Vol. 22, No. 2(2023) Sim2399
Revista Mexicana de Ingeniería Química

Modeling NPK nutrients release via nanoparticle/hydrogel system

Modelado de liberación de nutrientes de tipo NPK a través del sistema nanopartícula/hidrogel

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Received: June 1, 2023; Accepted: July 22, 2023

Abstract

In this work, we present a detailed mathematical modeling of the controlled release of nutrients encapsulated in a nanoparticle/hydrogel system. The main objective was to investigate how hydrogels can be used to sustainably release water and nutrients, keeping the soil moist and improving nutrient availability for plants. Experimental reference data were used, which underwent rigorous numerical and statistical treatment. The mass transfer equation in spherical coordinates was employed to obtain concentration profiles and released fraction of each nutrient. Additionally, the effective diffusion coefficients of the nutrients were determined through an optimization process controlled by the mean squared error (MSE) statistic. The results revealed that the nanoparticle/hydrogel system demonstrated efficient controlled release of the studied nutrients. The obtained effective diffusion coefficients were 1.3×10^{-11} m^2/s for nitrogen in the form of ammonium (MSE=0.0125), 7.2×10^{-10} m^2/s for potassium ion (MSE=0.0697), and 5.8×10^{-12} m^2/s for phosphorus in the form of hydrophosphate (MSE=0.2023), consistent with typical values observed in similar mass transfer processes. These findings have significant implications for sustainable agriculture as the use of nanoparticle/hydrogel systems can reduce nutrient loss, promote microbial life in the rhizosphere, and enhance nutrient uptake by plants.

Keywords: nanoparticle, hydrogel, modeling, release, NPK nutrients.

Resumen

En este trabajo, se presenta el modelado matemático detallado de la liberación controlada de nutrientes encapsulados en un sistema de nanopartícula/hidrogel. El objetivo principal fue investigar cómo los hidrogeles pueden ser utilizados para liberar agua y nutrientes de manera sostenida, manteniendo el suelo húmedo y mejorando la disponibilidad de nutrientes para las plantas. Se utilizaron datos experimentales de referencias, que fueron sometidos a un riguroso tratamiento numérico y estadístico. La ecuación de transferencia de masa en coordenadas esféricas se empleó para obtener perfiles de concentración y fracción liberada de cada nutriente. Además, se determinaron los coeficientes de difusión efectiva de los nutrientes a través de un proceso de optimización controlado por el estadístico del error cuadrado medio (MSE). Los resultados revelaron que el sistema de nanopartícula/hidrogel demostró una liberación controlada eficiente de los nutrientes estudiados. Los coeficientes de difusión efectiva obtenidos fueron: 1.3×10^{-11} m^2/s para el nitrógeno en forma de amonio (MSE=0.0125), 7.2×10^{-10} m^2/s para el ion potasio (MSE=0.0697) y 5.8×10^{-12} m^2/s para el fósforo en forma de hidrofosfato (MSE=0.2023), consistentes con los valores típicos observados en procesos de transferencia de masa similares. Estos hallazgos tienen implicaciones significativas para la agricultura sostenible, ya que el uso de sistemas nanopartícula/hidrogel puede reducir la pérdida de nutrientes, promover el desarrollo de la vida microbiana en la rizosfera y mejorar la absorción de nutrientes por parte de las plantas.

Palabras clave: nanopartícula, hidrogel, modelado, liberación, nutrientes NPK.

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https://doi.org/10.24275/rmiq/Sim2399
ISSN:1665-2738, *issn-e*: 2395-8472

1 Introduction

In agriculture, the traditional application of fertilizers leads to considerable nutrient wastage, which is harmful to the environment and costly for farmers (Rakhimol *et al*., 2021). To address this challenge, the synthesis of agricultural products and inputs at the nanoscale, such as nanofertilizers, has emerged as a promising alternative due to their potential impact in utilizing the high surface-to-volume ratio of nanoparticles, enabling more efficient nutrient delivery to plants (Kottegoda *et al*., 2011; Flores-Hernández *et al*., 2020). Additionally, controlled release techniques have been explored to meet the nutrient requirements of plants at different growth stages (Vejan *et al*., 2021).

