Porous inorganic nanoparticles for Improved Nutrient Delivery and Environmental Sustainability

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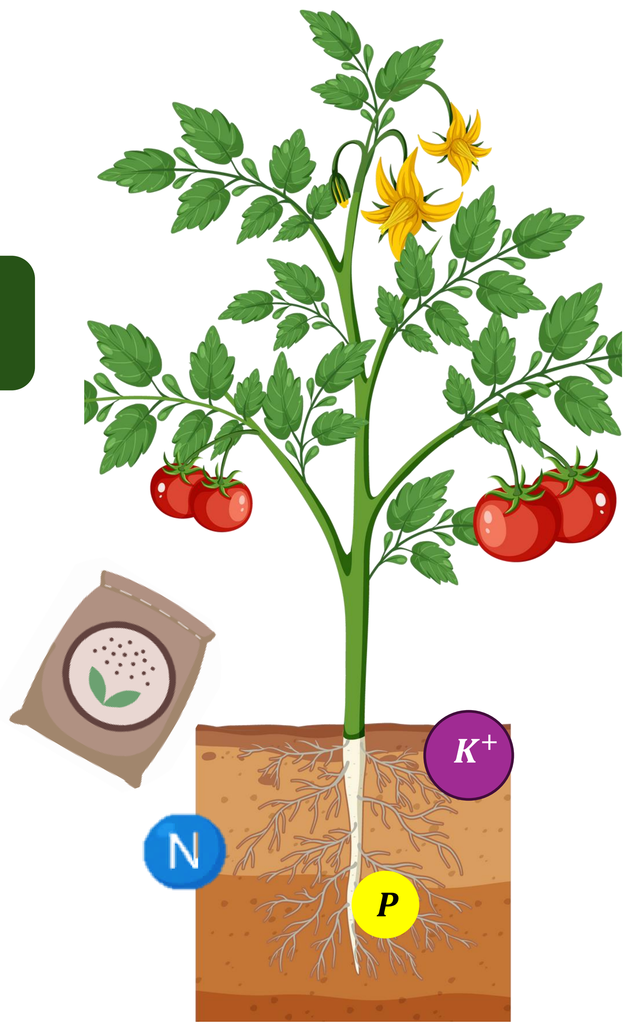
Introduction & Objective

Precision agriculture requires sustainable nutrient delivery systems, as conventional fertilization leads to significant nutrient losses and environmental contamination. Traditional agrochemicals present several limitations, including low bioavailability, poor target precision, high environmental impact, and considerable economic losses due to their inefficiency.

In this context, porous inorganic nanomaterials, as nanoclay (NCL) and porous silica nanoparticles (NPs), emerge as promising alternatives to enhance nutrient use efficiency and promote more sustainable agricultural practices. Therefore, it is essential to evaluate these inorganic nanoparticles as sustainable nanoplatforms for slow and controlled nutrient delivery.

Our main objective is to evaluate and characterize nanoclay and porous silica nanoparticles as sustainable biobased nanoplatforms for slow and controlled fertilizers delivery, aiming to improve nutrient efficiency while minimizing fertilizers lixiviation and their environmental impact. To achieve this objective, laboratory-scale assays have been used to evaluate the performance of release systems based on inorganic nanoparticles in both water and soil.



Materials & Methods

Both inorganic nanoparticles were impregnated with fertilizers such as urea and ammonium nitrate via mechanical stirring to ensure uniform nutrient loading.

A filtration step was carried out to remove non-incorporated fertilizer from the structure of nanoclay and porous silica nanoparticles.

The fertilizers impregnated into nanoparticles were dried and ground to reduce and homogenize the particle size for further application.

Results

Physicochemical characterization of nanoparticles delivery systems

Table 1. TGA analysis of urea-impregnated into nanoparticles.

