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MAESTRÍA EN INGENIERÍA QUÍMICA

INFORMACIÓN CORTA

Unidad de Investigación

Modelamiento y Simulación de Procesos Aplicada a la Termodinámica de Soluciones en la Recuperación de Nutrientes

Natividad-Marin, Leynard (Investigador Peruano-Australiano)

Doctor of Philosophy (Ph.D.) – Chemical Engineering

Ingeniero Químico (UNAC) – Magister en Ciencia y Tecnología de Alimentos (UNAC)

Docente de la James Cook University (Townsville – Australia)

JAMES COOK UNIVERSITY AUSTRALIA

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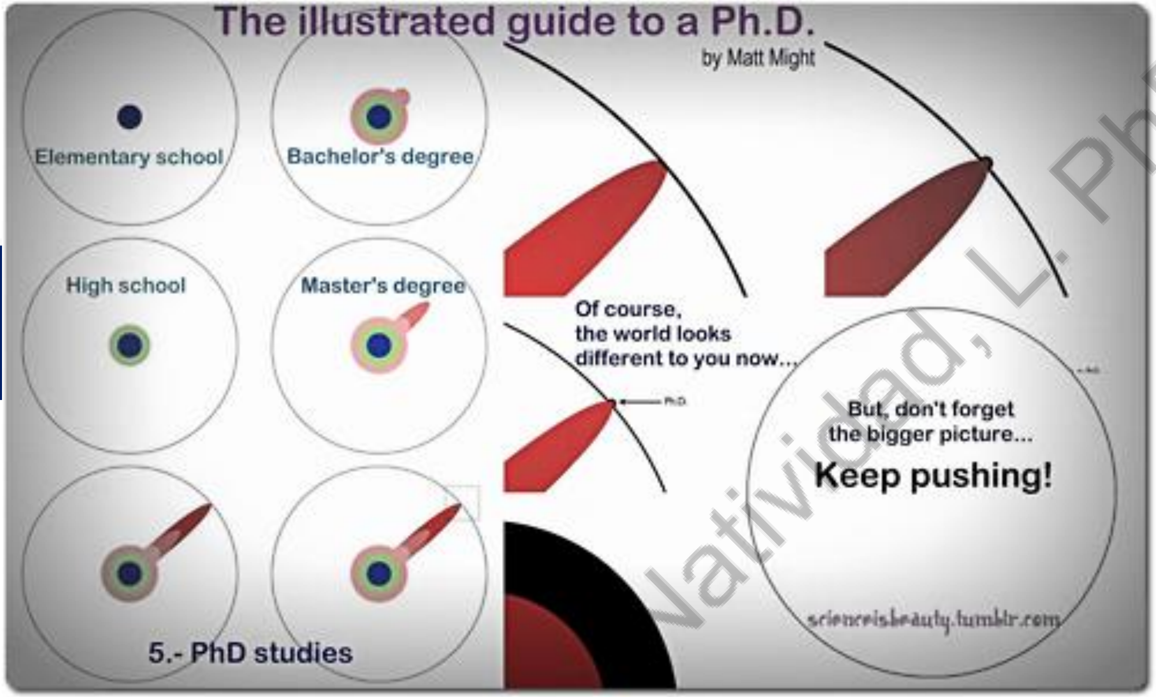
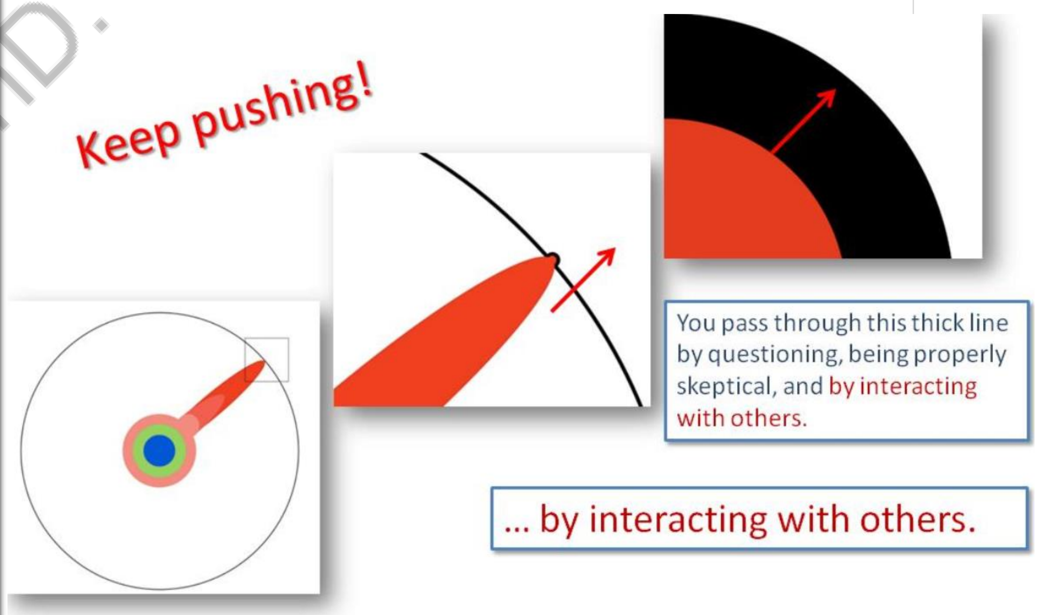
No coursework, only high-level research





Top Universities

The percentage of students who don't complete their PhD varies hugely; some institutions report ***as high as 71% and some as low as 9%.***

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Perth

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Queensland – Australia (2014-2017

College of Science, Health, Engineering and Education - Murdoch University (2017-2019)

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Research Group at JCU


Dr. Phil Schneider

Study better ways to do things

(implementing or improving a specific technology)

Dr. Imtiaj Ali

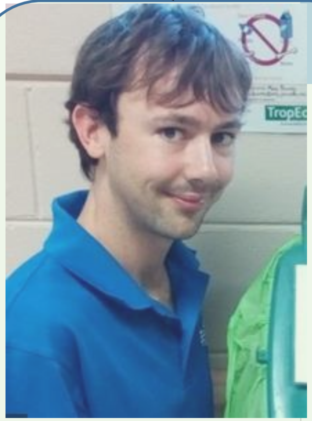
Fed-Batch

Precipitation rate without considering nucleation, only growth

Precipitation rate considering nucleation

Dr. Shaun Galbraith

Continuous reactor



Dr. Max Burns

Continuous reactor


Dr. Leynard Natividad

Continuous reactor
(hybrid)

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Acknowledgments

"James Cook University Postgraduate Research Scholarship (JCUPRS)"

Supervisors

Dr. Philip A. Schneider Principal supervisor– Murdoch Uni (Australia)

Dr. Madoc Sheehan Secondary advisor– JCU (Australia)

PHD = only research External reviewers

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Dr. Saifur Rahaman Yale University (USA)

Dr. Stephan Tait University of Southern Queensland (Australia)

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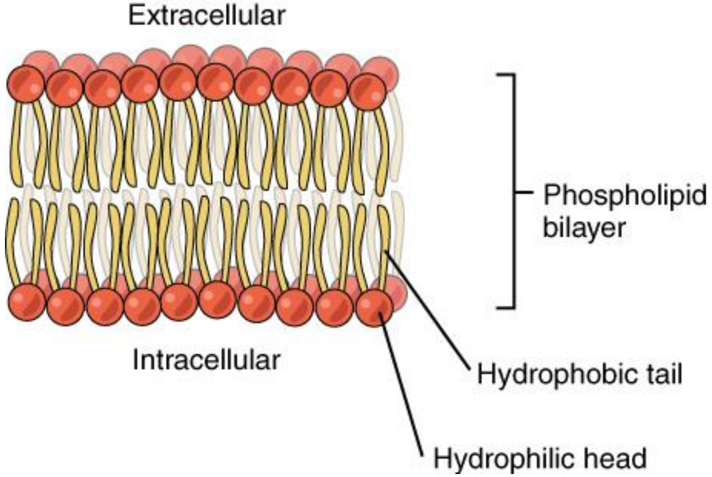
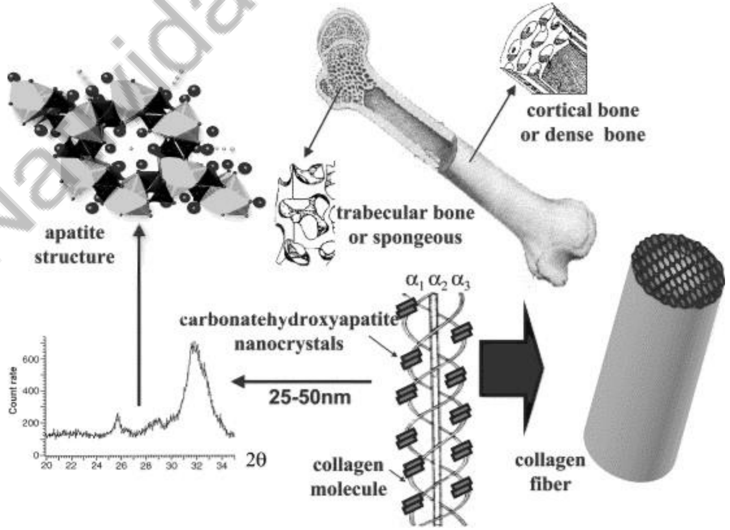
Why do we need to recover nutrients?

