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Facultad de Ciencias Químicas

FACULTAD DE INGENIERIA

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DE LA REPÚBLICA
URUGUAY

Modelling the thermodynamic equilibrium of struvite precipitation using a hybrid optimization technique

Claudia Santiviago Petzoldt
csantiviago@qui.una.py

Iván López Moreda
ivanl@fing.edu.uy

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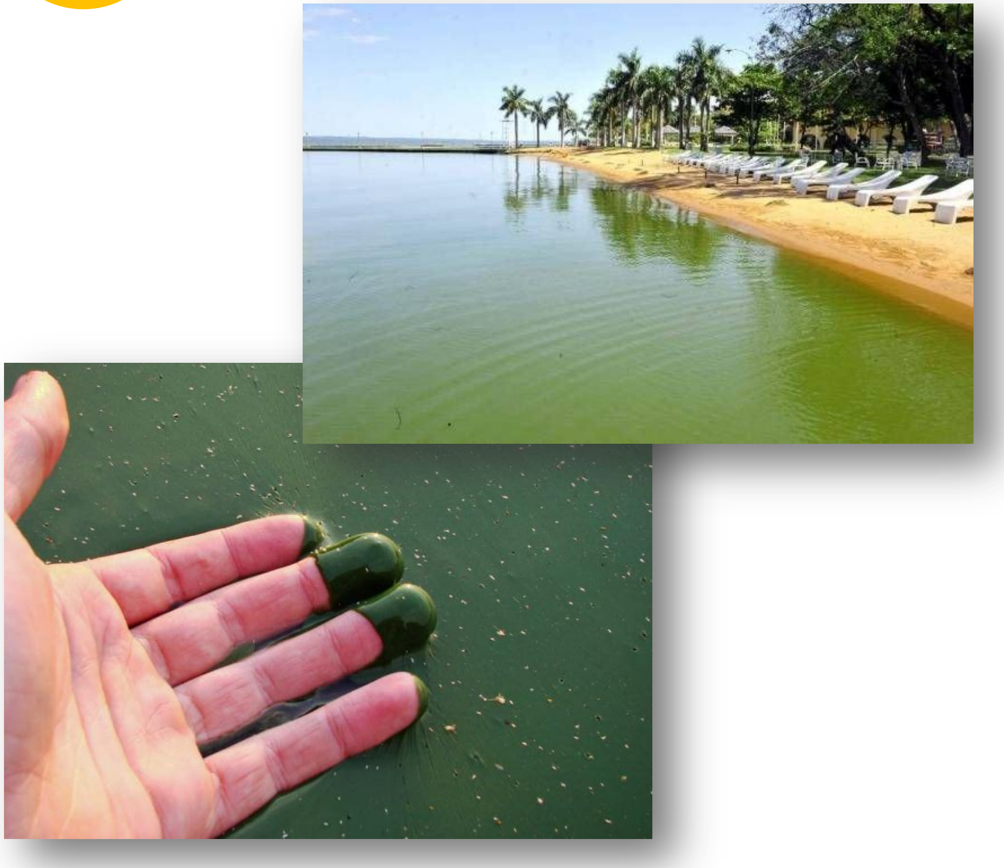
NUTRIENTS IN WASTEWATER

“Agro-industrial wastewater streams, such as concentrated slaughterhouse wastewater, present high concentrations of nutrients that generally exceed those accepted for the discharge standards”

NEGATIVE IMPACTS OF NUTRIENT DISCHARGED

01 Eutrophication



Excessive richness of nutrients in bodies of water, causes a dense growth of plant life and death of animal life from lack of oxygen.