As the application of nanoparticles in agriculture progresses, understanding how factors such as crop type, environmental conditions, and soil properties can influence the effectiveness of these nanofertilizers becomes evident (Zhao *et al*., 2020). In this regard, green synthesis of nanoparticles has gained interest as a more environmentally friendly alternative compared to conventional chemical and physical methods (Bandeira *et al*., 2020; González-Fernández *et al*., 2022; Makarov *et al*., 2014).

The integration of nanoparticulate and superabsorbent materials into high-value substrates, such as NPK fertilizers, has demonstrated multiple agroforestry benefits. However, understanding how these substances are absorbed, retained, and released for utilization in crops is crucial. In this regard, predicting the kinetics of the behavior of these systems is essential for optimizing their effectiveness (Alharbi *et al*., 2018).

This article focuses on the mathematical modeling of the controlled release of NPK nutrients from nanoparticles contained in a hydrogel used in agriculture. The main objective is to obtain an accurate estimation of the fertilizer release over time, which will enable proper formulation and application. To achieve this, the mass conservation equation has been adapted to a spherical geometry representing the fertilizer particle, taking into account diffusional effects from the interior of the particle. The Lines method has been used to solve the differential equation governing the mass transport phenomenon. During the study, limitations related to the accuracy of the experimental data used to calibrate the proposed model have been encountered, which were taken from previous studies (Huang *et al*., 2019; Zhang *et al*., 2018).

The results obtained through this modeling technique have been compared with experimental values, based on the statistical parameter of mean squared error (MSE). Minimizing its value has allowed for the proper representation of the experimental and simulated data, validating the effectiveness of the model in simulating nutrient release processes (Melgarejo-Torres *et al*., 2022). This simulation technique proves to be a useful tool for optimizing crop performance and improving resource efficiency, providing precise information about the quantity and availability of nutrients released at specific moments. Ultimately, the technique employed in this study can be a valuable tool for the agricultural industry and research in the field of nanoparticles and their application in agriculture.

2 Materials and methods

The objective of this study was to simulate the controlled release of NPK nutrients from spherical nanoparticles using a mass balance-based approach. The nanoparticles were characterized as having a spherical morphology with an average diameter of approximately 50 nm. The macronutrient layer consisted of urea, phosphates, and chlorides, which dissociate in the soil according to Equations (1) and (2) (Basu *et al*., 2010). The nitrogen, phosphorus, and potassium input values were taken from widely used commercial fertilizers in agriculture, specifically $(NH_4)_2SO_4$, $Ca(H_2PO_4)_2$ and KCl (Liu & Lal, 2015).

The simulation was based on the mass balance applied to a spherical geometry, represented by Equation (3). To simplify the model, it was assumed that the particles are spherical, there is no convective transport, and the densities are constant in all phases. In addition, no chemical reactions were considered during the release process, and a radially homogeneous concentration gradient was established within the particles. The external medium to the particles was assumed to be homogeneous, the mass transport coefficient between phases was constant, and the transport followed a Fickian behavior, resulting in Equation (4).

The initial and boundary conditions were defined according to Equations (5) - (7), taking into account the physical and kinetic properties of the system. The experimental data required for the simulation were obtained from previous works by Zhang, Alharbi, and Huang (Alharbi *et al*., 2018; Huang *et al*., 2019; Zhang *et al*., 2018) and were presented in Table 1. Auxiliary Equations (8) - (13) were used to estimate the overall mass transfer coefficient using dimensionless numbers such as Sh, Re, and Sc. To validate the proposed model, the fraction of released nutrients was calculated using Equation (14), which compares the nutrient mass at a specific time with the initial mass. Additionally, the mean squared error (MSE) statistic was used to assess the accuracy of the fit between experimental data and simulation results.

