International Conference on Nanotechnology for Renewable Materials

Synthesis and Characterization of Microencapsulated Controlled Release Fertilizers (CRFs) by Spray-Drying

Gutierrez Cesar, Juarez-Luna Gregorio; Rivera-Toledo Martin, Neri-Torres, Elier, Quevedo Ivan R.

UNIVERSIDAD IBEROAMERICANA
CIUDAD DE MÉXICO ®

TAPPI NANO DIVISION

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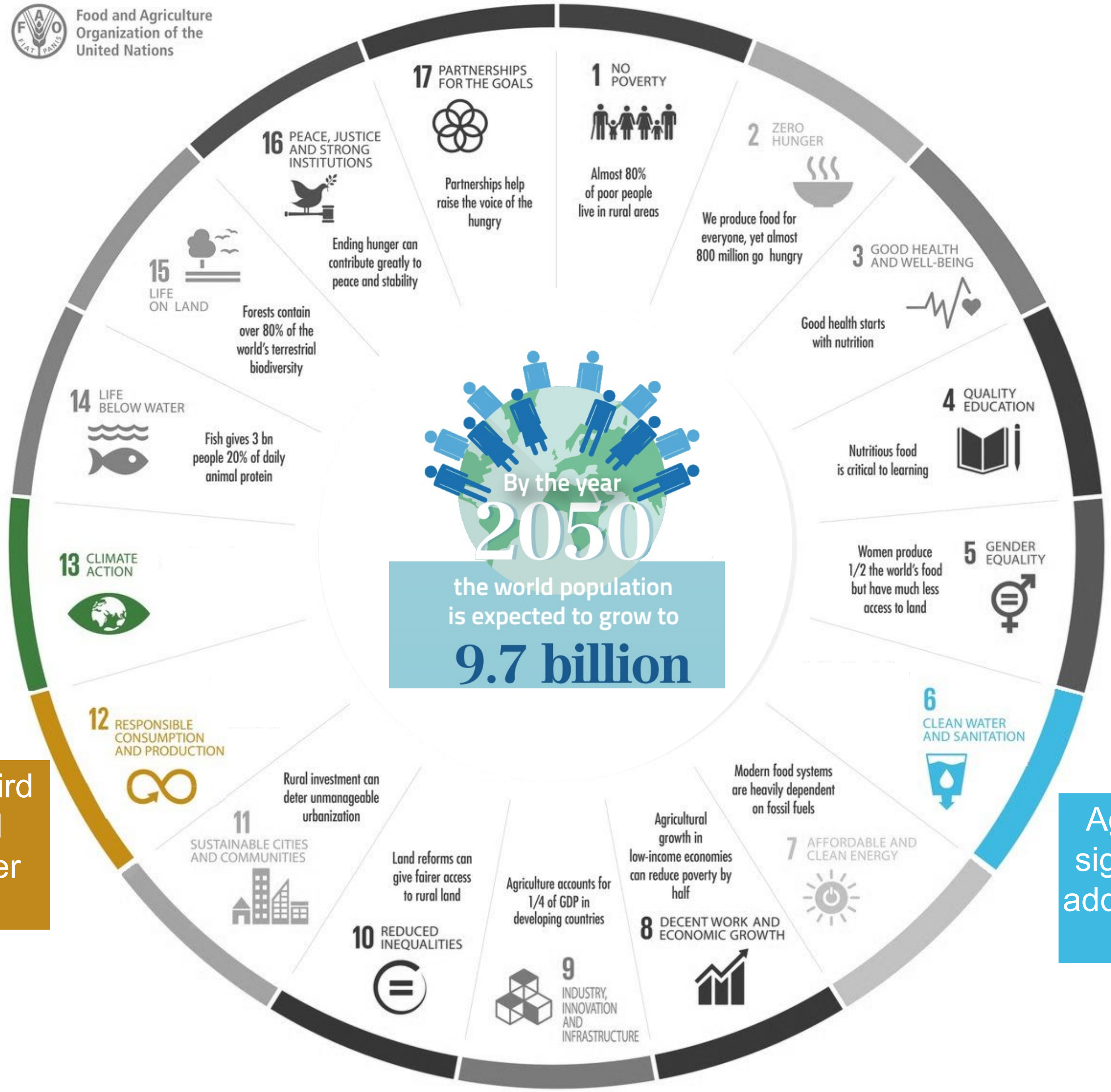
Agenda

- Conventional vs. Controlled-Release Fertilizers (CRFs)
- Objectives of this Investigation
- Experimental Results
- Simulation Model Proposed
- Preliminary Conclusions

The Future of Food and Agriculture

Agriculture plays a substantial role in the exacerbation of global warming

More than one-third of the total food produced is either lost or wasted



1 NO POVERTY

Almost 80% of poor people live in rural areas

2 ZERO HUNGER

We produce food for everyone, yet almost 800 million go hungry

3 GOOD HEALTH AND WELL-BEING

Good health starts with nutrition

4 QUALITY EDUCATION

Nutritious food is critical to learning

5 GENDER EQUALITY

Women produce 1/2 the world's food but have much less access to land

6 CLEAN WATER AND SANITATION

7 AFFORDABLE AND CLEAN ENERGY

Modern food systems are heavily dependent on fossil fuels

8 DECENT WORK AND ECONOMIC GROWTH

Agricultural growth in low-income economies can reduce poverty by half

9 INDUSTRY, INNOVATION AND INFRASTRUCTURE

Agriculture accounts for 1/4 of GDP in developing countries

10 REDUCED INEQUALITIES

Land reforms can give fairer access to rural land

11 SUSTAINABLE CITIES AND COMMUNITIES

Rural investment can deter unmanageable urbanization

12 RESPONSIBLE CONSUMPTION AND PRODUCTION

13 CLIMATE ACTION

14 LIFE BELOW WATER

Fish gives 3 bn people 20% of daily animal protein

15 LIFE ON LAND

Forests contain over 80% of the world's terrestrial biodiversity

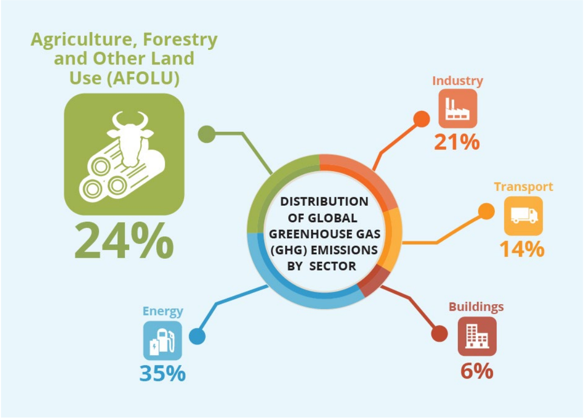
16 PEACE, JUSTICE AND STRONG INSTITUTIONS

Ending hunger can contribute greatly to peace and stability

17 PARTNERSHIPS FOR THE GOALS

Partnerships help raise the voice of the hungry

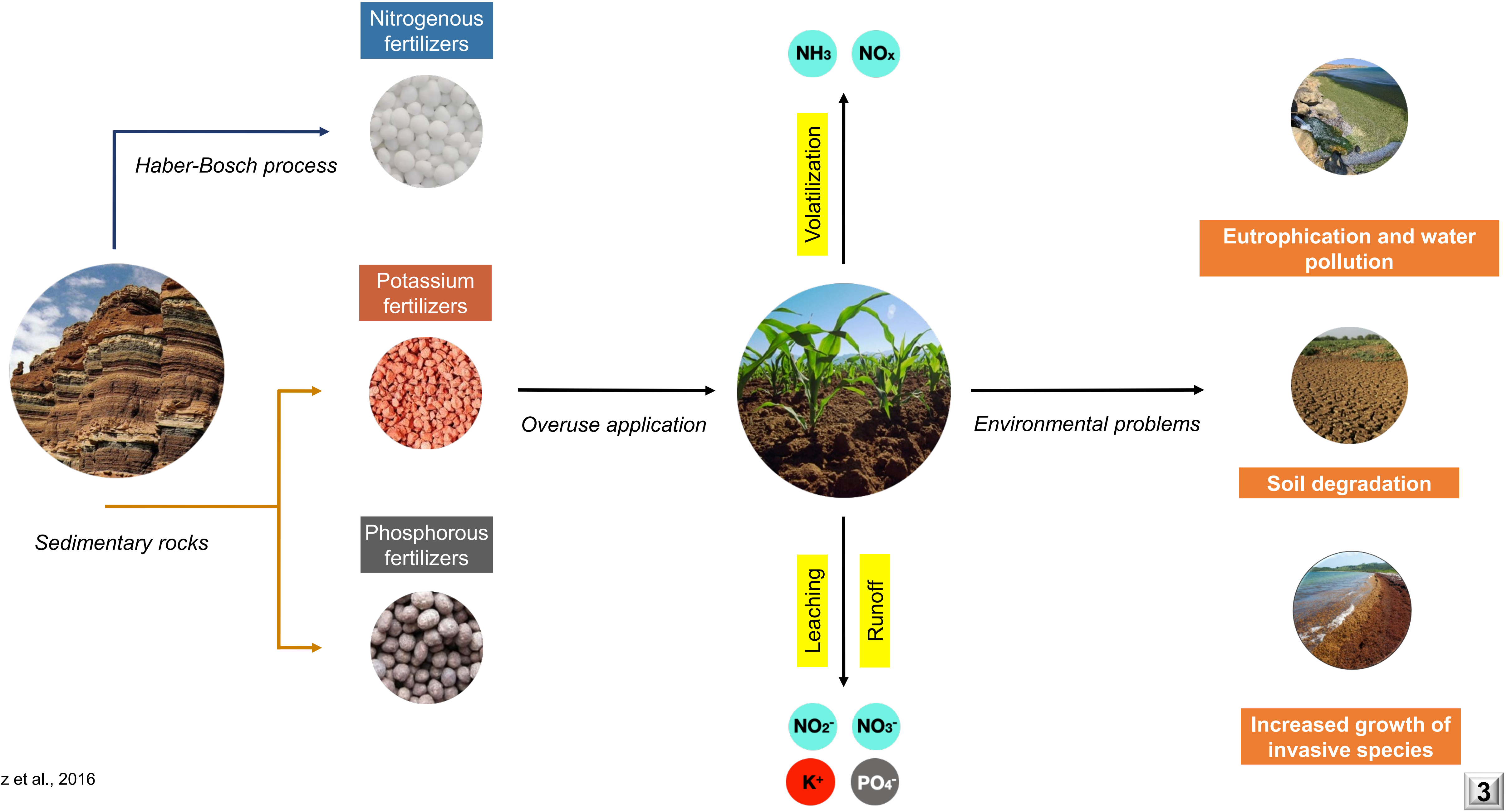
By the year 2050 the world population is expected to grow to 9.7 billion



Agriculture presents significant potential in addressing the issue of water scarcity