NEGATIVE IMPACTS OF NUTRIENT DISCHARGED

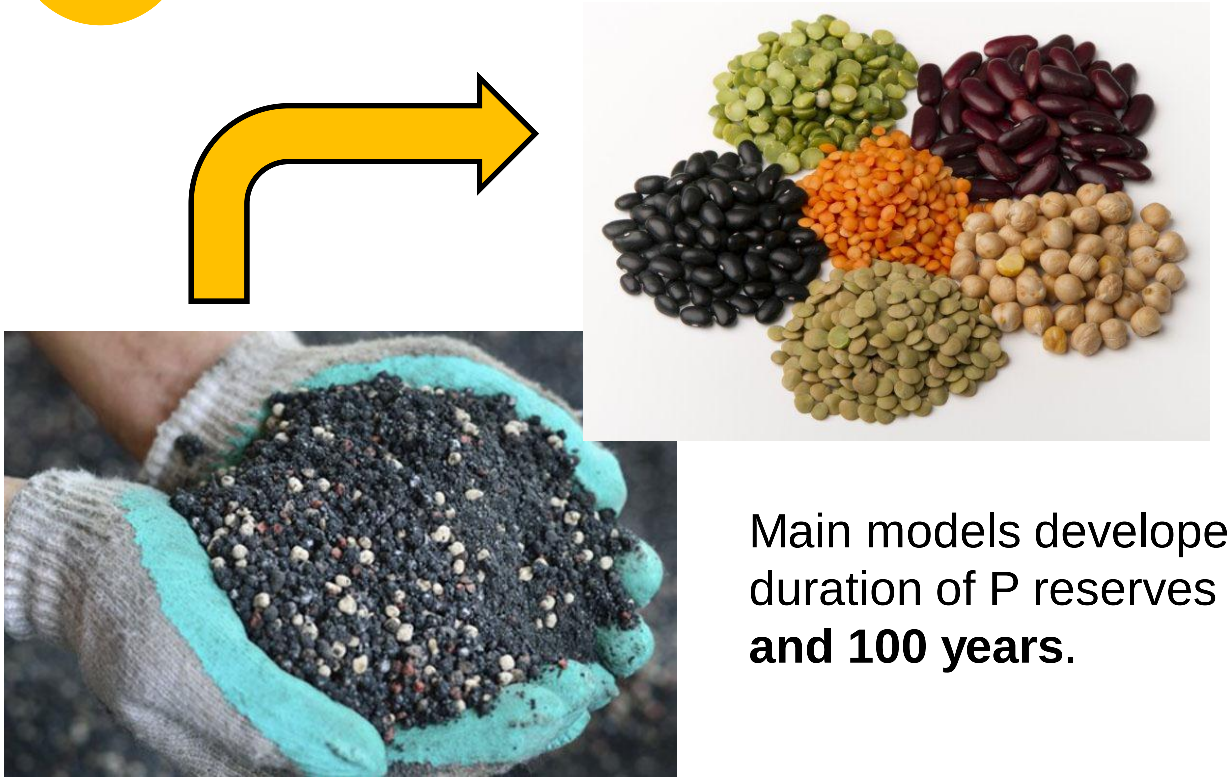
02

Crystalline deposits by uncontrolled deposition of phosphate salts in wastewater treatment systems

[1] *Bowers, 2011.*

NEGATIVE IMPACTS OF NUTRIENT DISCHARGED

03 Phosphorus: an increasingly limited resource



"**Phosphorus** is the **limiting resource**, the bottleneck of agriculture and therefore of the **global food security**"

Main models developed estimate that the duration of P reserves will be **between 50 and 100 years**.

Consumption in 2015: 43.7 million MT [2]

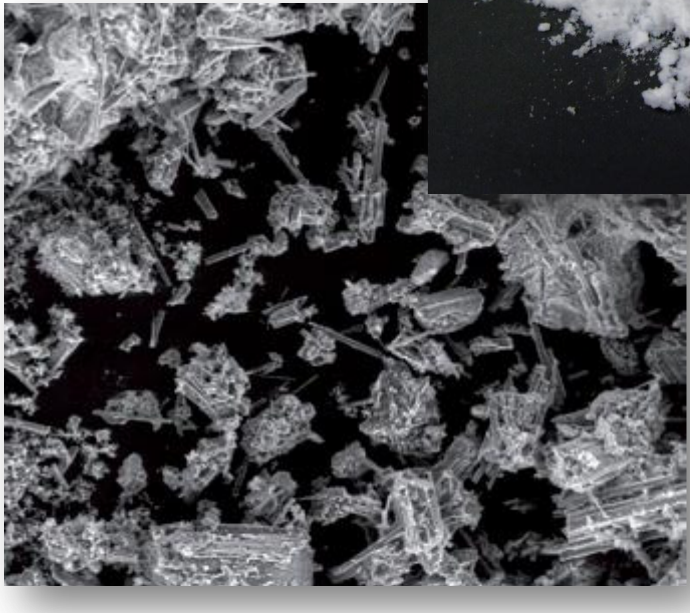
[2] *U.S. Geological Survey (2016)*

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.

An alternative solution that allows the recovery of nutrients in wastewater is the crystallization as struvite.

STRUVITE PRECIPITATION

> “Precipitation of ***struvite*** can be conceived as one of the main processes for recovery P and N from agro-industrial wastewater streams”

