

Zinc Layered Hydroxide 2-methyl-4-chlorophenoxyacetate: Synthesis via ZnO, Characterization and Effect on Seed Germination

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Abstract

2-methyl-4-chlorophenoxyacetic acid (MCPA) was successfully intercalated into zinc layered hydroxide (ZLH) by anion exchange technique followed by hydrothermal treatment, resulting in the formation of nanoherbicide, zinc-layered hydroxide-2-methyl-4-chlorophenoxyacetic acid (ZMCPA). Fourier-transform infrared spectroscopy (FTIR) and Powder X-ray diffraction (PXRD) was used to confirm the intercalation of herbicide into ZLH, while Ultraviolet-visible spectroscopy (UV-vis) was employed to assess the plant's protein content and amino acid composition before and after 1 h treatment with ZnO, MCPA and ZMCPA via the foliar technique and direct soil application. The basal spacing of ZMCPA in this study is 21.6 Å at 4.0815°, revealing the triumphant incorporation of MCPA into the ZLH host. The zinc oxide (ZnO) fingerprint from 30° to 60° that certainly vanished in the ZMCPA diffractogram indicates that all ZnO has successfully converted to ZLH matrices. The FTIR spectrum of ZMCPA shows the similarity of most MCPA spectra, but with the COO⁻ peaks at 1610 and 1700 cm⁻¹ replacing the intense C=O band at 1742.21 cm⁻¹, implying that the herbicide has assimilated into the host. The protein level of the plant treated with ZMCPA was discovered to be more significant, which signifies that ZLH has effectively acted as a herbicide carrier. This study has depicted the potential of ZMCPA as a more unassailable agrochemical agent in increasing crop productivity while minimizing environmental consequences.

Keywords: Layered double hydroxide, Herbicide, MCPA, Seed germination, Amino acid, Protein biosynthesis

Introduction

The world's population is expanding, which is driving up the demand for agricultural products. It was broadly acknowledged that the agriculture industry, which encompasses everything from plant or farm crops to animal husbandry, is crucial to assure food availability for everyone around the globe. Nevertheless, the predominance of weeds, which afflict farmers with an unending barrage, including their proneness to grow faster than cultivated plants has significantly constrained crop productivity [1]. The weeds that plague crops today have been related to their capacity to exert competition for soil nutrients, water, minerals, light, space and other resources [2]. The serious threat of weeds to the plants also includes with the way they act as an alternate host, harbouring insects, pests and diseases [3,4]. Consequently, it also hampers agricultural operations, necessitating additional time, resources and labour to remove it.

In spite of all the problems driven by weeds, the herbicide has evolved into the solution for fostering agriculture's sustainable growth [5-7]. However, the indiscriminate and irrational use of these compounds

in the past few decades to control pests and enhance food production has created another conflict since less than 0.1 % of pesticides only are available to reach the targets. The remainder of more than 99 % was anticipated to head directly to the environment through leaching, evaporation, destruction by light and microorganisms, all of which would simultaneously lessen productivity, adversely affect public health and raise related ecological concerns [8,9]. Apparently, it has been discovered that vast quantity of herbicide formulation has been applied because of the low active ingredient adherence to leaves, high soil sorption and physicochemical instability [10]. Regarding that, it is imperative to devise an effective herbicide delivery system that can lower the dosage of herbicide used and overwhelm the current limitations of conventional herbicides.

Recently, it has been proclaimed that the use of delivery systems based on nanotechnology has created remarkable prospects for a sustainable agricultural practice, principally because of their increased effectiveness and environmental benefits [11]. Its potential to show improved cell membrane penetration, boost bioavailability, reduce toxicity and control the release of active components to prevent unintended harm to non-targets has thus sparked interest in the agricultural sector [12-14]. Additionally, it can offer stability and defend the active compounds it carries from degradation [15,16]. Various polymeric and inorganic nanomaterials have been used as a course for pesticide delivery. The study of intercalating atrazine (ATZ) herbicide into poly(ϵ -caprolactone) (PCL) has demonstrated better and rapid absorption rates of ^{14}C -atrazine in mustard leave in comparison to commercial atrazine, with 80 % absorption within 24 h [17]. Besides, the influence of weed control agent, clopyralid integrated into zinc/aluminium layered double hydroxide (Zn/AL-LDH) also was reported to exhibit a satisfactorily result when 25.39 % of this substance was successfully loaded into the interlayer of Zn/AL-LDH host [18]. A major finding from the study on the controlled release of abamectin from porous silica nanoparticles was that it substantially released at a slower pace in an ethanol medium with a rate of 0.01 mg/h as opposed to pure abamectin [19]. These studies exemplify how useful nanoparticles are as carriers for protecting and enhancing the activity of active substances.