Fao.org

Conventional Fertilizers



Haber-Bosch process

Nitrogenous fertilizers

Potassium fertilizers

Phosphorous fertilizers

Sedimentary rocks

Overuse application

Volatilization

NH_3 NO_x

Leaching

Runoff

NO_2^- NO_3^-

K^+ PO_4^-

Environmental problems

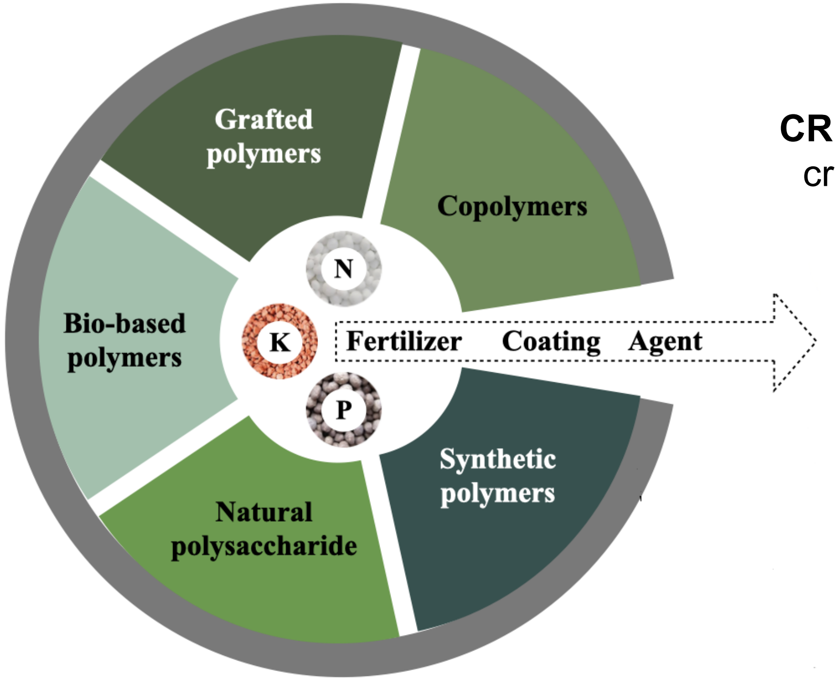
Eutrophication and water pollution

Soil degradation

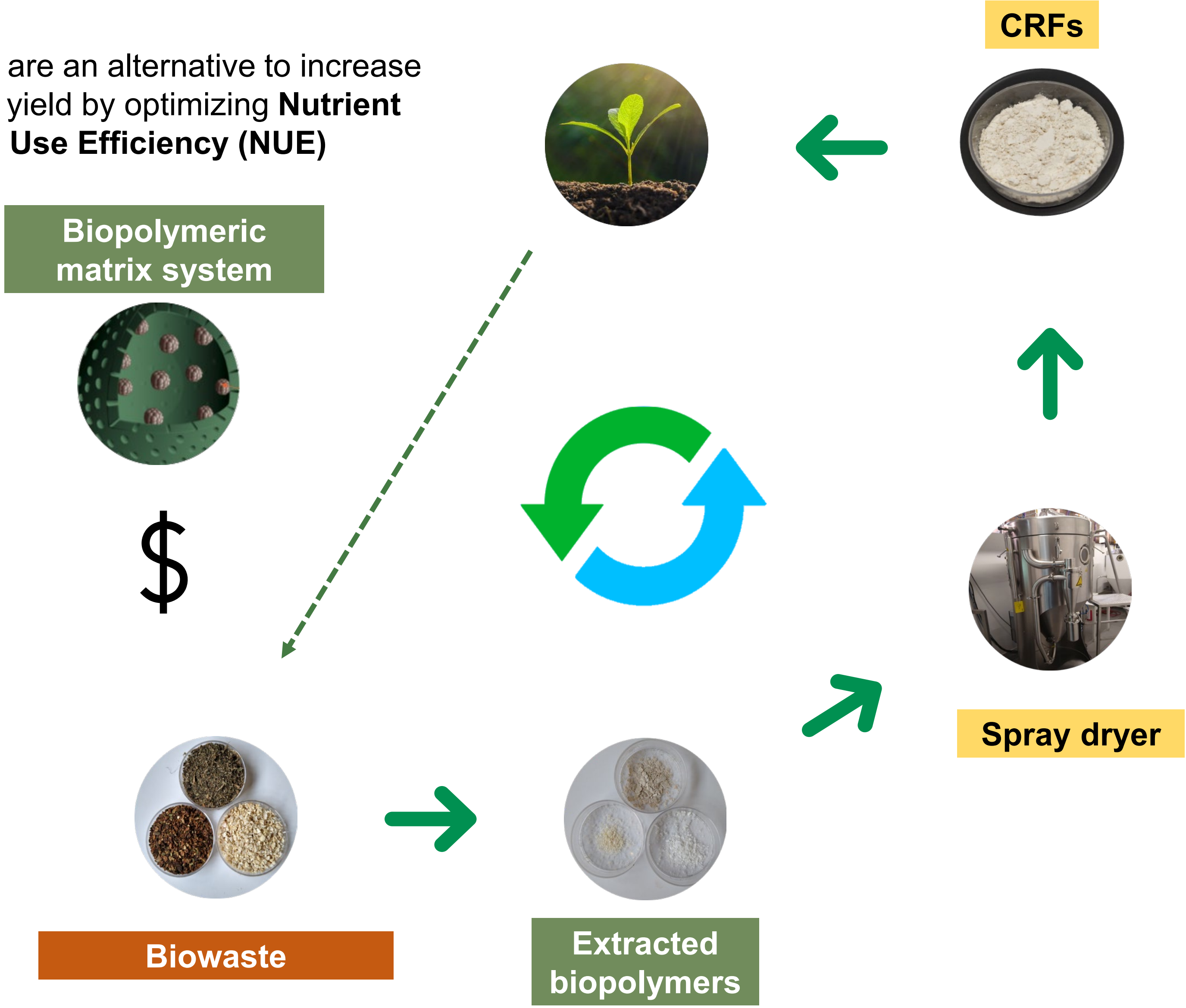
Increased growth of invasive species

Naz et al., 2016

Controlled-Release Fertilizers (CRFs)



CRFs are an alternative to increase crop yield by optimizing **Nutrient Use Efficiency (NUE)**



Biopolymeric matrix system

$

CRFs

Spray dryer

Biowaste

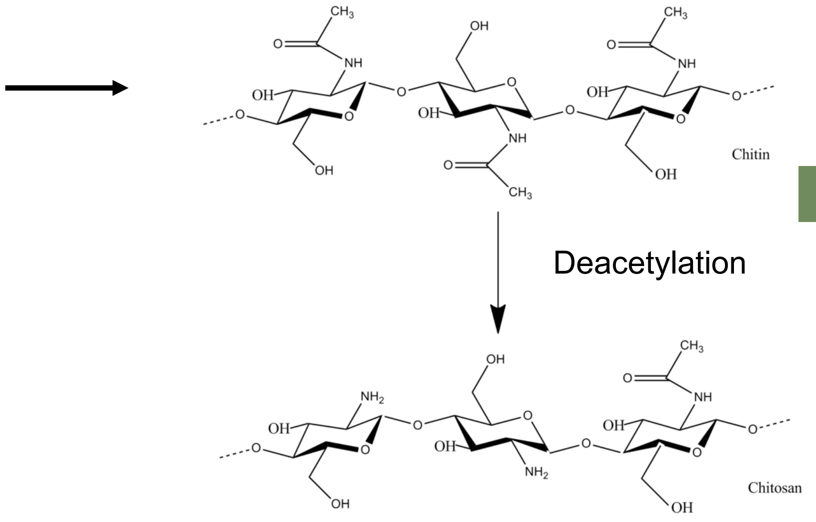
Extracted biopolymers

Lignocellulosic materials	Biopolymers	Biobased polymers
Lignin	Sodium alginate	Biobased polyurethane
Acetylated lignin	k-Carregeenan	Polyvinyl alcohol
Cotton stalk	Starch	Biobased epoxy
Wheat straw	Chitosan	Poly-eugenol sulfone
Cellulose	Maltodextrin	Epoxy resin
Ethyl cellulose	Sodium alginate	Polyhydroxyalkanoates
Carboxymethyl cellulose	Gelatin	Polylactic acid

Gutiérrez et al., 2022

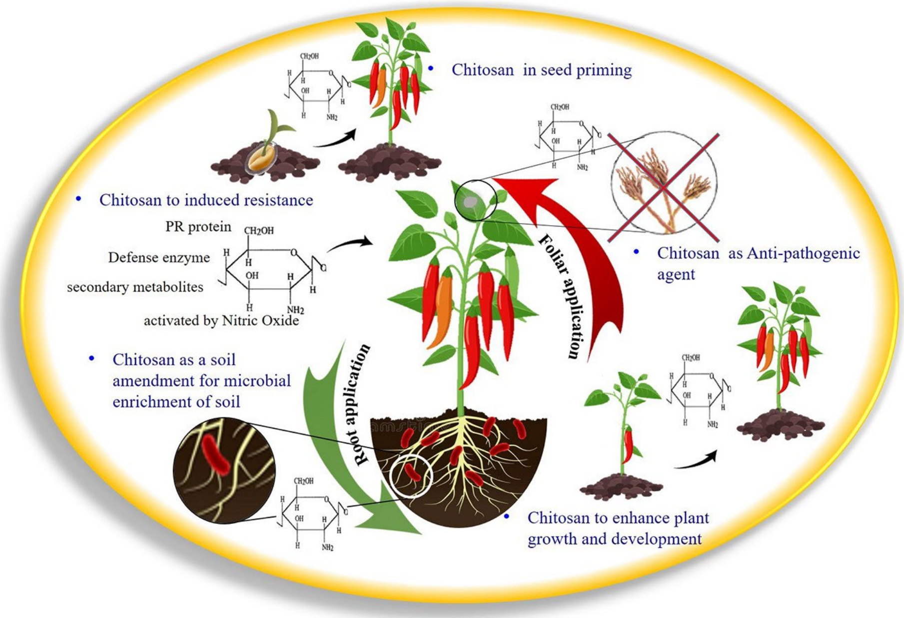
CRF Based on Chitosan

Food waste



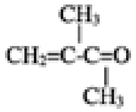
Chitin

Chitosan



+

MMA



$CH_2=\overset{CH_3}{C}-\underset{CH_3}{C}=O$

Co-polymerization chitosan-MMA

+

Urea

Chitosan is a promising encapsulating agent for CRF due to its biocompatibility, lack of toxicity, antibacterial activity, high availability, and natural compound to control plant diseases.