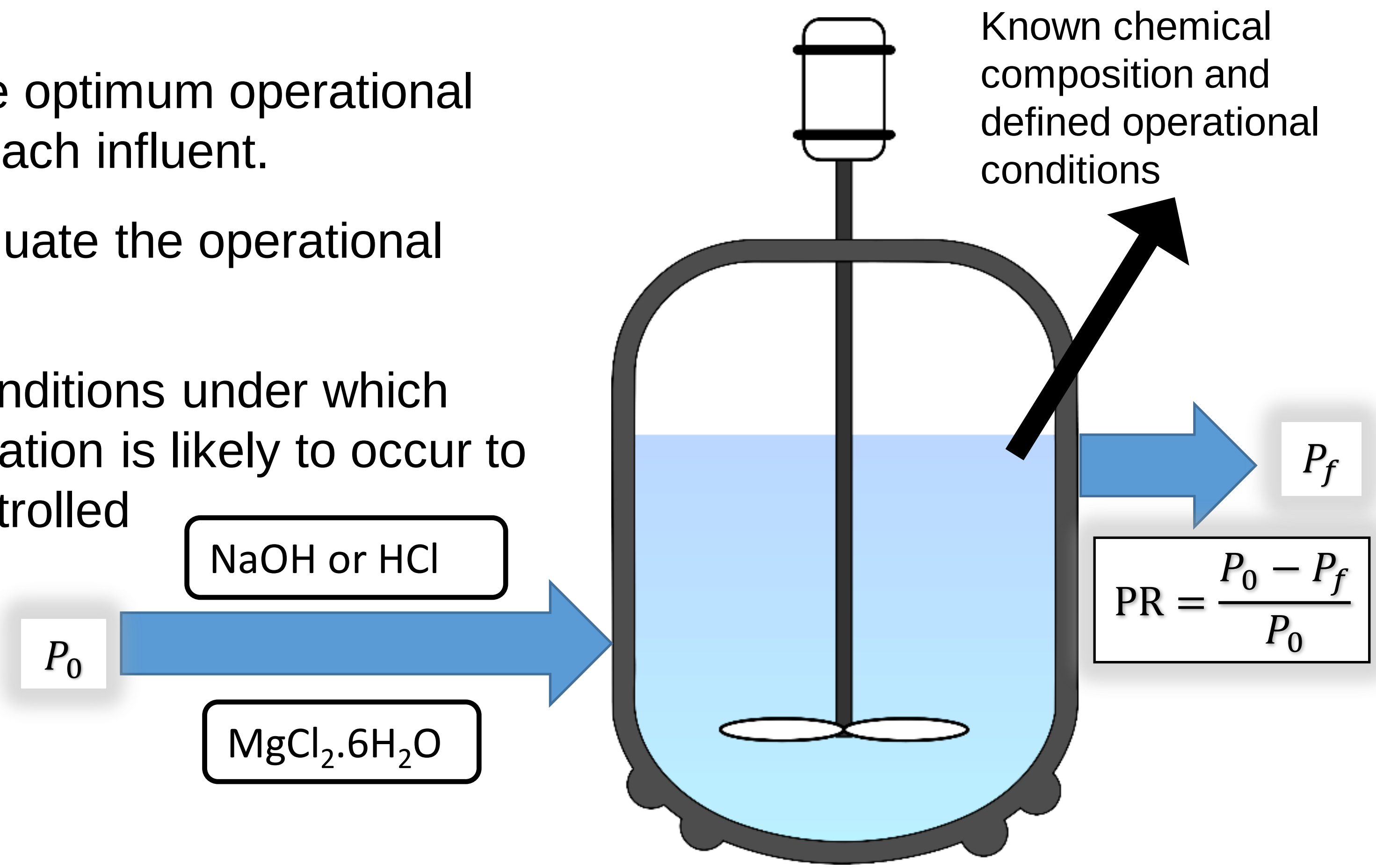


Struvite crystals

Magnesium ammonium phosphate hexahydrate: **$MgNH_4PO_4.6H_2O$**

PREDICTION OF POTENTIAL NUTRIENT REMOVAL FROM WASTEWATER STREAM

- Essential tool for design crystallization reactors.
- Definition of the optimum operational conditions for each influent.
- It allows to evaluate the operational efficiency.
- To know the conditions under which struvite precipitation is likely to occur to avoid its uncontrolled deposition.



Known chemical composition and defined operational conditions

NaOH or HCl

$MgCl_2.6H_2O$

P_0

P_f

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

STRUVITE PRECIPITATION THERMODYNAMIC

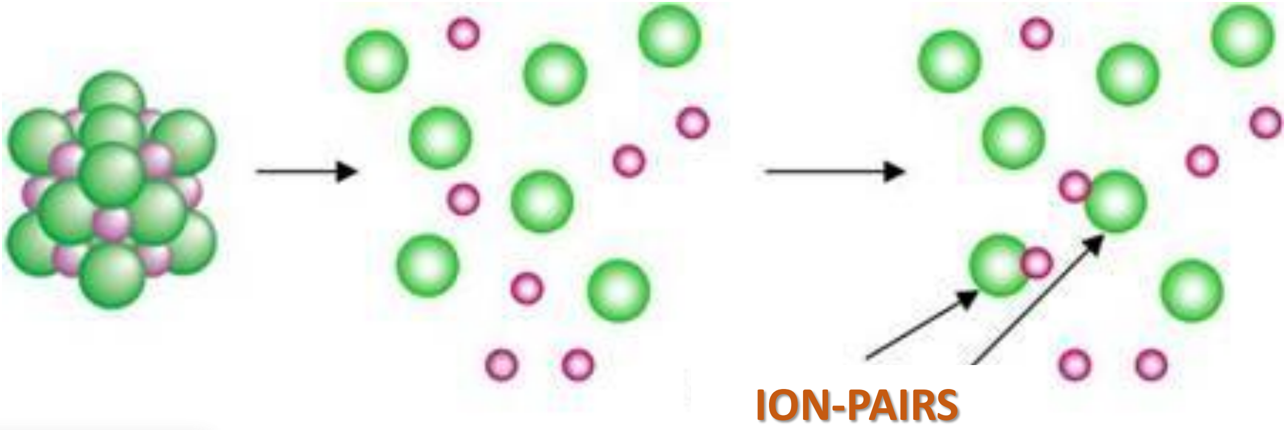
- Mg^{2+}, NH_4^+ and PO_4^{3-} concentrations
- pH
- Supersaturation ratio
- Ionic strength
- Temperature
- Reaction time

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

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

Struvite solubility product

STRUVITE PRECIPITATION THERMODYNAMIC



$$a_i = \gamma_i \cdot [C_i]$$

Calculated with Davies Equation:

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

Lewis and Randall Equation:

$$I = 0.5 \sum C_i\, Z_i^{\,2}$$

Debye-Hückel constant:

$$A_{DH} = 1.82\ 10^6 (\varepsilon T)^{3/2}$$

STRUVITE PRECIPITATION THERMODYNAMIC

Supersaturation of the solution is the key parameter leading to crystallization

The supersaturation ratio (Sc) is calculated using the equation:

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

Product of analytical molar concentration

Equilibrium conditional solubility product

Sc > 1.0 indicates that supersaturated conditions exist and that precipitation is possible

Sc = 1 characterizes the saturated condition

Sc < 1 indicates an undersaturated solution

MODEL FORMULATION

A struvite precipitation model at least requires the incorporation of concentrations of :

- Ionic species: Mg^{2+}, NH_4^+ and PO_4^{3-}
- Dissolved species: NH_3 (aq) and H_3PO_4
- Solid compound: $MgNH_4PO_4.6H_2O$

The complexity of the models depends on the number of soluble and solid species considered.

- Ionic species: $H_2PO_4^-$, HPO_4^{2-}, $MgH_2PO_4^+$, $MgOH^+$, $MgPO_4^-$
- Dissolved species: NH_3 (gas), $MgHPO_4$
- Solid compounds: $Mg(OH)_2$ (brucite), $Mg_3(PO_4)_2{\cdot}8H_2O$ (bobierrite), $Mg_3(PO_4)_2{\cdot}22H_2O$ (cattiite), and $MgHPO_4.3H_2O$ (newberyite)

MODEL FORMULATION

This research considers the equations for ions, dissolved and solids species given in the table:

j	**Reaction *j***	**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)	$MgH_2PO_4^+ \leftrightarrows H_2PO_4^- + Mg^{2+}$	1.51
(5)	$MgHPO_4 \leftrightarrows HPO_4^{2-} + Mg^{2+}$	2.91
(6)	$MgPO_4^- \leftrightarrows PO_4^{3-} + Mg^{2+}$	6.59
(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

$$pK_j = -log\ e^{\Delta G^{\circ}/(RT)}$$

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

MODEL ASSUMPTIONS

The thermodynamic model is formulated with the following assumptions:

1. **Precipitate** which may be formed in assay recovery conditions is **only struvite**. Precipitates such as **cattiite** and **newberyite** were not taken into account. The presence of Mg(OH)$_2$ in the system, which compete with struvite formation at pH>10 **is neglected**.
2. All reactions are in equilibrium state. The **reactions are rapid**; therefore, **the dynamics of the reactions are ignored** and equilibrium relationships are used to determine the species concentrations.

