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

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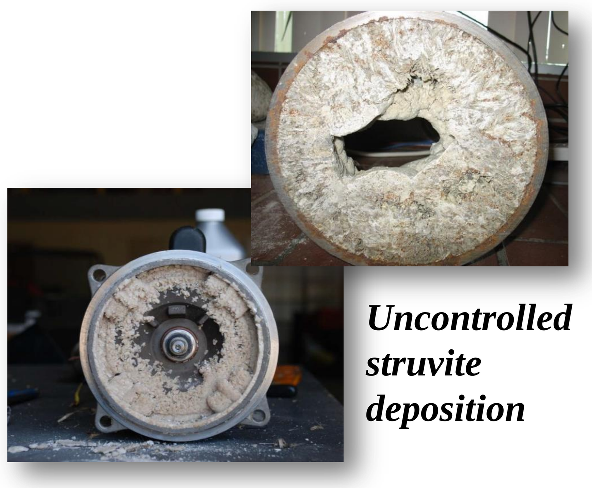
PROBLEM STATEMENT

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

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

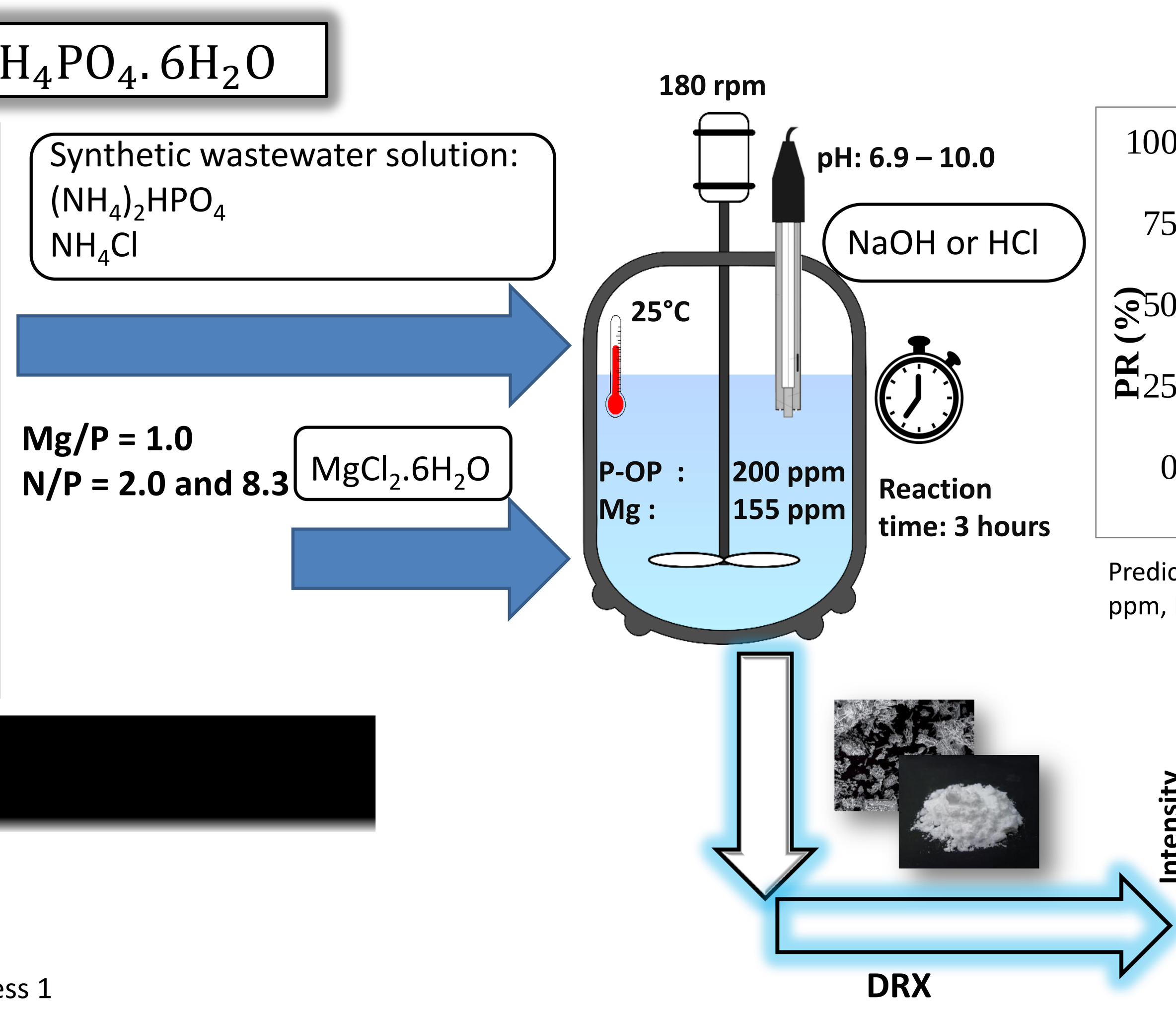
Ionization fraction:

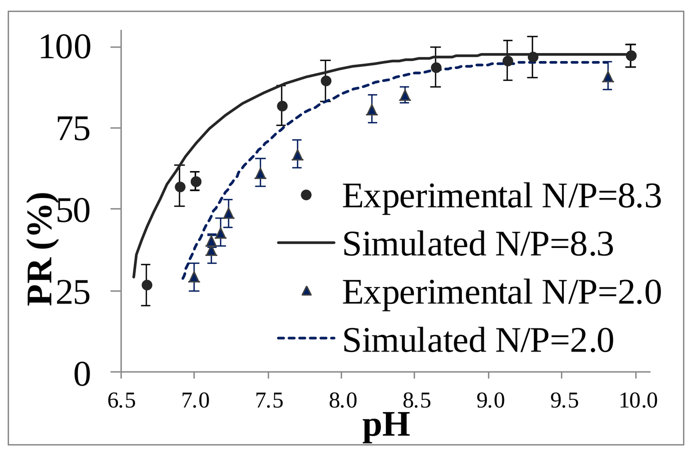
$$\alpha_{ion^{charge}} = \frac{C_{free\_ion}}{C_{T,\,free+combined}}$$

To precipitate Supersaturation>1:

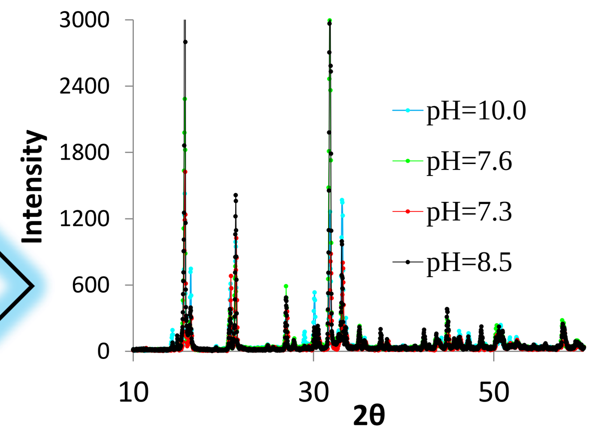
$$S_C = \left(\frac{P_S}{P_{Seq}}\right)^{1/3} > 1$$