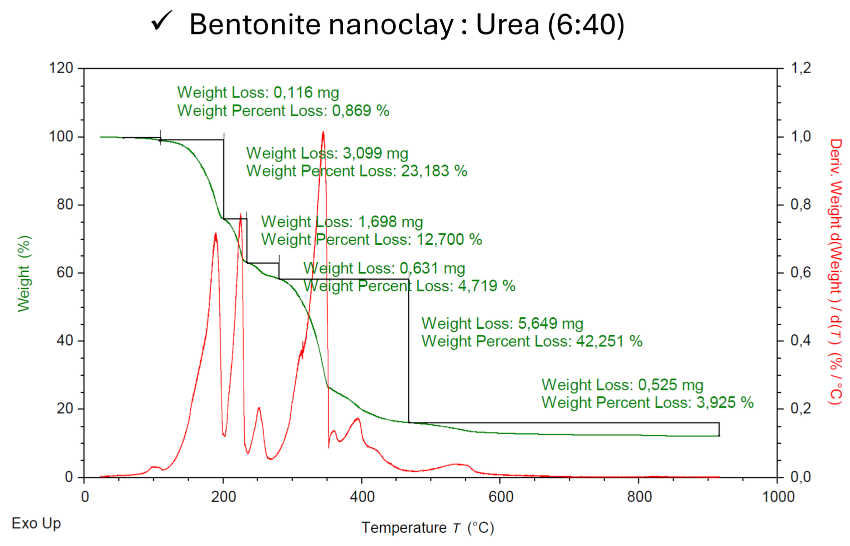
Nanocarrier : Fertilizer	Ratio	Temperature range (°C)	Weight Loss (%)
Nanoclay: Urea	2:40	220 - 900	**76.47**
	4:40	220 - 900	**70.04**
	6:40	220 - 900	**82.85**
Porous silica: Urea	2:40	220 - 900	**89.63**
	4:40	220 - 900	**95.87**

✓ Silica NPs

Surface area: **Porous silica ≈ 145 m²/g** and **Bentonite ≈ 49 m²/g** determined by the BET adsorption isotherm

✓ Nanoclay

✓ Bentonite nanoclay : Urea (6:40)