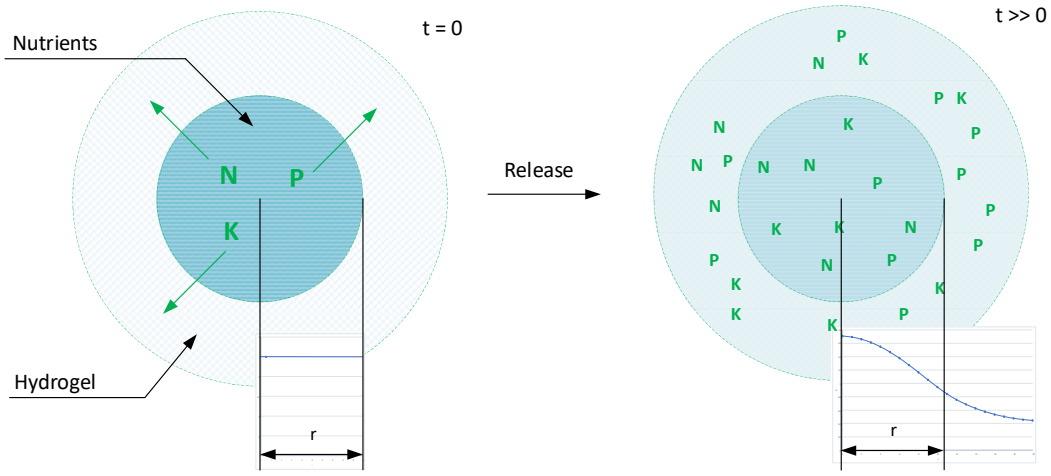

Figure 1: Scheme of the proposed release system.

The mathematical model based on Equation (4) was used to estimate the effective diffusion coefficient (D_{eff}), which characterizes the mass transport in the NPK release system. The estimation of D_{eff} was carried out using a trial-and-error approach, assuming an initial value and solving the ordinary differential equations of the system. Subsequently, the results were compared with the experimental data.

Equations of ion dissociation:

$$(NH_4)_2HPO_{4(s)} \rightarrow 2NH^{+}_{4(ac)} + HPO^{-2}_{4(ac)} \quad (1)$$

$$KCl_{(s)} \rightarrow K^{+}_{(ac)} + Cl^{-}_{(ac)} \quad (2)$$

Equations for the development of the mathematical model:

$$\frac{\partial C}{\partial t} + v_n \frac{\partial C}{\partial r} + v_\theta \frac{\partial C}{\partial \theta} + \frac{v_\phi}{r \sin\phi} \frac{\partial C}{\partial \phi} = D\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial C}{\partial r}\right) + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial C}{\partial \theta}\right) + \frac{1}{r^2 \sin^2\phi}\frac{\partial^2 C}{\partial \phi^2}\right] \quad (3)$$

$$\frac{\partial C}{\partial t} = D_{eff}\left(\frac{\partial^2 C}{\partial r^2} + \frac{2}{r}\frac{\partial C}{\partial r}\right) \quad (4)$$

Initial and boundary conditions:

$$t = 0, \quad C = C_s, \quad \forall r > 0 \quad (5)$$

$$r = 0, \quad \frac{\partial C}{\partial r} = 0, \quad \forall t > 0 \quad (6)$$

$$r = R, -D_{eff}\frac{\partial C}{\partial r} = h_m(C - C_\infty), \quad \forall t > 0 \quad (7)$$

Auxiliary equations:

$$h_m = \frac{A_p Sh D_p}{V_p} \quad (8)$$

$$Sh = 2.0 + 0.6 Re^{0.5} Sc^{0.33} \quad (9)$$

$$Re = \frac{v(V_p/A_p)}{\mu} \quad (10)$$

$$Sc = \frac{\mu}{D} \quad (11)$$

$$V_p = \frac{4}{3}\pi R^3 \quad (12)$$

$$A_p = 4\pi R^2 \quad (13)$$

Validation equations:

$$y_{icalc} = \frac{m_0 - m_t}{m_0} \quad (14)$$

$$MSE = \frac{\sum_{i=1}^{n}(y_i - y_{icalc})^2}{n} \quad (15)$$

The flowchart illustrates the iterative calculation sequence starting from the effective diffusion coefficient until the minimum MSE condition is satisfied.