Phosphate + sugar + nitrogenous base = nucleic acid



Phosphorus (P)

*"Life can multiply until all the **phosphorus** has gone and then there is an inexorable halt which nothing can prevent. That's because **phosphorus** is essential to all living organisms.*



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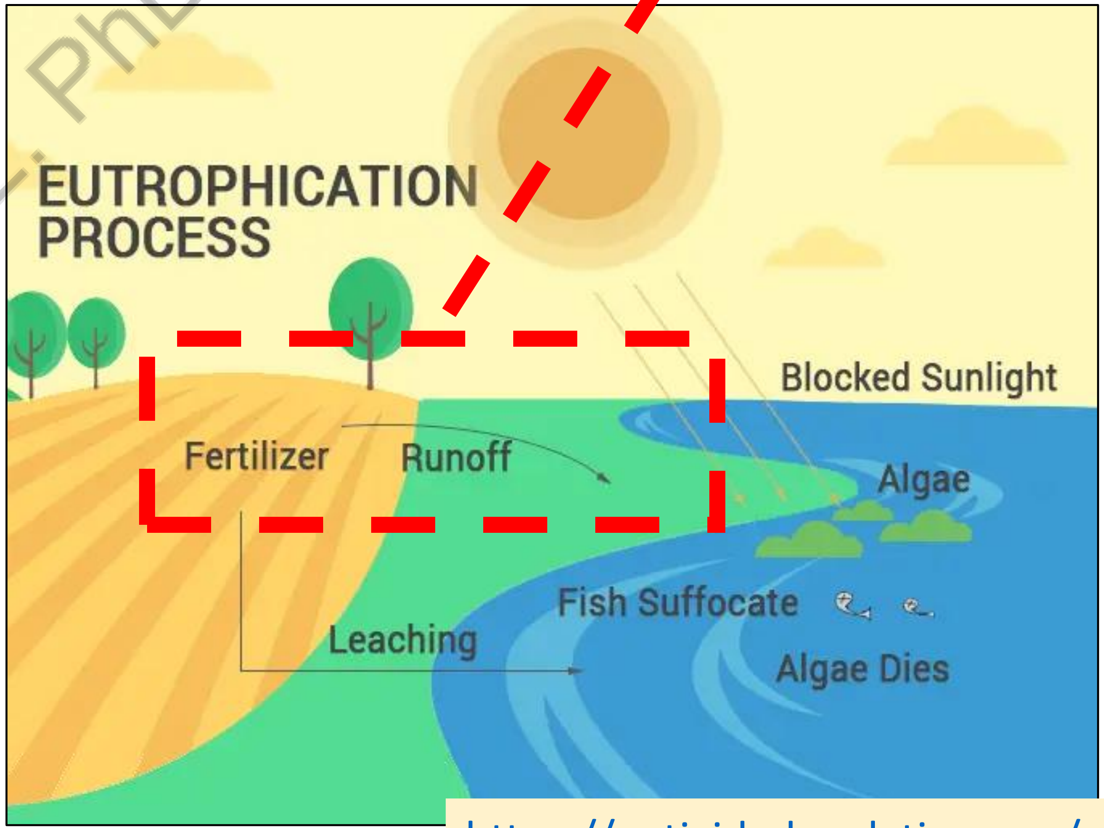
Isaac Asimov (1974)

Source: Vallet-Regi (2004). Calcium phosphates as substitution of bone tissues

The Eutrophication Issue

1. *Excess nutrients*
2. *Algae bloom*
3. *Oxygen depletion*
4. *Dead zones*

This could be also non-treated effluent



Source: https://earthhow.com/eutrophication-causes-process-examples/

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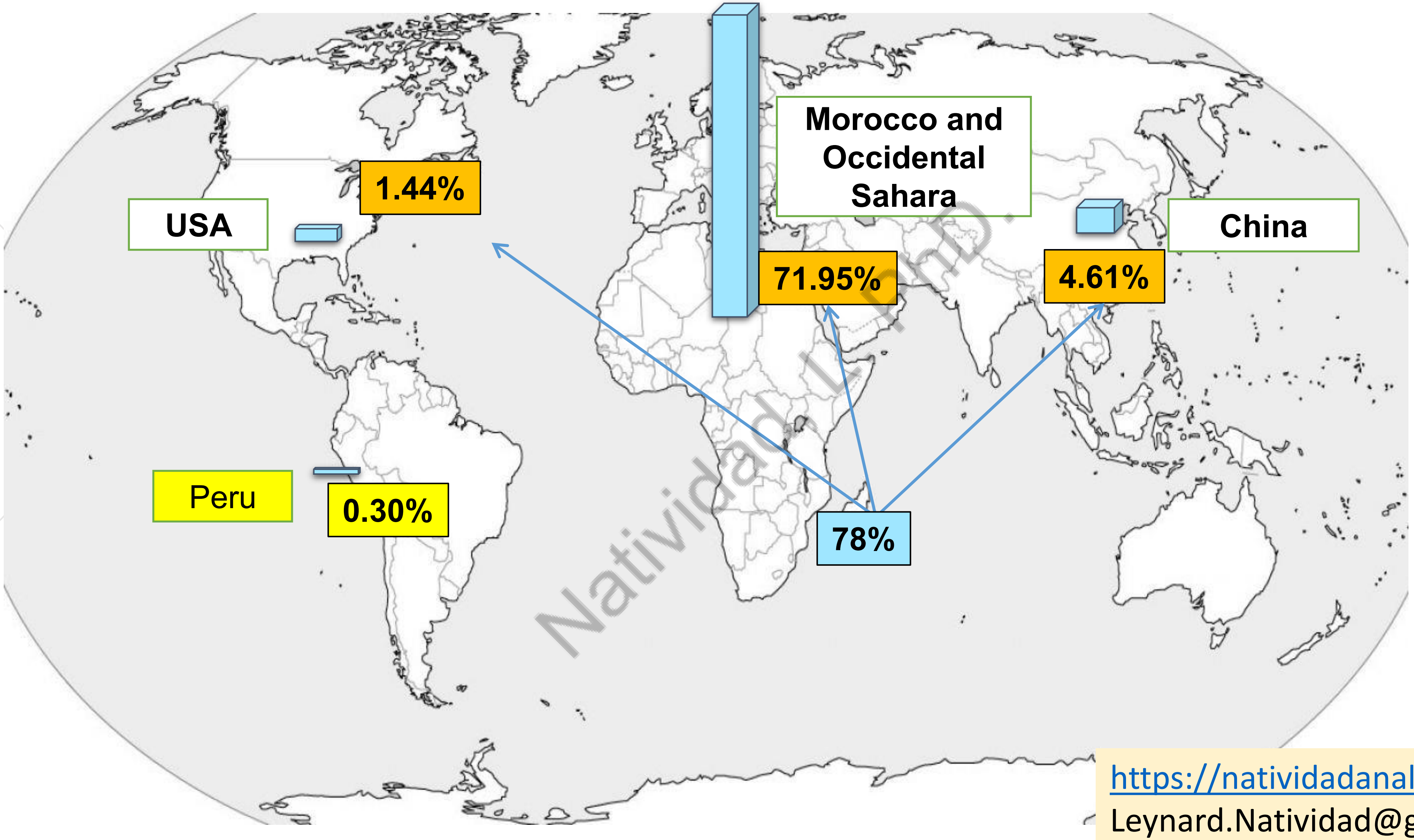
Rock Phosphate Mineral Reserves



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USGS. Mineral Commodity Summaries

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Nutrient Recovery – Closing the Loop

Phosphorus
3 million Tons of P/year

Struvite

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International Policies - UN

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Global implications (6)

Source: https://www.un.org/

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Possible Solutions

Alternative P sources

Biosolids,

Food waste,

Human waste,

Urine

Components	Fresh urine [mg/L]
Cl	6620
Urea ($CO(NH_2)_2$)	4450
Na	3240
K	1870
SO_4	878
NH_4-**N**	438
PO_4-P	388
Ca	89.2
Mg	45.4
Total Carbonates(CO_3)	8.53

Struvite!!!