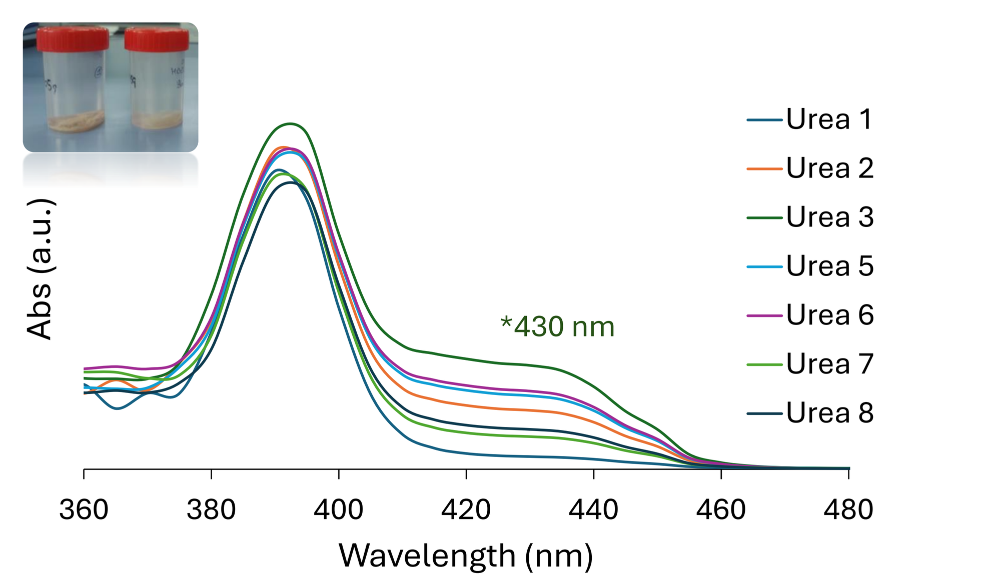


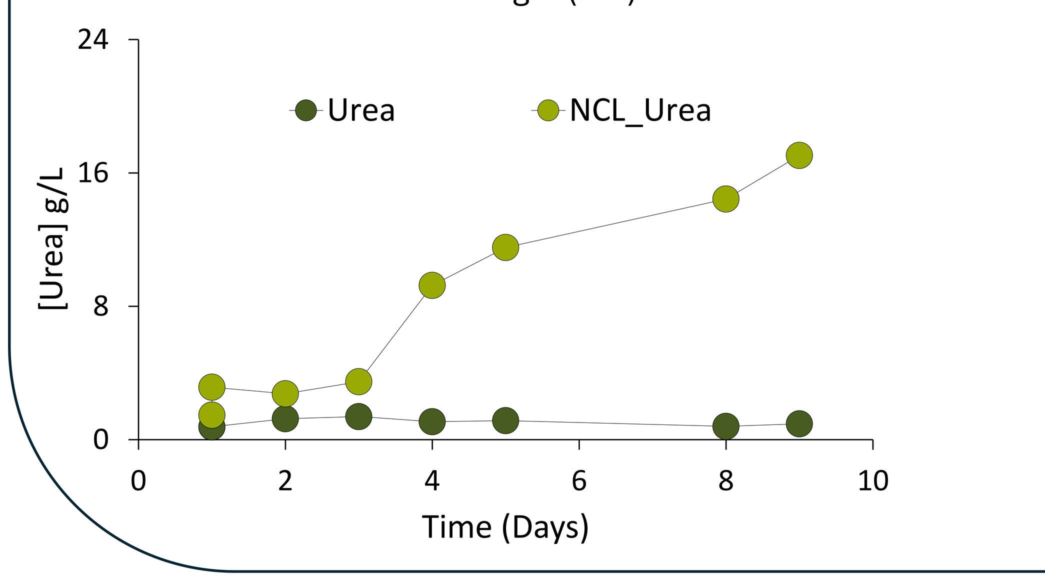
Water release test and characterization at laboratory scale

Water release test involved the incubation of fertilizers impregnated into inorganic nanostructures in water, followed by monitoring their release through the analysis of aliquots. The fertilizers release was evaluated using two different experimental methods.

✓ UV–Vis spectrophotometry

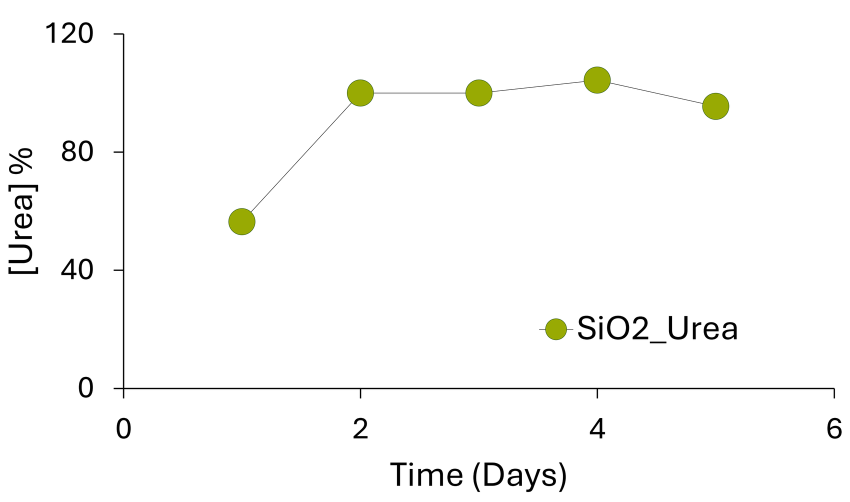
$$(N_2H_2)_2CO + PDAB \xrightarrow{H^+} Yellow\ Schiff\ base\ complex$$