MODEL ASSUMPTIONS

The thermodynamic model is formulated with the following assumptions:

3. The system is run at isothermal and isobaric conditions: **25°C** and **101.325 kPa**.
4. **Non-reactive ionic species are represented by NaCl** to study the impact of ionic strength in the phosphorus removal.
5. **pH** is kept constant (**6.9 - 10.0**) by addition of NaOH or HCl, which meant that the concentration of protons and OH^- are known.
6. The formation of **complexes with Cl^- or Na^+** is **neglected**, just like complexes created since more than two ions.

MODEL FORMULATION

In a reaction system the equilibrium condition at constant temperature and pressure occurs when the Gibbs Free Energy (G) reaches a minimum

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

Objective Function

$$\mu_{iL} = \overset{\circ}{\mu}_{iL}(T) + RT\ln(C_i\gamma_i)$$

$$\mu_{is} = \overset{\circ}{\mu}_{is}(T)$$

MASS AND ELECTRONEUTRALITY BALANCES

Mass balance for Mg:

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

Mass balance for orthophosphate phosphorus:

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

Mass balance for ammonium:

$$C_{T,NH_4} = C_{NH_4^+} + C_{NH_3} + PR \cdot C_{T,OP}$$

Electroneutrality:

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

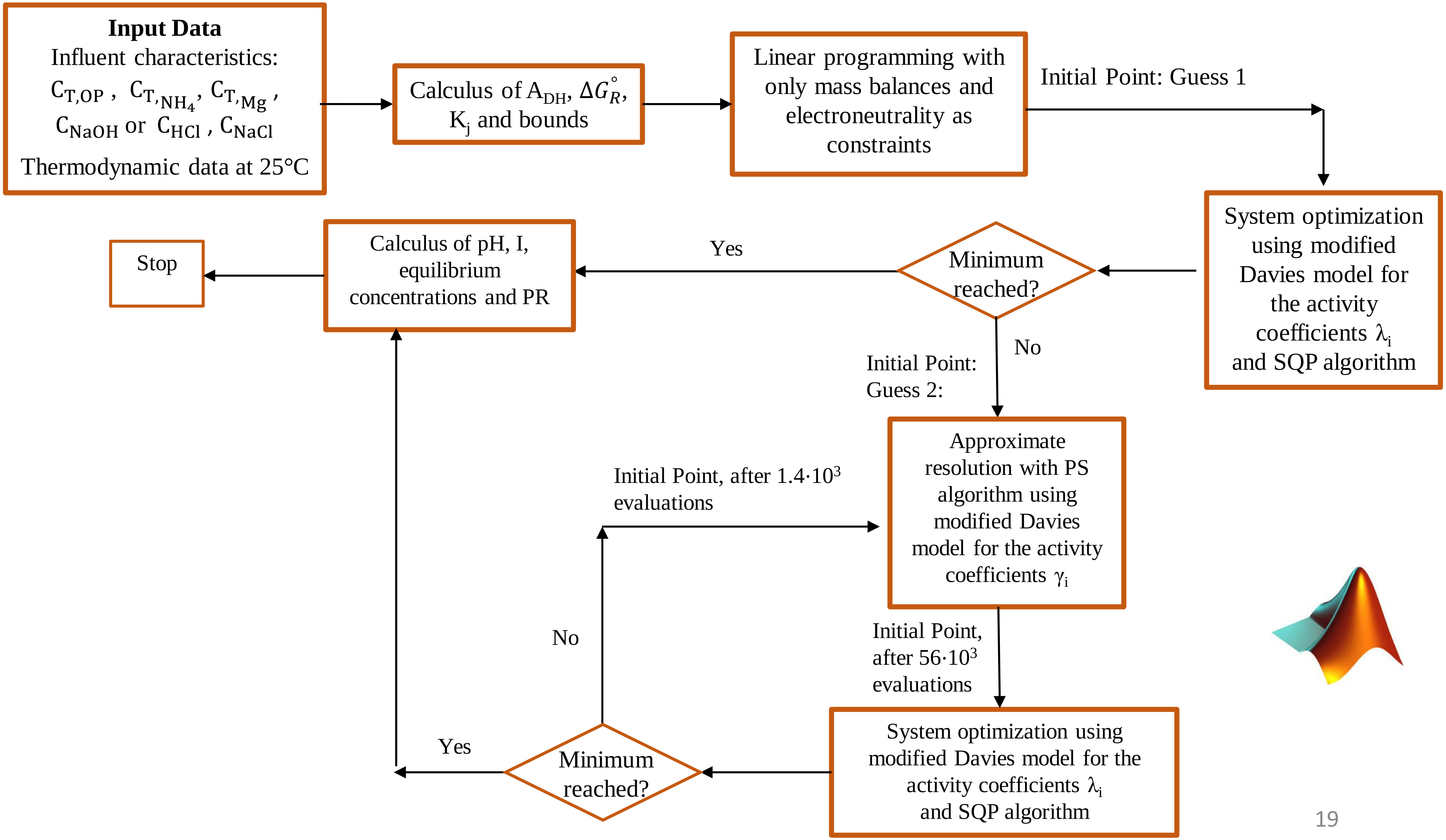
4 linear equality constraints in the proposed optimization problem

