engineering proceedings

MDPI

Proceeding Paper

Green Synthesis of Zinc Oxide Nanoparticles Using *Lepidium sativum* Seed Extract Embedded in Sodium Alginate Matrix for Efficient Slow-Release Biofertilizers †

Yasmina Khane [1,2,*], Zoulikha Hafsi [1,2], Fares Fenniche [1,2], Djaber Aouf [1,2], Marwa Laib [1], Abdelkrim Gagi [1] and Sofiane Khane [3]

[1] Faculty of Sciences and Technology, University of Ghardaïa, P.O. Box 455, Ghardaïa 47000, Algeria; hafsidoc@yahoo.fr (Z.H.); fennichefares@yahoo.fr (F.F.); djaberaouf@gmail.com (D.A.)
[2] Materials, Energy Systems Technology and Environment Laboratory, Faculty of Sciences and Technology, University of Ghardaïa, P.O. Box 455, Ghardaïa 47000, Algeria
[3] Faculty of Sciences, University of Djillali Liabes, Sidi Bel Abbes 48000, Algeria
* Correspondence: yasminekhane@yahoo.fr or khane.yasmina@univ-ghardaia.dz; Tel.: +213-540575638
† Presented at the 3rd International Electronic Conference on Processes—Green and Sustainable Process Engineering and Process Systems Engineering (ECP 2024), 29–31 May 2024; Available online: https://sciforum.net/event/ECP2024.

Abstract: In this research, we developed a novel slow-release biofertilizer by utilizing an environmentally friendly method to synthesize ZnO-NPs using sodium hydroxide, zinc acetate salt, and *Lepidium sativum* seed extract. The commercial fertilizer urea 46% was encapsulated in the nano-ZnO/alginate beads. The structural and morphological characteristics of the nanocomposites were confirmed using X-ray diffraction (XRD) and scanning electron microscopy, which confirmed the successful creation of nanocomposite alginate beads. The results indicated that the ZnO/alginate/urea beads exhibited a steady and continuous release of urea for up to one hour and extended nutrient availability over time. This research demonstrates the potential of ZnO-NP/alginate composites as a promising platform for developing slow-release biofertilizers, combining the beneficial properties of ZnO nanoparticles with the controlled-release capabilities of alginate matrices. This research highlights the potential of ZnO-NP/alginate composites as a sustainable and efficient solution for agricultural applications, providing a controlled release of nutrients that could minimize their environmental impact and enhance crop productivity.

Keywords: biosynthesis; *Lepidium sativum*; zinc oxide nanoparticles; alginate; fertilizers; urea; encapsulation; slow release; sustainable agriculture

Citation: Khane, Y.; Hafsi, Z.; Fenniche, F.; Aouf, D.; Laib, M.; Gagi, A.; Khane, S. Green Synthesis of Zinc Oxide Nanoparticles Using *Lepidium sativum* Seed Extract Embedded in Sodium Alginate Matrix for Efficient Slow-Release Biofertilizers. *Eng. Proc.* **2024**, *67*, 35. https://doi.org/10.3390/engproc2024067035

Academic Editor: Juan Francisco García Martín

Published: 6 September 2024

1. Introduction

Agrochemical fertilizers are employed to augment crop yields and soil remediation; nonetheless, the agricultural sector is the primary origin of escalating chemical contaminants as a result of the excessive demand and unregulated application of synthetic chemical fertilizers [1]. Although agricultural fertilizers provide significant benefits globally and are crucial for agricultural progress, certain areas and farmers experience the adverse effects of these fertilizers on the environment and sustainable agriculture, as well as the economic consequences associated with their high prices [2]. Specifically, plants utilize only 50% to 70% of the added amounts of conventional fertilizers, which are compounds larger than 100 nanometers. The remaining amount is lost through leaching into the soils, which can have detrimental impacts on soils, water, and biodiversity. These effects include climate change, soil acidification, nitrogen depletion, soil fertility degradation, groundwater pollution, species extinction, and excessive energy consumption in the manufacturing process [3–5]. Moreover, the accumulation of chemical residues in crops can pose health hazards to individuals [6,7].