In addition to the aforementioned studies, research on how nanoherbicides simulate plant gene expression also was employed. It was discovered that herbicides affect plant genes by altering the amount of protein, chlorophyll and enzymatic/non-enzymatic activity [9]. The finding from ATZ loaded PCL nanocapsules have proved a significant diminution of protein content in both roots and shoot tissues, even at a low exposure concentration, revealing that nanomaterials can affect a plant's ability to synthesize proteins [20]. Similarly, for plant development, the study of ATZ-loaded PCL nanocapsules also has shown a decrease in both the root and shoot growth of *B. pilosa* and *A. viridis* more than the commercial formulation. This has highlighted the efficacy of nanomaterial in rising the herbicidal activity of herbicide against weeds [21].

Recent years have seen the emergence of zinc-layered hydroxide (ZLH) as a potential material for the intercalation of different compounds in a diverse range of industries. This goes to the point where it includes formulations for sunscreen, agricultural herbicides, pharmaceutical drug carriers, anti-corrosion agents and flame retardants [22]. This nanocompound has been classified under layered hydroxide salt (LHS) with a 2-dimensional inorganic nanostructure that resembles the brucite-like system ($\text{Mg}(\text{OH})_2$). It comprised a tetrahedral sheet with charged hydroxide that coordinates with divalent (M^{2+}) cations. The tetrahedral structure is edge-share above and below the vacant octahedral sheet, with the interlayer of this nanostructure dominated by a water molecule (H_2O), and anionic guest (A^{n-}) [23]. The generic formula to describe this nanocompound can be represented as $\text{M}^{2+}(\text{OH})_{2-x}(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$ [24], while **Figure 1** defines its proposed structure.

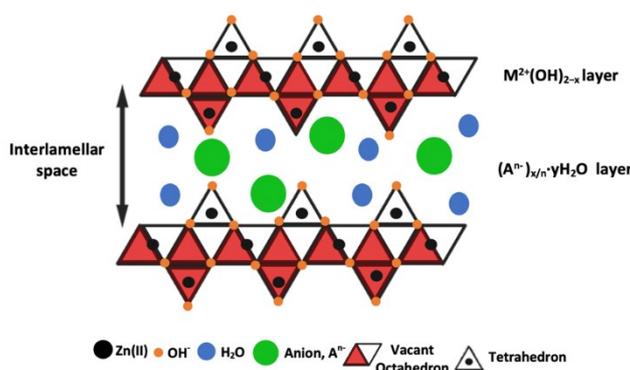


Figure 1 Structure of ZLH.

This study aims to generate nanoherbicides using ZLH as a host to encapsulate MCPA. The anion exchange technique was principally used to create the cationic layer as the foundation for the ZLH host's synthesis. Subsequently, hydrothermal treatment was employed to increase the product's crystallinity. To clarify, there are few studies on intercalating MCPA into ZLH that have been employed [25,26], but there haven't been any published studies investigating the effect of protein and amino acid content of plant samples treated by this nanoherbicide yet. Due to this reason, in this present study, the protein and amino acid composition in leaves of bean sprout samples was reported following the application of herbicide with aimed to broaden the limited scientific knowledge by supporting the impact of nanoherbicides on plant gene expression. **Figure 2** exhibits the MCPA structure which acts as an herbicide that suppresses broadleaf weeds such as dock and thistle, in pasture and cereal crops [26].

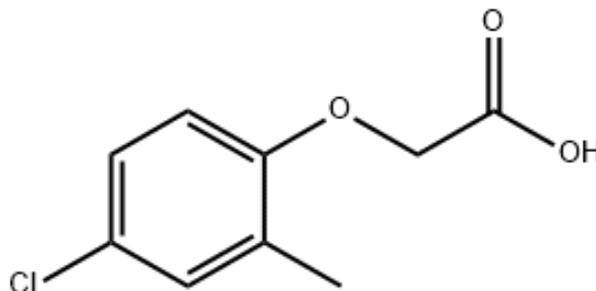


Figure 2 Chemical structure of MCPA.

Materials and methods

Materials

The reagents used throughout the MCPA intercalation and extraction for the sample were utilized without further purification. MCPA (95 %, Sigma-Aldrich), zinc oxide (99 %, R & M Chemicals), 1.0 M sodium hydroxide (99.8 % R & M chemicals), 1.0 M hydrochloric acid (37 %, R & M Chemicals), methanol (95 %, R & M Chemicals) and deionized water were used in synthesizing the nano hybrid zinc layered hydroxide-MCPA (ZMCPA). Methanol was also utilized, primarily to extract the sample for protein content and amino acid composition assessment.