Borges-Valle et al., 2020; Roohallah et al., 2022

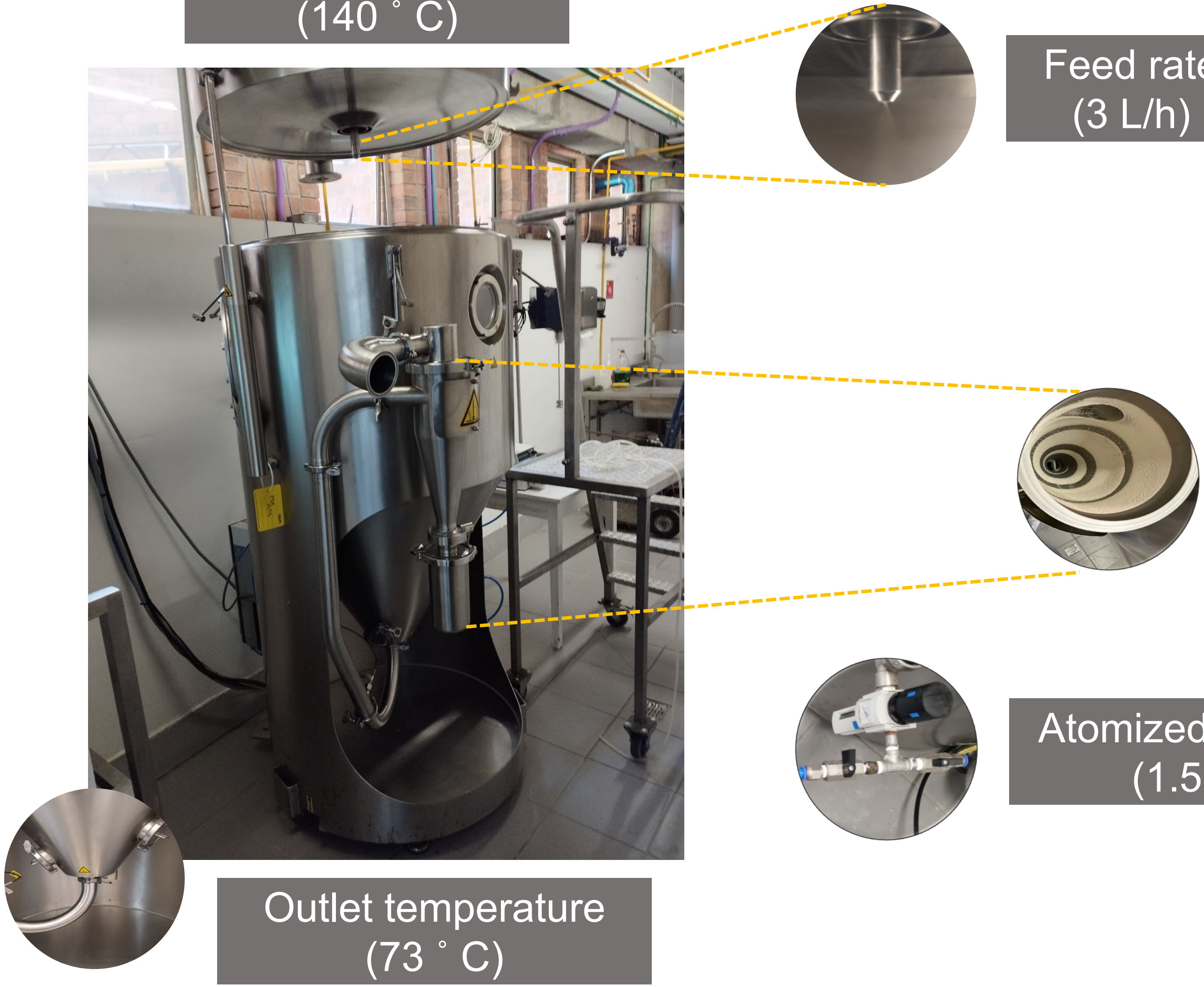
Objectives of this Investigation

- To synthesize a CRF by employing chitosan, MMA (methyl methacrylate), and urea through the process of spray drying. This objective focuses on the production of a fertilizer that releases nutrients gradually over time.

- Modelling the spray drying process to obtain controlled-release fertilizers, enabling the prediction of particle properties and thus enhancing the product's quality.

Ali Aslam et al, 2022

Spray Dryer (MM-PSR GEA-NIRO)



Inlet temperature
(140 ° C)

Feed rate
(3 L/h)

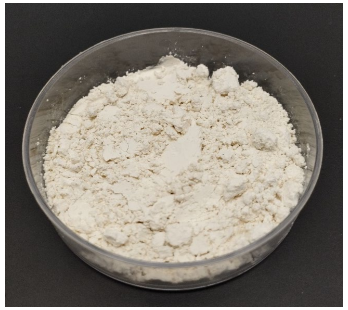
Atomized pressure
(1.5 bar)

Outlet temperature
(73 ° C)

Peristaltic pump

Biopolymeric solution

Solution
temperature
(22 ° C)