Recently, new avenues for tackling these issues have been made possible by the development of nanotechnology [8]. Considerable effort has been dedicated to replacing synthetic agrochemical fertilizers with sustainable and eco-friendly natural ones. Over the last decade, scientists have concentrated on the development of novel nano-enabled agrochemical products. This involved the creation of nano-fertilizers using environmentally benign materials. These nano-fertilizers have the ability to operate as plant biostimulants, antioxidants, antimicrobials, or combinations of these for various agronomical techniques [9,10]. In this regard, zinc oxide nanoparticles (ZnO-NPs) have attracted a lot of interest as a potentially useful technology because of their substantial ability to successfully treat biotic and abiotic stressors [11]. Zinc oxide (ZnO) nanoparticle synthesis encompasses several techniques, such as chemical and physical methods [12,13], as well as environmentally benign methods that circumvent dangerous chemicals and harsh environments [14]. Typically, these techniques utilize natural sources, such as microorganisms or plant extracts (such as those present in green tea, neem, or aloe vera), together with other environmentally benign compounds that function as stabilizers, reducing agents, or templates for the synthesis of nanoparticles [15,16]. Although each of these preparation processes has its own set of benefits and drawbacks, when combined, they provide a plethora of possibilities for utilizing ZnO nanoparticles to address both living and non-living stresses [17]. The production of metallic nanoparticles entails the amalgamation of a plant extract with a solution of metallic salt, followed by a period of incubation [18]. These plant extracts include bioactive chemicals that have the dual function of reducing and capping agents, therefore stabilizing the recently synthesized metallic nanoparticles (NPs) [19,20]. The reduction mechanism is significantly influenced by the phytochemical makeup of these extracts, which includes terpenoids, flavones, quinones, ketones, and aldehydes. Furthermore, these chemicals function as electron donors, promoting the conversion of metal ions into nanoparticles in aqueous solutions [21]. In order to produce stable and functionally varied metallic nanoparticles, this green synthesis method exploits the inherent reducing power of chemicals obtained from plants.

We aim to obtain an effective product while ensuring that the production process will be sustainable and natural, without any harmful chemical substances, in addition to being an affordable price for all. The use of plant-growth-promoting substances in encapsulated beads with nutritive mineral salts or fertilizers is an effective alternative to traditional fertilizers, as it presents many advantages, such as the use of smaller quantities of these substances and a longer storage duration. This allows us to bring numerous benefits to plants and the environment while supporting the agricultural economy under current conditions [22].

The nutritional components in nanofertilizers might be enclosed by nanomaterials, coated with a thin layer, or administered as nanoparticles (NP). The objective of encapsulation is to guarantee the safeguarding, compatibility, and stability of an active component within a formulation, which area contingent upon the specific domains and circumstances of its use. Encapsulation enables the modification and regulation of the release profile of an active ingredient, therefore providing the potential for it to provide a sustained or triggered pharmacological action [23,24]. Biologically degradable, bioavailable, and biocompatible natural polymers, such as chitosan, alginate, starch, and cellulose, are the primary components in formulations for bio- and nano-fertilizers [25,26]. Particles within a size range of 10 to 100 nm are combined with these polymers. The nanoscale size of these particles results in a remarkably high surface area-to-volume ratio, which provides numerous sites for metabolic processes in plants. This bigger reactive surface area enables improved nutrient penetration and use, perhaps leading to increased photosynthetic rates. Collaboratively, biodegradable polymers and nanoparticles form a delivery system that optimizes the availability of nutrients, promotes plant development, and minimizes their environmental footprint.

The focus of this study was the synthesis of a nanofertilizer via the encapsulation of urea 46% in beads formed after embedding ZnO nanoparticles in an Alginate-Based

Hydrogel. We have biologically synthesized and characterized these ZnONPs using *Lepidium sativum* (*L. sativum*) seed extract and evaluated their plant growth and compatibility standards in terms of other biofertilizers.

2. Materials and Methods

2.1. Materials

All chemicals and reagents used in this study were of analytical grade and obtained from Sigma-Aldrich. The following materials were used without further purification. These included alginate, calcium chloride, sodium hydroxide, and zinc acetate dihydrate.

Granular urea (46% Nitrogen), a commercial fertilizer widely used in agricultural crop production, was supplied by Ritchie Feed and Seed Inc. (Ottawa, ON, Canada). This fertilizer contains the highest nitrogen percentage (46%) among all solid fertilizers and serves as a primary nitrogen source for plants. It is characterized by its complete water solubility and high mobility in soil, moving with soil moisture until soil microorganisms initiate the nitrification process.

2.2. Preparation of L. sativum Extract

In this work, zinc oxide nanoparticles (ZnO NPs) was synthesized using a green method and with an extract of *L. sativum* seeds, which were purchased from a local market (herb seller) in the state of Ghardaia, Algeria.

The *L. sativum* seeds were thoroughly washed multiple times with distilled water to remove impurities and dust. After washing, the seeds were dried in the shade at room temperature for 1–3 days. The dried *L. sativum* seeds were then ground into a fine powder using a grinder to increase their surface area and enhance their interaction with the solvent. To prepare the extract, 5 g of the ground seeds were added to 50 mL of distilled water in a 100 mL glass beaker. This mixture was stirred for 35 min at 60 °C. The resulting extract was filtered using filter paper and stored in a glass bottle.

2.3. Biosynthesis of ZnO Nanoparticles

Under high-speed stirring for 2 h at 60 °C, we combined 20 mL of *L. sativum* seed extract with 80 mL of an aqueous solution of 0.1 mol zinc acetate dihydrate. Then, a 0.5 M NaOH water solution was added dropwise to the mixture until it reached the desired consistency. The solution was left to settle overnight, the supernatant was removed, and the precipitate was washed with a mixture of water and ethanol. Lastly, the ZnO nanoparticles that had precipitated were air-dried at 60 °C before being calcined for 2 h at 400 °C.