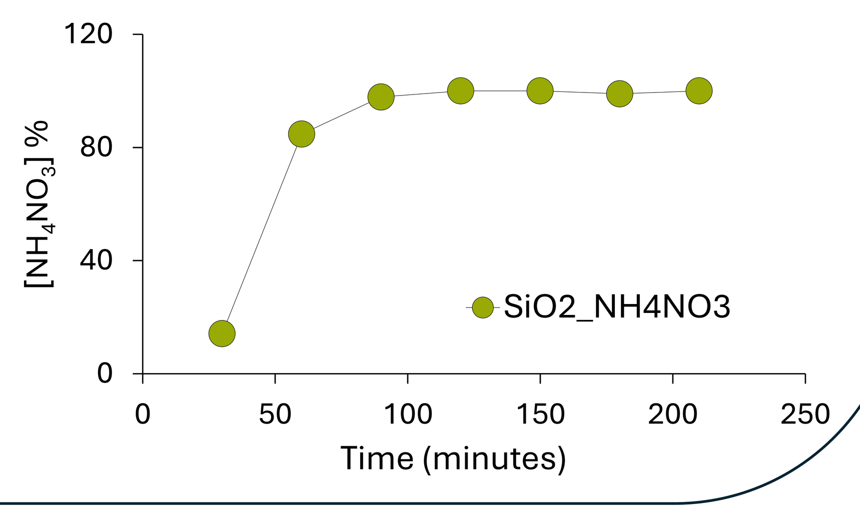




✓ Electrical Conductivity

$$(N_2H_2)_2CO + 2H_2O \xrightarrow{Urease} NH_4^+ + NH_3 + HCO_3^-$$

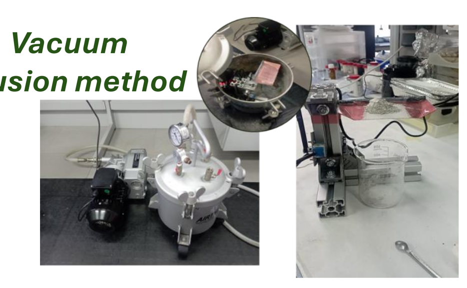


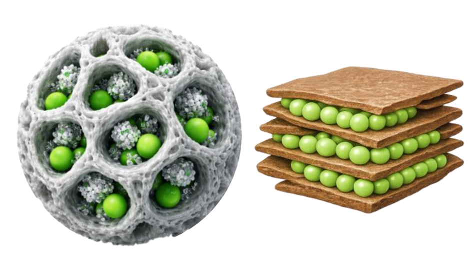


Optimization of fertilizers loading into inorganic nanoparticles

Two different strategies to enhance the absorption capability of fertilizers, such as urea and ammonium nitrate, into nanoclay and porous silica nanoparticles have been tested.

✓ *Vacuum infusion method*





✓ *Impregnation method*

The most effective method of loading fertilizers into the inorganic nanoparticles (Bentonite-NCL and porous silica) that were evaluated was the impregnation method by mechanical stirring mixing at room temperature. The properties and performance of the resulting product were evaluated using various techniques, including thermogravimetric analysis (TGA–DSC), as shown in Table 2.

✓ Nanoclay

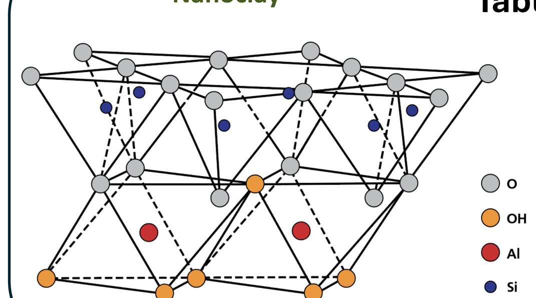
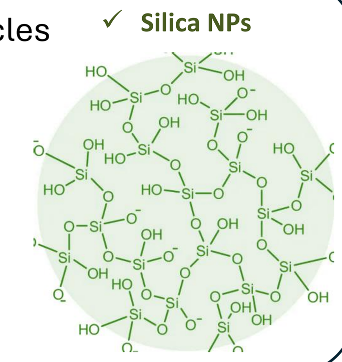


Table 2. Active substance adsorption ratio for evaluated nanoparticles

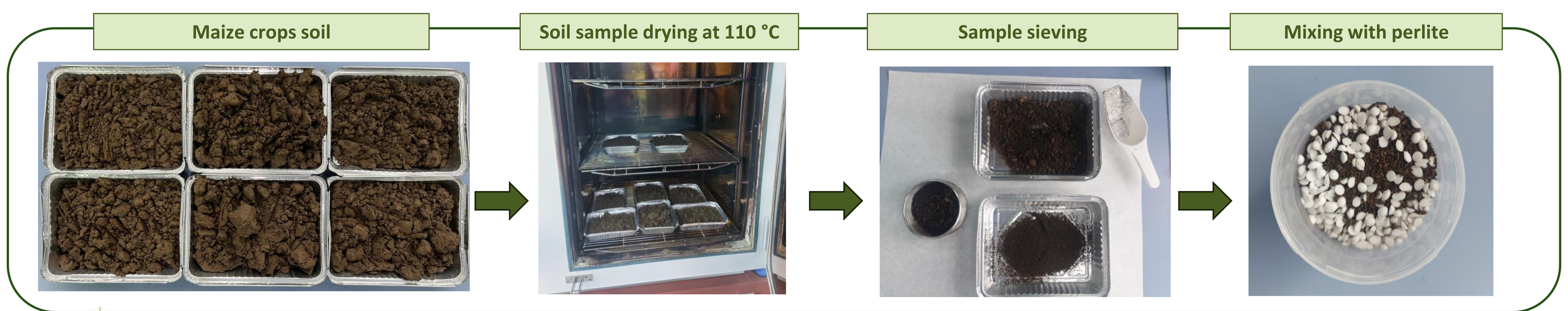
Nanocarrier	N fertilizer	Ratio	ASAR, wt.%
Nanoclay	Urea	4:40	**96 %**
Nanoclay	Urea	6:40	**95%**
Silica NPs	Urea	4:40	**58%**