Synthesis of nano hybrid

This method developed by Salleh *et al.* [26] and Ahmad *et al.* [27] was followed with some modifications. To synthesize the nano hybrid material (ZMCPA), the ion-exchange technique was first utilized in the production of the ZLH, by which the anionic guest solution was incorporated into this aqueous solution containing the ZLH. The synthesis was started by dissolving 0.075 M of MCPA with methanol in a 250 mL conical flask. Consequently, 1.0 g of zinc oxide was added to the solution. Then, 1.0 M sodium hydroxide was added drop by drop with vigorous stirring until the pH of the solution reached $\text{pH } 7.00 \pm 0.05$.

Within 24 h, the solution was continuously mixed to ensure that the intercalation process occurred. It was then aged for 18 h in an oil bath shaker at 70 °C and 80 rpm before being chilled for 10 min. Correspondingly, the resulting slurry was centrifuged at 300 rpm for 30 min before being rinsed with deionized water and centrifuged again for 15 min at the same condition. The solid precipitate obtained was dried in a vacuum oven at 70 °C for 48 h before being collected for further use and characterization for ZMCPA confirmation.

Plant treatment procedure

The 3.00 g of dried solid collected was used to generate a fresh solution with 15 mL 1.0 M hydrochloric acid, whereby this solution was applied to a bean sprout that had been germinating for 9 days to see how effective it was. The application of this herbicide involves foliar spraying and direct soil administration to the plant sample to ensure maximized uptake of these substances by plants [13]. All the 15 mL solution prepared was sprayed directly onto the leaves of the plant and the soil. After 1 h, the plant's leaves were collected and cut into tiny pieces before being dried in a 100 °C oven and pulverized with a mortar and pestle. The dried leaves were then used for further analysis.

Determination of protein content and amino acid composition

The protein content and amino acid composition of bean sprout leave treated with ZnO, MCPA and ZMCPA were measured using the same method, which involved pulverizing the samples using a fresh mortar and pestle. First, 0.10 g of each sample was extracted with 1 mL methanol. Next, the solution was warmed in an electro-thermal heater while stirring for 15 min before being filtered into a 100 mL volumetric flask and brought up to the mark with methanol. Finally, the UV-vis spectrophotometer assessed each treated sample's protein content and amino acid composition [28].

Before placing the sample in the sample chamber, the instrument was zeroed to adjust to the imputed parameters and the wavelength range was set to 200 to 600 nm. Methanol was used as a blank solution, and it was placed into the chamber together with the sample solution. The auto track is employed to obtain a specific wavelength of absorption for protein and various amino acid, and the protein content was determined through the below equation [28].

$$\text{The percentage concentration} = \frac{\text{Absorbance}}{\epsilon_{\text{percent}}} \quad (1)$$

$$\text{Concentration in mg/mL} = \left(\frac{\text{Absorbance}}{\epsilon_{\text{percent}}} \right) \times 50 \quad (2)$$

where $\epsilon_{\text{percent}} = 10$

Characterization methods

The FTIR absorption spectra of each sample were recorded from 3000 to 400 cm^{-1} using Perkin Elmer Spectrum 100 spectrometer. In addition, the PXRD patterns of the samples were recorded on Panalytical model Empyrean (Panalytical, Almelo, Netherlands) using Ni-filtered Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$), with the data collected in the range of $2\theta = 2.5 - 70^\circ$. Note that the protein contents and amino acid composition of host ZnO, MCPA and its nanocomposite were determined using a UV-vis spectrophotometer with the wavelength range set at 200 to 600 nm.

Results and discussion

Fourier transform infrared spectroscopy

The FTIR spectra for ZnO, MCPA and ZMCPA are depicted in **Figure 3**. The ZnO spectra are dominated by 1 strong band at around 560 cm^{-1} , which is attributed to the zinc-oxygen sublattices [25]. Other than that, the FTIR absorption bands for the MCPA show multiple peaks, with the most intense and identifiable band belonging to the C=O carboxylic acid functional group at 1742.21 cm^{-1} . Besides, the hydroxyl primary OH in-plane bending vibration of the carboxylic acid functional group also can be evidenced by bands at 1247.06 cm^{-1} . The presence of a C=C stretching vibration aromatic ring is indicated by the appearance of a strong band at 1494.50 cm^{-1} . Meanwhile, the existence of a C-Cl bond is suggested by the presence of a peak located at 685.90 cm^{-1} .

The absorption band of nanohybrid ZMCPA is shown in **Figure 3(c)**. The C-Cl stretching vibration of MCPA can still be observed at the peak of 725.33 cm^{-1} . Meanwhile, the peak at 1191.18 cm^{-1} suggested the sight of ether C-O-C of MCPA in ZMCPA. Furthermore, the absorption band of the C=C aromatic ring, which occurred at 1492.51 cm^{-1} could also provide proof of the presence of MCPA in ZMCPA. The most notable feature of these spectra is the disappearance of the MCPA C=O carboxylic acid band at 1742.21 cm^{-1} and the appearance of new bands at around 1610 cm^{-1} , attributed to the asymmetric C=O carboxylate anion [27]. This immediately proved that intercalation of MCPA in the anionic form did occur in the ZLH layer. A prominent band detected at 560 cm^{-1} in ZnO spectra that is diminished in ZMCPA spectra also suggests that ZnO has been successfully diverted to ZLH, allowing the MCPA to retain.