MODEL VALIDATION

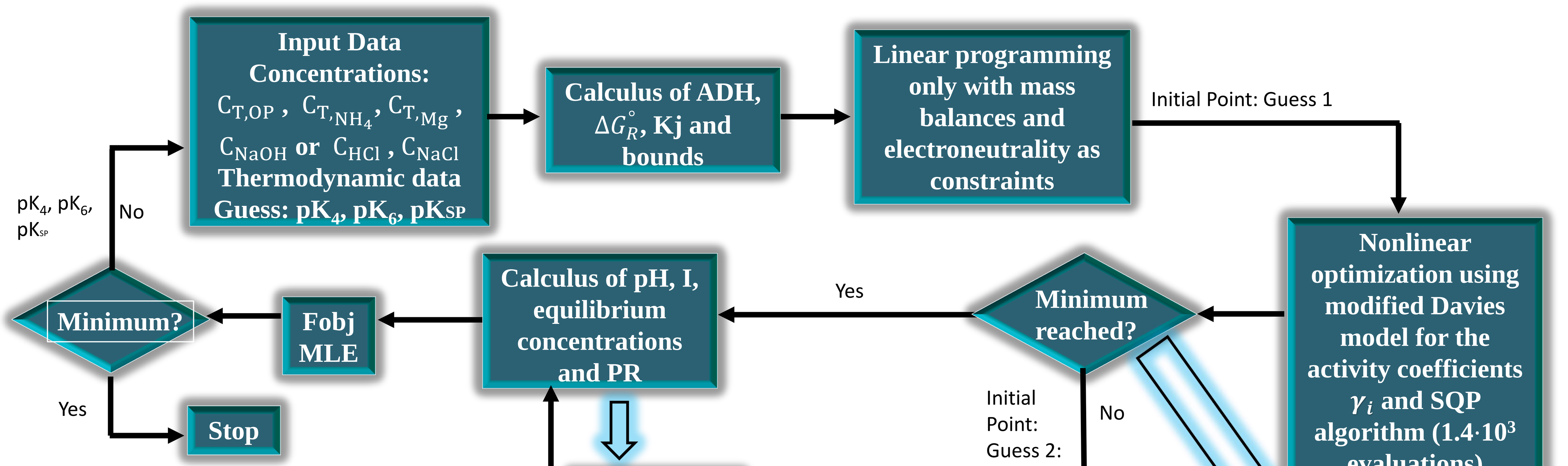


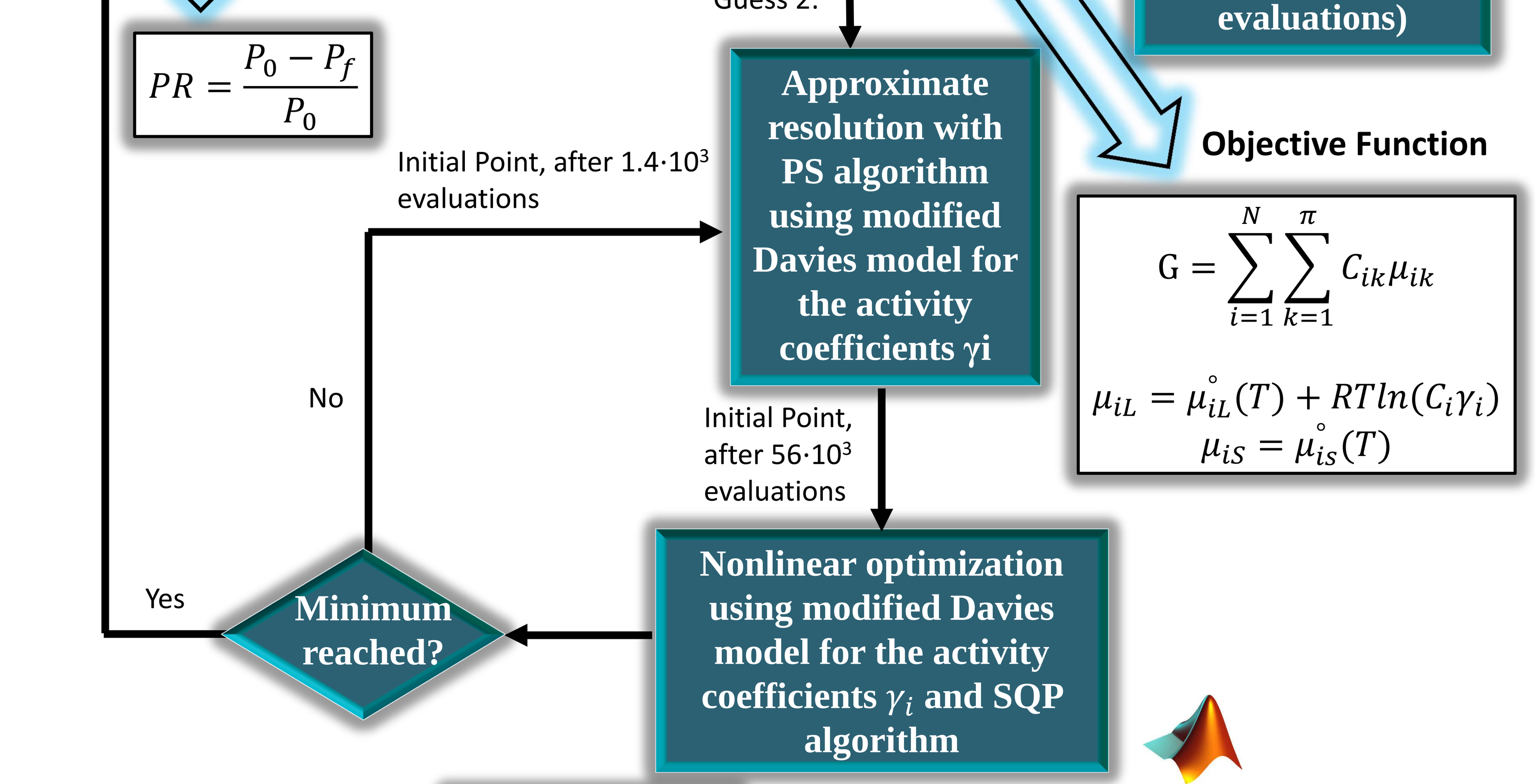


Predicted and measured PR (%) as struvite for P-OP=200 ppm, Mg/P=1for N/P=2.0 and N/P=8.3 at T=25°C.



THERMODYNAMIC MODEL FORMULATION





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)	$HPO_4^{2-} \leftrightarrows PO4^{3-} + H+$	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

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 pKPS** 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-NH_4^+ 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-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**.