2.4. Synthesis of ZnO-NPs/Alginate Beads

Dissolve a specified amount of alginate in distilled water, stirring thoroughly with a magnetic stirrer at 800 rpm for 5 h to ensure complete dissolution. In a separate container, disperse 1% (w/v) of zinc oxide nanoparticles (ZnO-NPs) in distilled water to prevent agglomeration. Slowly add this ZnO-NP dispersion to the alginate solution and mix with rapid agitation for 1 h.

Using a syringe, drop the alginate/ZnO gel solution into a calcium chloride bath while maintaining gentle magnetic stirring. This process facilitates the formation of alginate beads. After formation, rinse the beads several times with distilled water to remove impurities. Allow the beads to air dry to obtain uniform spherical gel beads based on sodium alginate (SA) and ZnO-NPs.

2.5. Preparation of Urea-Encapsulating Alginate/ZnO-NPs Beads

To synthesize urea-encapsulating beads, reproduce the identical beginning procedures as described above. Once the ZnO-NPs have been evenly distributed in the alginate solution, introduce a predetermined quantity of urea (46% nitrogen) powder into the mixture. Maintain optimal dispersion in distilled water to prevent the aggregation of urea. Follow the previously stated process of bead generation by introducing the urea/ZnO-NPs/alginate

combination into the calcium chloride solution. The outcome of this procedure is the formation of urea-encapsulating Alginate/ZnO-NPs beads.

2.6. Characterization of Biosynthesized ZnO Nanoparticles and Urea-Encapsulating Alginate/ZnO-NPs Beads

A diffractometer (Bruker D2 Phaser SSD 160; Bruker AXS, Madison, WI, USA) was used to analyze the beads' crystalline structure. This device uses Cu Kα radiation (λ = 1.54184 Å) and a LYNXEYE scintillation detector, operating at 30 KV and 10 mA of current. The SEM used to analyze our samples was a "SU3500" model equipped with an X-ray detector.

2.7. Kinetic Study of the Release of the Active Ingredient, Urea 46%

The liberation of the encapsulated urea 46% from the alginate/ZnO-NPs beads was evaluated using a UV-Vis spectrometer that had been calibrated to the highest wavelength (μmax) of the active components (urea fertilizer) present in the medium being studied. To conduct our kinetic investigations, we prepared a physiological medium with a pH equal to 7.4. To prepare the solution, we combined 20 mL (0.1 N) of hydrochloric acid with 500 mL (0.025 N) of sodium tetraborate decahydrate in 1 L of distilled water. Loaded beads weighing 100 mg were submerged in a pH 7.4 physiological medium in a 100 mL beaker and subjected to controlled magnetic stirring at 500 rpm at 30 °C. A total of 1 mL of the samples was collected at predetermined time intervals. The spectral absorbance of urea 46% was measured using a Thermo Fisher Scientific UV-Vis instrument (UviLine 9400C, Waltham, MA, USA) within the wavelength range of 200 to 800 nm.

3. Results and Discussion

The fabrication of ZnO-NPs using plant extracts employs a green technique that utilizes the phytochemicals found in the *L. sativum* seed extract as both reducing and stabilizing agents [27,28]. This approach is ecologically sustainable and circumvents the utilization of hazardous substances commonly associated with traditional nanoparticle production [29]. The composition of *L. sativum* seed extract is characterized by a varied assortment of bioactive constituents, including tannins, proteins, flavonoids, and other phenolic derivatives [30]. Based on these key molecules, it is possible to determine the mechanism for the production pathway of ZnO NPs [31]. These compounds serve as natural reducing agents. When zinc acetate is dissolved in water, it breaks down into zinc ions (Zn^{2+}) and acetate ions. Upon the addition of the plant extract to the zinc salt solution, these phytochemicals engage with the zinc ions and effectively convert Zn^{2+} to elemental zinc (Zn^{0}). This process is typically followed by observable alterations in the solution's color, suggesting the formation of nanoparticles. Zinc atoms undergo aggregation to form tiny nuclei, marking the earliest stage of nanoparticle creation. The zinc nuclei experience oxidation when exposed to oxygen (either from water or dissolved oxygen in the solution), resulting in the formation of ZnO nanocrystals. ZnO nanoparticles are formed via the growth of these nanocrystals, which occurs as more Zn^{2+} is reduced and introduced to the developing particles. The phytochemicals included in the plant extract function as stabilizers for the generated ZnO-NPs by covering their surfaces and preventing them from clumping together, therefore regulating the size and shape of the particles [20,32].