In particular, the ZMCPA nanohybrid's FTIR absorption bands mimic a combination of MCPA characteristics, indicating that the MCPA anion was successfully intercalated into the ZLH interlayer. The altered position of each functional group band in ZMCPA represents the new bond that has been formed in the ZMCPA nanomaterials as a result of the triumphant interaction between MCPA and ZLH [27,22]. However, since this FTIR can only determine the functional group and hence cannot be used to discern the material's character properly, additional instruments such as PXRD have thus been utilized to determine the successful intercalation processes.

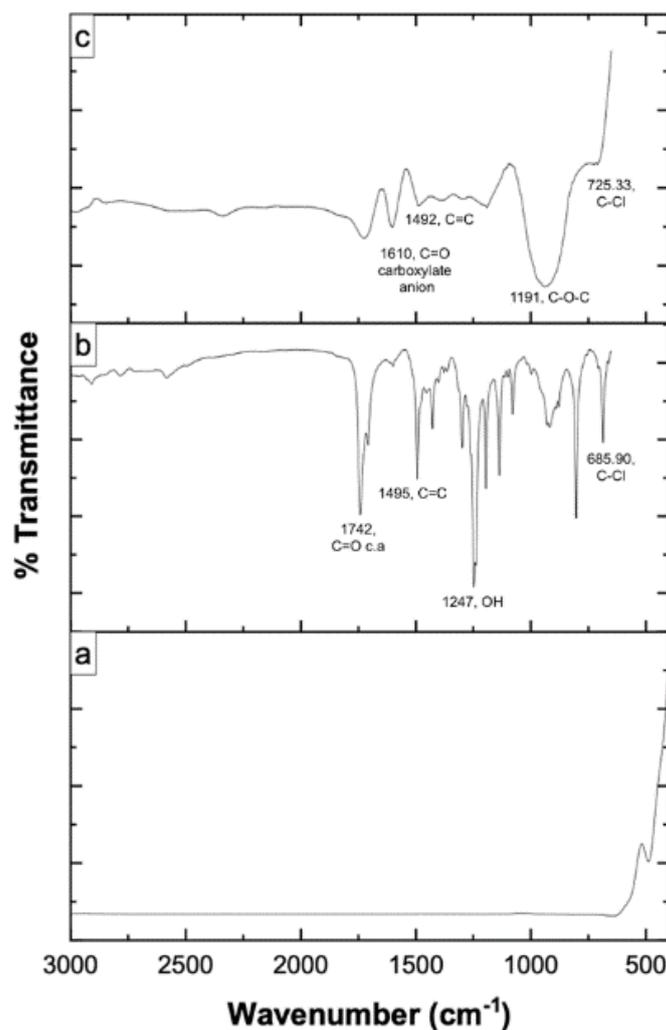


Figure 3 IR spectra for (a) ZnO, (b) MCPA and (c) ZMCPA.

Powder x-ray diffraction analysis

The PXRD patterns of ZnO, MCPA and ZMCPA are shown in **Figure 4**. The result for ZnO demonstrates the formation of 5 peaks spanning from 30 to 60 °, with the 5 peaks representing the lattice planes 100, 002, 101, 102 and 110. This implies that the ZnO was in a pure phase with high crystallinity [27]. Upon the conversion of ZnO to ZLH in an aqueous environment and intercalation of MCPA anion into this ZLH matrix, the basal spacing of ZMCPA using the Bragg's Law formula has yielded the value of 21.6 Å at 2θ of 4.0815 °, which was comparable with the previous study made by Foad *et al.* [25]. Thus, this result has proven the entrapment of the MCPA anion between the interlayer region of ZLH.

The dissociation-deposition mechanism explains the transition of ZnO into ZLH matrices in an aqueous environment [22]. When ZnO particles are soaked in water, their surface will begin to hydrolyze, generating a Zn(OH)₂. In the presence of acid (MCPA), Zn(OH)₂ will become much more soluble, dissociating into Zn²⁺ and 2OH⁻. All the components in the solution, including the Zn²⁺ species, water, hydroxyls and MCPA anions, will react together to generate the multilayer intercalation complex (Zn²⁺(OH)_{2-x}(MCPA⁻)_x·nH₂O).

The emergence of intense and sharper peaks in ZMCPA diffractograms extending from 2 to 30 ° concludes that nanohybrid intercalation was successful, resulting in high crystallinity. Furthermore, no traces of the ZnO fingerprint peaks were seen in the ZMCPA diffractogram, showing that all ZnO had been converted into ZLH matrices, and was ready to be the host for MCPA intercalation.