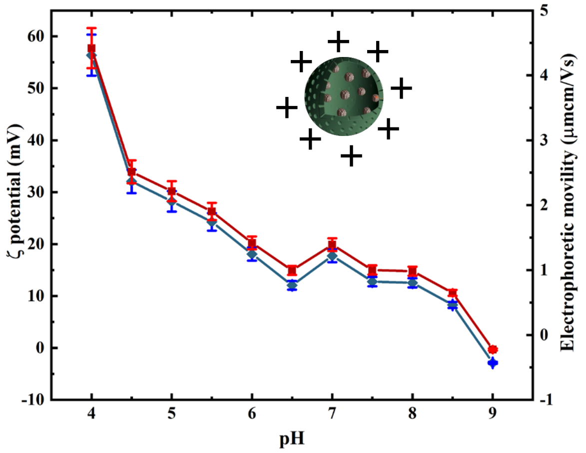


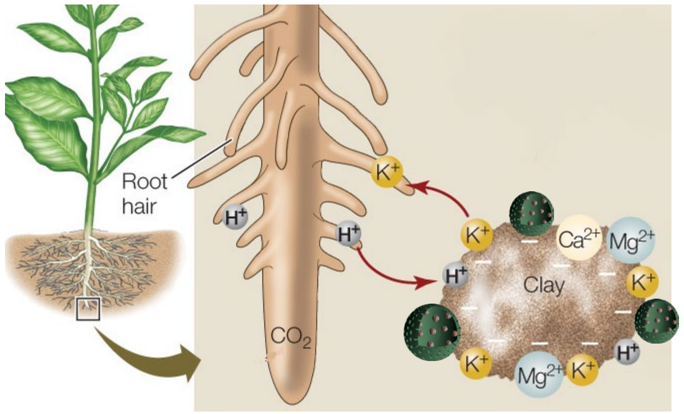
CRF

Yield
25-75 %

Physicochemical Properties

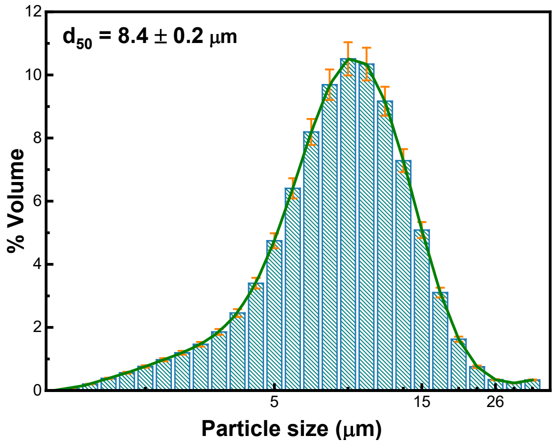
Net surface charge



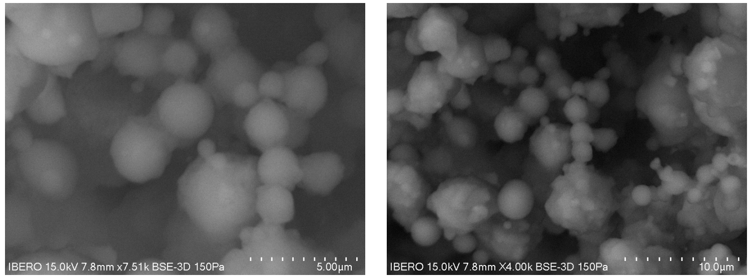


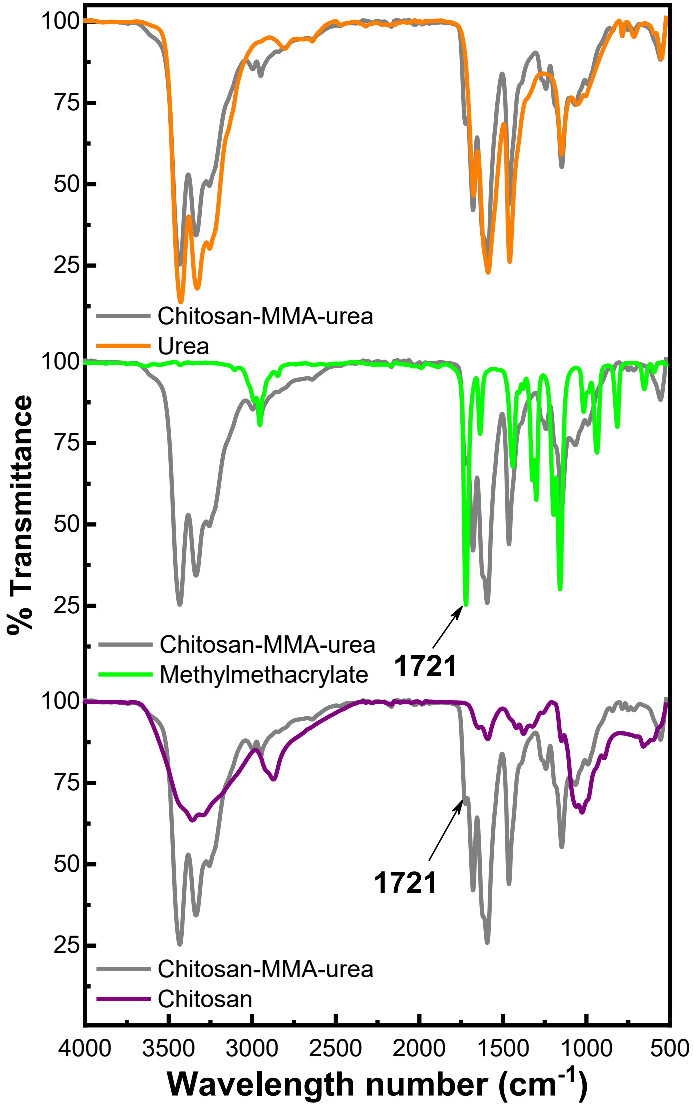
https://www.macmillanhighered.com/

Particle size

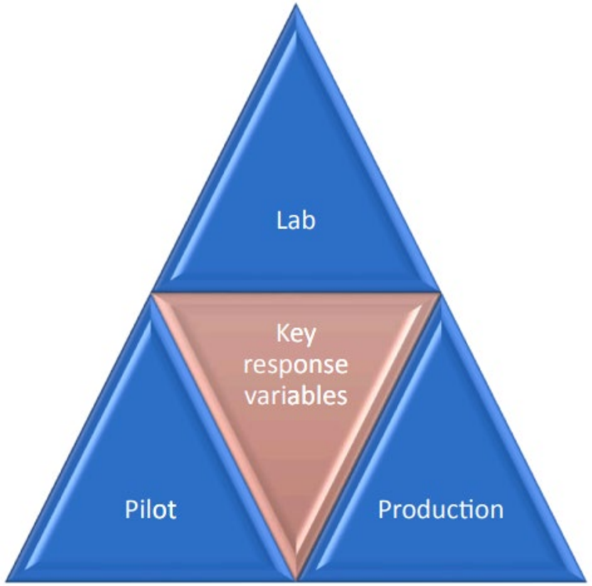


Morphology





Simulation of Spray Dryer Performance



Simulation

Mini spray dryer

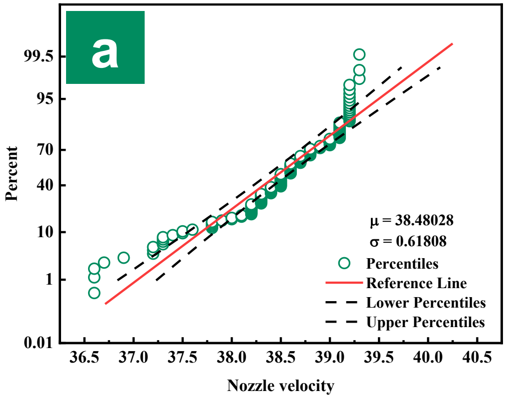
Pilot spray dryer

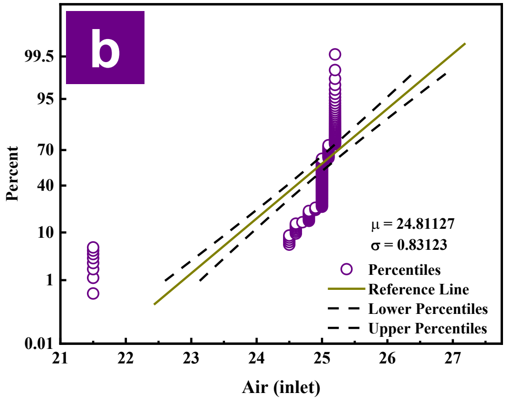
Industrial spray dryer

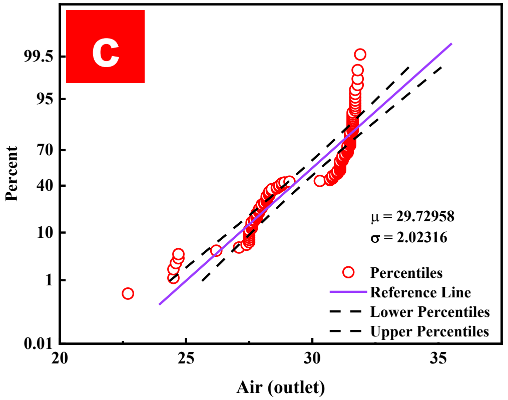
Scalability process

Poozesh et al., 2019; buchi.com; gea.com

Operational parameters



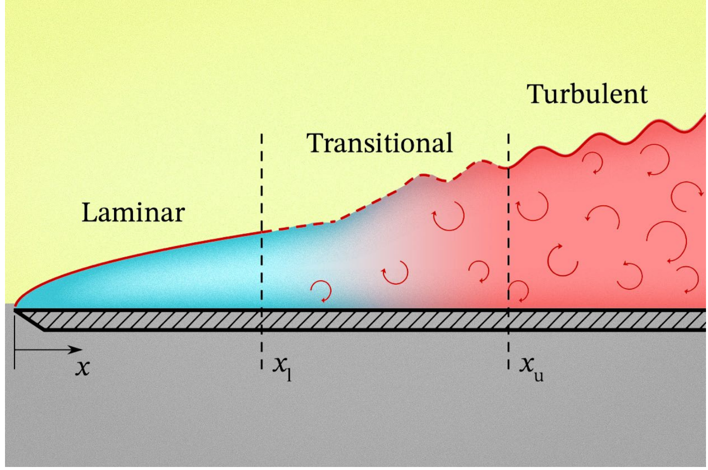


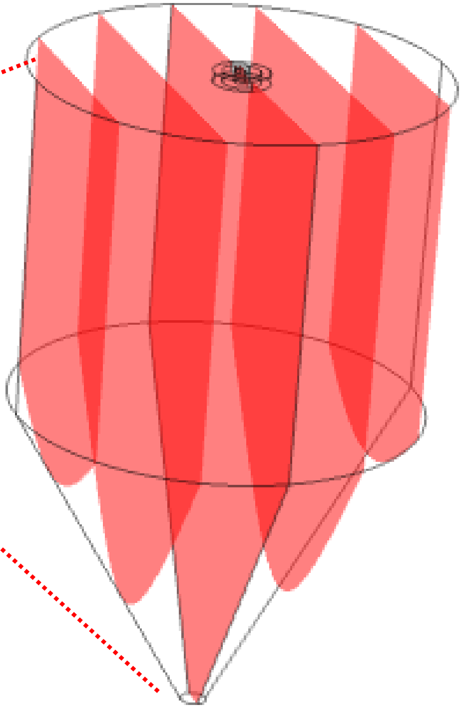


Process Parameters	
Nozzle velocity (a)	38.5 m/s
Drying gas velocity (b)	24.8 m/s
Outlet gas velocity (c)	29.7 m/s

Response Variables
Particle mass, size, and velocity
Humidity content
Outlet temperature
Velocity profile (drying gas)

Turbulent flow





Reynolds stress

$$\overline{\rho u'v'} = \mu_t \frac{\partial \bar{u}}{\partial y}$$

Turbulent viscosity

$$\mu_T = \rho C_\mu \frac{k^2}{\varepsilon}$$

Turbulent viscosity (μ_T) is obtained using de ***k*-ε model**

Computational Fluid Dynamics (CFD)

k-ε model

(widely employed in industrial processes)

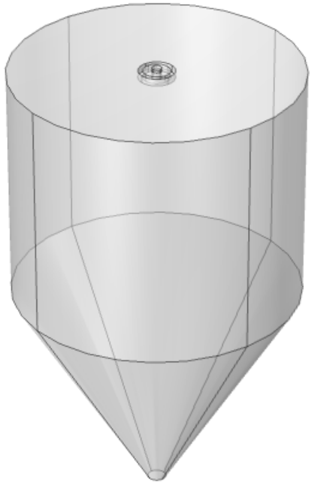
Turbulent kinetic energy (*k*)

$$\rho \frac{\partial k}{\partial t} + \rho u \cdot \nabla k = \nabla \cdot \left(\left(\mu + \frac{\mu_T}{\sigma_k} \right) \nabla k \right) + P_k - \rho \varepsilon$$

Turbulent dissipation rate (ε)

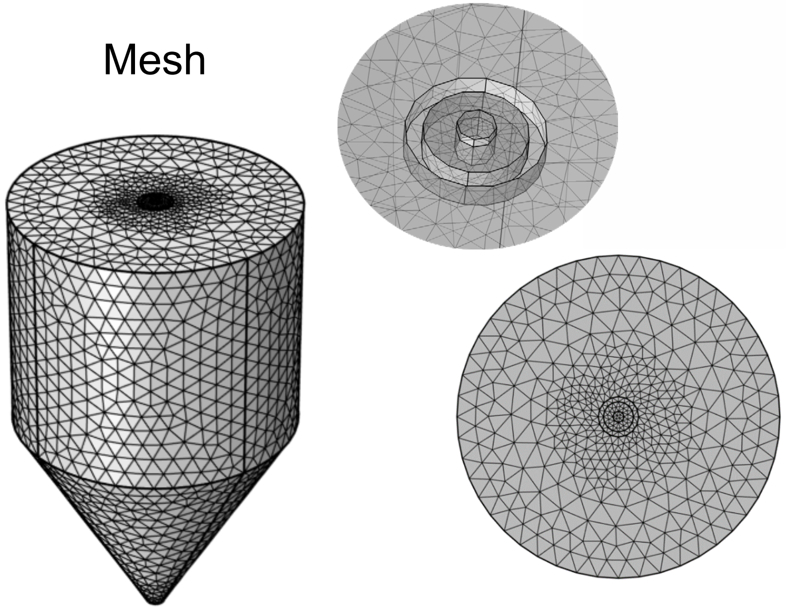
$$\rho \frac{\partial \varepsilon}{\partial t} + \rho u \cdot \nabla \varepsilon = \nabla \cdot \left(\left(\mu + \frac{\mu_T}{\sigma_\varepsilon} \right) + C_{\varepsilon 1} \frac{\varepsilon}{k} P_k - C_{\varepsilon 2} \rho \frac{\varepsilon^2}{k} \right)$$