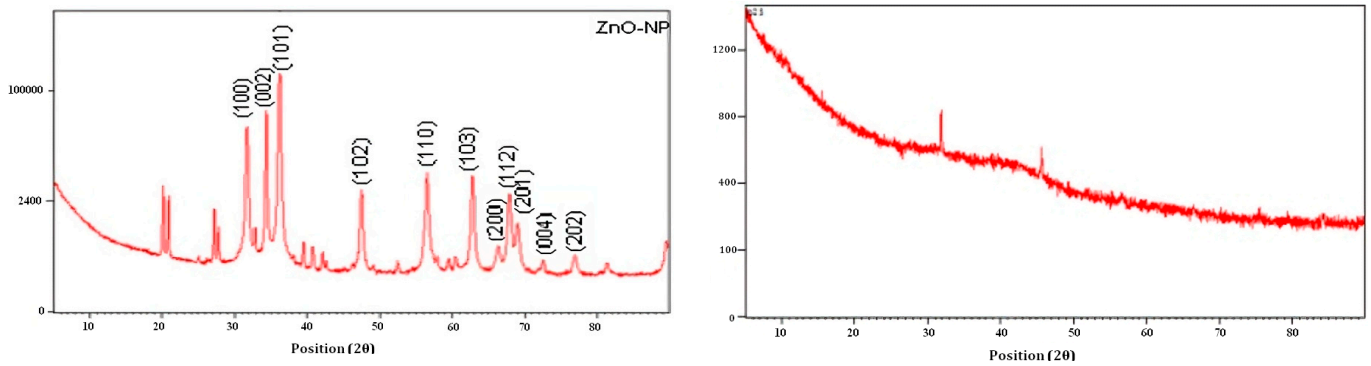
3.1. Characterization

The L. sativum seed extract-mediated ZnO nanoparticles were characterized by X-ray diffraction (XRD) in the 2θ range of 20° to 80°, as shown in Figure 1a. Sharp diffraction peaks were observed at 2θ values of 31.5°, 34.2°, 38°, 47.56°, 57°, 62.8°, 65.42°, 67°, 69.5°, 71.64°, and 76.98°, corresponding to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004), and (202) crystal planes, respectively. All observed peaks can be indexed to the hexagonal wurtzite structure of zinc oxide, in agreement with JCPDS data card No. 36-1451. The sharpness and narrow width of the peaks indicate that the biosynthesized ZnO NPs are

highly crystalline. These results are consistent with previous research characterizing well-formed ZnO-NP structures [33,34]. The average crystallite size of the ZnO nanoparticles (ZnO-NPs) was estimated using the Debye–Scherrer equation [27]:

$$D = K\lambda/(\beta \cos \theta) \quad (1)$$

where D = mean crystallite size, K = shape factor (0.9, assuming spherical particles), λ = X-ray wavelength of the Cu Kα radiation (1.5406 Å), β = Full Width at Half Maximum (FWHM) of the diffraction peak (in radians), and θ = Bragg diffraction angle.



(**a**) (**b**)

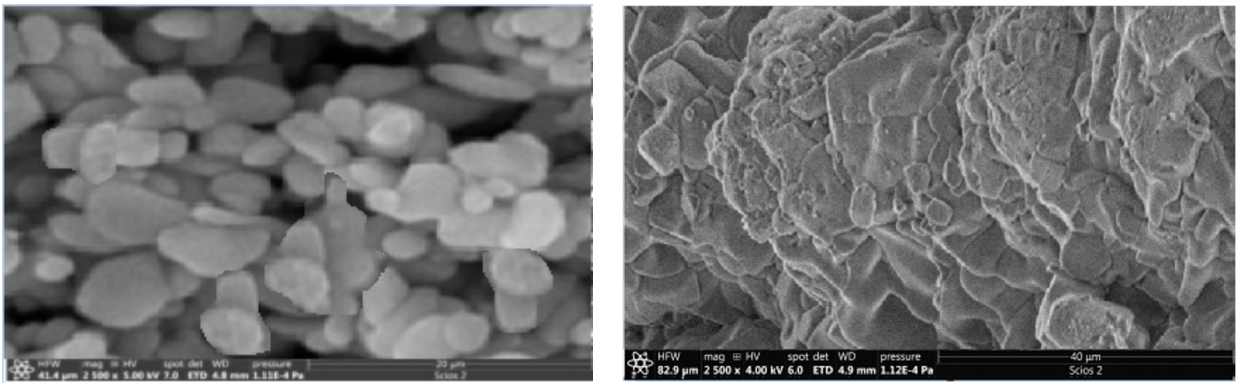
Figure 1. XRD pattern of (**a**) biosynthesized ZnO nanoparticles and (**b**) alginate/ZnO/fertilizer beads.

The FWHM was determined from the most intense peak in the XRD pattern, typically the (101) reflection for ZnO. After careful analysis and calculation using this equation, the average crystallite size of the biosynthesized ZnO-NPs was found to be 15.6 ± 2 nm.