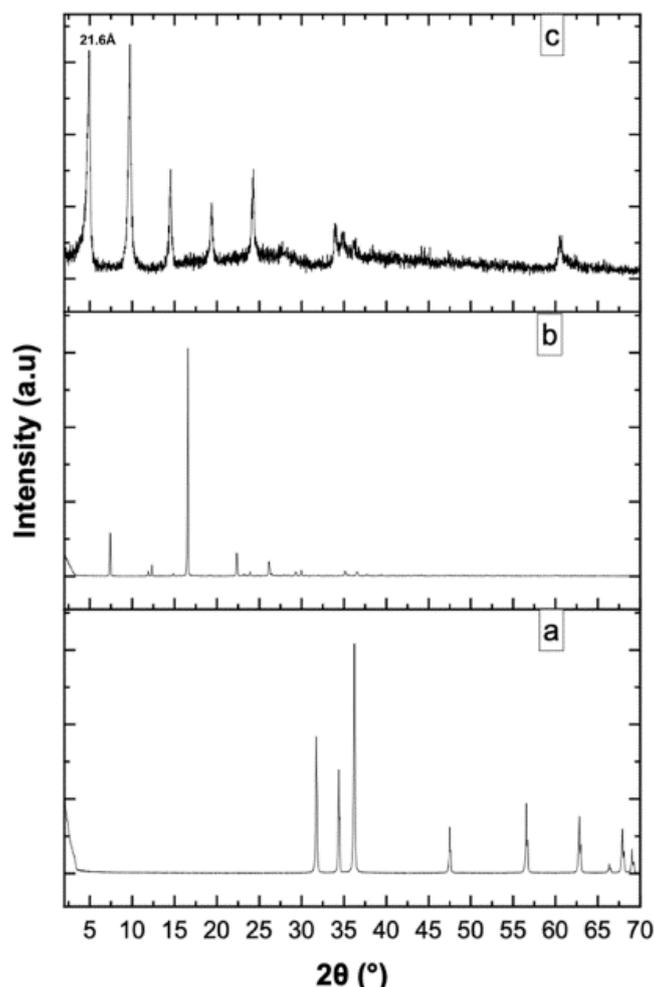


Figure 4 XRD Diffractograms for (a) ZnO, (b) MCPA and (c) ZMCPA.

Protein content

The percentage concentration and concentration in mg/mL of the bean sprout samples before and after treatment with ZnO, MCPA and ZMCPA obtained from the UV-vis spectra are shown in **Table 1**. Before receiving any treatment, the protein percentage concentration was 0.0211 %, with the concentration in mg/mL being 1.0550. However, after this bean sprout was treated with MCPA, the percentage concentration and the concentration of protein contents were found to be 0.0348 % and 1.7400 mg/mL, respectively. The protein content continues to rise and reaches its peak after being treated with ZMCPA, where the percentage is 0.0941 %, and the concentration is 4.705 mg/mL. It was discovered that the treatment used on the bean sprout caused the increment of protein content, rather than decreased it, indicating that the herbicide and the nanoherbicide had a favourable impact on the plant sample since the synthesis of protein continued.

While some herbicides are designed to disrupt the protein biosynthetic pathways, MCPA has been thought to stand as the one administering a contradicting effect of protein synthesis in the plant. Parallel with its class, which is categorized as synthetic auxin herbicide, its mimicry as plant growth hormone auxin known as indole acetic acid (IAA) has thus been expected [29]. The presence of this compound in the plant has been reported to interfere with nucleic acid metabolism and cell wall stability through the activation of the adenosine triphosphate (ATP)ase proton pump, which consequently raises the enzyme activity in the cell wall. The persistence of this mechanism in stimulating the DNA, mRNA and protein biosynthesis activity within the plant cell (to the extent of uninhibited vascular growth) [29], has explained why the protein content of plants treated with MCPA is higher than the control and ZnO.

Considering ZLH as a carrier for MCPA, its capability in increasing the bioavailability of this herbicide upon the encapsulation has thus been met since the protein content of the plant treated with this nanocompound is higher than conventional MCPA, with a larger disparity displayed.

Table 1 The percentage concentration and concentration in mg/mL of the bean sprout samples before and after treatment with ZnO, MCPA and ZMCPA.