Table 1: Nomenclature

Symbol	Description
D_{eff}	Effective diffusion coefficient
h_m	Global mass transfer coefficient
C_∞	Nutrient concentration in the substrate
C	Nutrient concentration in the nanoparticle
C_s	Initial nutrient concentration
MSE	Mean square error
y_{icalc}	Fraction released as a result of the simulation
y_i	Fraction released taken from the literature
m_0	Initial mass of nutrient
m_t	Mass of nutrient at time t
n	Number of data points
r	Radial position
R	Nanoparticle radius
t	Time

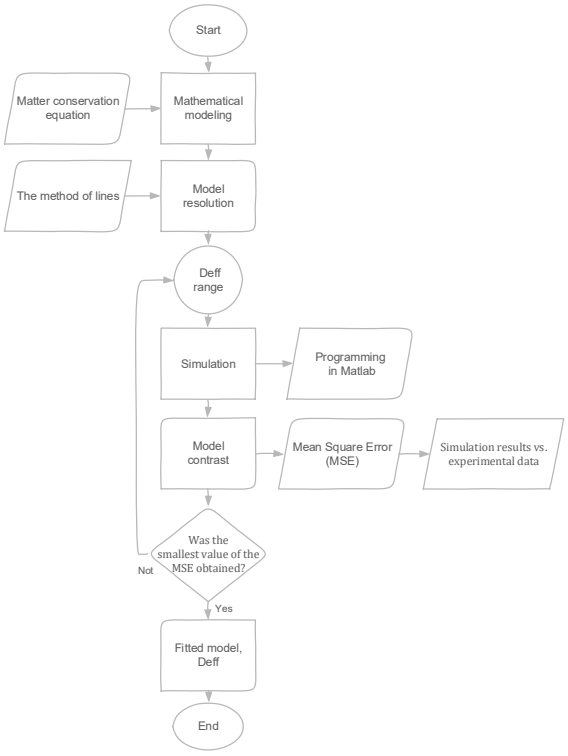

Figure 2: Flowchart of controlled release through modeling and simulation.

3 Results and discussion

Figure 3 depicts concentration profiles over time generated from Equation (4). Different behavior patterns were observed for each nutrient in terms of release times. After a certain period, the fertilizer concentration tends to deplete, indicating no further concentration gradients are occurring. This demonstrates the effectiveness of the controlled release system in gradually delivering nutrients.

In Figure 4, the release profiles obtained from Equation (14) are presented, comparing the simulation results (solid line) with the experimental data (dotted lines). The simulated release fraction reached approximately 90% for potassium, 99% for nitrogen, and 95% for phosphorus during the fertilizer delivery period. These values were compared to the experimental release fraction, showing a difference of 10% for potassium, 0.1% for nitrogen, and 7% for phosphorus. These results validate the model for the time periods considered in relation to the experimental data.

Table 3 presents the diffusion coefficients obtained from the fitting between the mathematical model and the experimental data collected from the literature, along with the MSE value for each fit. The low MSE values for each nutrient indicate a good fit of the model, supporting the validity and accuracy of the proposed mathematical model in simulating the controlled release of NPK nutrients.

These findings demonstrate the model's ability to predict nutrient release behavior in the studied system and validate the effectiveness of the proposed methodology. The numerical simulation employed in this study provides a valuable tool for optimizing fertilizer formulation and improving nutrient delivery efficiency in agriculture.

In general, the results of this study highlight the potential of the mathematical model to provide insights into nutrient release dynamics and optimize fertilizer use strategies. Future research could focus on validating the model with additional experimental data and exploring its application in other nutrient release systems and agricultural scenarios.

Table 2: Modeling parameters.

Description	Symbol	Nutrient		
		N	P	K
Diffusion coefficient (m^2/s)	D_i	1.32×10^{-8}	1.80×10^{-13}	5.80×10^{-11}
Initial concentration (kg/kg)	C_{i0}	2.35	0.02	0.17
Water's rate (m/s)	v	0.1	0.1	0.1
Viscosity of water at T=20 °C (m^2/s)	μ	1.15×10^{-6}	1.15×10^{-6}	1.15×10^{-6}
Particle radius (m)	R	0.0001	0.0001	0.0001
Particle volume (m^3)	Vp	4.1888×10^{-12}	4.1888×10^{-12}	4.1888×10^{-12}
Particle surface area (m^2)	Ap	1.2566×10^{-7}	1.2566×10^{-7}	1.2566×10^{-7}
Schmidt number	Sc	87.0754	6.3889×10^{6}	6.0526×10^{3}
Reynolds number	Re	2.8986	2.8986	2.8986
Sherwood number	Sh	6.4607	181.9004	20.0835
Mass transfer coefficient (m^2/s)	h_{mi}	2.6×10^{-3}	9.8226×10^{-7}	1.1448×10^{-4}

