Nano World Journal

https://doi.org/10.17756/nwj.2024-131

Research Article

Open Access

Characterizing Nano-encapsulated Pretilachlor: A Multifaceted Approach Using TEM, XRD, FTIR, TGA, and GC-MS Analyses

A. Sundari* **and G. Bhargavi**

Department of Agronomy, Faculty of Agriculture, Annamalai University, Chidambaram, Tamil Nadu, India

***Correspondence to:**
A. Sundari
Department of Agronomy,
Faculty of Agriculture,
Annamalai University,
Chidambaram, Tamil Nadu, India.
E-mail: sundariagronomy@gmail.com

Received: February 16, 2024
Accepted: March 21, 2024
Published: March 26, 2024

Citation: Sundari A, Bhargavi G. 2024. Characterizing Nano-encapsulated Pretilachlor: A Multifaceted Approach Using TEM, XRD, FTIR, TGA, and GC-MS Analyses. *NanoWorld J* 10(1): 22-28.

Copyright: © 2024 Sundari and Bhargavi. This is an Open Access article distributed under the terms of the Creative Commons Attribution 4.0 International License (CC-BY) (http://creativecommons.org/licenses/by/4.0/) which permits commercial use, including reproduction, adaptation, and distribution of the article provided the original author and source are credited.

Published by United Scientific Group

Abstract

Weed management remains a critical challenge in modern agriculture, necessitating innovative approaches to enhance the efficacy of herbicides. Nanotechnology offers a promising avenue for the synthesis of herbicides with improved performance and reduced environmental impact. This study underscores the importance of employing nanotechnological methods in the synthesis of herbicides, emphasizing their potential to revolutionize weed management practices. The nano-encapsulated pretilachlor materials were synthesized using solvent evaporation method at the Centre for Agricultural Nanotechnology, Coimbatore (Tamil Nadu, India). This research explores the synthesis and characterization of nano-encapsulated pretilachlor utilizing the solvent evaporation method. Through transmission electron microscope (TEM), X-ray diffraction (XRD), Fourier-transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), and gas chromatography-mass spectrometry (GC-MS) analyses, we investigated the presence of nanoparticles, crystal structure, functional group, thermal stability, and composition of the nano-encapsulated pretilachlor herbicide. According to the results of characterization techniques on encapsulated pretilachlor, the TEM analysis confirmed the presence of pretilachlor, XRD analysis confirmed the nano-encapsulated pretilachlor exhibits amorphous nature and the polymer peak showed semi crystalline nature, FTIR validated the functional group of pretilachlor, TGA showed that double stage decomposition with high stable temperature and GC-MS analysis of different compounds of nano-encapsulated pretilachlor were detected representing with 100% concentration.

Keywords

Nano-encapsulation, Pretilachlor, Thermogravimetric analysis, Gas chromatography, X-ray diffraction

Introduction

Herbicides play a pivotal role in modern agriculture by serving as essential tools in weed management. These chemical compounds are designed to control or eliminate unwanted vegetation, preventing weeds from competing with crops for nutrients, sunlight, and water [1]. Efficient weed management is crucial for maximizing agricultural productivity, ensuring crop yield stability, and ultimately addressing global food security challenges. The significance of herbicides in maintaining the health and productivity of cultivated areas, underscoring their integral role in contemporary agriculture. In modern agriculture, herbicides emerge as crucial tools in the realm of weed management, playing a pivotal role in sustaining crop health, and optimizing yields. Weeds, by nature voracious competitors for essential resources, pose a persistent threat to crop productivity, necessitating effective management strategies. As we delve into the complexities of herbicide

application, the goal is to highlight their role in maintaining agricultural efficiency, ensuring food security, and contributing to sustainable farming practices.

In the dynamic landscape of agricultural innovation, nanotechnology has emerged as a promising frontier, particularly in the realm of weed management [2]. It sets the stage for a comprehensive exploration of the importance of nanotechnology in weed management within the context of contemporary research. By harnessing the unique properties of nanomaterials, researchers aim to revolutionize weed control strategies, offering precise and environmentally sustainable solutions [3]. The synthesis of progressive research findings will shed light on the transformative potential of nanotechnology in mitigating weed-related challenges in crop production. Technology such as smart delivery, encapsulation and slow release can also be used to create herbicides that suppress weeds [4]. In the process of nano-encapsulation, microscopic particles called nanoparticles are employed to encapsulate active ingredients like chemicals. Its use is not limited solely to conventional microcapsules; it encompasses all other systems of microscopic particulates, including self-assembling structures that need prior manipulation. In the pursuit of enhancing precision and efficacy in weed management, the integration of nano-encapsulated herbicides stands at the forefront of agricultural innovation [5]. Due to the nanoscale size range of nanoparticles, they may enter plants and deliver substances where they are needed. Encapsulation improves the stability, controlled release and toxicity of the herbicide while also increasing its efficacy.