	Treatments			
	Control	ZnO	MCPA	ZMCPA
Percentage Concentration (%)	0.0211	0.0322	0.0348	0.0941
Concentration (mg/mL)	1.0550	1.6100	1.7400	4.705

Amino acid composition

The amino acid composition of a plant sample prior to treatment was compared to the amino acid composition of all plant samples treated via the UV-vis spectra with the wavelength observed from 200 - 346 nm. **Table 2** shows the outcome with only 2 distinct amino acids detected in the plant samples, namely tryptophan and histidine. These 2 compositions can be seen in the untreated and plant samples treated with ZnO and ZMCPA. Meanwhile, when this plant sample was exposed to MCPA, the histidine could not be spotted, leaving only tryptophan visible. To the best of our knowledge, no study concerning the influence of MCPA herbicide against amino acid biosynthesis has yet been conducted. This is because different type of herbicide has different class that is distinguished based on their modes of action [30]. MCPA's mode of action entails plant growth regulator, whereby its function is to stimulate protein biosynthesis and cause the plant to grow uncontrollably until it ultimately breaks down the critical structure of the plant [29]. Different from group 9 herbicide (glyphosate), the mode of action implicates the inhibition of amino acids. So many studies are focused on this herbicide in explaining the mechanism [31,32].

The fact that the amino acid contributes to the formation of protein, however, made this conclusion clear of its relation [33,34]. Since MCPA mimics the auxin hormone, therefore stored sugar and amino acids may then be discharged from the chloroplast [35]. These chemicals' mobilization has encouraged the augmentation of protein in an integral cell component. So, with this fact in hand, the protein content that rose in the plant sample treated with nanoherbicide, ZMCPA explains why both amino acids appeared, and none of them is invisible as the conventional herbicide (MCPA).

Table 2 Comparison of amino acid identified at different wavelengths in each of the treatments.

Treatment	Observation (nm)				
	200 - 220 Cysteine	240 - 265 Phenylalanine	274 - 300 Tyrosine	280 - 312 Tryptophan	346 Histidine
Control	-	-	-	+	+
ZnO	-	-	-	+	+
MCPA	-	-	-	+	-
ZMCPA	-	-	-	+	+

Note: "+" indicates that the amino acids detected at the wavelength specified are present, whereas "-" indicates that the amino acids identified at the wavelength indicated are not present.

Plant morphology

Figures 5(a) and **5(b)** illustrate the morphology of a bean sprout before and after 1 h treatment with 15 mL 0.075 M nano hybrid ZMCPA, respectively. The untreated plant sample is plainly unwithered, but the treated plant sample appears wilted. This concludes the efficiency of ZMCPA, which contains the MCPA herbicide within its interlayer, in successfully destroying the chlorophyll of the plant through the uninhibited vascular growth and cell bursts, leading it to be unable to process photosynthesis and so cease to survive.



Figure 5 Bean sprout's morphology (a) before being treated and (b) after being treated with ZMCPA.

Conclusions

The zinc layered hydroxide-MCPA (ZMCPA) nanohybrids were successfully synthesized utilizing the ion-exchange approach from the intercalation of 2-methyl-4-chlorophenoxyacetic acid (MCPA) into ZnO in methanol. The findings of this conformity came from FTIR spectroscopy, which revealed that significant bands like the one in MCPA were likewise seen in the spectra of ZMCPA, with a minor shift in wavenumber owing to the configuration in host and host-guest interactions. Furthermore, PXRD analysis was also able to confirm the positive result of intercalation since the ZnO fingerprint peaks vanished from the ZMCPA diffractogram, indicating that all the ZnO molecules were successfully converted into the ZLH matrices. Furthermore, the basal spacing of 21.6 Å demonstrated that effective intercalation of MCPA into the ZLH matrices resulted in considerable alterations in the height of the host's interlayer.

The objective of examining ZMCPA's effects as a potential eco-friendly nanocarrier for the delivery of agricultural herbicides has been accomplished. It was discovered that the amount of protein in the bean sprout increased significantly following treatment with ZMCPA compared to other treatments and the control, suggesting that ZLH potentially boost the active substances it carries after encapsulation. In addition, the amino acid profiles of the bean sprouts that were left after being exposed to ZMCPA for an hour show how effective this nanoherbicide is at stimulating plant samples' biological pathways to the point where the organelle structure is destroyed, and the plants die. Accordingly, this research proposes the ZLH potential as a host carrier in enhancing the bioavailability of herbicides. Hence, reducing the number of agrochemicals applied in agriculture and minimizing the impact of ecological concerns.

Though this experiment has given a satisfactory result, it can be suggested that more parameters may be embedded, such as the time taken for the adsorption to take place after the treatment, the different concentrations used, as well of using another plant as a sample to be tested on. Additionally, perhaps other methods can be utilised for plant treatment procedures, considering the current method (heat-based drying) are not suitable for protein assays since it can decompose the protein complexes.