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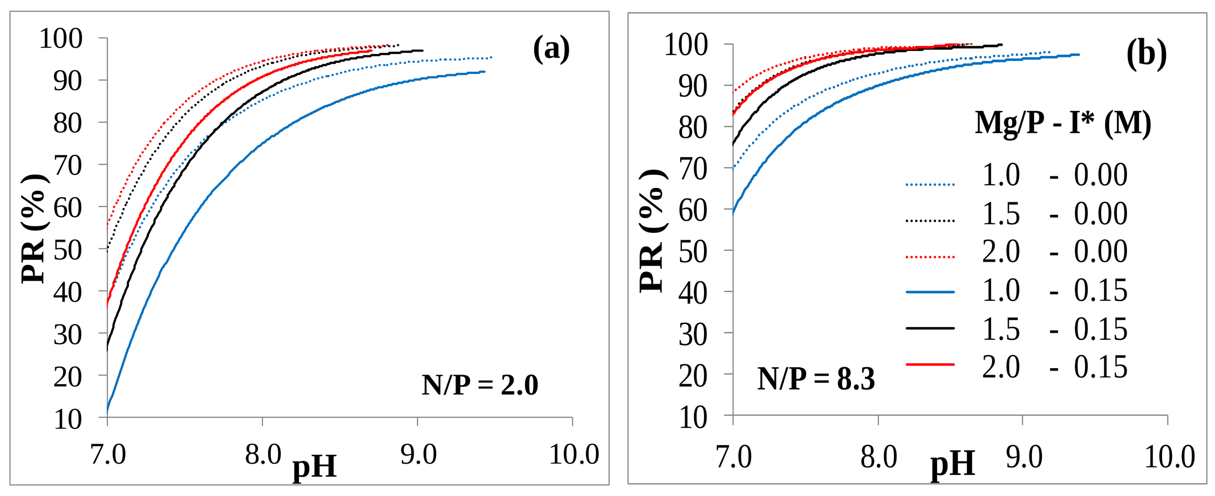
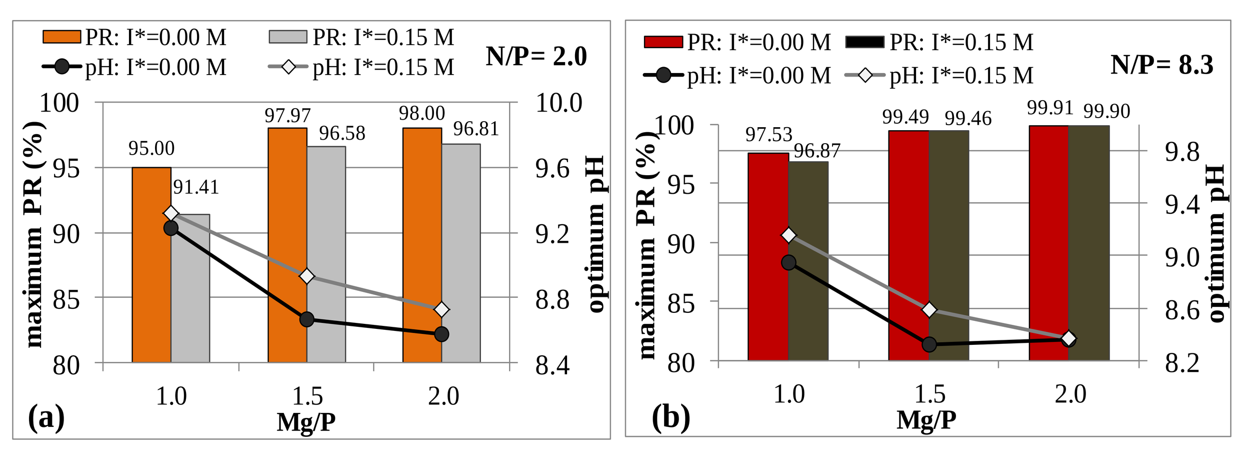