MASS AND ELECTRONEUTRALITY BALANCES

Reaction j	Nonlinear equality constraints
(1)	$\mathrm{pK_1} + \log\left(\frac{\alpha_{\mathrm{H_2PO_4^-}} \cdot \alpha_{\mathrm{H^+}}}{\alpha_{\mathrm{H_3PO_4}}}\right) = 0$
(2)	$\mathrm{pK_2} + \log\left(\frac{\alpha_{\mathrm{HPO_4^{2-}}} \cdot \alpha_{\mathrm{H^+}}}{\alpha_{\mathrm{H_2PO_4^-}}}\right) = 0$
(3)	$\mathrm{pK_3} + \log\left(\frac{\alpha_{\mathrm{PO_4^{3-}}} \cdot \alpha_{\mathrm{H^+}}}{\alpha_{\mathrm{HPO_4^{2-}}}}\right) = 0$
(4)	$\mathrm{pK_4} + \log\left(\frac{\alpha_{H_2PO_4^-} \cdot \alpha_{Mg^{2+}}}{\alpha_{MgH_2PO_4^+}}\right) = 0$
(5)	$\mathrm{pK_5} + \log\left(\frac{\alpha_{HPO_4^{2-}} \cdot \alpha_{Mg^{2+}}}{\alpha_{MgHPO_4}}\right) = 0$
(6)	$\mathrm{pK_6} + \log\left(\frac{\alpha_{\mathrm{PO_4^{3-}}} \cdot \alpha_{\mathrm{Mg^{2+}}}}{\alpha_{\mathrm{MgPO_4^-}}}\right) = 0$
(7)	$\mathrm{pK_7} + \log\left(\frac{\alpha_{\mathrm{OH^-}} \cdot \alpha_{\mathrm{Mg^{2+}}}}{\alpha_{\mathrm{MgOH^+}}}\right) = 0$
(8)	$\mathrm{pK_8} + \log\left(\frac{\alpha_{\mathrm{NH_3}} \cdot \alpha_{\mathrm{H^+}}}{\alpha_{\mathrm{NH_4^+}}}\right) = 0$
(9)	$\mathrm{pK_9} + \log\left(\frac{\alpha_{OH^-} \cdot \alpha_{H^+}}{\alpha_{H_2O}}\right) = 0$
(10)	$\mathrm{pK_{SP}} + \log\left(\mathrm{a_{Mg^{2+}}} \cdot \mathrm{a_{NH_4{}^+}} \cdot \mathrm{a_{PO_4{}^{3-}}}\right) = 0$

10 nonlinear equality constraints in the proposed optimization problem

SOLVING THE THERMODYNAMIC MODEL



Input Data
Influent characteristics:
$C_{T,OP}$, C_{T,NH_4}, $C_{T,Mg}$,
C_{NaOH} or C_{HCl} , C_{NaCl}
Thermodynamic data at 25°C

Calculus of A_{DH}, ΔG_R°, K_j and bounds

Linear programming with only mass balances and electroneutrality as constraints

Initial Point: Guess 1

System optimization using modified Davies model for the activity coefficients λ_i and SQP algorithm

Minimum reached?

Yes

Calculus of pH, I, equilibrium concentrations and PR

Stop

No

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

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

System optimization using modified Davies model for the activity coefficients λ_i and SQP algorithm

Minimum reached?