✓ Silica NPs



Soil release test and characterization at laboratory scale

Soil samples were taken from maize crops and used to prepare soil columns, in which the controlled release of fertilizers was evaluated using a bentonite nanoclay-based release system.

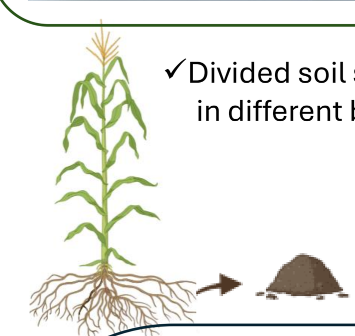


✓Divided soil samples in different batches

✓Reduction of water content (moisture) and autoclave soil

✓Improved soil homogeneity

✓Enhances drainage during irrigation



Schematic representation of soil column

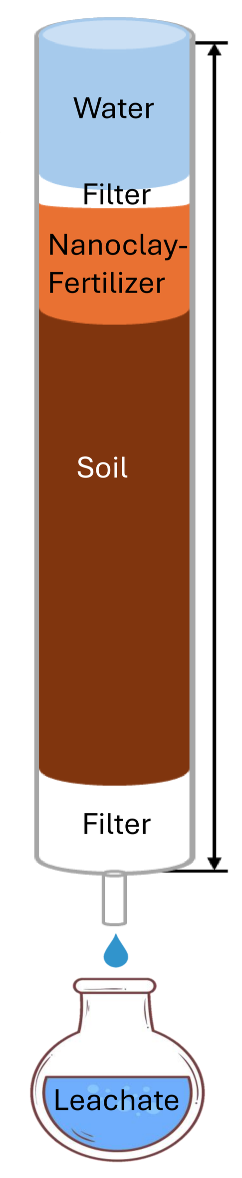


Table 3. Desorption time of fertilizers based on evaluated delivery systems.

System	Fertiliser	Ratio	Desorption in water	Desorption in soil
Without NPs	Urea	-	Few seconds	1 day
Bentonite - NCL	Urea	6:40	9 days	4 days**
Silica NPs	Urea	4:40	Few seconds	-
Without NPs	NH_4NO_3	-	Few seconds	1 day
Bentonite - NCL	NH_4NO_3	6:40	2 days	4 days**
Silica NPs	NH_4NO_3	4:40	<2 hours	-

***The analysis is ongoing. Results obtained after four days indicate a progressive and controlled release of fertilizer in soil for Bentonite-NCL urea and NH_4NO_3. The release time in soil is expected to be longer than in the water assay because of the reduced water contact.*

Fertilizers incorporated into nanoclay demonstrated a slower release profile than either non-impregnated fertilizers or those loaded into porous silica nanoparticles. This could be due to the ion exchange that occurs within the nanoclay structure and the flexibility of its framework, which enables it to hold fertilizers such as urea inside it.

In soil column studies, desorption proceeded even more slowly, likely owing to reduced water interaction during irrigation.

Main Conclusions

- Bentonite nanoclay serves as an efficient nanocarrier for controlled nutrient release, as demonstrated by the results obtained from laboratory-scale water and soil release tests. Its high surface area, layered structure, and cation-exchange capacity enable effective nutrient retention and controlled desorption.
- Although porous silica nanoparticles are excellent nanocarriers for fertilizer adsorption, the laboratory release tests showed that fertilizers are released within a few seconds, limiting their effectiveness for controlled delivery compared with bentonite nanoclay.
- Laboratory-scale release tests in water and soil showed that both spectrophotometric and electrical conductivity measurements are suitable for monitoring the release of fertilizers impregnated into nanostructures.
- Soil release tests for the evaluated systems indicate that Bentonite nanoclay is a promising nanoplatform for the development of controlled-release fertilizer systems.

Acknowledgments

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