wastes -like slaughterhouse wastewater- is a powerfull technology to remove the organic content. However the nutrient content of the treated wastewater or the anaerobically digested dewatering liquid remains almost unchanged. Excess of nutrients may cause eutrophication of aquatic systems, difficulties for water supply and crystalline deposits by uncontrolled deposition of phosphate salts in the treatment systems. Nutrient recovery has become more important in recent years as demand increases. Recovery is particularly important for P, as it is becoming an increasingly limited resource.

OBJECTIVE

Predict potential nutrient removal from a wastewater stream of known chemical composition and under defined operating precipitation conditions to design the crystallization reactors and to define the optimum operating conditions for each influent and to evaluate the operational efficiency.

STRUVITE PRECIPITATION

$$Mg^{2+} + NH_4^+ + PO_4^{3-} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O$$

Ionization fraction:

$$\alpha_{ion^{charge}} = \frac{C_{free\_ion}}{C_{T,free+combined}}$$

To precipitate Supersaturation>1:
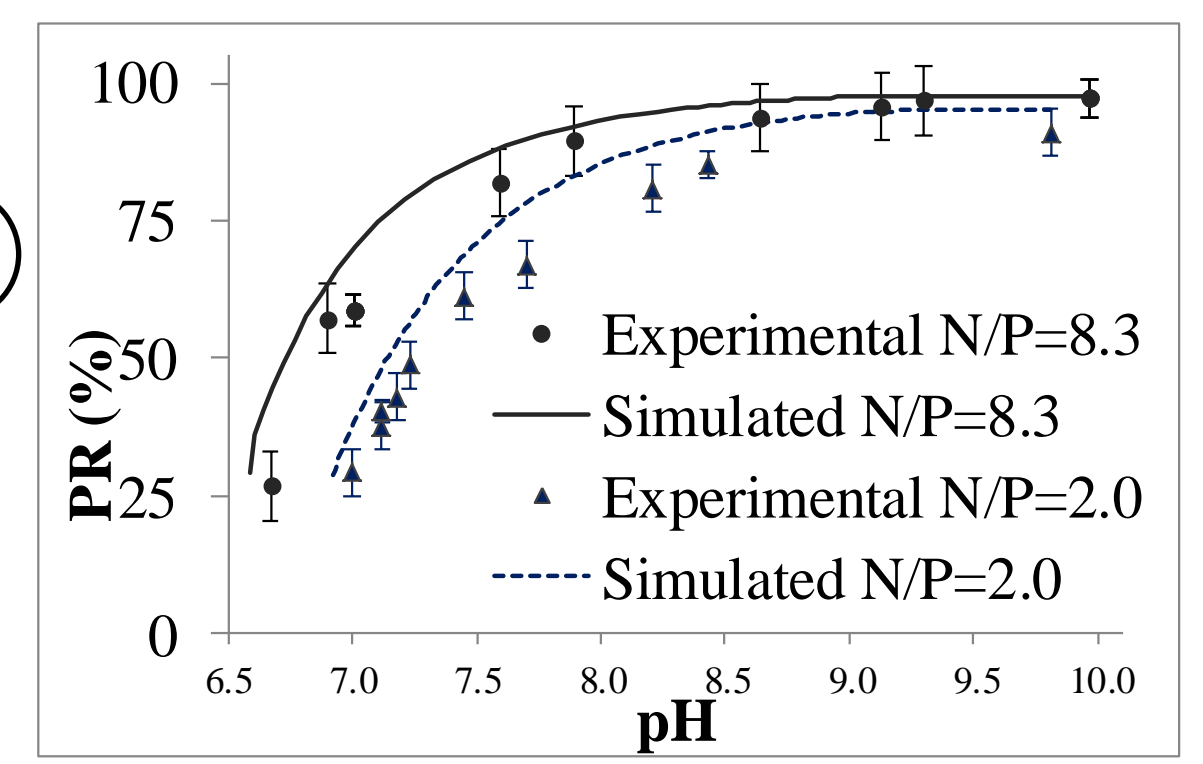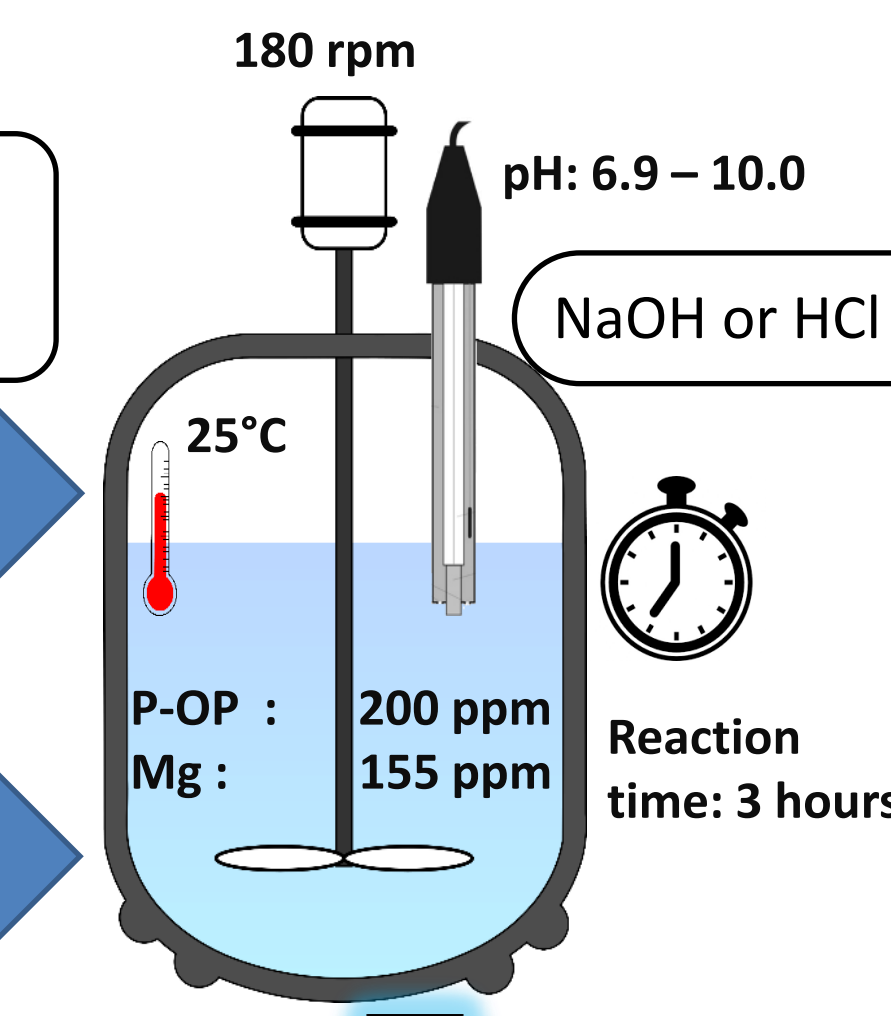
$$S_C = \left(\frac{P_S}{P_{seq}}\right)^{1/3} > 1$$