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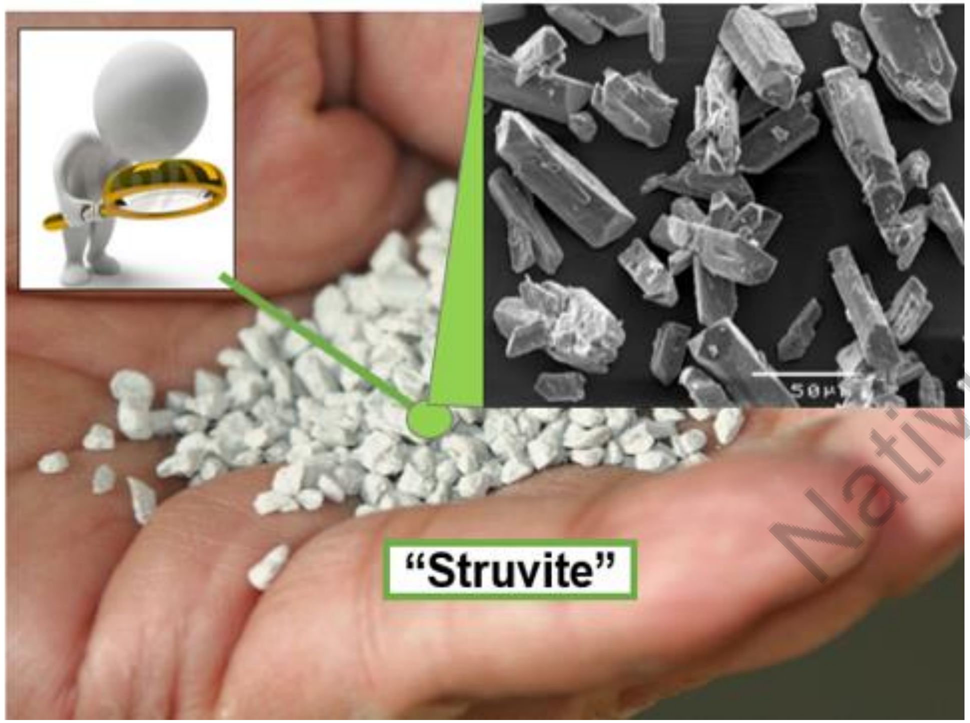
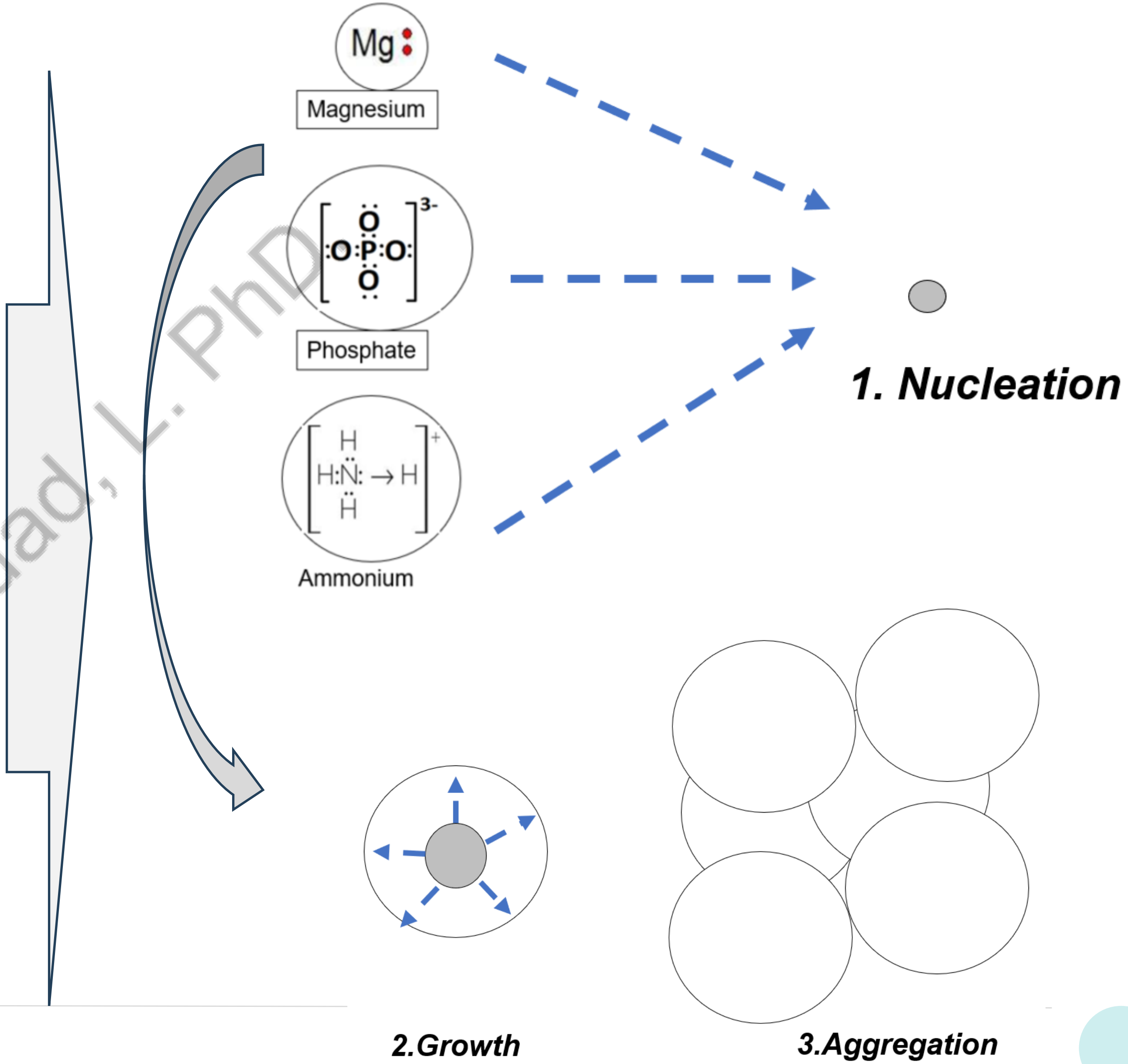
How does it happen?