Acknowledgements

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References

- [1] S Kumar, MK Bhowmick and P Ray. Weeds as alternate and alternative hosts of crop pests. *Indian J. Weed Sci.* 2021; **53**, 14-29.
- [2] A Syeda, KR Alharby, H Alharby and MI Qureshi. *Weed control through herbicide-loaded nanoparticles*. In: Nanomaterials and plant potential. Springer Cham, Switzerland, 2019, p. 507-27.
- [3] JL Capinera. Symposium relationships between insect pests and weeds: An evolutionary perspective weeds are a food resource for insects. *Weed Sci.* 2005; **53**, 892-901.
- [4] W Taye. Effect of weed management on insect pest population on cotton (*Gossypium Hirsutum* L.) at Werer, Ethiopia. *Int. J. Res. Stud. Agric. Sci.* 2021; **7**, 24-31.
- [5] WH Leong, SY Teh, MM Hossain, T Nadarajaw, Z Zabidi-Hussin, SY Chin, KS Lai and SHE Lim. Application, monitoring, and adverse effects in pesticide use: The importance of reinforcement of Good Agricultural Practices (GAPs). *J. Environ. Manage.* 2020; **260**, 109987.
- [6] S Xiao, Y Gong, Z Li and P Fantke. Improving pesticide uptake modeling into potatoes: Considering tuber growth dynamics. *J. Agric. Food Chem.* 2021; **69**, 3607-16.
- [7] Indu, AS Baghel, A Bhardwaj and W Ibrahim. Optimization of pesticides spray on crops in agriculture using machine learning. *Comput. Intell. Neurosci.* 2022; **2022**, 9408535.
- [8] F Peng, X Wang, W Zhang, X Shi, C Cheng, W Hou, X Lin, X Xiao and J Li. Nanopesticide formulation from Pyraclostrobin and graphene oxide as a nanocarrier and application in controlling plant fungal pathogens. *Nanomaterials* 2022; **12**, 1112.
- [9] MML Forini, MS Pontes, DR Antunes, PHCD Lima, JS Santos, EF Santiago and R Grillo. Nano-enabled weed management in agriculture: From strategic design to enhanced herbicidal activity. *Plant Nano Biol.* 2022; **1**, 10008.
- [10] J Dong, X Liu, Y Chen, W Yang and X Du. User-safe and efficient chitosan-gated porous carbon and nanoherbicides. *J. Colloid Interface Sci.* 2021; **594**, 20-34.
- [11] V Takeshita, LB Carvalho, JA Galhardi, GV Munhoz-Garcia, RF Pimpinato, HC Oliveira, VL Tornisielo and LF Fraceto. Development of a preemergent Nanoherbicide: From efficiency evaluation to the assessment of environmental fate and risks to soil microorganisms. *ACS Nanosci. Au* 2022; **2**, 307-23.
- [12] G Chugh, KHM Siddique and ZM Solaiman. Nanobiotechnology for agriculture: Smart technology for combating nutrient deficiencies with nanotoxicity challenges. *Sustainability* 2021; **13**, 1781.
- [13] C An, C Sun, N Li, B Huang, J Jiang, Y Shen, C Wang, X Zhao, B Cui, C Wang, X Li, S Zhan, F Gao, Z Zeng, H Cui and Y Wang. Nanomaterials, and nanotechnology for the delivery of agrochemicals: Strategies towards sustainable agriculture. *J. Nanobiotechnol.* 2022; **20**, 11.
- [14] K Neme, A Nafady, S Uddin and YB Tola. Application of nanotechnology in agriculture, postharvest loss reduction and food processing: Food security implication and challenges. *Heliyon* 2021; **7**, e08539.
- [15] M Chaud, EB Souto, A Zielinska, P Severino, F Batain, J Oliveira-Junior and T Alves. Nanopesticides in agriculture: Benefits and challenge in agricultural productivity, toxicological risks to human health and environment. *Toxics* 2021; **9**, 131.
- [16] LA Paramo, AA Feregrino-Pérez, R Guevara, S Mendoza and K Esquivel. Nanoparticles in agroindustry: Applications, toxicity, challenges and trends. *Nanomaterials* 2020; **10**, 1654.
- [17] V Takeshita, BT Sousa, AC Preisler, LB Carvalho, ADES Pereira, VL Tornisielo, G Dalazen, HC Oliveira and LF Fraceto. Foliar absorption and field herbicidal studies of atrazine-loaded polymeric nanoparticles. *J. Hazard. Mater.* 2021; **418**, 126350.
- [18] SNM Sharif, N Hashim, IM Isa, M Mamat, NM Ali, SA Bakar, MZ Hussein and S Mustafar. The intercalation behaviour and physico-chemical characterisation of novel intercalated nanocomposite from zinc/aluminium layered double hydroxides and broadleaf herbicide clopyralid. *Chem. Chem. Tech.* 2020; **14**, 38-46.
- [19] Y Wang, H Cui, C Sun, X Zhao and B Cui. Construction, and evaluation of controlled-release delivery system of Abamectin using porous silica nanoparticles as carriers. *Nanoscale Res. Lett.* 2014; **9**, 655.
- [20] J Wu, Y Zhai, FA Monikh, D Arenas-Lago, R Grillo, MG Vijver and WJGM Peijnenburg. The differences between the effects of a nanoformulation and a conventional form of atrazine to lettuce: Physiological responses, defense mechanisms, and nutrient displacement. *J. Agr. Food Chem.* 2021; **69**, 12527-40.
- [21] GFM Sousa, DG Gomes, EVR Campos, JL Oliveira, LF Fraceto, R Stolf-Moreira and HC Oliveira. Post-emergence herbicidal activity of nanoatrazine against susceptible weeds. *Front. Environ. Sci.* 2018; **6**, 12.
- [22] SMN Mohsin, MZ Hussein, SH Sarijo, S Fakurazi, P Arulselvan and TYY Hin. Synthesis of (cinnamate-zinc layered hydroxide) intercalation compound for sunscreen application. *Chem. Cent. J.* 2013; **7**, 26.