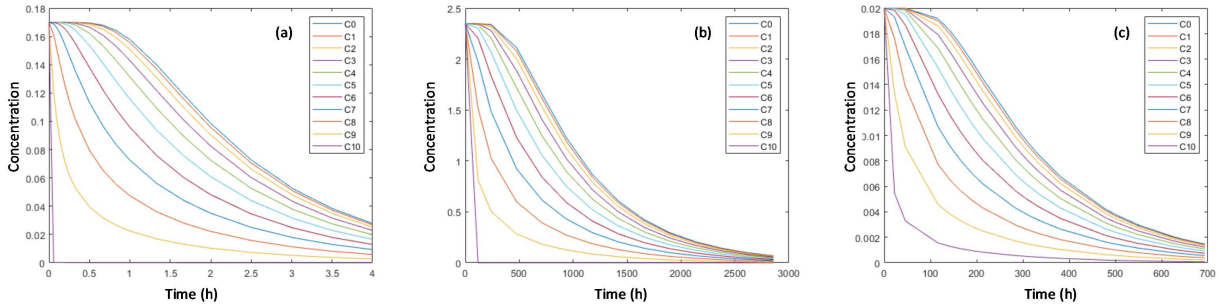

Figure 3: Concentration profiles in the aqueous medium contained in the hydrogel for different ions as a function of time and particle radius (a) potassium, (b) ammonium, and (c) hydrophosphate.

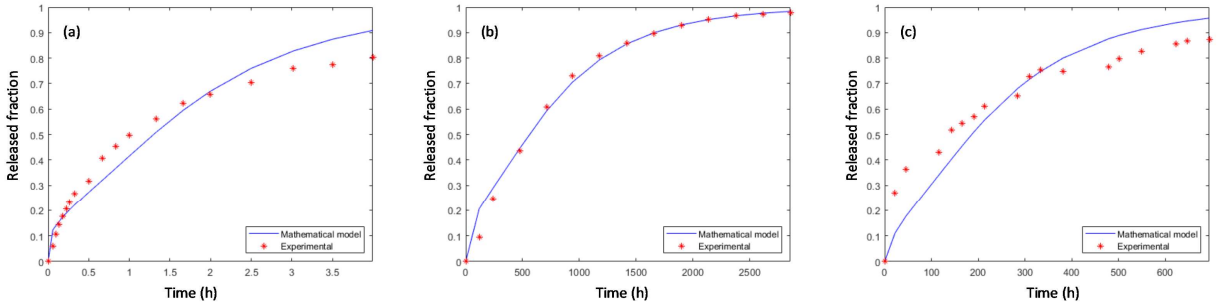

Figure 4: Experimental profiles and modeling of the release fraction of the different ions (a) potassium, (b) ammonium, and (c) hydrophosphate.

Table 3: Effective diffusion coefficient values and mean squared error for each simulation.

Compound released	D_{eff} (m^2/s)	MSE
Potassium	7.2×10^{-10}	0.0697
Ammonium	1.3×10^{-11}	0.0125
Hydrophosphate	5.8×10^{-12}	0.2023

*Note: The effective diffusion coefficients were obtained through the simulation, and the mean squared error represents the accuracy of the model in relation to the experimental data.

The study by Alharbi *et al.* (2018) focuses on controlled release from carboxymethyl phosphate grafted with polyacrylamide (P-CMS-g-PAM), aiming to deliver phosphate fertilizer to the plant at a constant rate to increase phosphorus use efficiency and maintain proper hydration for the plant. In their study, a 600-hour profile achieved 85% nutrient release. In contrast, in the current research, the 600-hour profile achieves a nutrient release of 92%, which exceeds the experimental value.

Zhang *et al.* (2018) in their study focus on the use of biomass ashes as fertilizer and their transformation into tablets to control potassium release. The experimental study shows that biomass ash tablets can decrease the potassium release rate compared to powdered ashes but fail to meet the required values for slow-release fertilizers according to standards. The results indicate that for a time of 4 hours, 80% of the nutrient is released, while in the current research, the release reaches 90% for the same time. This indicates that controlling potassium release presents a greater challenge for improving the delivery technique.