MODEL VALIDATION
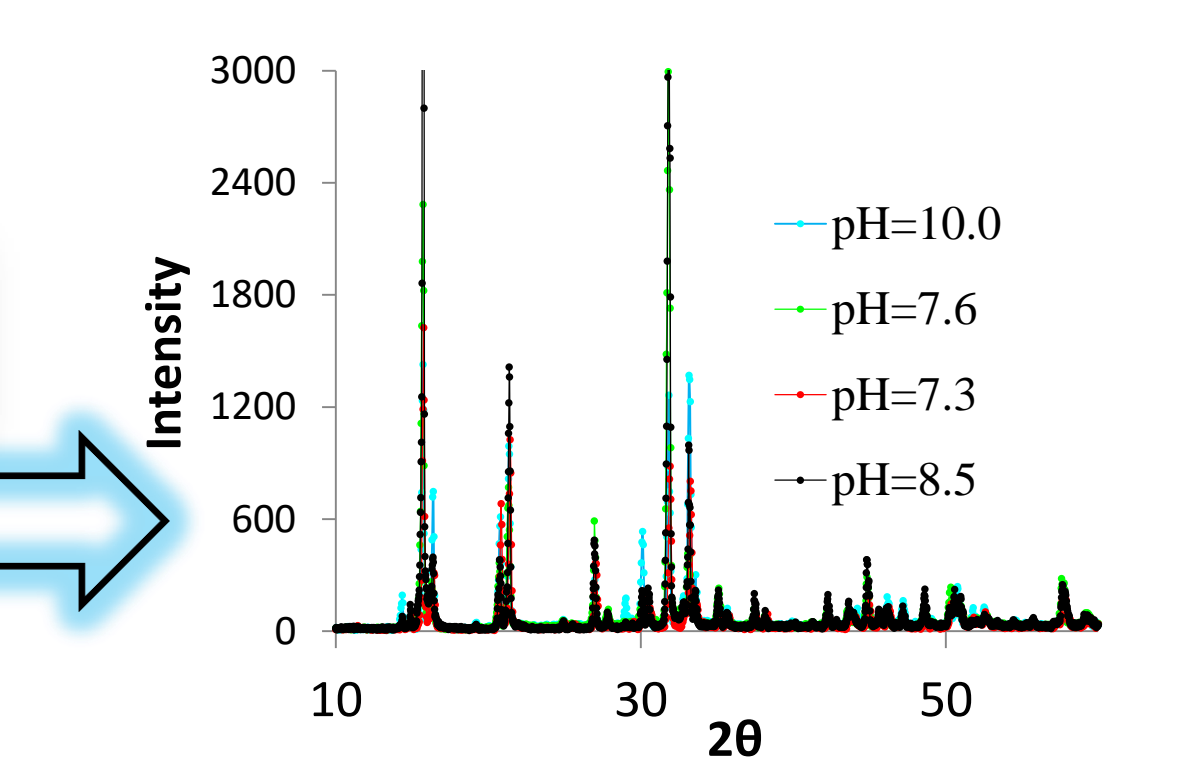
Synthetic wastewater solution: $(NH_4)_2HPO_4$, NH_4Cl