$$MgNH_4PO_4 \cdot 6H_2O(s)$$





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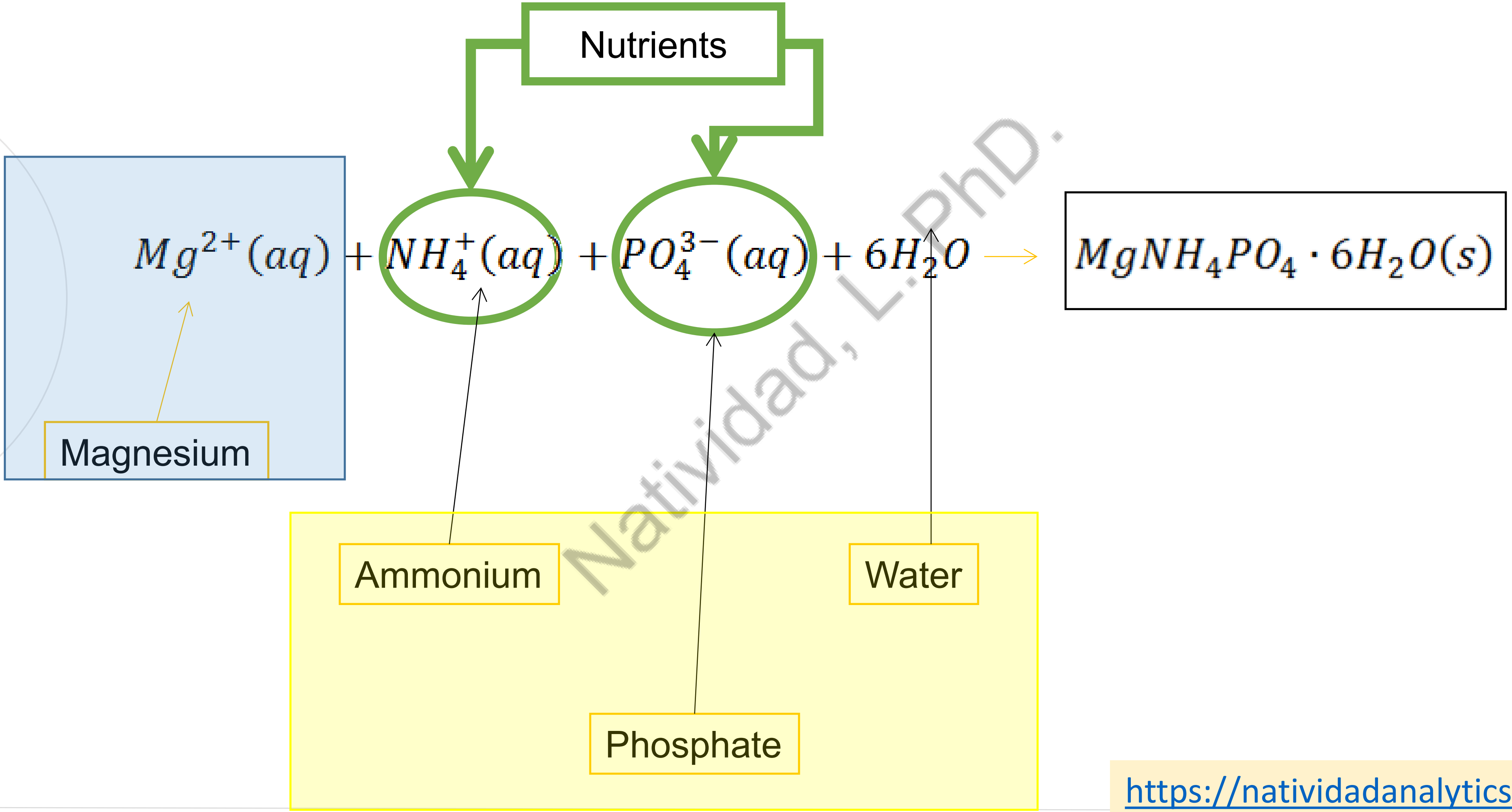
Struvite Chemical Reaction



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Overall Process System Engineering Approach

Dynamic model

Thermodynamic model

- *Elemental mass balance*
- *Struvite mass balance*
- *Reaction kinetics*

- *Equilibrium*
- *Chemical speciation*
- *Charge balance*
- *Activity coefficients*

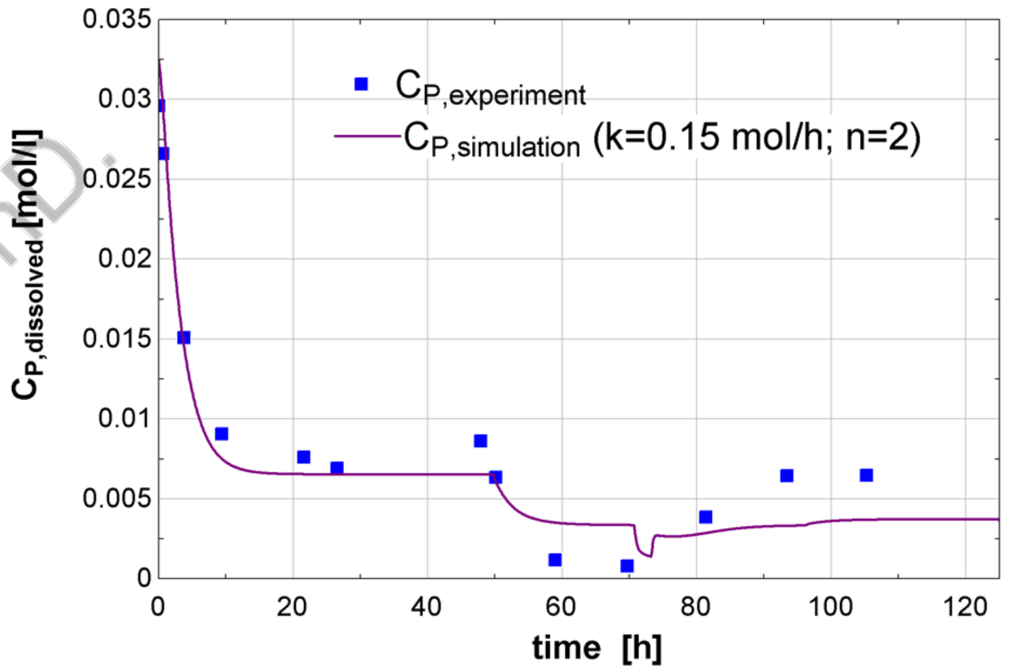

Figura. Concentration del Fósforo disuelto a través del tiempo

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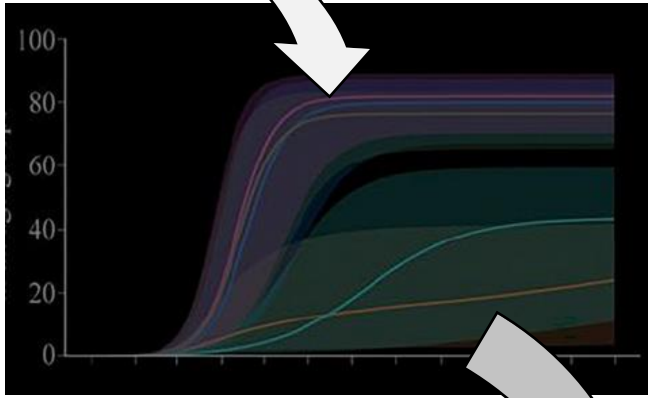
Modelling - Simulation