There are two phases involved in emulsification-solvent evaporation. Emulsifying the polymer solution into an aqueous phase is necessary for the first step. The second stage involves evaporating the polymer solvent, which causes the polymer to precipitate as nanospheres. High-energy homogenization of a dispersing agent is used to disperse a polymer organic solution containing the dissolved dosage into micro droplets [6]. Although many emulsion types can be employed, using oil or water as the non-solvent simplifies and enhances process economics by removing the need for recycling, making the washing step easier and reducing agglomeration [7]. After cellulose, starch is the second most common natural polymer. It is inexpensive and simple to extract from a wide range of plants [8]. All natural polymers, including starch, are totally biodegradable because microorganisms have hundreds of millions of years to develop the enzymes needed to digest them. Extended agrochemical activity, cost-effective encapsulation, a biodegradable matrix, reduced environmental pollution, shortened application times and amounts, enhanced plant and handling safety, efficient agrochemical control over targets and decreased agrochemical losses are all displayed by starch-encapsulated agrochemicals [9]. With improved weed control, the pesticide encased in nanoparticles posed no environmental harm. It could be the result of nanoencapsulation enhanced mechanism of action, which preserved the product's effectiveness even when the administered dosage was lowered.

The synthesis of research findings will illuminate its potential to redefine weed management practices, providing sustainable solutions with reduced environmental impact. The research study aims to contribute to the evolving discourse on sustainable agriculture by unraveling the multifaceted role of nanotechnology in weed management [10]. Solvent evaporation method is a novel approach surpassing conventional techniques. By utilizing this method, we achieve precise encapsulation, enhancing pretilachlor efficacy and environmental sustainability. This innovative process represents a significant advancement in synthesis, demonstrating the transformative power of nanotechnology in agro-chemicals production. The valuable insights to the evolving discourse on nano-encapsulated herbicides, positioning them as a transformative tool in the pursuit of efficient and sustainable weed control. However, the literature involving encapsulated herbicides usage is limited.

In the light of the above facts, the present study was carried out to determine the synthesis and characterization of nano-encapsulated pretilachlor using solvent evaporation method through TEM, XRD, FTIR, TGA and GC-MS analyses.

Materials and Method

Materials

Technical grade pretilachlor (MW-311.85, purity - 98%), acetone (dimethyl ketone/2-propanone, MW - 58.08), polyethylene glycol (PEG) (18-ethoxyoctadec-3-ene, MW - 296.5), dichloromethane (dichloromethane, MW - 84.93) and starch (soluble, MW - 342.3) were purchased from Sigma-Aldrich (Bengaluru, India), while its commercial formulation Rifit® 50 EC was obtained from Syngenta (India). Borosil-made glassware and analytical-grade chemicals were both employed in the investigation without any additional purification. In order to make the solutions, double distilled water was used.

Solvent evaporation method

In organic phase preparation, analytical grade of pretilachlor (5 mg) was dissolved in acetone solvent of 6 ml and stirred using magnetic stirrer for 15 min to form a homogenized mixture and then sonicated for 120 sec. 25 mg of PEG polymer was added to a different beaker and dissolved in 10 ml of dichloromethane and agitated using magnetic stirrer for 15 min and sonicated for 120 sec. To prepare aqueous phase, 6 ml of starch polymer (six percent concentration) is added to a beaker and stirred with magnetic stirrer for 60 min. Both the organic and aqueous phase are gradually mixed and stirred continuously in magnetic stirrer under room temperature for the next 24 h. The resulting nanoparticles are removed from acetone, dried in vacuum desiccator, and collected in vial for storage. The schematic representation of nano-encapsulated pretilachlor is given in figure 1.

Characterization

The nano-encapsulated pretilachlor was characterized using TEM, XRD, FTIR, TGA, and GC-MS to ascertain the crystal structure, thermal stability, and composition of the nano-encapsulated pretilachlor.