NaOH or HCl

180 rpm — pH: 6.9 – 10.0

25°C — P-OP: 200 ppm — Mg: 155 ppm — Reaction time: 3 hours

Mg/P = 1.0
N/P = 2.0 and 8.3 — $MgCl_2 \cdot 6H_2O$

DRX

Predicted 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.

PR (%) vs pH: Experimental N/P=8.3, Simulated N/P=8.3, Experimental N/P=2.0, Simulated N/P=2.0

Intensity vs 2θ: pH=10.0, pH=7.6, pH=7.3, pH=8.5

THERMODYNAMIC MODEL FORMULATION

Input Data Concentrations: $C_{T,OP}$, C_{T,NH_4}, $C_{T,Mg}$, C_{NaOH} or C_{HCl}, C_{NaCl}
Thermodynamic data Guess: pK_4, pK_6, pK_{SP}

Calculus of ADH, ΔG_R°, Kj and bounds

Linear programming only with mass balances and electroneutrality as constraints — Initial Point: Guess 1

pK_4, pK_6, pK_{ip} — No

Minimum? — Fobj MLE — Calculus of pH, I, equilibrium concentrations and PR

$$PR = \frac{P_0 - P_f}{P_0}$$

Minimum reached? — Yes / No

Nonlinear optimization using modified Davies model for the activity coefficients γ_i and SQP algorithm ($1.4 \cdot 10^3$ evaluations)

Initial Point: Guess 2

Approximate resolution with PS algorithm using modified Davies model for the activity coefficients γ_i — Initial Point, after $1.4 \cdot 10^3$ evaluations

Objective Function

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

$$\mu_{iL} = \mu_{iL}^\circ(T) + RTln(C_i\gamma_i)$$
$$\mu_{iS} = \mu_{iS}^\circ(T)$$

Initial Point, after $56 \cdot 10^3$ evaluations

Nonlinear optimization using modified Davies model for the activity coefficients γ_i and SQP algorithm

Minimum? — Yes — Stop

Minimum reached? — Yes

j	Considered Reactions	pK_j
(1)	$H_3PO_4 \leftrightarrows H_2PO_4^- + H^+$	2.15
(2)	$H_2PO_4^- \leftrightarrows HPO_4^{2-} + H^+$	7.21
(3)	$HPO_4^{2-} \leftrightarrows PO_4^{3-} + H^+$	12.34
(4)	$MgH_2PO_4^+ \leftrightarrows H_2PO_4^- + Mg^{2+}$	?
(5)	$MgHPO_4 \leftrightarrows HPO_4^{2-} + Mg^{2+}$	2.91
(6)	$MgPO_4^- \leftrightarrows PO_4^{3-} + Mg^{2+}$	?
(7)	$MgOH^+ \leftrightarrows Mg^{2+} + OH^-$	2.56
(8)	$NH_4^+ \leftrightarrows NH_{3(aq)} + H^+$	9.25
(9)	$H_2O \leftrightarrows OH^- + H^+$	14.00

$$K_{PS} = a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}$$

$$a_i = \gamma_i \cdot [C_i] \qquad pK_{PS} = ?$$

Calculated with Davies Equation:

$$log\gamma_i = -A_{DH}\, Z_i^2\left[\left(\frac{I^{0.5}}{1+I^{0.5}}\right) - 0.3I\right]$$