+



Source: Simulation in Chemical Engineering - 2024-A - UNAC

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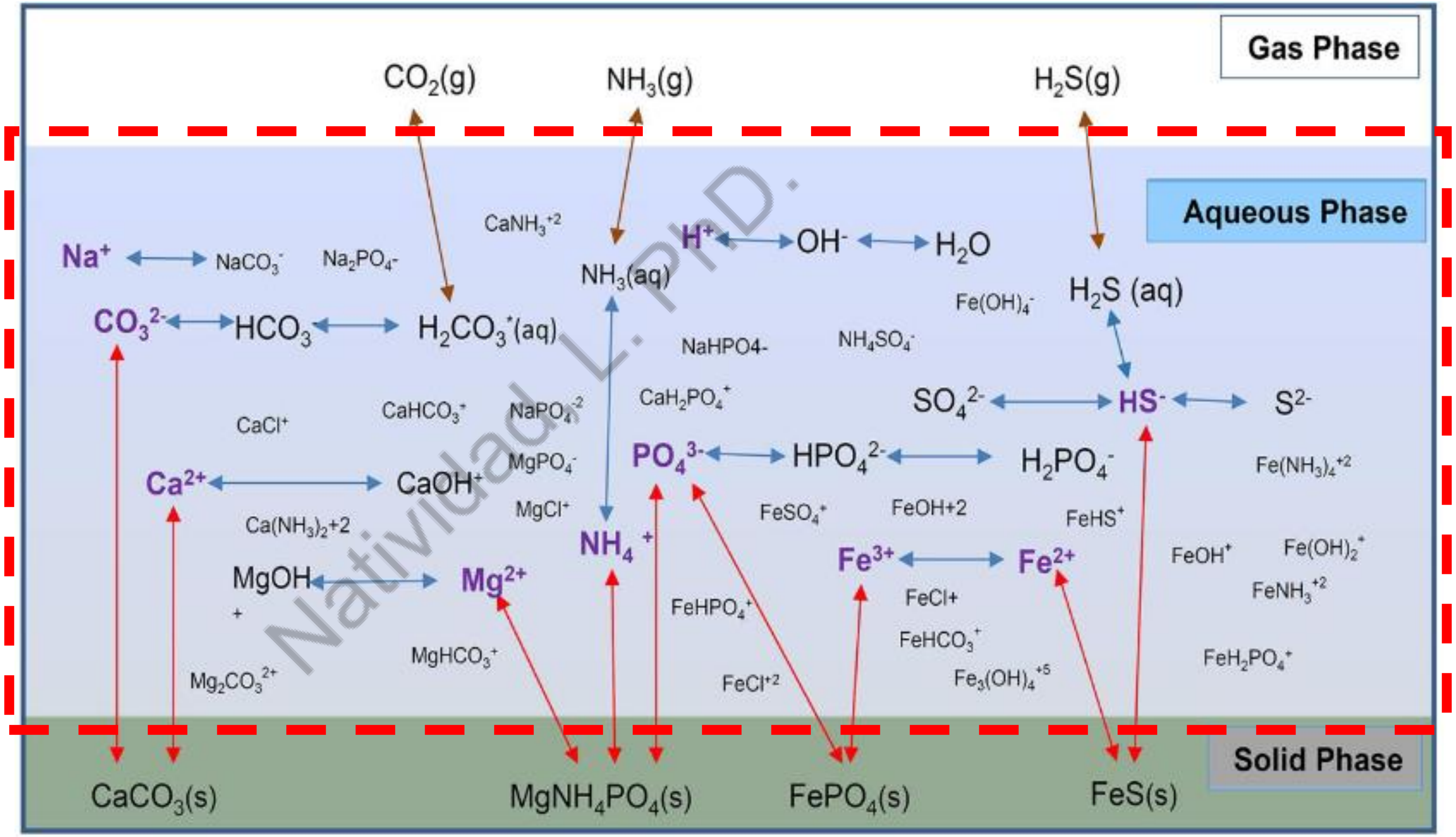
Chemical Speciation Basis

Elements will dissociate in ions, depending on the pH and solution composition



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Source: Kazadi, C. (2016). Dynamic modelling of minerals precipitation in wastewater

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Constant Solubility Product (K_{sp}) and Saturation Index (SI)

$$Mg^{2+}(aq) + NH_4^{+}(aq) + PO_4^{3-}(aq) + 6H_2O \overset{K_{sp}}{\rightleftharpoons} MgNH_4PO_4 \cdot 6H_2O(s)$$

$$\mathbf{SI} = \log_{10}\left(\frac{IAP}{K_{sp}}\right) = \log_{10}\left(\frac{a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}}}{\mathbf{K_{sp}}}\right)$$

Debye-Hückel modified by Davies

$$a_i = \gamma_i \cdot \mathbf{C_i}$$

Chemical Speciation

$$-\log_{10}\gamma_i = A \cdot Z_i^2\left[\frac{\mu^{1/2}}{1 + a \cdot \mu^{1/2}} + b \cdot \mu\right]$$

$$\mu = \sum \mathbf{C_i} \cdot Z_i^{\,2}$$

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Presenter’s Research Work

Water Science & Technology

Water Science & Technology Vol 87 No 6, 1393 doi: 10.2166/wst.2023.061

A comparison of struvite precipitation thermodynamics and kinetics modelling techniques

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ABSTRACT

Solution thermodynamics and kinetic modelling applied to struvite crystallisation–precipitation were reviewed from diverse references to determine proximity between predicted and cited experimental measurements. These simulations show the expected variability range of struvite saturation calculation when only limited solution compositional information is given, showing acceptable agreement between predicted and experimental struvite mass. This work also compares results from struvite crystallisation kinetic studies on liquid phase species depletion, crystallisation induction time, primary nucleation, secondary nucleation, crystal growth, and crystal aggregation. Large inconsistencies between reported kinetics were observed in many scenarios. Variations in species depletion models highlighted that they are only suitably applied to the specific system from which they were regressed. Spontaneous primary nucleation was predicted to occur in the range of $SI = 0.237$–0.8. Predicted primary nucleation rates vary over at least 10 orders of magnitude (depending on supersaturation) because of uncertainties in interfacial tension and maximum achievable nucleation rate. Secondary nucleation rates are more agreeable, varying over approximately two orders of magnitude. Growth rates varied over five orders of magnitude due to variations in experimental conditions. Aggregation rates are not thoroughly examined enough to make any inferences.

Key words: aggregation, growth, kinetic, nucleation, struvite recovery, thermodynamics

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$$\Omega = \frac{IAP}{K_{sp}}$$

$$S_a = \sigma = \Omega^{1/v} = \left(\frac{IAP}{K_{sp}}\right)^{1/v}$$

$$S_r = S_a - 1 = \Omega^{1/v} - 1$$

$$SI = \log_{10}(\Omega) = \log_{10}\left(\frac{IAP}{K_{sp}}\right)$$

$$SI^* = \log_{10}(S_a) = \log_{10}\left[\left(\frac{IAP}{K_{sp}}\right)^{1/3}\right] = \frac{1}{3}\log_{10}\left(\frac{IAP}{K_{sp}}\right)$$

$$S_h = IAP^{1/3} - K_{sp}^{1/3}$$

$$-\log_{10}\gamma = 0.5Z_i^2\mu^{1/2}$$

$$-\log_{10}\gamma = 0.5Z_i^2\left[\frac{\mu^{1/2}}{1+\mu^{1/2}}\right]$$

$$-\log_{10}\gamma = AZ_i^2\left[\frac{\mu^{1/2}}{1+a\cdot\mu^{1/2}} + b\cdot\mu\right]$$

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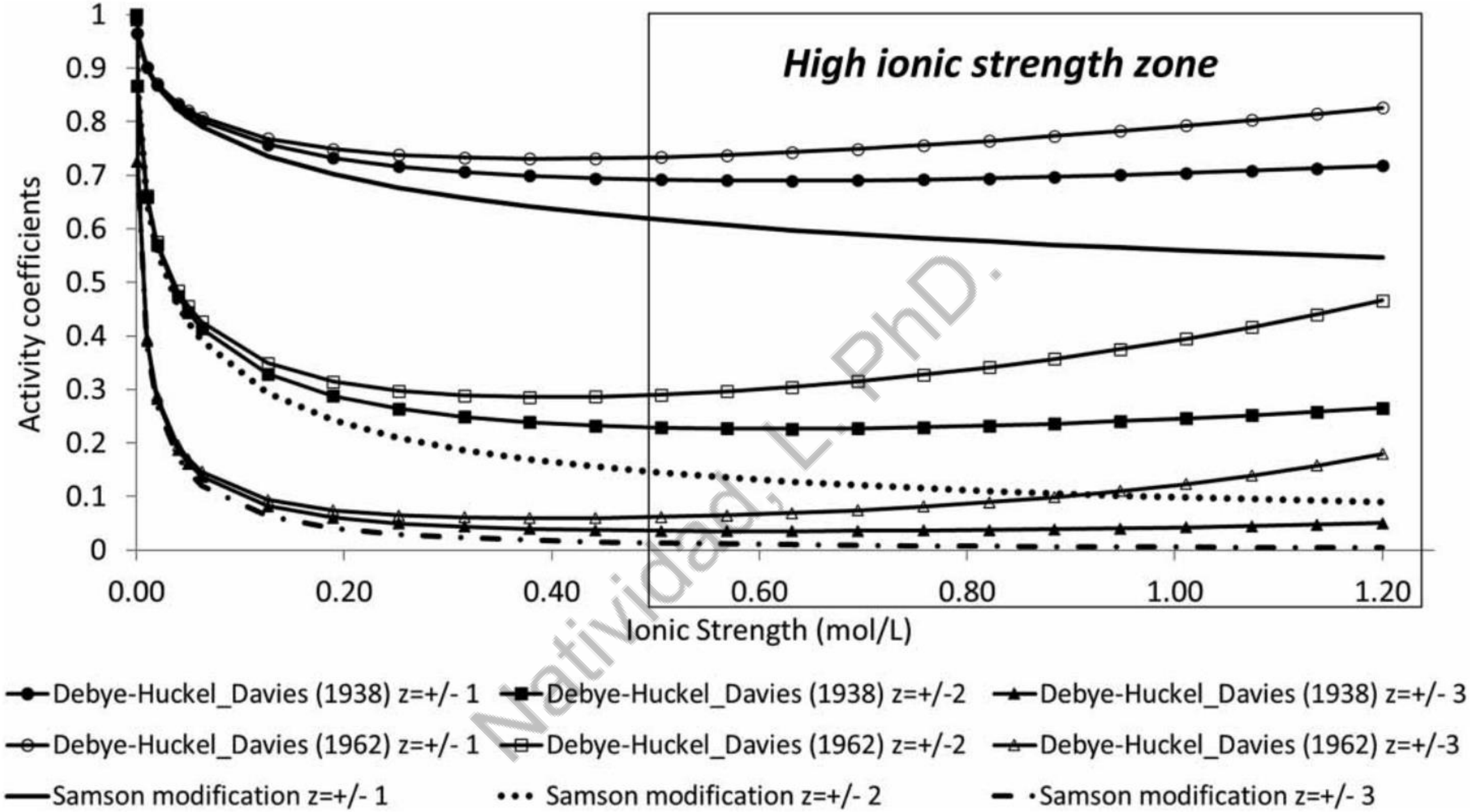