Preliminary results with CFD Modelling

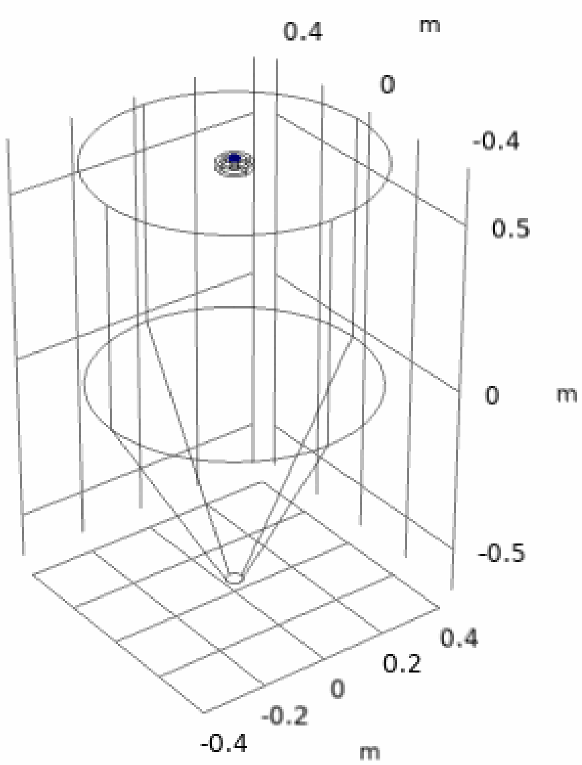


Geometry

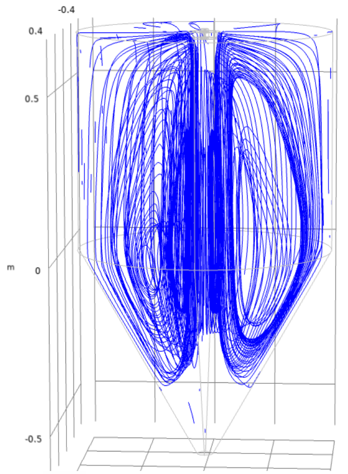
Mesh



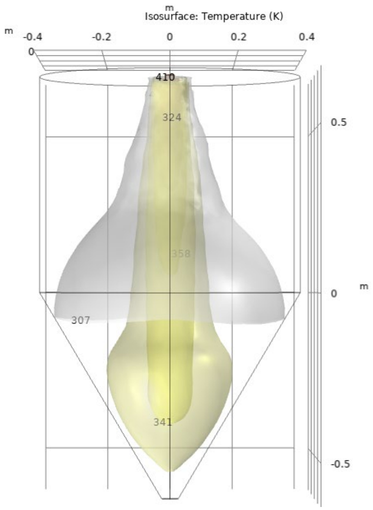
Particle trajectories



Air velocity field

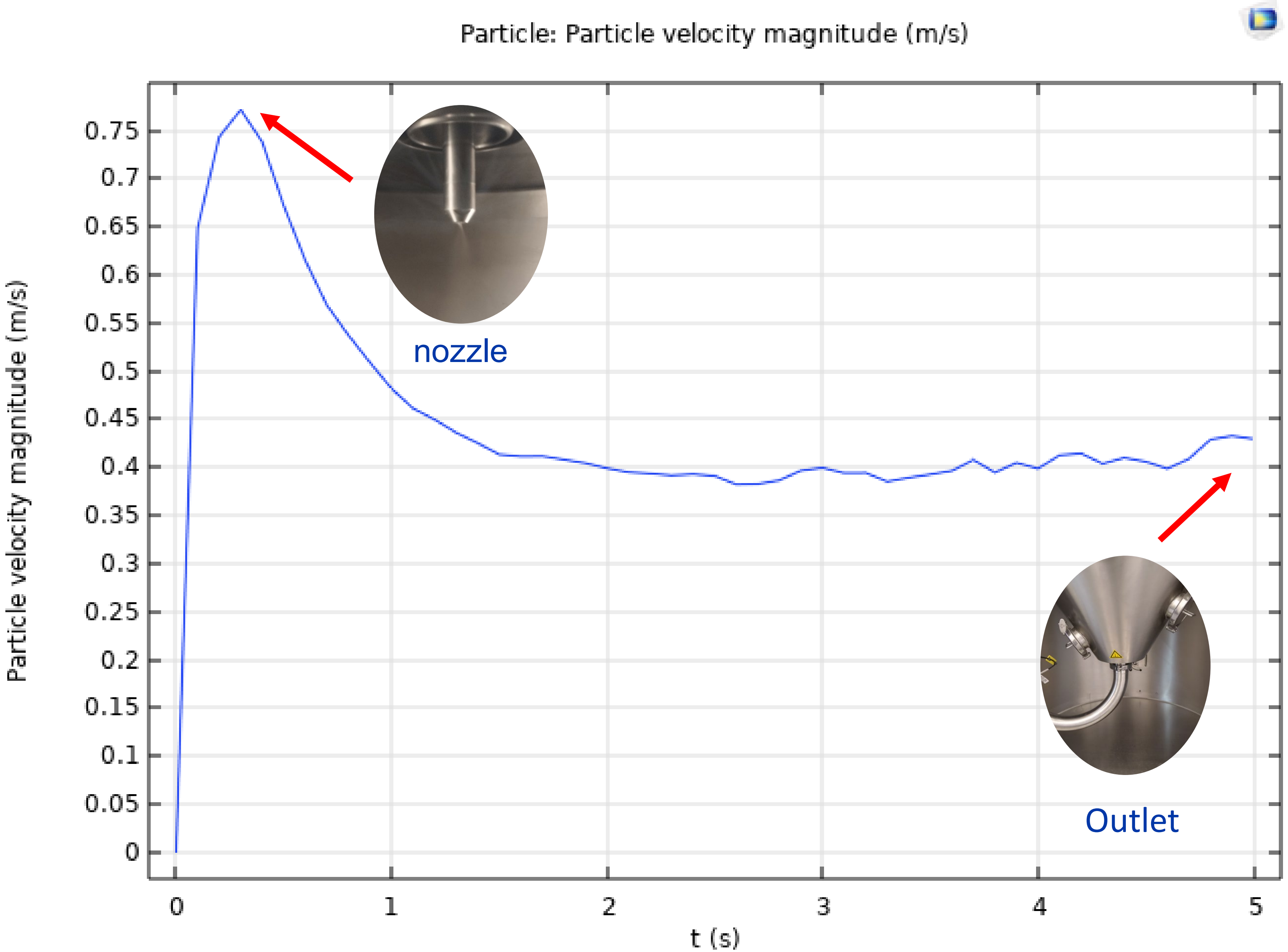


Isosurface temperature

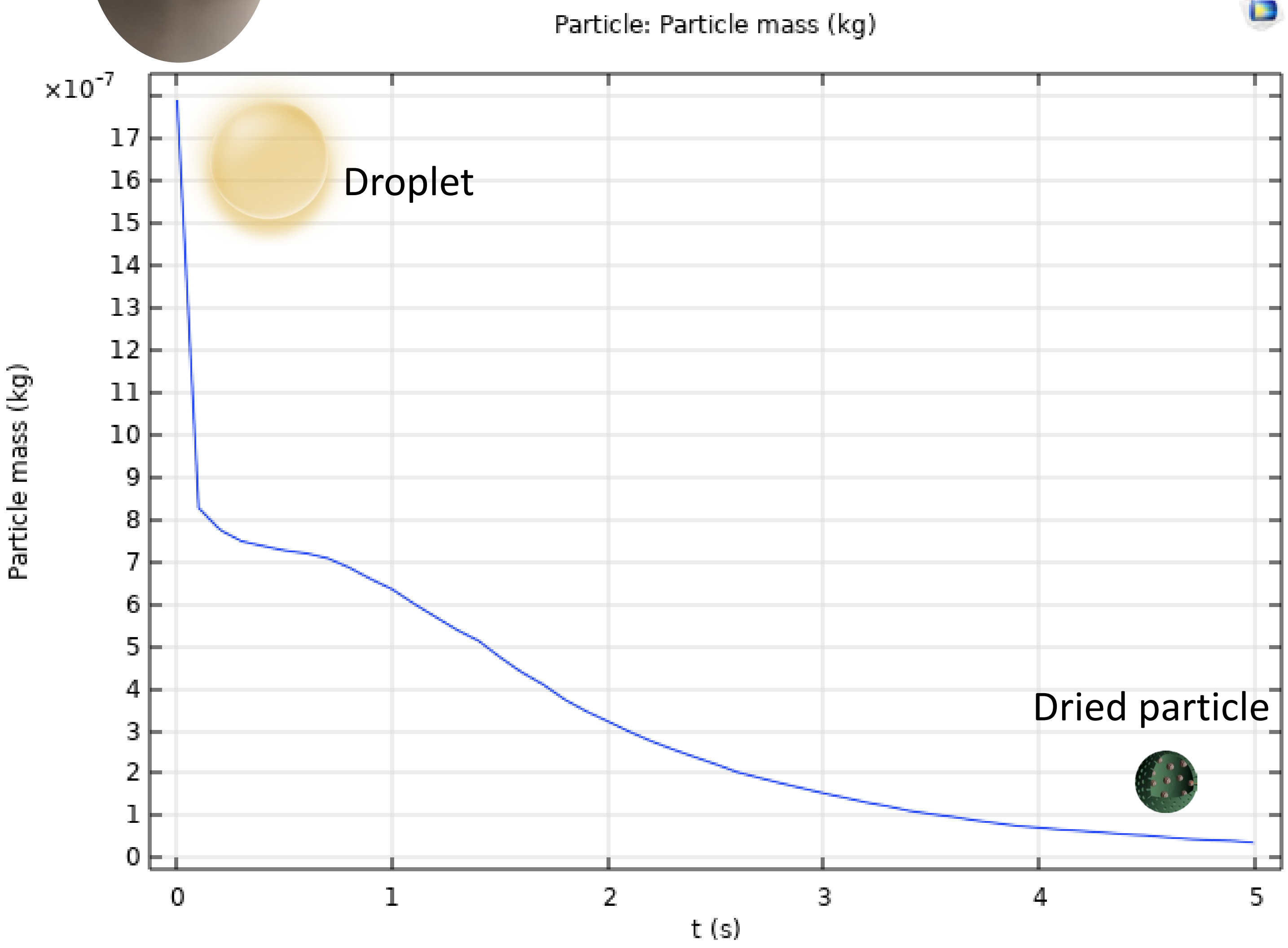


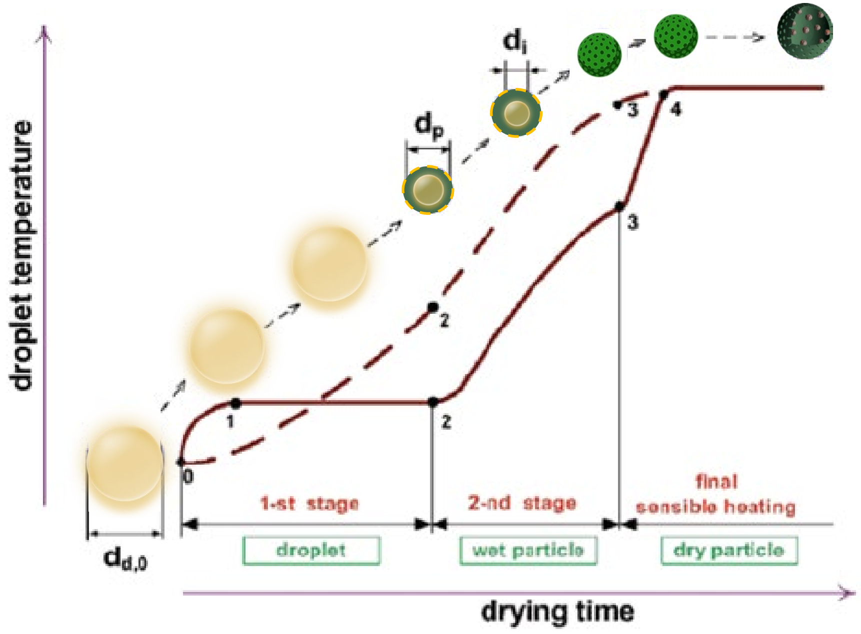
Gutiérrez et al., 2023 (*In preparation*)

Preliminary results with CFD software



Preliminary results with CFD software





Preliminary Conclusions

- Controlled-release fertilizers (CRFs) derived from biopolymers present a viable solution for implementing sustainable agricultural practices.

- The process of spray drying enables the conversion of controlled-release agrochemicals (like CRFs) into powder form. This conversion is anticipated to enhance storage, transportation, and application procedures of these products in the field.

- Employing Computational Fluid Dynamics (CFD) offers the possibility of accurately predicting the properties of dried CRFs. This technique could potentially assist in scaling up the spray drying process, resulting in more efficient resource utilization.