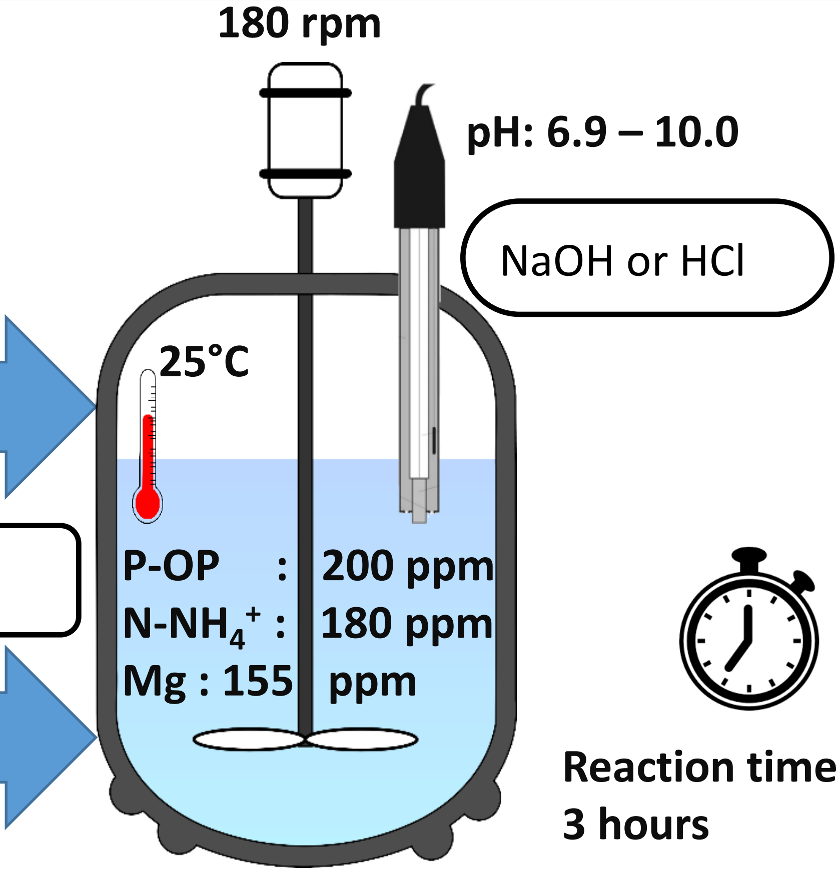
No

Yes

Model Validation. Experimental Procedure

Synthetic wastewater solution:
$(NH_4)_2HPO_4$
NH_4Cl

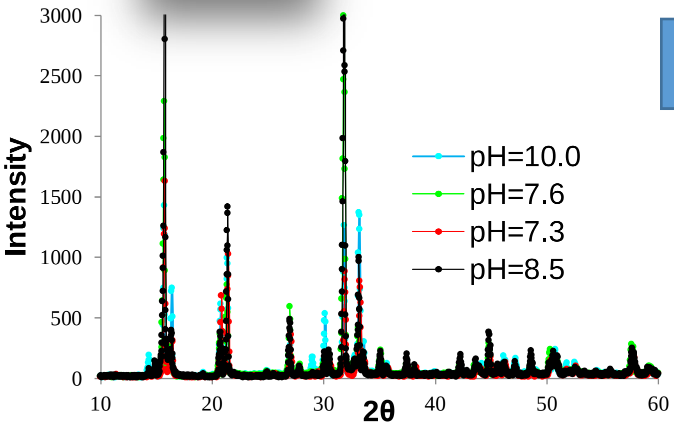
$MgCl_2.6H_2O$



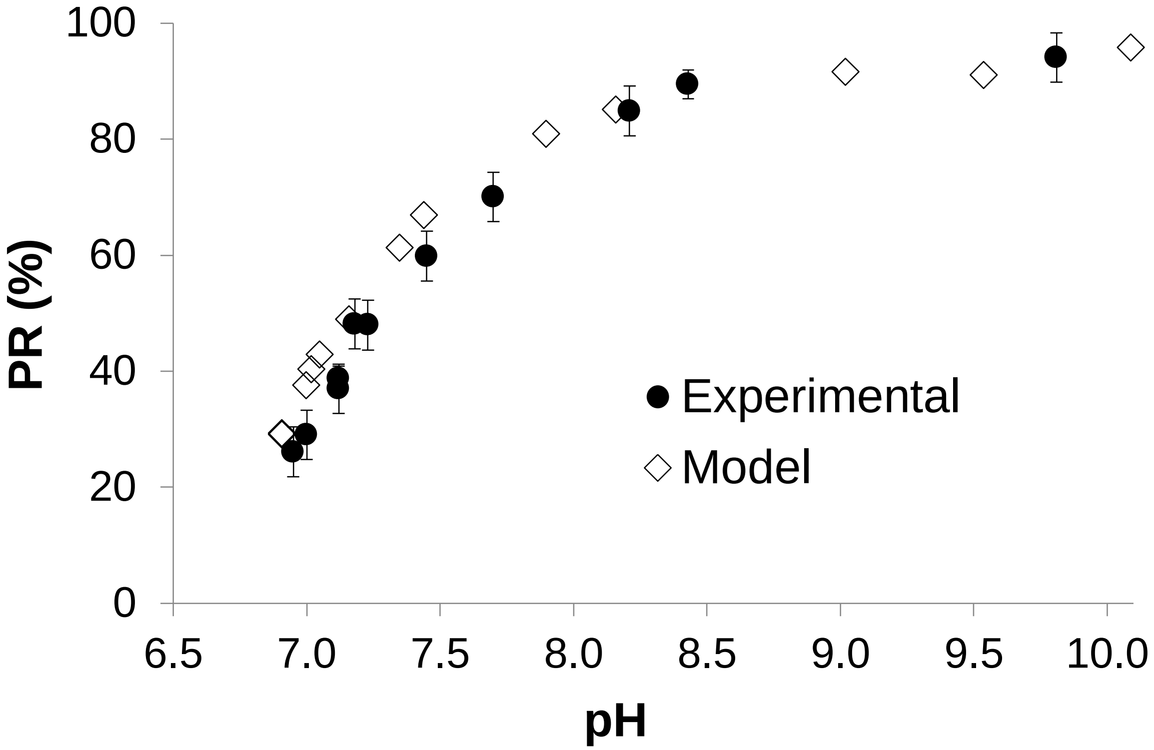
Reaction time:
3 hours

Mg/P and N/P were 1.0 and 2.0

DRX



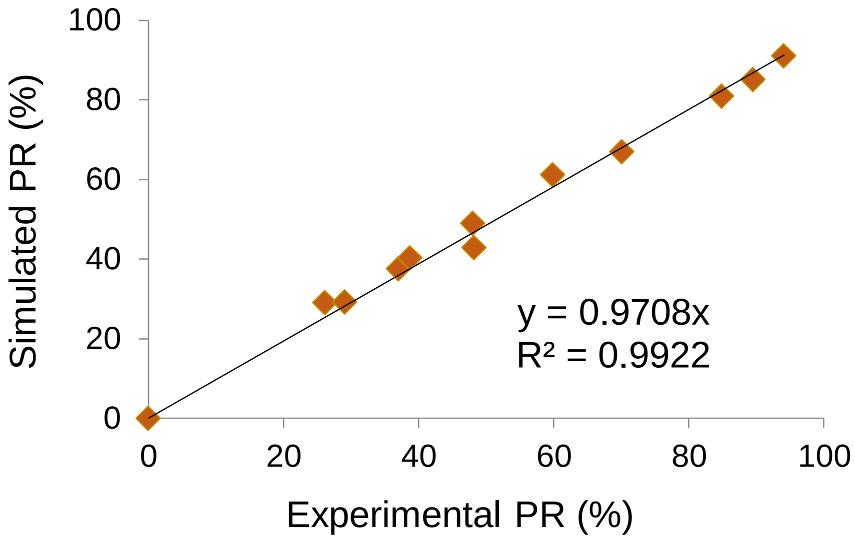
VERIFICATION OF THE PROPOSED MODEL



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**.