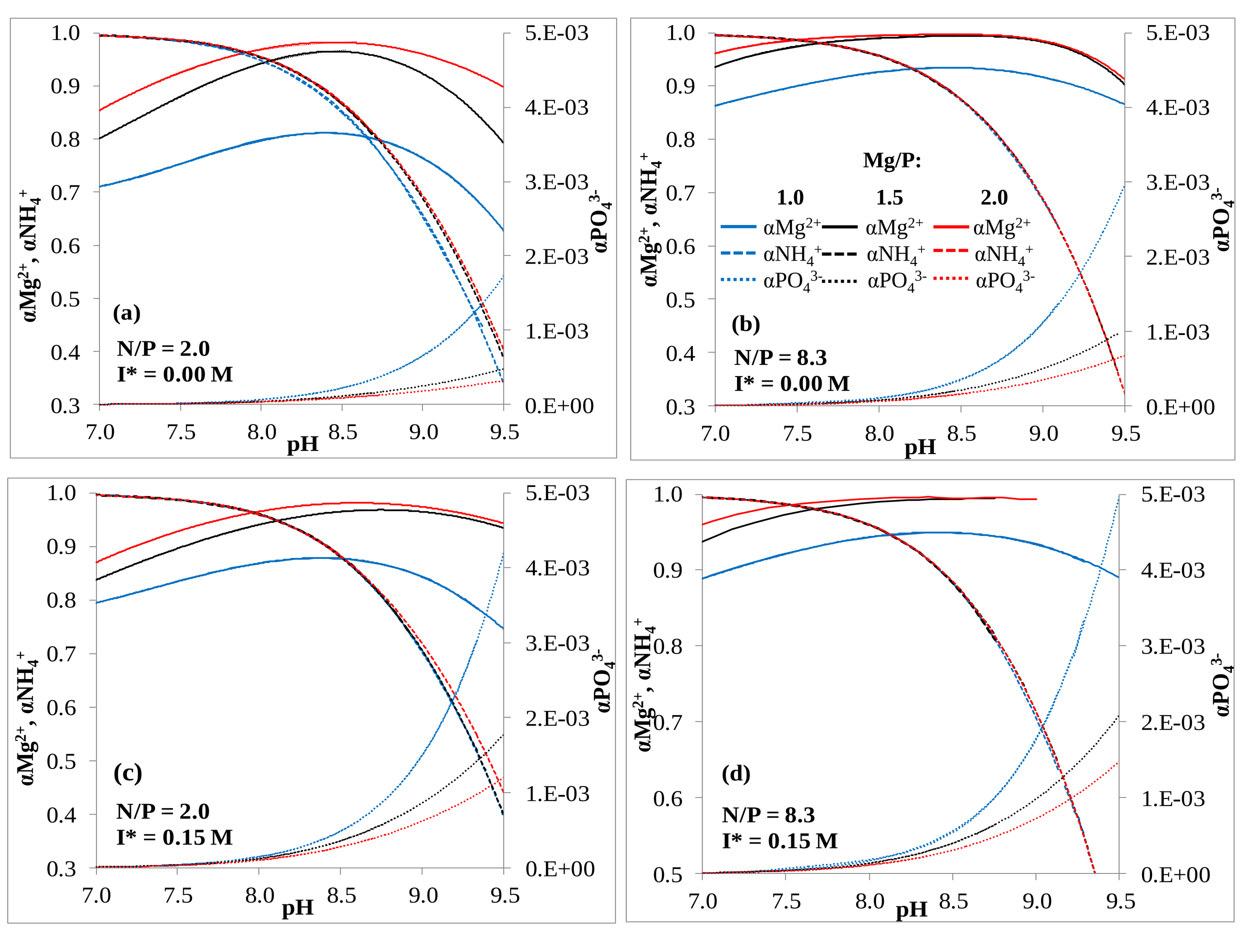
RESULTS AND DISCUSSION



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.