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CONAHCYT
CONSEJO NACIONAL DE HUMANIDADES
CIENCIAS Y TECNOLOGÍAS

Thank you

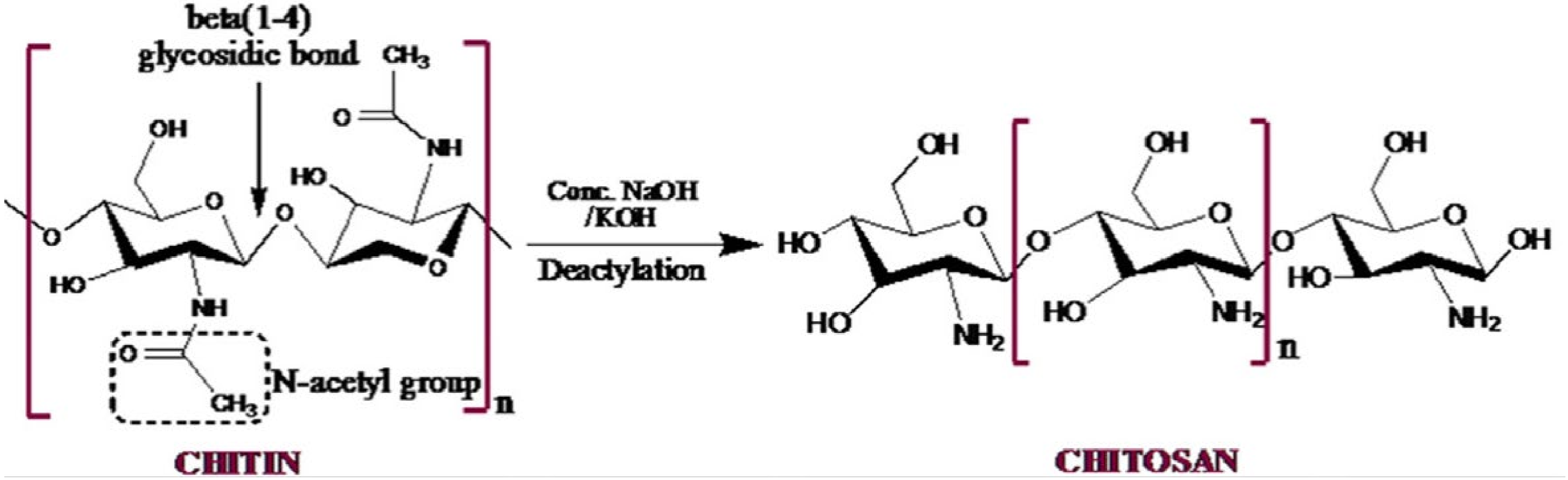
Dr. Martín Rivera

Dr. Elier E. Neri

Dr. Gregorio Juárez

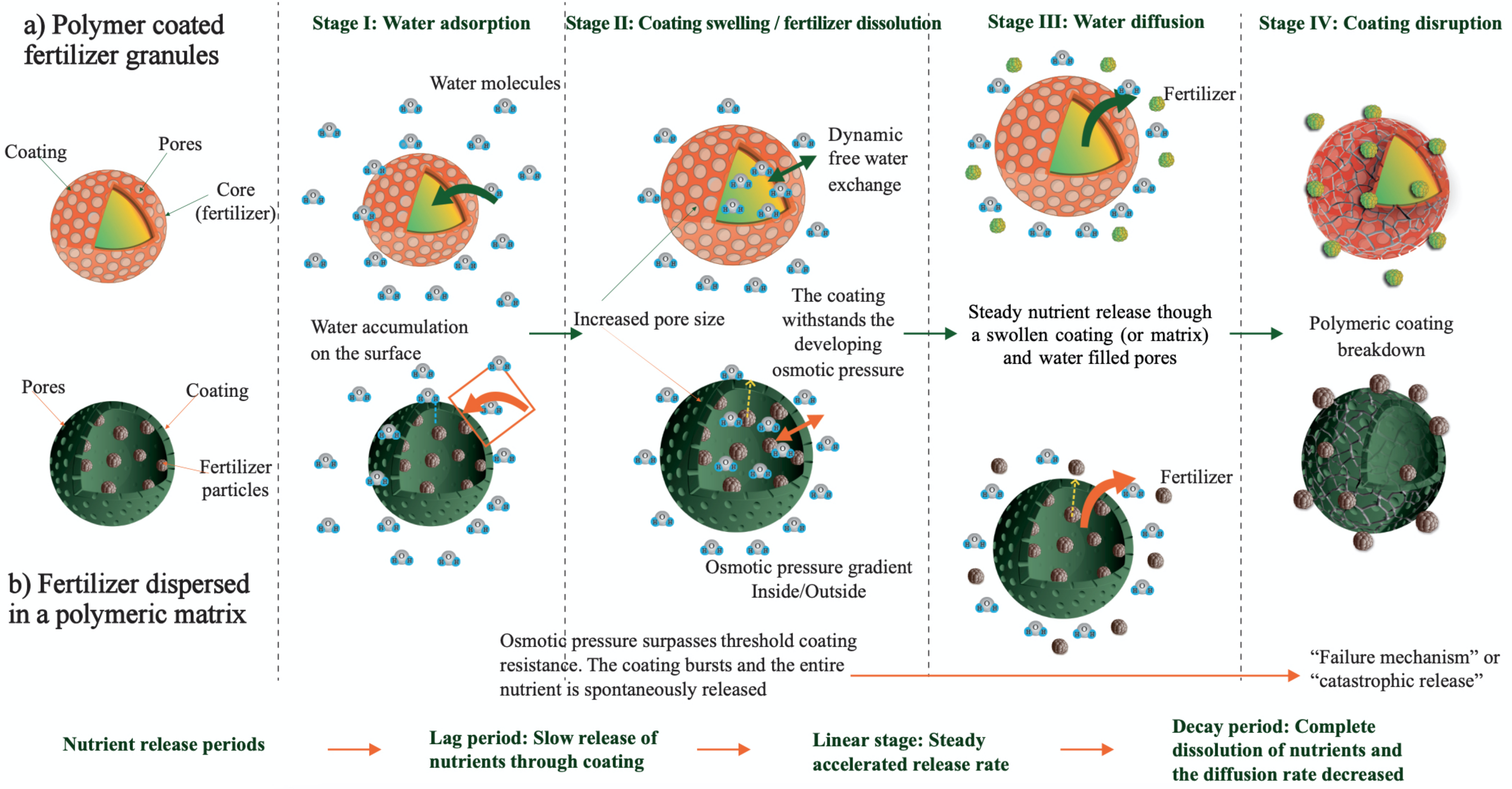
Dr. Iván R. Quevedo

Chemical deacetylation has many disadvantages like high energy consumption and environmental pollution problems. An alternative method of enzyme deacetylation has been developed to overcome these drawbacks.



The solubilization occurs by protonation of the –NH2 group on the C-2 position of the D-glucosamine repeat unit, whereby the polysaccharide is converted to a polyelectrolyte in acidic media

Representing schematics for nutrient release stages in two different CRFs configurations: (a) fertilizer (core) covered by a biobased polymer (coating) to form a granule; and (b) fertilizer particles dispersed into the biobased polymer matrix.



a) Polymer coated fertilizer granules

b) Fertilizer dispersed in a polymeric matrix

Stage I: Water adsorption

Stage II: Coating swelling / fertilizer dissolution

Stage III: Water diffusion

Stage IV: Coating disruption

Water accumulation on the surface

The coating withstands the developing osmotic pressure

Steady nutrient release though a swollen coating (or matrix) and water filled pores

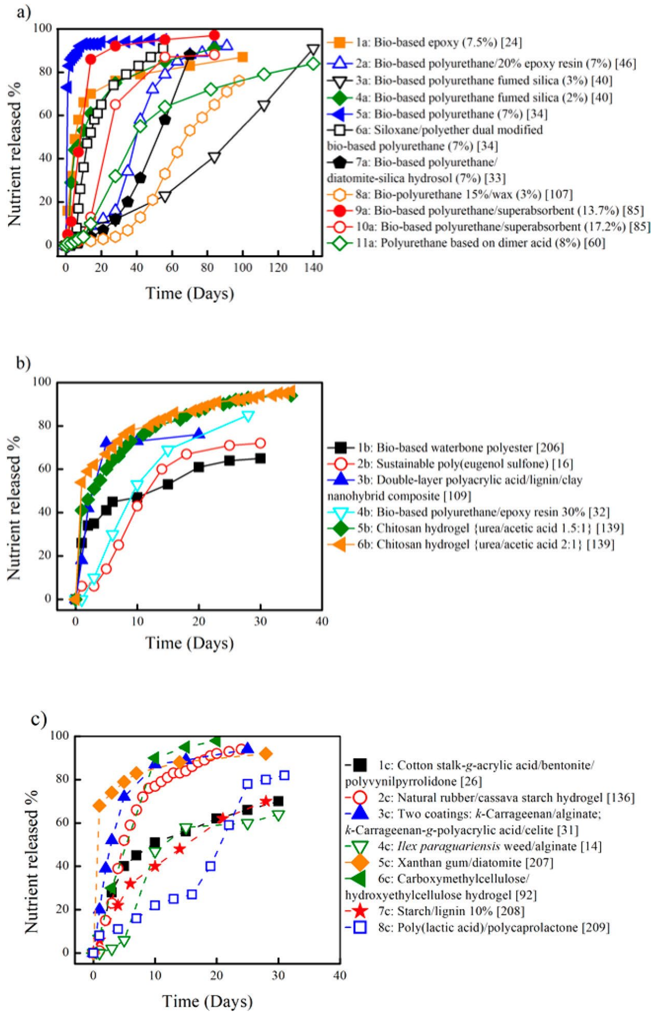
Polymeric coating breakdown

Osmotic pressure surpasses threshold coating resistance. The coating bursts and the entire nutrient is spontaneously released

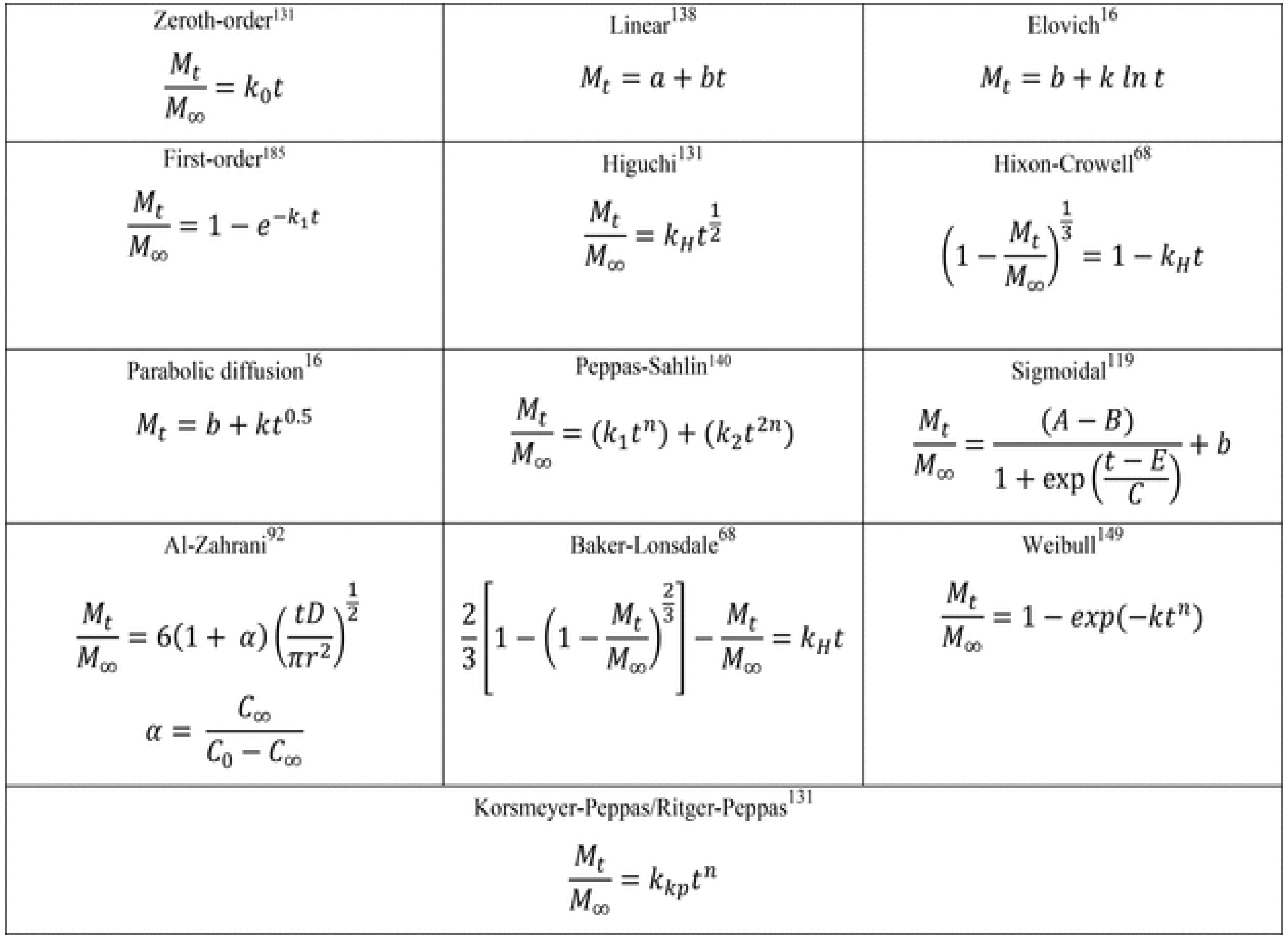
"Failure mechanism" or "catastrophic release"

Nutrient release periods → **Lag period: Slow release of nutrients through coating** → **Linear stage: Steady accelerated release rate** → **Decay period: Complete dissolution of nutrients and the diffusion rate decreased**

Nutrient Release Behavior in CRFs



Urea release behavior in water at different time scales in water at (a) 140 days and 35 days (b); in soil at (c) 35 days. In the legend, the coating percentage in the formulation is indicated in parentheses.