With ionic strength calculated by Lewis and Randall Equation:

$$I = 0.5\sum C_i Z_i^2$$

I^* represents the ionic strength produced by nonreactive ions in the system

RESULTS AND DISCUSSION

(a) PR (%) vs pH, N/P = 2.0; (b) PR (%) vs pH, N/P = 8.3. Mg/P - I* (M): 1.0 - 0.00; 1.5 - 0.00; 2.0 - 0.00; 1.0 - 0.15; 1.5 - 0.15; 2.0 - 0.15

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.

Optimum 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.
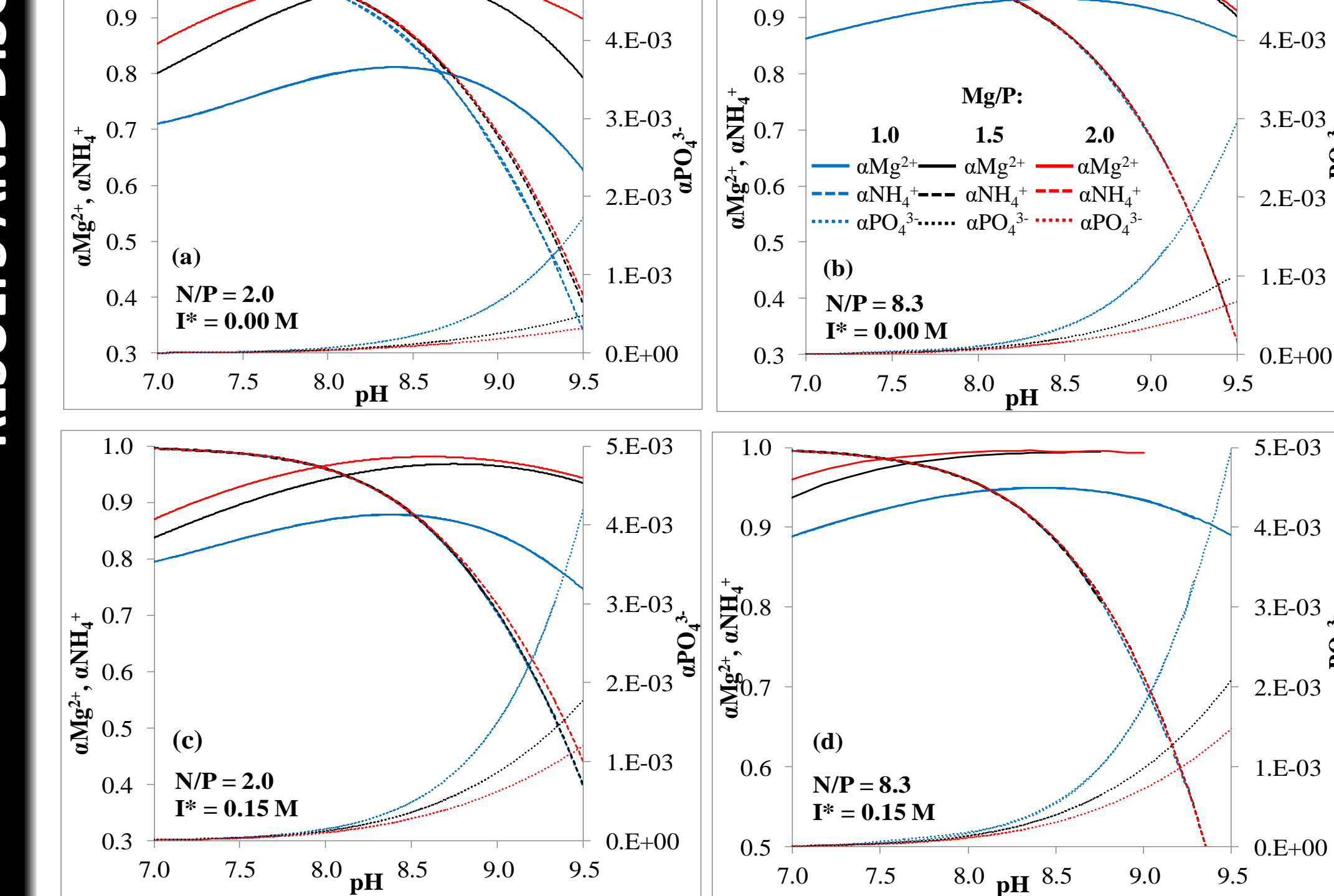
Ionization fraction at different equilibrium pH and Mg/P molar ratios for P-OP=200 ppm and T=25°C with (a) N/P=2.0, I*=0.00 M; (b) N/P=8.3, I*=0.00 M; (c) N/P=2.0, I*=0.15 M; (d) N/P=8.3, I*=0.15 M.