The crystallographic structure of the alginate/ZnO/fertilizer composite beads (Figure 1b) was investigated using X-ray diffraction (XRD) analysis. The diffraction pattern obtained has a remarkably simple profile, comprised of only three clearly defined peaks of modest intensity. The X-ray diffraction (XRD) profile indicates numerous significant characteristics of the composite beads. The existence of a limited number of low-intensity peaks suggests that the composite has quite a low level of crystallinity. This may be attributed to the prevalence of amorphous components, most likely originating from the alginate matrix. The beads' composite composition, which includes alginate (an amorphous polymer), ZnO nanoparticles, and fertilizer components, may have led to a complicated structural configuration that is not readily discernible by X-ray diffraction (XRD). The limited presence of observable peaks may also be attributed to the overlapping diffraction patterns of several crystalline phases inside the composite material. Additionally, the low intensity and possible widening of the peaks (if detected) may indicate the presence of crystalline components (probably ZnO) in a nanocrystalline form. The structural complexity of the alginate/ZnO/fertilizer composite beads is elucidated by this XRD investigation, which reveals their mostly amorphous character and a certain level of nanocrystallinity.

An analysis of the morphological properties of the ZnO nanoparticles (ZnO-NPs) produced by biological means and their integration into alginate beads following their encapsulation of urea fertilizer was carried out using scanning electron microscopy (SEM). The data shown in Figure 2a indicate that the ZnO-NPs have a mostly spherical morphology, with dimensions reaching from 80 to 100 nm. The particles have a homogeneous structure; however, there is some level of aggregation noted. Upon the analysis of the urea's encapsulation in the nano-ZnO alginate composite beads (Figure 2b), the scanning electron microscope (SEM) pictures unequivocally show the effective incorporation of ZnO-NPs into the alginate matrix. The nanoparticles are evenly distributed inside the alginate framework, with some particles clearly scattered on the surface and others incorporated into the dense matrix. Observations of this dispersion pattern indicate an intricate interplay among the

ZnO-NPs, the alginate polymer, and the enclosed urea fertilizer. The modest aggregation of ZnO-NPs detected in the pure nanoparticle sample is also apparent in the composite, suggesting that the process of incorporation does not completely inhibit the clustering of particles. The scanning electron microscopy (SEM) study sheds light on the structure of the biosynthesized ZnO-NPs and their spatial distribution in the alginate matrix containing urea fertilizer. These aspects are essential for comprehending the possible effectiveness of these nanocomposites in controlled-release fertilizer applications.



(**a**) (**b**)

Figure 2. SEM images of (**a**) biosynthesized ZnO nanoparticles and (**b**) alginate/ZnO/fertilizer beads.

3.2. Release of Urea Fertilizer from ZnO-NPs/Alginate Beads

We present kinetic curves that depict the liberation of urea molecules from alginate beads. These curves correlate to the experimental observation of the fertilizer content in a solution with respect to time. Specifically, the absorbance measured by UV–visible spectroscopy with time at the characteristic absorption wavelength for urea (usually approximately 200–210 nm) is shown in Figure 3. The percentage of molecule release from the beads containing fertilizer was quantified in a medium with a pH of 7.4, accurately replicating the somewhat alkaline conditions commonly encountered in soil habitats.

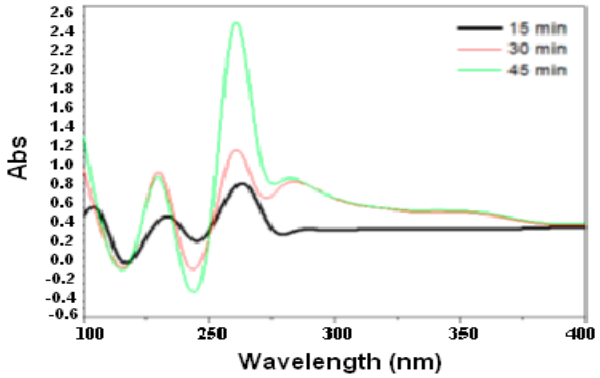


Figure 3. Kinetic curves of the liberation of urea molecules from alginate beads.

The rate at which the agent is released rises with time, exhibiting a non-linear trend. The release curves have a typical morphology, distinguished by three clearly defined phases:

1. Burst release phase: An initial fast liberation of urea, most likely caused by the breakdown of molecules attached to the surface or that are inadequately confined.
2. The diffusion-controlled phase involves a gradual and prolonged release of urea as it passes through the alginate matrix.
3. Plateau phase: A progressive stabilization as the concentration gradient diminishes and converges to equilibrium.

The observed release profile indicates that the diffusion of the active component through the polymer layers is a crucial factor in determining its release kinetics. This phenomenon may be elucidated by applying Fick's principles of diffusion, which assert that the rate of diffusion is directly proportional to the concentration gradient [35,36]. Upon contact with the medium, the beads undergo hydration or a swelling of their alginate matrix, allowing water to enter the system. Consequently, the urea molecules undergo disintegration. Due to its high water solubility (1080 g/L at 20 °C) and the comparatively modest initial molecule loading, it is anticipated that urea will dissolve quickly, resulting in a concentration gradient. Once dissolved, these bioactive compounds permeate the coated polymer and enter the dissolving media via diffusion. The last stage is frequently the slowest in terms of kinetics and might crucially determine the total rate of fertilizer release. Several parameters can determine the rate of diffusion [37]:

1. Polymer matrix characteristics: the pore size, crosslinking density, and hydrophilicity of the alginate.
2. Environmental conditions: the pH, temperature, and ionic strength of the release medium.
3. Urea molecule characteristics: the size, charge, and interactions of urea with the alginate matrix.