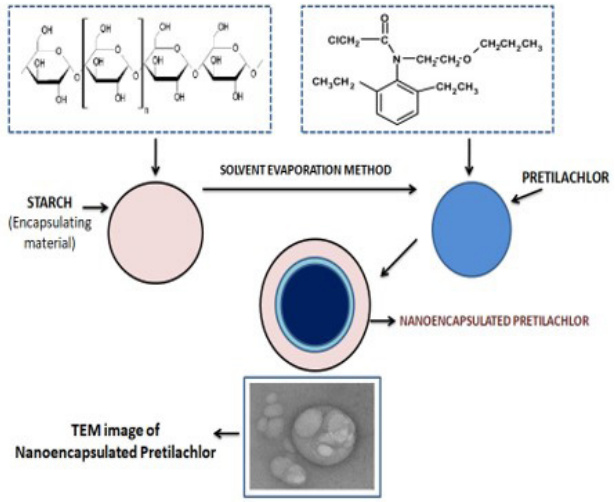


Figure 1: Schematic representation of nano-encapsulated pretilachlor by solvent evaporation method.

TEM

The nano-encapsulated herbicide sample was placed on a TEM grid coated with carbon. JEOL JEM-2100F TEM running at an accelerating voltage of 200 kV was employed in this investigation. A digital camera called Gatan Ultrascan 1000 was used to take the pictures. TEM pictures with high resolution were obtained at various magnifications. Particles of encapsulated nano-herbicide are dissolved in acetone using an ultrasonic bath, and after 30 min of solvent evaporation, the mixture is placed on a grid covered with carbon for examination.

XRD

XRD analysis was used to determine the crystal structure and identify possible impurities in the sample. The XRD analysis was performed using a Bruker D8 Advance diffractometer equipped with a 40 kV with CuKα radiation source. The scanning speed was 5° to 60° 2θ per sec, the step size was 0.02° 2θ and the counting time was 5 sec per step and wavelength (1.54 Å). The samples were finely ground and placed on foil. The XRD condition of the crystal is given by Bragg's law ($2d \sin\theta = n\lambda$). Diffraction peaks were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) database maintained by the International Center for Diffraction Data.

FTIR

FTIR was utilized to characterize the functional groups found in the sample. The Perkin Elmer Spectrum FTIR spectrometer, which has a 4 cm^{-1} resolution, was used. The FTIR data were obtained with 64 scans, and the detected wavelengths were within the range of 4000 cm^{-1} to 400 cm^{-1}. Perkin Elmer provided Opus software, which was used to process the data. Using a hydraulic press, the mixture was compressed into pellets by pressing it onto a hard plate. After that, the pellet was placed on a transfer frame and scanned, preferring a thickness of 0.5 - 1 mm.

TGA

TGA is used to determine the decomposition temperature of materials. TGA analysis was performed using a Q50 V20.6 Build 31 Universal Thermogravimetric Analyzer equipped with a simultaneous differential scanning calorimetry (DSC) system. DSC measurements were performed on a TA DSC V500 series at a heating rate of 15 °C/min. The encapsulated pretilachlor sample was weighed prior to measurement. The weight of the sample was about 7 - 10 mg. The sample was heated at 10 °C/min over a temperature range from 25 °C to 600 °C in a nitrogen atmosphere. The weight of the sample was continuously monitored as the temperature increased. The polymer content and its change at transition temperatures were investigated.

GC-MS

GC analysis was performed using a Shimadzu GC-2010 equipped with a dimension of 30 m x 0.25 mm x 0.25 µm 5% diphenyl/95% dimethyl poly siloxane stationary phase column. The energy of the electron ionization system was 70 eV, and the scan interval was 0.5 sec. The carrier gas was helium with a flow rate of 1.0 ml/min. The temperature program used was as follows: an initial temperature of 60 °C for 2 min, increased to 300 °C at a rate of 10 °C/min and held for 5 min. A 1 µl sample of nano-encapsulated pretilachlor was injected in the split-less mode. The detection limit for pretilachlor was 0.005 mg/kg. The retention time was 5.0 min.

Results

TEM

The TEM image (Figure 2) validates that nanoparticles of pretilachlor were found adhered with layers of starch polymer and size of their particles were in close proximity of 100 nm. No further impurities were observed in the encapsulated particles.