Initially ⇧ pH produces ⇧ PR likely due to ⇧ of free PO_4^{3-} as a consequence of the successive deprotonation of HPO_4^{2-}, $H_2PO_4^-$ and H_3PO_4. This ⇧ in PR is counteracted by ⇩ in the free NH_4^+ which is transformed to NH_3.

⇧ Mg/P ⇧ PR, due to a ⇧ of free Mg^{2+}. At higher pH, the ⇧ in PR is less sensitive to Mg/P, because the negative effect produced by ⇩ NH_4^+ prevails.

⇧ I produces ⇧ in free Mg^{2+}, PO_4^{3-} and NH_4^+. This ⇧ is not sufficient to counteract the ⇧ in γ of struvite components produced by the high charges Z from these ions.

CONCLUSIONS

▶ A **hybrid optimization procedure** combining **Pattern Search (PS) + Sequential Quadratic Programming (SQP)** algorithm has been developed to minimize Gibbs free Energy and to **predict the potential P-OP removal as struvite** from wastewater.

▶ The **maximum likelihood estimation method (MLE)** was applied to estimate the **pK for reactions 4, 6 and pK_PS** resulting: **0.45, 6.58** and **13.26** respectively, according to [1], [2] and [3].

▶ **Excess of Mg improve PR** although this improvement **is least significant as Mg/P increases**. The **positive impact** in PR produced **by increase in Mg/P** is **more significant at lower N/P and higher I***.