The overall release kinetics can often be modeled using various mathematical equations, such as the Korsmeyer–Peppas model or the Higuchi equation, which can provide insights into the dominant release mechanisms [38]. A possible benefit of this controlled-release method for agricultural applications is the possibility of reduced nutrient loss through leaching and a more sustained delivery of nitrogen to plants over time [39–41].

4. General Conclusions

This study sought to create a superior polymeric fertilizer compound. A matrix of micronutrient metal oxide nanoparticles and a natural biodegradable polymer encapsulates urea, a commercial fertilizer. This unique formulation was tested in terms of its micronutrient uptake and release to plants and the environment.

Zinc was chosen as the first test element for this nanofertilizer because zinc oxide nanoparticles are easy to synthesize and zinc is essential for plant health and development. This method permits the production of a multifunctional fertilizer system with controlled release and improved nutrient delivery.

The biosynthesized ZnO nanoparticles and urea-encapsulating alginate/ZnO-NP beads showed that the ZnO-NPs were incorporated in the alginate matrix and that the urea fertilizer was encapsulated. In water-based experiments, ZnO-NPs were released without impediment, whereas urea was released gradually and in a regulated manner. These nano-ZnO/alginate beads containing urea can link alginate chains with biogenic ZnO-NPs, according to our results. Since they include zinc, a micronutrient, they are ideal for plant growth. A flexible nanofertilizer that transports both major and minor nutrients might improve nutrient usage efficiency and reduce the environmental impact of standard fertilizers.