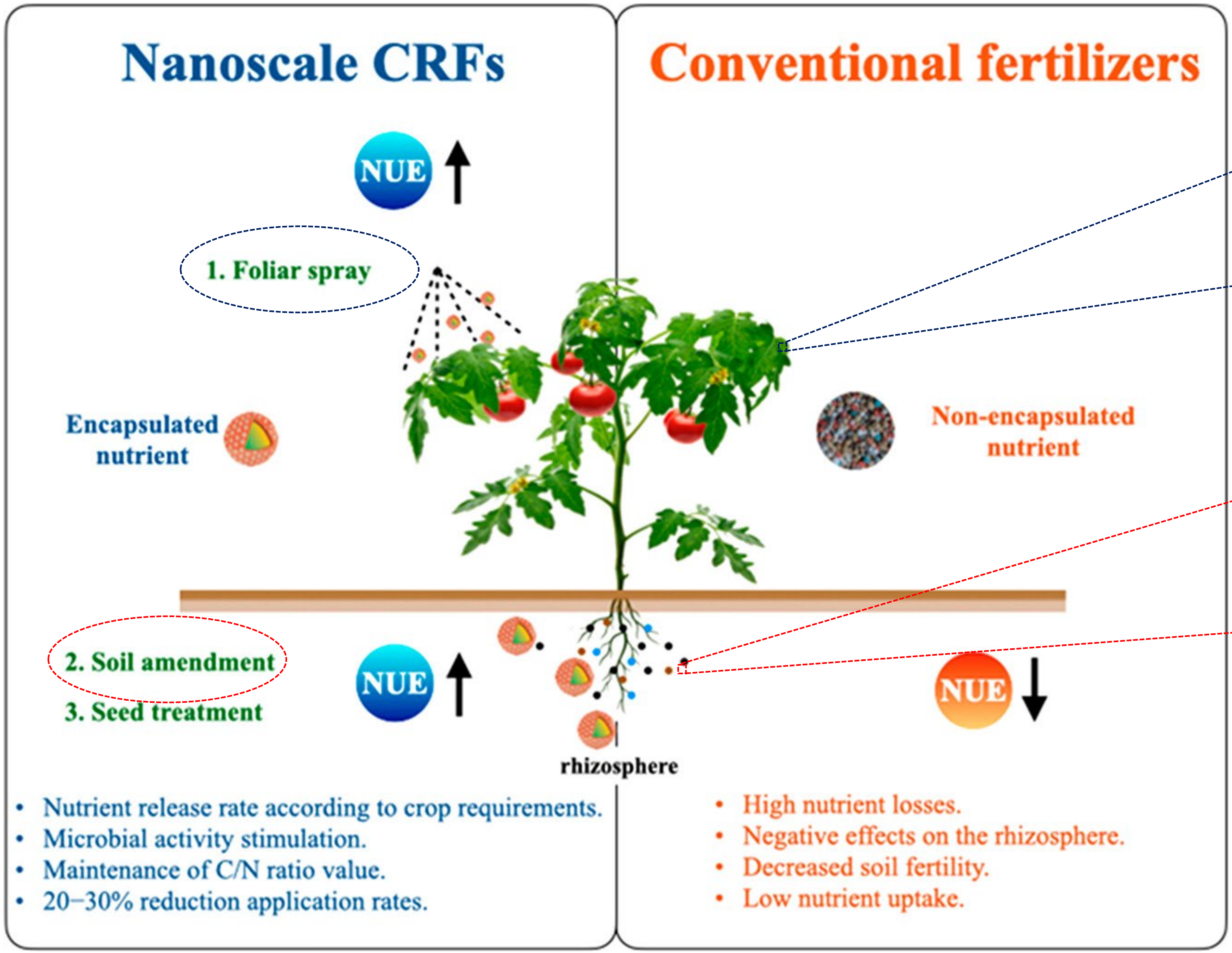


Zeroth-order[131] $\frac{M_t}{M_\infty} = k_0 t$	Linear[138] $M_t = a + bt$	Elovich[16] $M_t = b + k \ln t$
First-order[185] $\frac{M_t}{M_\infty} = 1 - e^{-k_1 t}$	Higuchi[131] $\frac{M_t}{M_\infty} = k_H t^{\frac{1}{2}}$	Hixon-Crowell[68] $\left(1 - \frac{M_t}{M_\infty}\right)^{\frac{1}{3}} = 1 - k_H t$
Parabolic diffusion[16] $M_t = b + kt^{0.5}$	Peppas-Sahlin[140] $\frac{M_t}{M_\infty} = (k_1 t^n) + (k_2 t^{2n})$	Sigmoidal[119] $\frac{M_t}{M_\infty} = \frac{(A - B)}{1 + \exp\left(\frac{t - E}{C}\right)} + b$
Al-Zahrani[92] $\frac{M_t}{M_\infty} = 6(1 + \alpha)\left(\frac{tD}{\pi r^2}\right)^{\frac{1}{2}}$ $\alpha = \frac{C_\infty}{C_0 - C_\infty}$	Baker-Lonsdale[68] $\frac{2}{3}\left[1 - \left(1 - \frac{M_t}{M_\infty}\right)^{\frac{2}{3}}\right] - \frac{M_t}{M_\infty} = k_H t$	Weibull[149] $\frac{M_t}{M_\infty} = 1 - exp(-kt^n)$
Korsmeyer-Peppas/Ritger-Peppas[131] $\frac{M_t}{M_\infty} = k_{kp} t^n$		

Mt: nutrient mass diffused up to time *t*; *M*∞: nutrient mass diffused after infinite time (equilibrium); *k*, *k*kp, *k*0, *k*1, and *k*: diffusion constants; *k*H, *k*2:
dissolution constants; *α*: initial nutrient released; *b*: release constant; *n*: diffusion exponent; *D*: diffusion coefficient, *r*: radius of the fertilizer granule;
*C*0: initial concentration of nutrient; *C*∞: concentration of the fertilizer in the sphere at infinite time, *A*, *B*, *C*, and *E*: sigmoidal equation parameters.

Gutierrez et al. 2022

Absorption Routes for Nanoscale CRFs



- Nutrient release rate according to crop requirements.
- Microbial activity stimulation.
- Maintenance of C/N ratio value.
- 20–30% reduction application rates.

- High nutrient losses.
- Negative effects on the rhizosphere.
- Decreased soil fertility.
- Low nutrient uptake.

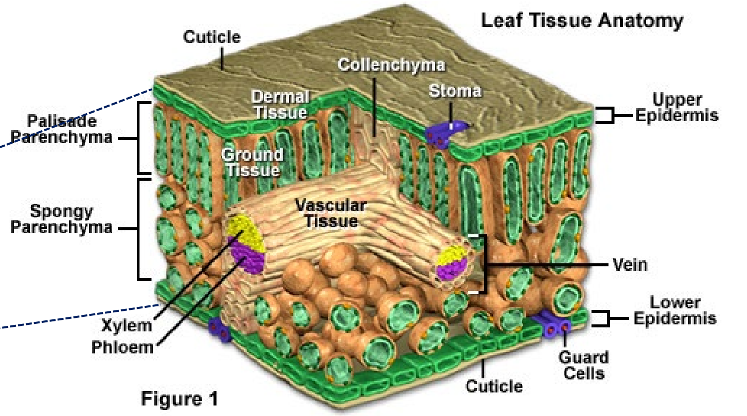
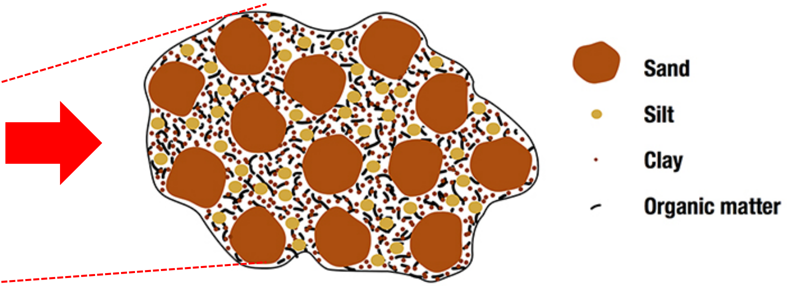
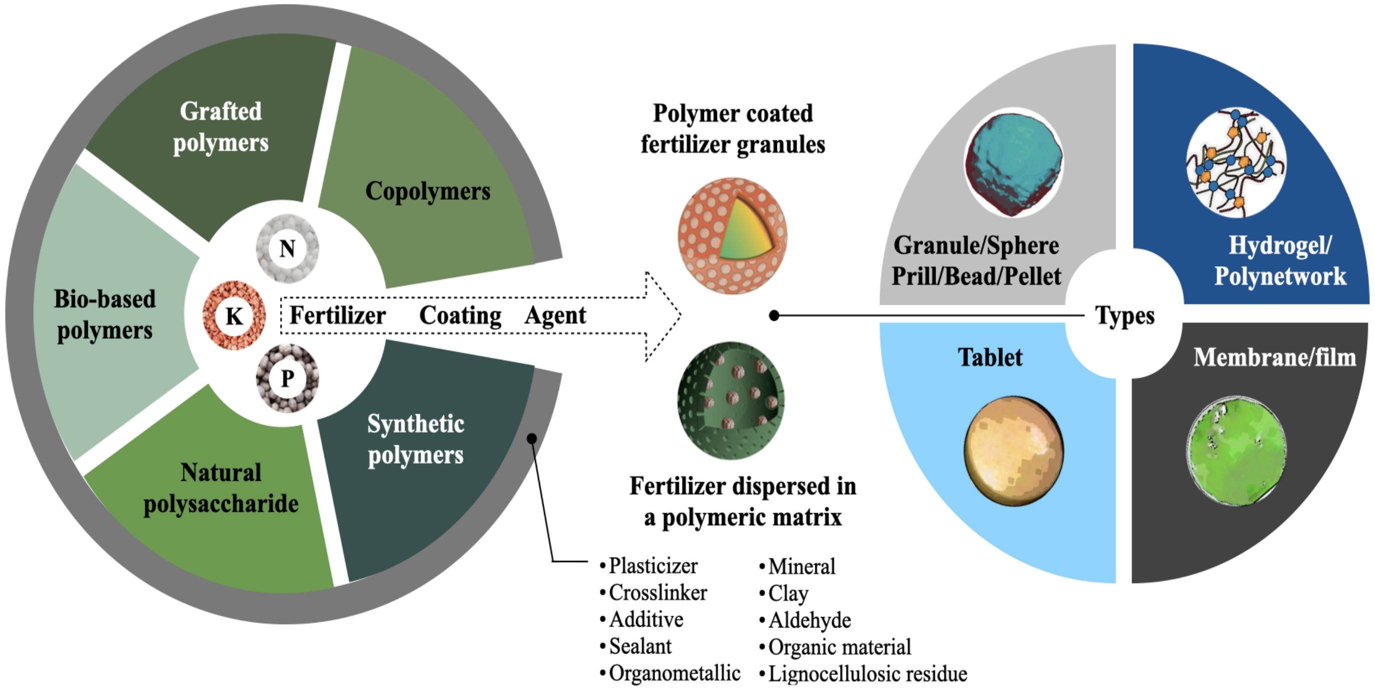