▶ **PR decreases with the N-NH₄⁺ concentration**. 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-NH₄⁺ = 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.
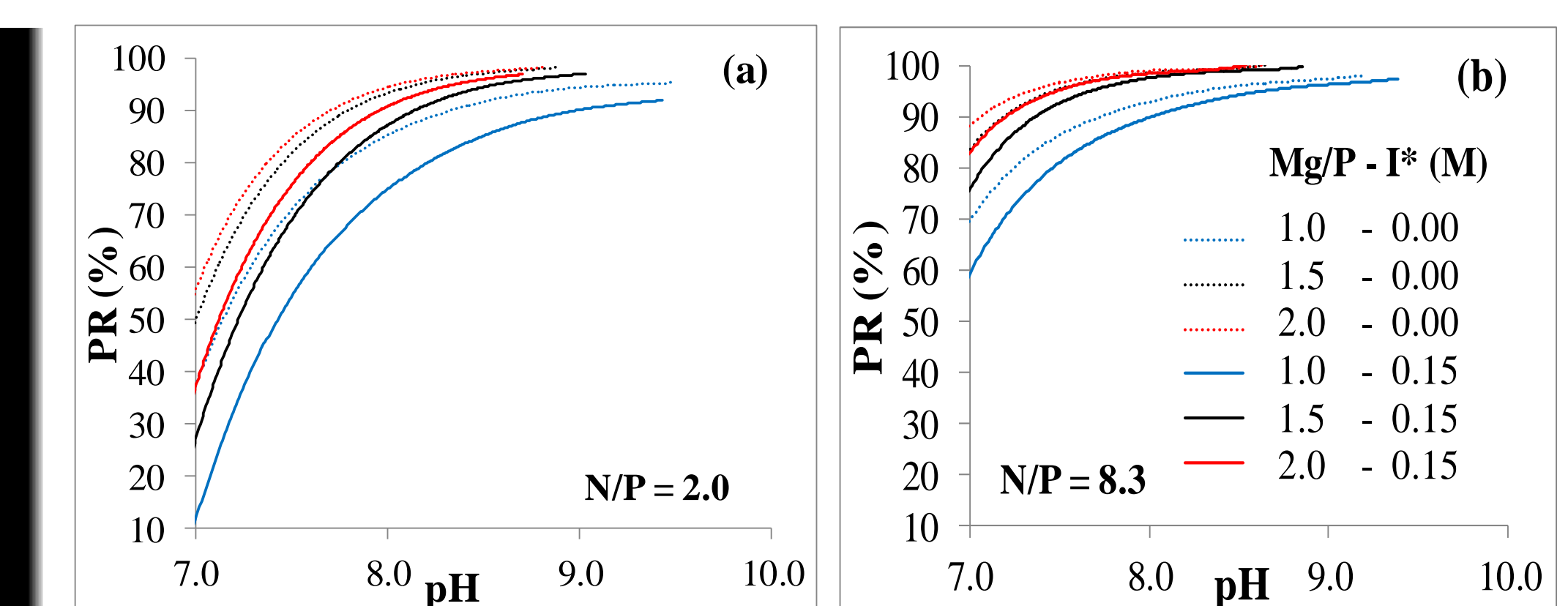
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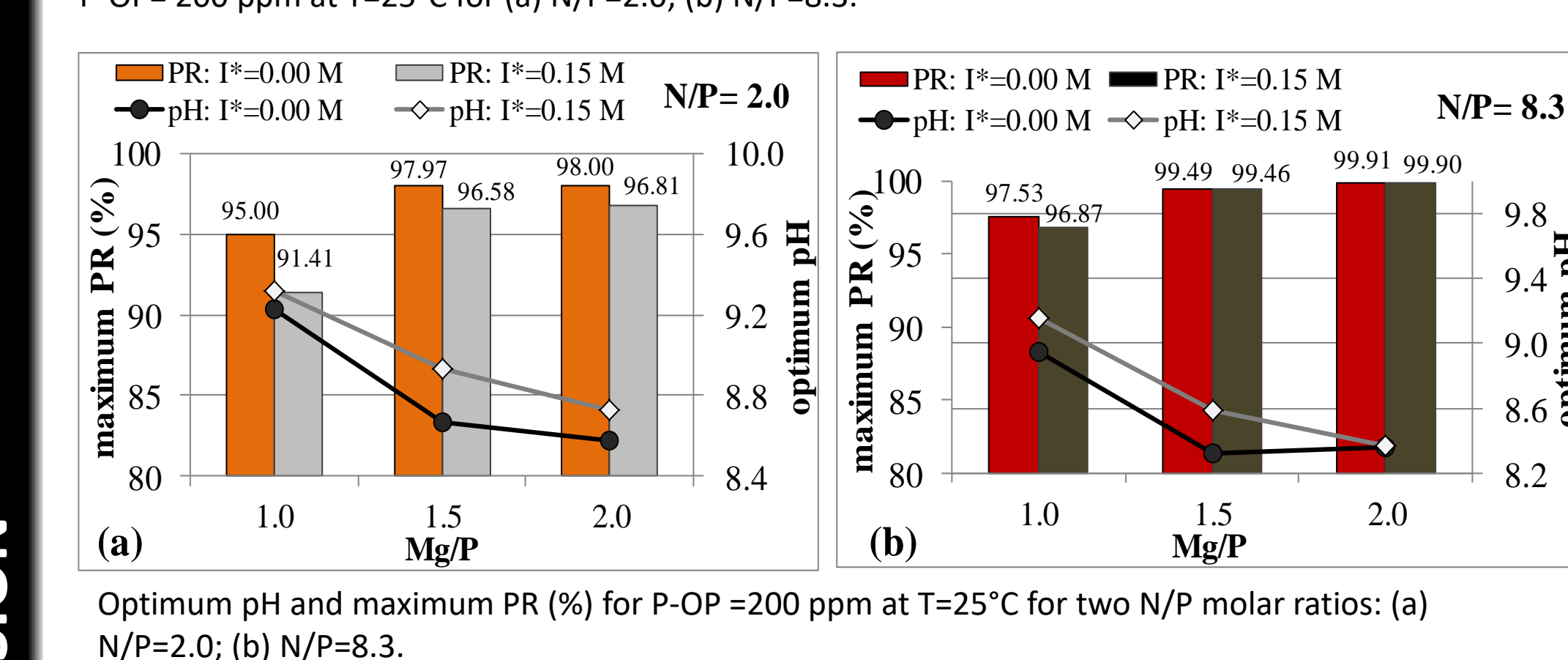
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