Author Contributions: Y.K.: methodology and formal analysis; Z.H.: investigation and resources; S.K.: data curation; Y.K., M.L. and A.G.: writing—original draft preparation; Y.K., F.F. and D.A.: writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data is unavailable due to privacy or ethical restrictions.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Hamed, R.; Jodeh, S.; Alkowni, R. Nano bio fertilizer capsules for sustainable agriculture. *Sci. Rep.* **2024**, *14*, 13646. [CrossRef] [PubMed]
2. Penuelas, J.; Coello, F.; Sardans, J. A better use of fertilizers is needed for global food security and environmental sustainability. *Agric. Food Secur.* **2023**, *12*, 5. [CrossRef]
3. Kumar, R.; Kumar, R.; Prakash, O. The impact of chemical fertilizers on our environment and ecosystem. *Chief Ed.* **2019**, *35*, 69.
4. Usman, M.; Farooq, M.; Wakeel, A.; Nawaz, A.; Cheema, S.A.; Rehman, H.U.; Ashraf, I.; Sanaullah, M. Nanotechnology in agriculture: Current status, challenges and future opportunities. *Sci. Total Environ.* **2020**, *721*, 137778. [CrossRef] [PubMed]
5. Govindasamy, P.; Muthusamy, S.K.; Bagavathiannan, M.; Mowrer, J.; Jagannadham, P.T.K.; Maity, A.; Halli, H.M.; GK, S.; Vadivel, R.; TK, D.; et al. Nitrogen use efficiency—A key to enhance crop productivity under a changing climate. *Front. Plant Sci.* **2023**, *14*, 1121073. [CrossRef]
6. Shukla, K.; Mishra, V.; Singh, J.; Varshney, V.; Verma, R.; Srivastava, S. Nanotechnology in sustainable agriculture: A double-edged sword. *J. Sci. Food Agric.* **2024**, *104*, 5675–5688. [CrossRef]
7. Tyagi, J.; Ahmad, S.; Malik, M. Nitrogenous fertilizers: Impact on environment sustainability, mitigation strategies, and challenges. *Int. J. Environ. Sci. Technol.* **2022**, *19*, 11649–11672. [CrossRef]
8. Tang, Y.; Zhao, W.; Zhu, G.; Tan, Z.; Huang, L.; Zhang, P.; Gao, L.; Rui, Y. Nano-Pesticides and Fertilizers: Solutions for Global Food Security. *Nanomaterials* **2023**, *14*, 90. [CrossRef]
9. Wahab, A.; Muhammad, M.; Ullah, S.; Abdi, G.; Shah, G.M.; Zaman, W.; Ayaz, A. Agriculture and environmental management through nanotechnology: Eco-friendly nanomaterial synthesis for soil-plant systems, food safety, and sustainability. *Sci. Total Environ.* **2024**, *926*, 171862. [CrossRef]
10. Khan, H.A.; Naqvi, S.R.; Mehran, M.T.; Khoja, A.H.; Niazi, M.B.K.; Juchelková, D.; Atabani, A. A performance evaluation study of nano-biochar as a potential slow-release nano-fertilizer from wheat straw residue for sustainable agriculture. *Chemosphere* **2021**, *285*, 131382. [CrossRef]
11. Gade, A.; Ingle, P.; Nimbalkar, U.; Rai, M.; Raut, R.; Vedpathak, M.; Jagtap, P.; Abd-Elsalam, K.A. Nanofertilizers: The Next Generation of Agrochemicals for Long-Term Impact on Sustainability in Farming Systems. *Agrochemicals* **2023**, *2*, 257–278. [CrossRef]
12. Malaiappan, S.; Priyangha, P.T.; Niveditha, S. Green Synthesis and Characterization of Zinc Oxide Nanoparticles Using Catharanthus roseus Extract: A Novel Approach. *Cureus* **2024**, *16*, e60407. [CrossRef] [PubMed]
13. Dhoke, S.K. Synthesis of nano-ZnO by chemical method and its characterization. *Results Chem.* **2023**, *5*, 100771. [CrossRef]
14. Zhou, X.Q.; Hayat, Z.; Zhang, D.D.; Li, M.Y.; Hu, S.; Wu, Q.; Cao, Y.F.; Yuan, Y. Zinc Oxide Nanoparticles: Synthesis, Characterization, Modification, and Applications in Food and Agriculture. *Processes* **2023**, *11*, 1193. [CrossRef]
15. Bhardwaj, K.; Singh, A.K. Bio-waste and natural resource mediated eco-friendly synthesis of zinc oxide nanoparticles and their photocatalytic application against dyes contaminated water. *Chem. Eng. J. Adv.* **2023**, *16*, 100536. [CrossRef]
16. Ragavendran, C.; Kamaraj, C.; Jothimani, K.; Priyadharsan, A.; Anand Kumar, D.; Natarajan, D.; Malafaia, G. Eco-friendly approach for ZnO nanoparticles synthesis and evaluation of its possible antimicrobial, larvicidal and photocatalytic applications. *Sustain. Mater. Technol.* **2023**, *36*, e00597. [CrossRef]
17. Wang, Z.; Wang, S.; Ma, T.; Liang, Y.; Huo, Z.; Yang, F. Synthesis of Zinc Oxide Nanoparticles and Their Applications in Enhancing Plant Stress Resistance: A Review. *Agronomy* **2023**, *13*, 3060. [CrossRef]
18. Ohiduzzaman, M.; Khan, M.; Khan, K.; Paul, B. Biosynthesis of silver nanoparticles by banana pulp extract: Characterizations, antibacterial activity, and bioelectricity generation. *Heliyon* **2024**, *10*, e25520. [CrossRef]
19. Villagrán, Z.; Anaya-Esparza, L.M.; Velázquez-Carriles, C.A.; Silva-Jara, J.M.; Ruvalcaba-Gómez, J.M.; Aurora-Vigo, E.F.; Rodríguez-Lafitte, E.; Rodríguez-Barajas, N.; Balderas-León, I.; Martínez-Esquivias, F. Plant-Based Extracts as Reducing, Capping, and Stabilizing Agents for the Green Synthesis of Inorganic Nanoparticles. *Resources* **2024**, *13*, 70. [CrossRef]
20. Al-Darwesh, M.Y.; Ibrahim, S.S.; Mohammed, M.A. A Review on Plant Extract Mediated Green Synthesis of Zinc oxide Nanoparticles and Their biomedical Applications. *Results Chem.* **2024**, *7*, 101368. [CrossRef]
21. Bairwa, P.; Kumar, N.; Devra, V.; Abd-Elsalam, K.A. Nano-Biofertilizers Synthesis and Applications in Agroecosystems. *Agrochemicals* **2023**, *2*, 118–134. [CrossRef]
22. Easwaran, C.; Moorthy, G.; Christopher, S.R.; Mohan, P.; Marimuthu, R.; Koothan, V.; Nallusamy, S. Nano hybrid fertilizers: A review on the state of the art in sustainable agriculture. *Sci. Total Environ.* **2024**, *929*, 172533. [CrossRef] [PubMed]
23. Garg, D.; Sridhar, K.; Inbaraj, B.S.; Chawla, P.; Tripathi, M.; Sharma, M. Nano-Biofertilizer Formulations for Agriculture: A Systematic Review on Recent Advances and Prospective Applications. *Bioengineering* **2023**, *10*, 1010. [CrossRef] [PubMed]
24. Nongbet, A.; Mishra, A.K.; Mohanta, Y.K.; Mahanta, S.; Ray, M.K.; Khan, M.; Baek, K.H.; Chakrabartty, I. Nanofertilizers: A Smart and Sustainable Attribute to Modern Agriculture. *Plants* **2022**, *11*, 2587. [CrossRef] [PubMed]
25. Jha, A.; Pathania, D.; Damathia, B.; Raizada, P.; Rustagi, S.; Singh, P.; Rani, G.M.; Chaudhary, V. Panorama of biogenic nanofertilizers: A road to sustainable agriculture. *Environ. Res.* **2023**, *235*, 116456. [CrossRef] [PubMed]
26. Goyal, S.; Kumar, R.; Beniwal, V. Biogenic synthesis of nanoparticles for sustainable crop production: A review. *Nanobioletters* **2023**, *12*, 10.
27. Matinise, N.; Fuku, X.G.; Kaviyarasu, K.; Mayedwa, N.; Maaza, M.J.A.S.S. ZnO nanoparticles via Moringa oleifera greensynthesis: Physical properties & mechanism of formation. *Appl. Surf. Sci.* **2017**, *406*, 339–347.