Figure 1 | Activity coefficients' prediction with different models as a function of ionic strength. *Note*: This plot has been elaborated by the authors of this paper with EES software using Equations (13) and (14).

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Table 1 | Saturation index prediction of solid phases in nutrient recovery scenarios, using different databases provided by PHREEQC software package

Struvite precipitation cases and considered input data for simulations		Prediction of Saturation Index using diverse databases within PHREEQC							References
		minteq.v4	wateq4f	phreeqC	sit	minteq	llnl	iso	
1) Swine wastewater: 23 °C, units (*mol/L*): *Mg* (1.92×10^{-3}), *N* (1.01×10^{-2}), *P* (1.63×10^{-3})	a) *pH* = 8.4	0.77, $(0.01)^2$	−27.97	−27.97	1.04, $(1.94)^1$	0.68	−28.1	−27.97	(Nelson *et al.* 2003)
	b) *pH* = 8.7	−1, $(0.61)^2$	−28.95	−28.95	1.27, $(2.55)^1$, $(0.38)^2$, $(0.45)^3$	−1.16	−29.08	−28.95	
	c) *pH* = 9.0	−3.09, $(1.21)^2$	−29.97	−29.97	−0.22, $(3.13)^1$, $(0.96)^2$, $(1.03)^3$	−3.37	−30.11	−29.97	
2) a) Synthetic digested liquor: 25 °C, *pH* (8.4), units (mol/L): *Mg* (2.62×10^{-3}), *N* (4.50×10^{-2}), *P* (1.74×10^{-3}), *Cl* (4.64×10^{-2})		0.84	−27.82	− 27.82	1.56 $(1.77)^1$	0.79	−27.87	−27.83	(Quintana *et al.* 2005)
b) Real digested liquour: 25 °C, *pH* (8.81), units (*mol/L*): *Mg* (2.62×10^{-3}), *N* (4.50×10^{-2}), *P* (1.74×10^{-3}), *Ca* (1.22×10^{-3}), *C* (2.11×10^{-2})		−2.02 (*)	−29.24 (*)	−29.24 (*)	1 (*)	−2.18 (*)	−29.29 (*)	−29.24 (*)	
3) Synthetic nutrient solution: 25 °C, *pH* (9.0), units (*mol/L*): *Mg* (3.5×10^{-3}), *N* (7×10^{-3}), *P* (7×10^{-3}), *Cl* (7×10^{-3})		−3.38, $(2.4)^2$, $(0.25)^4$	−29.75	−29.75	−0.70, $(4.21)^1$, $(2.29)^2$, $(2.10)^3$, $(0.18)^4$	−3.78	−29.81	−29.75	(Le Corre *et al.* 2007)
4) Raw wastewater adjusted with chemical reagents: 37 °C, *pH* (8.5), units (*mol/L*): *Mg* (1.00×10^{-1}), *N* (1.00×10^{-1}), *P* (1.00×10^{-1}), *Ca* (5.29×10^{-4}), *K* (5.50×10^{-2})		−1.30, $(5.61)^2$, $(1.83)^4$ (*)	−26.86 (*)	−26.86 (*)	1.36, $(7.09)^1$, $(6.64)^2$, $(4.96)^3$, $(1.61)^4$ (*)	−1.56 (*)	−26.45 (*)	−26.86 (*)	(Türker & Celen, 2007)
5) Synthetic supernatant: 20 °C, *pH* (8.51), units (*mol/L*): *Mg* (1.28×10^{-3}), *N* (4.28×10^{-2}), *P* (9.85×10^{-4})		1.12	−28.06	−28.06	1.35 $(1.18)^1$	1.07	−28.31	−28.06	(Rahaman *et al.* 2008)
6) Synthetic nutrient: 25 °C, *pH* 8.0, units (*mol/L*): *Mg* (8.27×10^{-3}), *N* (4.78×10^{-2}), *P* (6.52×10^{-3})		2.09, $(1.23)^2$, $(0.44)^4$	−25.74	−25.74	2.07, $(3.08)^1$, $(1.16)^2$, $(0.97)^3$, $(0.38)^4$	2.04	−25.80	−25.75	(M. Iqbal *et al.* 2008)

Notes: Struvite *SI* are the unparenthesis values; and parenthesis values with superscripts indicate: (1) Bobierite $Mg_3(PO_4)_2.8H_2O$, (2) Magnesium Phosphate $Mg_3(PO_4)_2$, (3) Cattite $Mg_3(PO_4)_2.22H_2O$, (4) Newberyite $MgHPO_4.3H_2O$. Additionally: (*) Positive saturation index in solid phases containing Calcium.

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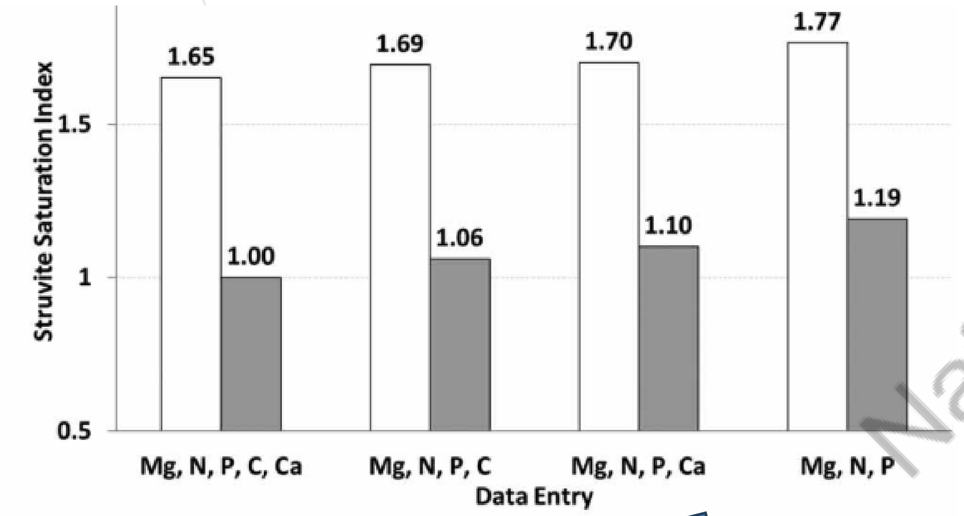
Water Science & Technology Vol 87 No 6, 1393 doi: 10.2166/wst.2023.061

A comparison of struvite precipitation thermodynamics and kinetics modelling techniques