The research conducted by Huang *et al.* (2019) reveals that the release of nitrogen from controlled-release urea exhibits a parabolic profile, while the release of nitrogen from conventional urea shows a sigmoidal profile. In contrast to the present study, the obtained release profile for nitrogen release in the form of ammonium ions also exhibits a parabolic profile, reaching 96% release at 2500 hours, consistent with the findings reported by Huang *et al.* This indicates that the model successfully replicates the nitrogen release behavior.

The study by Suratman *et al.* (2020) focused on the development of a new encapsulated NPK fertilizer in the form of hydrogel granules using chitosan crosslinked with glutaraldehyde. This novel fertilizer demonstrated good performance as a controlled-release fertilizer, with the hydrogel granules capable of

absorbing and storing significant amounts of NPK and gradually releasing it over time. Additionally, it was observed that the release of NPK from the granules tended to decrease with an increase in pH within a range close to the average soil pH (neutral to basic). The mathematical modeling approach proposed in this research has the potential to improve fertilization efficiency and reduce environmental pollution caused by conventional fertilizers.

The study by Bauli *et al*. (2021) focuses on the use of nanocellulose-filled hydrogels as soil conditioners and nutrient carriers. The results highlight the high water and nutrient retention capacity of these hydrogels, as well as their efficiency in the controlled release of NPK nutrients, which helps prevent leaching and wastage of fertilizers. This research supports the notion that hydrogels are a sustainable and efficient solution for agriculture. These findings have the potential to have a positive impact on agricultural practices, improving productivity and resource sustainability.

The study by Albuquerque *et al*. (2022) focused on the use of a biodegradable hydrogel called HEDTA as a substrate for a controlled-release NPK fertilizer in a field study with *Eucalyptus urograndis* seedlings. Four different treatments were compared, including HEDTA hydrogel alone, HEDTA hydrogel with NPK fertilizer, a commercial potassium polyacrylate hydrogel, and a solid NPK fertilizer. The results indicate that the HEDTA + NPK treatment shows positive responses and superior growth compared to the other treatments, demonstrating a slow release of the fertilizer according to the crop's needs. The use of hydrogels and nanoparticles can be explored in the context of mathematical modeling for a deeper understanding and improvement of controlled-release nutrient delivery, to assess their impact on plant growth and development under real conditions.

Conclusions

The proposed mathematical model for controlled release of nutrients in the nanoparticle/hydrogel system in agricultural applications was successfully validated in this study. Solving the mass conservation equation allowed us to obtain the effective diffusion coefficients for the studied nutrients. The estimated effective diffusion coefficients were D_{eff} = 1.3 $\times 10^{-11}$ m^2/s for nitrogen, D_{eff} = 7.2 $\times 10^{-10}$ m^2/s for potassium, and D_{eff} = 5.8 $\times 10^{-12}$ m^2/s for phosphorus. These values represent the transport-related properties in the analyzed nutrient release system. The concentration profiles generated by the model showed good agreement with previously reported experimental curves in the literature. A more precise fit was observed for the nitrogen release experimental data, with an MSE value of 0.0125, compared to the results obtained for potassium and phosphorus. These results confirm the ability of the proposed mathematical model to accurately predict nutrient release from non-metallic particles. This predictive capability is highly relevant in the field of agriculture as it can contribute to the design and development of more efficient and sustainable controlled-release nutrient systems. Additionally, it is important to note that this study relied on selected experimental data from the literature. Further research and validation with additional experimental data are recommended to strengthen the model's robustness and applicability in different agricultural contexts.

Acknowledgment

Authors are grateful to Concytec-Peru and the Iberoamerican Program of Science and Technology to development - CYTED for the financial support of this project under the call "Proyectos en Temas Estratégicos CYTED", through PROCIENCIA grant 207-2020 FONDECYT. Also, the authors are grateful to Dr. J. Quispe and Dr. D. Pinzón for their enriching discussions and valuable support, and to the Centro de Investigaciones Tecnológicas, Biomédicas y Medioambientales (CITBM).

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