28. Hassan, D.; Khalil, A.T.; Saleem, J.; Diallo, A.; Khamlich, S.; Shinwari, Z.K.; Maaza, M. Biosynthesis of purehematite phase magnetic iron oxide nanoparticles using foralextracts of Callistemon viminalis (bottlebrush): Their physicalproperties and novel biological applications. *Artifcial Cells Nanomed. Biotechnol.* **2018**, *46*, 693–707. [CrossRef]
29. Alnehia, A.; Al-Sharabi, A.; Al-Odayni, A.B.; Al-Hammadi, A.H.; Al-Ostoot, F.H.; Saeed, W.S.; Abduh, N.A.; Alrahlah, A. Lepidium sativum Seed Extract-Mediated Synthesis of Zinc Oxide Nanoparticles: Structural, Morphological, Optical, Hemolysis, and Antibacterial Studies. *Bioinorg. Chem. Appl.* **2023**, *2023*, 1–11. [CrossRef]
30. Al-Snafi, A.E. Chemical constituents and pharmacological effects of Lepidium sativum—A review. *Int. J. Curr. Pharm. Res.* **2019**, *11*, 1–10. [CrossRef]
31. Alnehia, A.; Al-Sharabi, A.; Al-Hammadi, A.-B.; Al-Odayni, W.; Saeed, S.; Alrahlah, A. Structural, optical, and bio-activity properties of silver-doped zinc sulfde nanoparticlessynthesized using plectranthus barbatus leaf extract. *J. Chem.* **2023**, *10*, 1399703.
32. Abdelbaky, A.S.; Mohamed, A.M.H.A.; Sharaky, M.; Mohamed, N.A.; Diab, Y.M. Green approach for the synthesis of ZnO nanoparticles using Cymbopogon citratus aqueous leaf extract: Characterization and evaluation of their biological activities. *Chem. Biol. Technol. Agric.* **2023**, *10*, 63. [CrossRef]
33. AlHarethi, A.A.; Abdullah, Q.Y.; AlJobory, H.J.; Anam, A.M.; Arafa, R.A.; Farroh, K.Y. Zinc oxide and copper oxide nanoparticles as a potential solution for controlling Phytophthora infestans, the late blight disease of potatoes. *Discov. Nano* **2024**, *19*, 105. [CrossRef] [PubMed]
34. Mendes, A.R.; Granadeiro, C.M.; Leite, A.; Pereira, E.; Teixeira, P.; Poças, F. Optimizing Antimicrobial Efficacy: Investigating the Impact of Zinc Oxide Nanoparticle Shape and Size. *Nanomaterials* **2024**, *14*, 638. [CrossRef] [PubMed]
35. Madhumitha, G.; Fowsiya, J.; Gupta, N.; Kumar, A.; Singh, M. Green synthesis, characterization and antifungal and photocatalytic activity of Pithecellobium dulce peel-mediated ZnO nanoparticles. *J. Phys. Chem. Solids* **2018**, *127*, 43–51. [CrossRef]
36. Shinn, E.J.; Tajkhorshid, E. Generating Concentration Gradients across Membranes for Molecular Dynamics Simulations of Periodic Systems. *Int. J. Mol. Sci.* **2024**, *25*, 3616. [CrossRef]
37. Paarakh, M.P.; Jose, P.A.; Setty, C.M.; Peterchristoper, G.V. Release Kinetics—Concepts And Applications. *Int. J. Pharm. Res. Technol.* **2018**, *10*, 10–20.
38. Lavrentev, F.V.; Shilovskikh, V.V.; Alabusheva, V.S.; Yurova, V.Y.; Nikitina, A.A.; Ulasevich, S.A.; Skorb, E.V. Diffusion-Limited Processes in Hydrogels with Chosen Applications from Drug Delivery to Electronic Components. *Molecules* **2023**, *28*, 5931. [CrossRef]
39. Zhu, W.; Long, J.; Shi, M. Release Kinetics Model Fitting of Drugs with Different Structures from Viscose Fabric. *Materials* **2023**, *16*, 3282. [CrossRef]
40. Chen, J.; Wei, X. Controlled-Release Fertilizers as a Means to Reduce Nitrogen Leaching and Runoff in Container-Grown Plant Production. In *Nitrogen in Agriculture—Updates*; Intech: Rijeka, Croatia, 2018.
41. Govil, S.; Van Duc Long, N.; Escribà-Gelonch, M.; Hessel, V. Controlled-release fertiliser: Recent developments and perspectives. *Ind. Crops Prod.* **2024**, *219*, 119160. [CrossRef]