Figure 1



Raliyah et al. 2018

Potential Biowaste for Obtaining Controlled-Release Fertilizers (CRFs)



Grafted polymers

Copolymers

Bio-based polymers

Natural polysaccharide

Synthetic polymers

N

K

P

Fertilizer Coating Agent

Polymer coated fertilizer granules

Fertilizer dispersed in a polymeric matrix

- Plasticizer
- Crosslinker
- Additive
- Sealant
- Organometallic
- Mineral
- Clay
- Aldehyde
- Organic material
- Lignocellulosic residue

Types

Granule/Sphere Prill/Bead/Pellet

Hydrogel/ Polynetwork

Tablet

Membrane/film

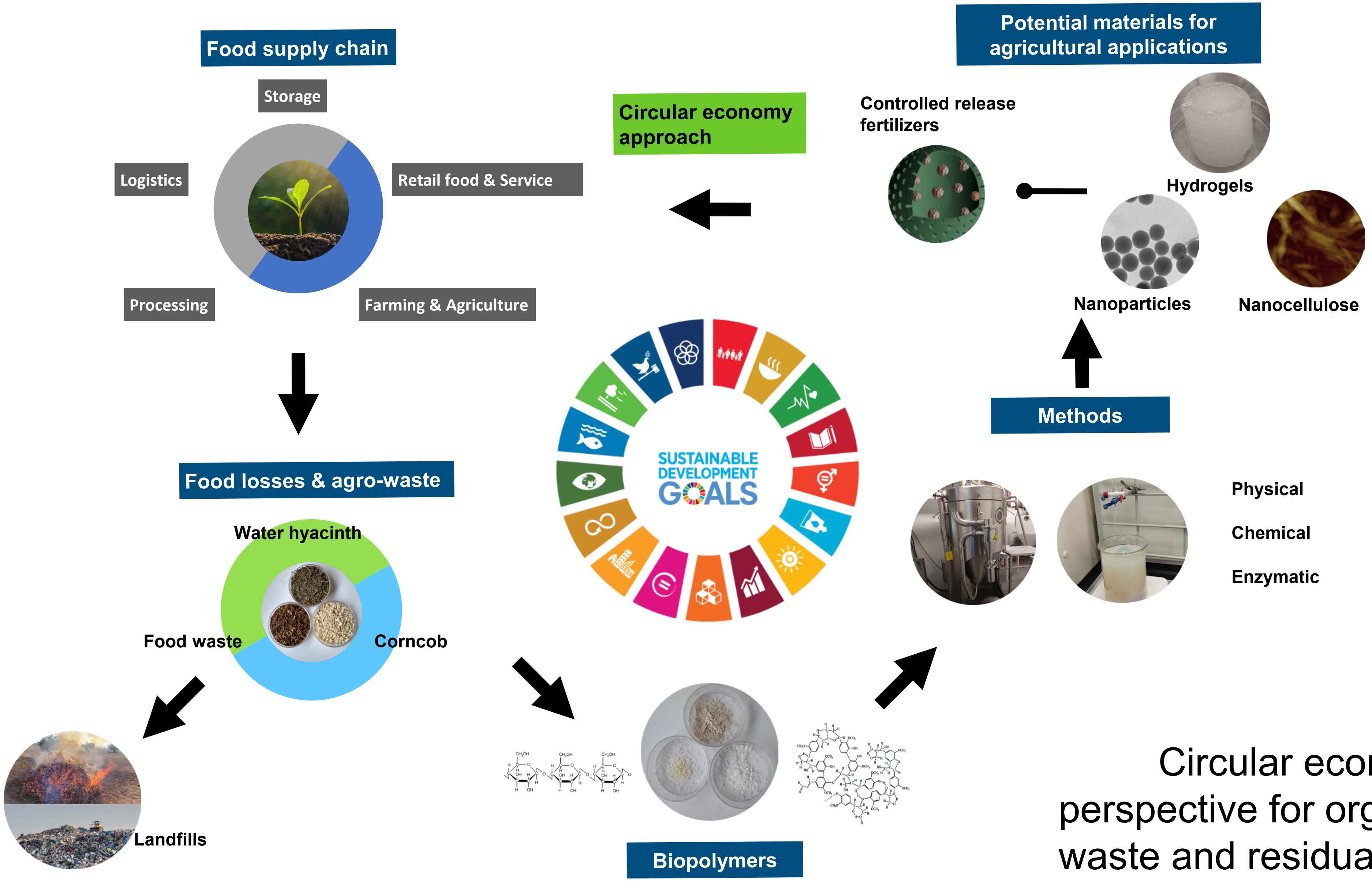
Agriculture

Forestry

Industrial Activities

Food Industry

“Biodegradable materials come from a broad range of sources: agriculture (e.g., wheat straw, rice husk, starches, corn stover, corn cob, branches, sugarcane bagasse), forestry (e.g., forest litter, oat hull, birch wood), industrial activities (e.g., Kraft and sulfite liquors from pulp and papers), and food industry (e.g., leftovers, peels, waste frying oil, chicken residues). The value-added products that could be obtained from organic waste are dependent on the primary components present” (Gutierrez et al., 2022)



Food supply chain

Storage

Logistics

Retail food & Service

Processing

Farming & Agriculture

Food losses & agro-waste

Water hyacinth

Food waste

Corncob

Landfills

Circular economy approach

Biopolymers

Methods

Physical

Chemical

Enzymatic

Potential materials for agricultural applications

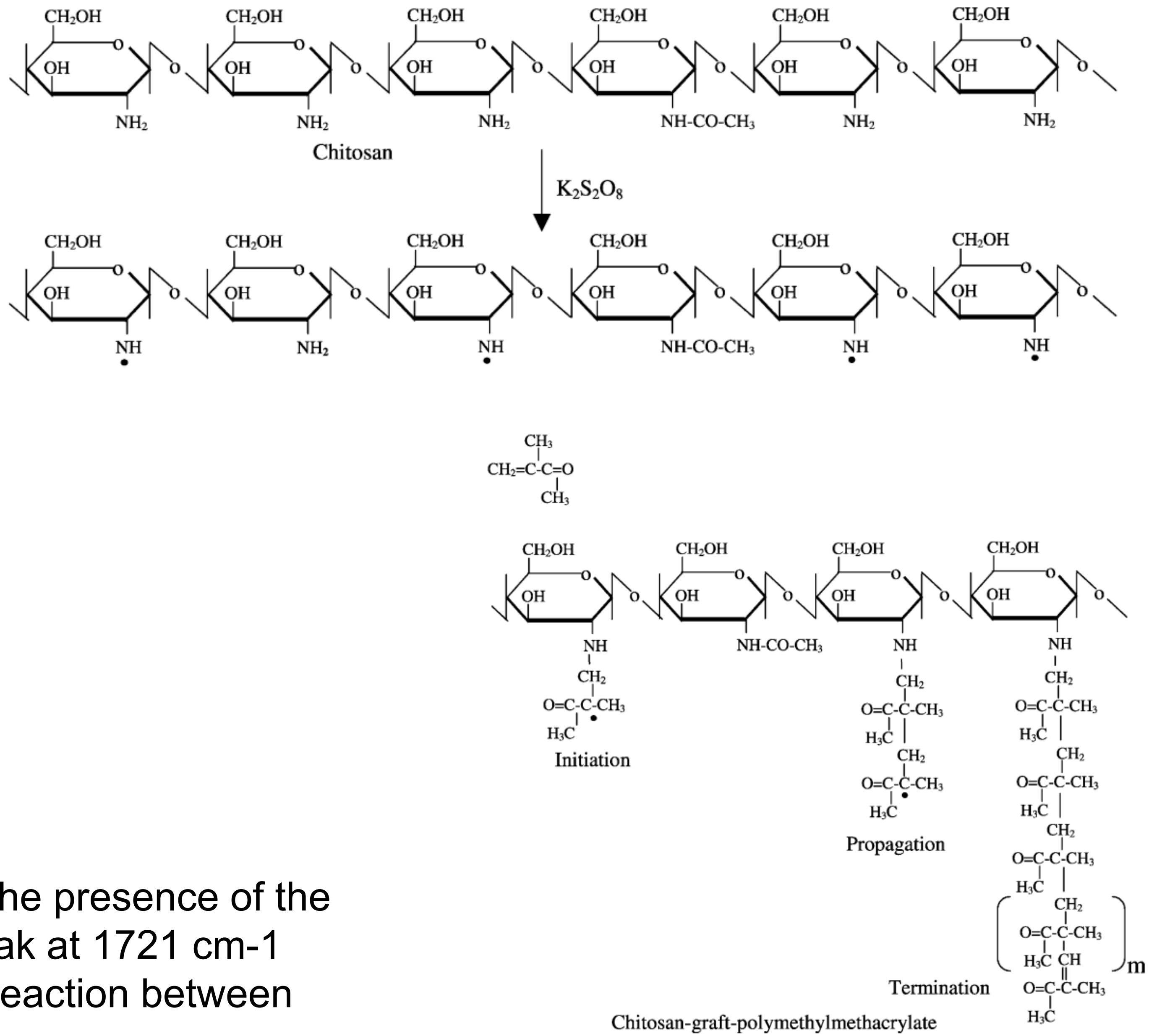
Controlled release fertilizers

Hydrogels

Nanoparticles

Nanocellulose

Circular economy perspective for organic food waste and residual biomass



In the graft copolymer the presence of the carbonyl absorption peak at 1721 cm-1 confirmed the grafting reaction between chitosan and MMA

Chitosan is a biopolymer that reduces plant diseases through two main mechanisms: (1) Direct antimicrobial function against pathogens, including plasma membrane damage mechanisms, interactions with DNA and RNA (electrostatic interactions), metal chelating capacity, and deposition onto the microbial surface, (2) Induction of plant defense responses resulting from downstream signalling, transcription factor activation, gene transcription and finally cellular activation after recognition and binding of chitin and chitosan by cell surface receptors. This biopolymer have potential with capability to combating fungi, bacteria, and viruses phythopathogens.