Leynard Natividad-Marin*, Max William Burns and Phil Schneider



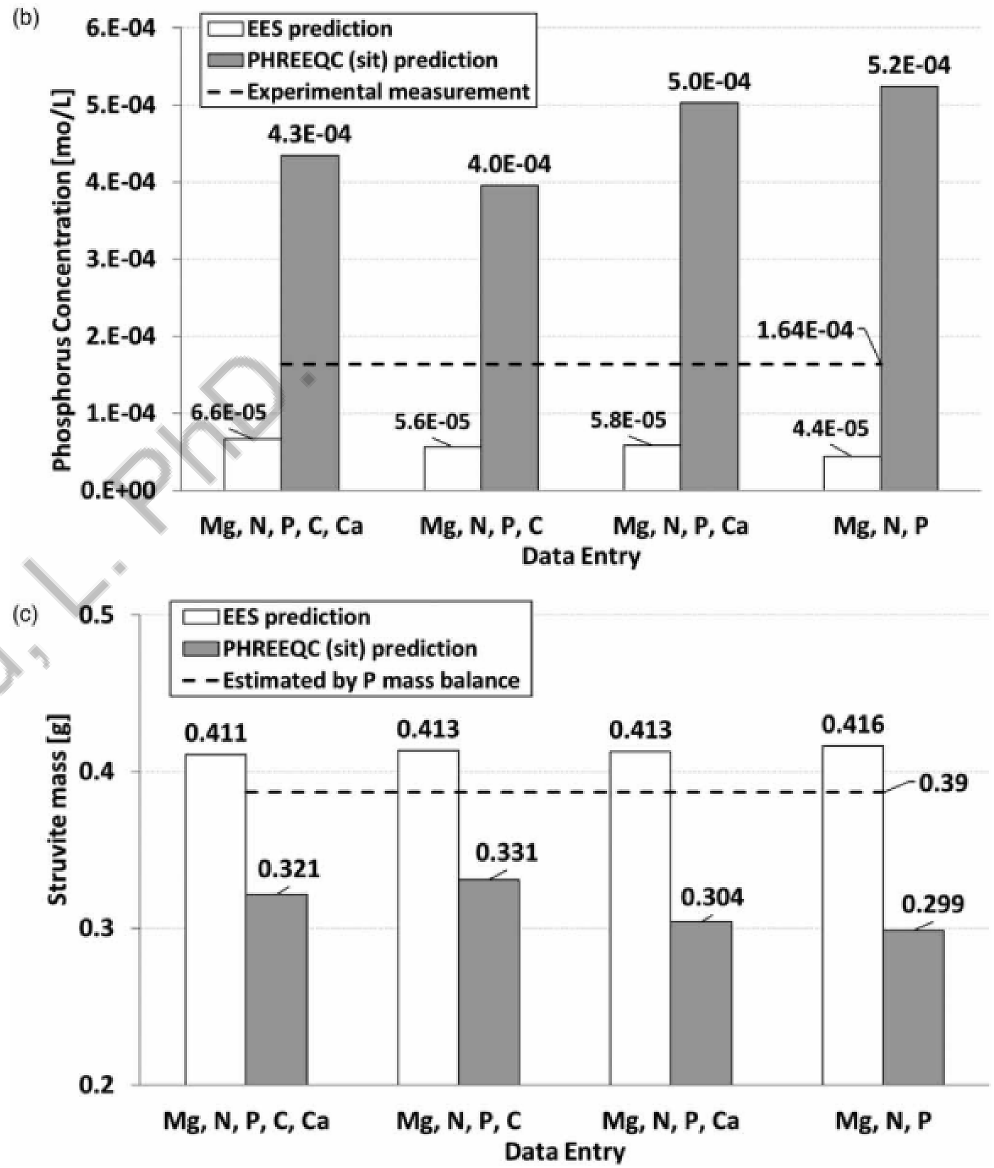


Figure 2 | Struvite precipitation from real digested liquour (case 2.b in Table 1) by discussing struvite *SI* at non-equilibrium (a), dissolved P (b), and struvite (c) at equilibrium conditions.

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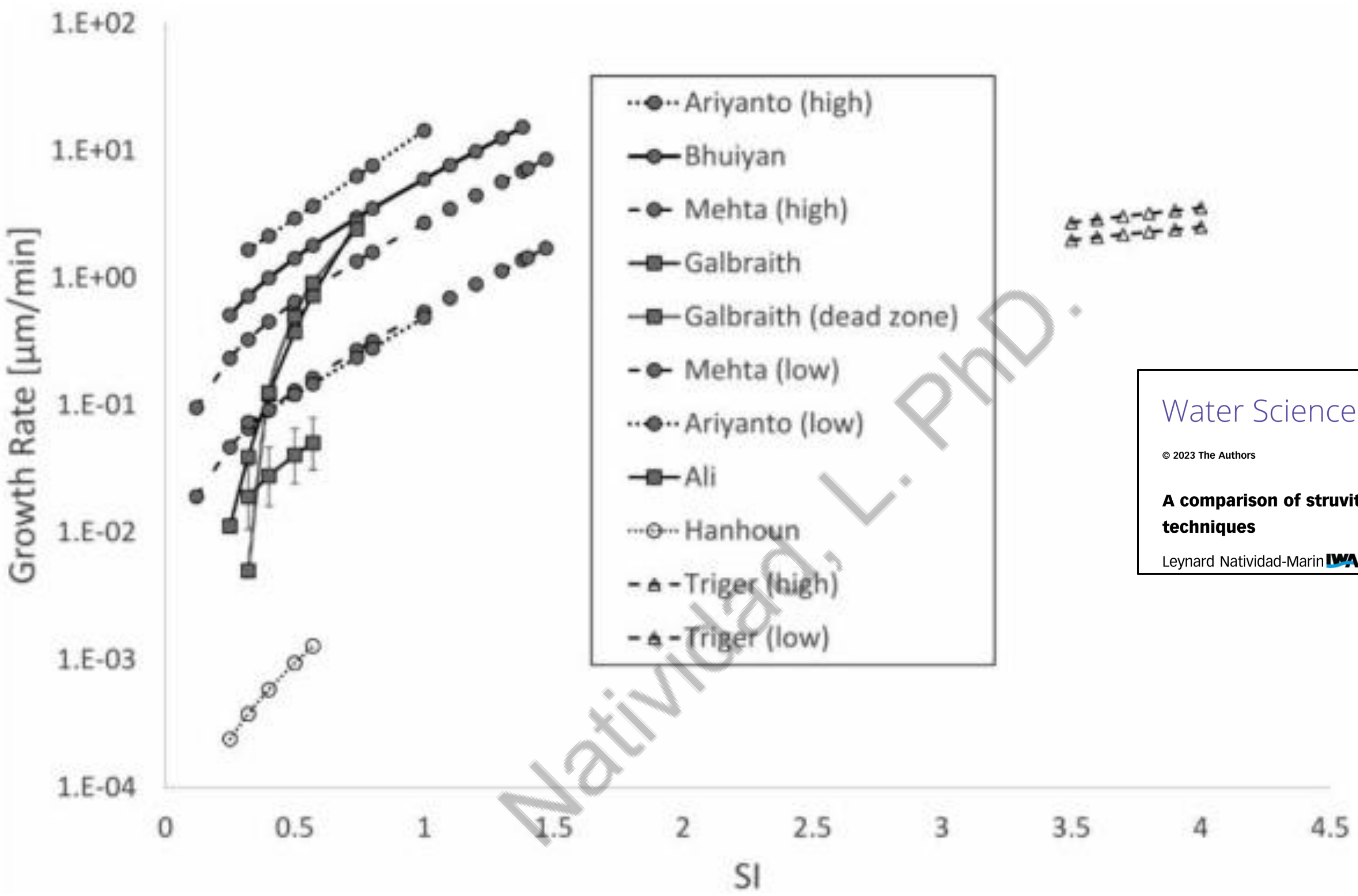

Figure 7 | Crystal linear growth rate comparison. Dashed and solid lines represent batch and continuous reactors, respectively. Circles indicate $C_{PO_4} < 5$ mM, squares indicate 5 mM $\leq C_{PO_4} < 10$ mM and triangles indicate $C_{PO_4} \geq 10$ mM. Filled and unfilled markers represent seeded and unseeded scenarios, respectively. Uncertainties in kinetic parameters were incorporated where available and significant enough to be visible.