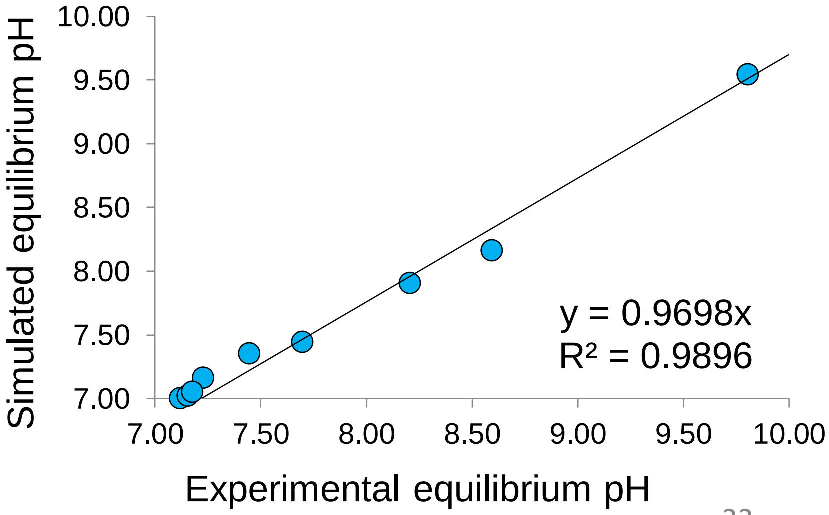
VERIFICATION OF THE PROPOSED MODEL

Conditions:
P-OP=200 ppm; Mg/P=1; N/P=2
T=25°C



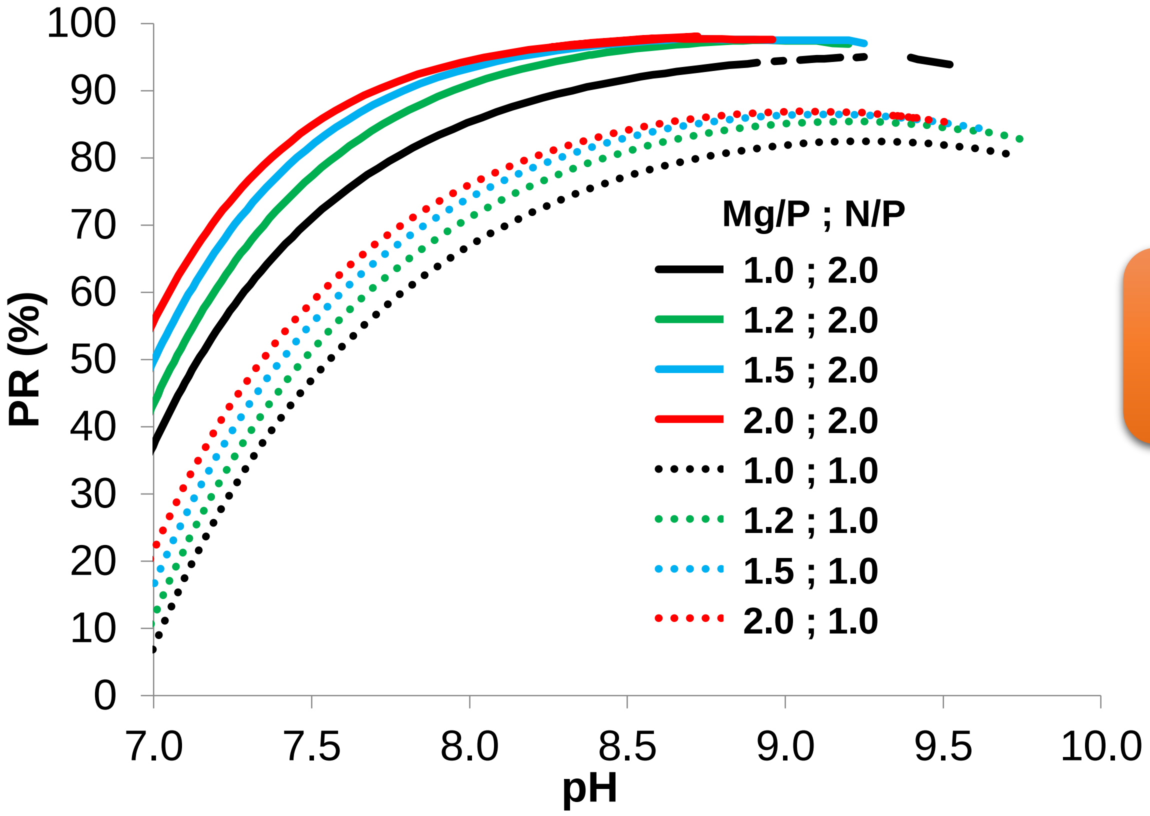
Linear correlations between PR (%) obtained by simulated and experimental data.

Data exhibit a high correspondence between the experimental and simulated sets



Linear correlations between pH obtained by the simulated data and experimental measurements.