- [23] A Gordeeva, YJ Hsu, IZ Jenei, PHBB Carvalho, SI Simak, O Andersson and U Häussermann. Layered zinc hydroxide dihydrate, $Zn_5(OH)_{10} \cdot 2H_2O$, from hydrothermal conversion of ϵ - $Zn(OH)_2$ at gigapascal pressures and its transformation to nanocrystalline ZnO. *ACS Omega* 2020; **5**, 17617-27.
- [24] NF Khadiran, MZ Hussein, R Ahmad, T Khadiran, Z Zainal, WRWA Kadir and SS Hashim. Preparation and properties of zinc layered hydroxide with nitrate and phosphate as the counter anion, a novel control release fertilizer formulation. *J. Porous Mater.* 2021; **28**, 1797-811.
- [25] NSIM Foad, NN Dzulkifli, A Abdullah, ML Jadam and SAISM Ghazali. Synthesis and characterisation of zinc layered hydroxide intercalated with 2-methyl-4-chlorophenoxyacetic acid and its controlled release application. *ASM Sci. J.* 2021; **15**, 1-10.
- [26] NM Salleh, SMN Mohsin, SH Sarijo and SAISM Ghazali. Synthesis and physico-chemical properties of zinc layered hydroxide-4-chloro-2-methylphenoxy acetic acid (ZMCPA) nanocomposite. *IOP Conf. Ser. Mater. Sci. Eng.* 2017; **204**, 12012.
- [27] SH Sarijo, SAISM Ghazali and MZ Hussein. Synthesis of dual herbicides-intercalated hydrotalcite-like nanohybrid compound with simultaneous controlled release property. *J. Porous Mater.* 2015; **22**, 473-80.
- [28] NE Okoronkwo, KC Mba and IC Nnorom. Estimation of protein content and amino acid compositions in selected plant samples using UV-vis spectrophotometric method. *Am. J. Food Sci. Health* 2017; **3**, 41-6.
- [29] SI Sherwani, IA Arif and HA Khan. *Modes of action of different classes of herbicides*. In: *Herbicides, physiology of action, and safety*. Intechopen, London, 2015, p. 165-86.
- [30] M Rutherford, J Flood and SS Sastroutomo. *Roundtable for sustainable palm oil (RSPO): Research project on integrated weed management strategies for oil palm*. Integrated Weed Management Strategies for Oil Palm, Kuala Lumpur, Malaysia, 2011, p. 1-189.
- [31] I Fatimah, G Purwiandono, I Sahroni, S Sagadevan, W Chun-Oh, SAISM Ghazali and R Doong. Recyclable catalyst of ZnO/SiO_2 prepared from salacca leaves ash for sustainable biodiesel conversion. *South Afr. J. Chem. Eng.* 2022; **40**, 134-43.
- [32] E Dor, S Galili, E Smirnov, Y Hacham, R Amir and J Hershenhorn. The effects of herbicides targeting aromatic and branched chain amino acid biosynthesis support the presence of functional pathways in broomrape. *Front. Plant Sci.* 2017; **8**, 707.
- [33] TM Hildebrandt, AN Nesi, WL Araújo and HP Braun. Amino acid catabolism in plants. *Mol. Plant* 2015; **8**, 1563-79.
- [34] GDL Ee, SA Izzaddin, M Rahmani, MA Sukari and HL Lee. γ -Mangostin and rubraxanthone, two potential lead compounds for anti-cancer activity against CEM-SS cell line. *Nat. Prod. Sci.* 2006; **12**, 138-43.
- [35] KDA Ghani, S Nayan, SAISM Ghazali, LA Shafie and S Nayan. Critical internal and external factors that affect firms strategic planning. *Int. Res. J. Finance Econ.* 2010; **51**, 50-8.