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What have we learned today?

i. Importance of the nutrient recovery topic around the world.

ii. We explored useful models to predict nutrient recovery.

iii. We learned the importance of computing tools (software) to estimate chemical speciation and then saturation index.

iv. We assessed the basis of solution thermodynamics and some ways to validate equilibrium equations selection

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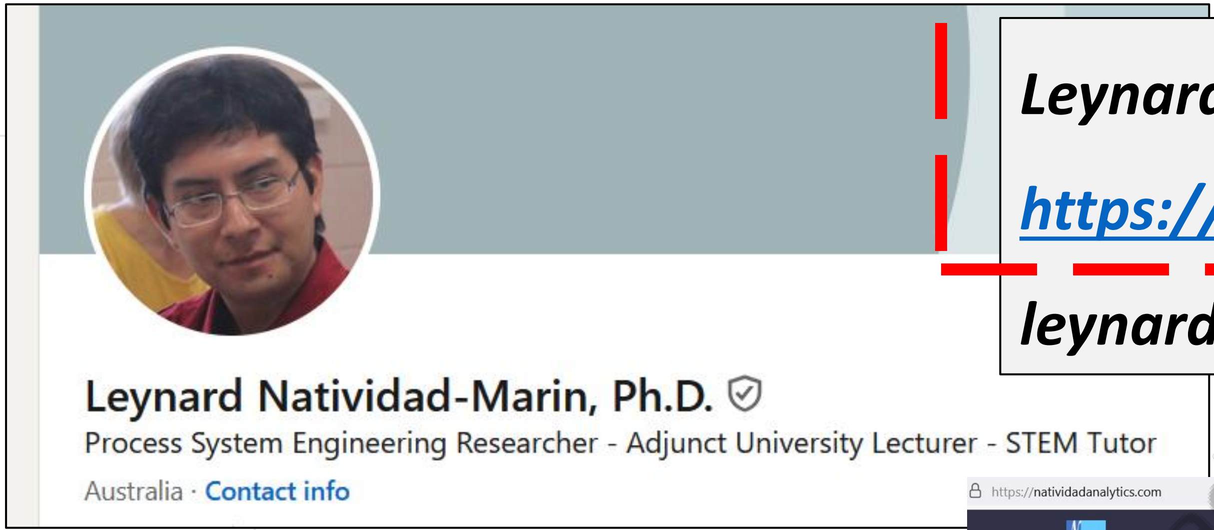
Contact



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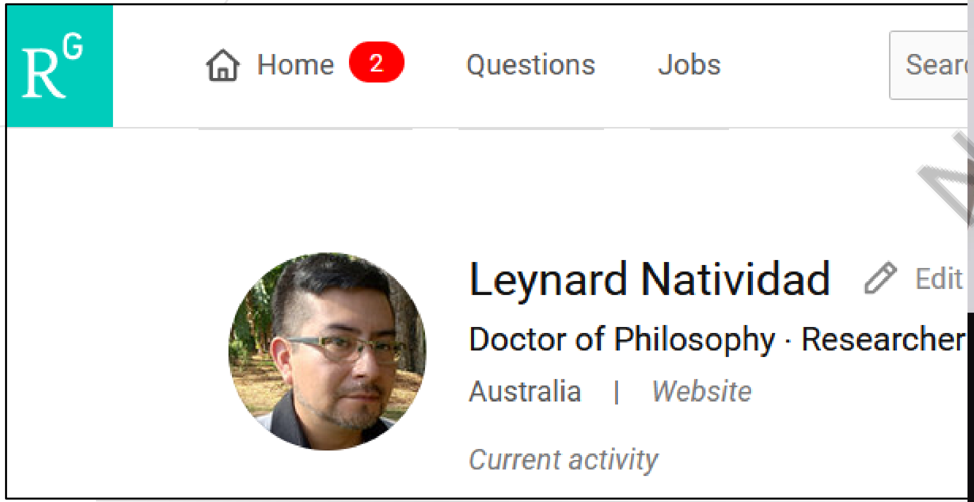

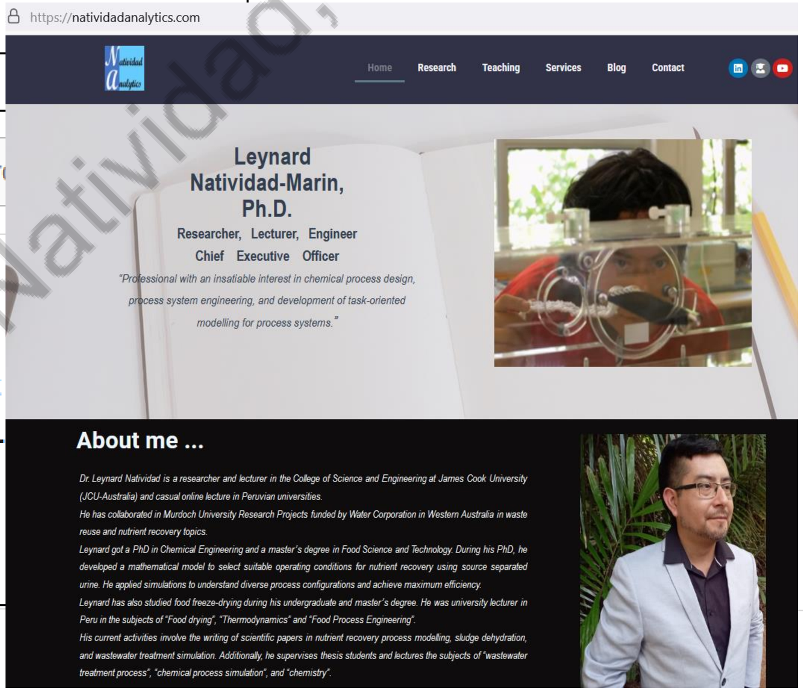

Enviarme un correo con dudas que no se hayan podido responder a tiempo

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Natividad Analytics

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***Natividad Analytics**, fundada en 2022 y liderada por Leynard Natividad-Marin, Ph.D., es una **consultoría y proveedora de educación con sede en Australia especializada en ingeniería de sistemas de procesos (simulación computacional) aplicada a procesos químicos, con un próximo énfasis en ciencia de datos e inteligencia artificial**. Con una profunda experiencia en diseño de **procesos químicos, modelado** orientado a tareas, recuperación de nutrientes y tratamiento de aguas residuales, ayudamos a industrias, investigadores y universidades a optimizar procesos, mejorar la sostenibilidad y convertir datos complejos en información accionable. También impartimos **cursos de ingeniería en línea atractivos y flexibles que hacen que los temas desafiantes sean prácticos y agradables.** Ya sea que necesite soluciones avanzadas de analítica, herramientas de modelado personalizadas, desarrollo profesional, **Natividad Analytics** entrega un soporte experto y orientado a resultados, diseñado para acelerar la innovación y el éxito en la ciencia y la ingeniería en todo el mundo.*

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ACERCA DEL EXPOSITOR Y GERENTE DE "NA":

Leynard Natividad-Marin, Ph.D., *es un investigador peruano-australiano y profesor en el College of Science and Engineering de la* ***James Cook University (JCU – Australia)****, además de instructor en línea ocasional para universidades en Perú. El Dr. Natividad es* ***Ingeniero Químico*** *egresado de la Universidad Nacional del Callao (UNAC-Perú), posee un* ***PhD en Ingeniería Química*** *(enfocado en modelado matemático avanzado y estudios experimentales para la recuperación de nutrientes de orina separada en la fuente) de la JCU y un* ***Máster en Ciencia y Tecnología de Alimentos*** *(UNAC – Perú).*

El Dr. Natividad-Marin aporta una profunda experiencia en diseño de procesos químicos, modelado orientado a tareas, tratamiento de aguas residuales y recuperación de nutrientes. Su objetivo es seguir mejorando profesionalmente para ***contribuir a la sostenibilidad mundial mediante la aplicación de conocimientos de ingeniería química,*** *mientras comparte continuamente su conocimiento a través de conferencias técnicas internacionales organizadas por "****The Institution of Chemical Engineers (IChemE)****", "****The American Institute of Chemical Engineers (AIChE) - PROCESA****" y "****The International Water Association (IWA)****", entre otras.*

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Se lo agradeceré mucho.

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Thanks, mate

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