EFFECT OF MOLAR RATIO Mg/P AND N/P AT DIFFERENT pH ON THE PHOSPHORUS REMOVAL

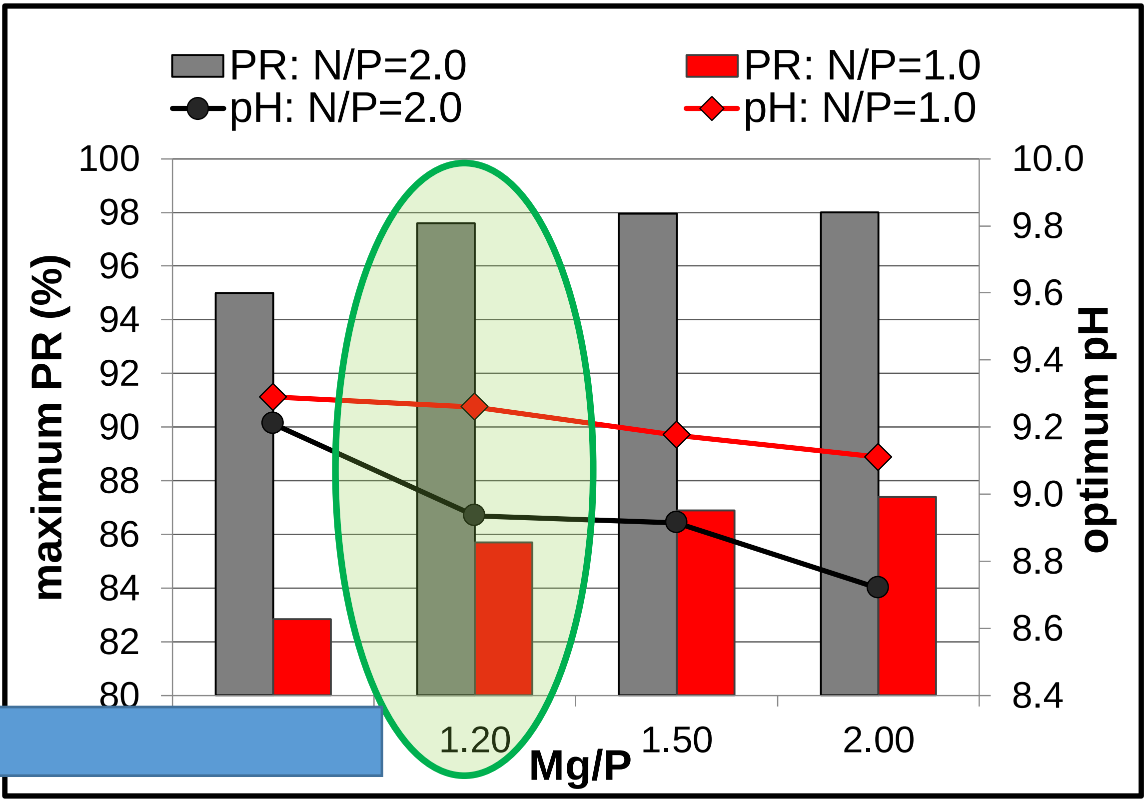


P-OP=200 ppm
T=25°C

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.

EFFECT OF MOLAR RATIO Mg/P AND N/P AT DIFFERENT pH ON THE PHOSPHORUS REMOVAL

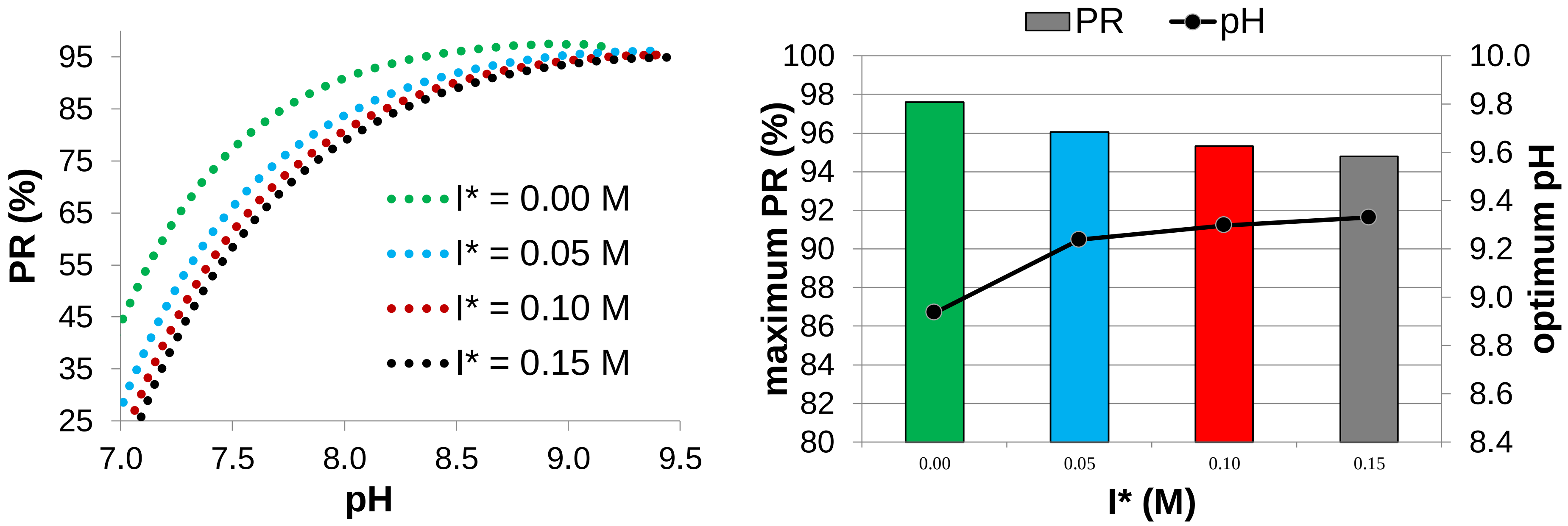
The higher relative improve ΔPR/(ΔMg/P) is obtained at molar ratio Mg/P=1.20 for both relations N/P evaluated.



P-OP=200 ppm
T=25°C

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).

Effect of Ionic Strength



Effect of ionic strength in the optimal pH operating conditions and maximum PR (%) at molar ratios Mg/P = 1.2, N/P = 2.

P-OP=200 ppm
T=25°C

CONCLUSIONS

1. 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**.
2. 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).
3. 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.
4. An **increment at ionic strength** **reduces the maximum PR** reached and increments the optimal pH.

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Facultad de Ciencias Químicas
VITAM IMPENDERE VERO
Ciudad Universitaria
San Lorenzo - Paraguay

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Claudia Santiviago Petzoldt
csantiviago@qui.una.py

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