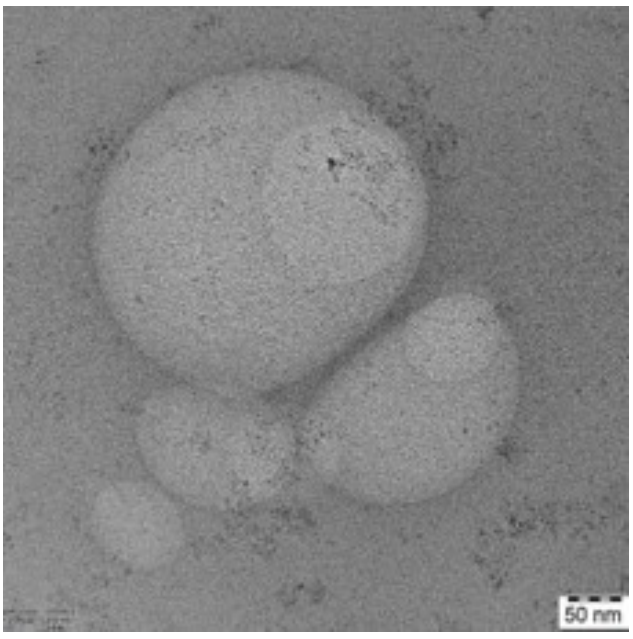


Figure 2: TEM image of nano-encapsulated pretilachlor.

XRD

The XRD pattern of nano-encapsulated pretilachlor sample peak was represented in figure 3. The XRD diffractogram of nano-encapsulated pretilachlor shows amorphous characteristic peaks at 2θ equal to 17.3°, 22.8°, and 25.7°. Based 2θ angles of nano-encapsulated sample represent the d spacing value of 0.51, 0.39, and 0.35. Thus, the nano-encapsulated sample with 2θ angles viz., 17.3° and 22.8° represents the starch and PEG polymers. The XRD analysis confirmed the nano-encapsulated sample exhibits amorphous nature and the polymer peak showed semi crystalline nature. The XRD pattern of the nano-encapsulated pretilachlor is consistent with standard pattern for the active ingredient of the herbicide and the polymer with JCPDS file no 00-003-0226 and 00-013-0686 correspondingly and no impurities detected in the sample.

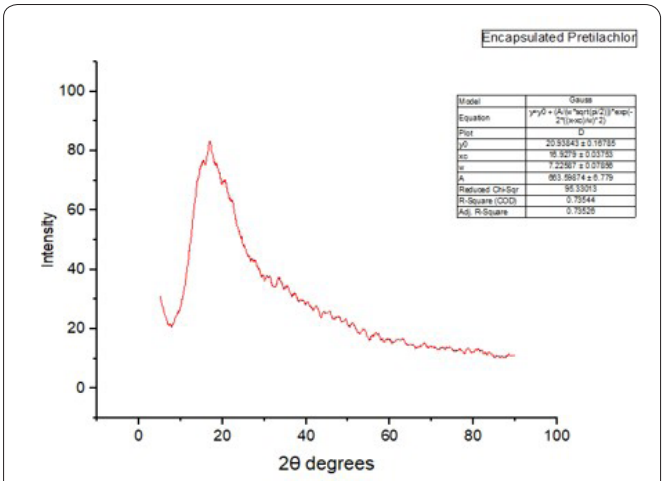


Figure 3: XRD diffractogram of nano-encapsulated pretilachlor.

FTIR

The pretilachlor nano-encapsulated spectra analyses in figure 4 signify the presence of active functional groups at the spectra peak. The alcohols with O-H stretching vibration were proven to be the peak that occurred at 3468 cm^{-1}. The peak that showed up at 2939 cm^{-1}, 2889 cm^{-1} and 2834 cm^{-1} with C-H stretching is verified with aldehydes group. The isothiocyanate molecule N=C=S stretching at 2071 cm^{-1} was verified to exist. A peak with C=O extending at 1637 cm^{-1} indicated the existence of an amide chemical. The presence of amine C-N stretching was confirmed by the development of three peaks at 1153 cm^{-1}, 1079 cm^{-1} and 1024 cm^{-1}. The smaller peak that displayed at 773 cm^{-1} stretching indicated that alkene compound. The C-Br stretching in the presence of alkyl halides was confirmed by the peak at 479 cm^{-1}.

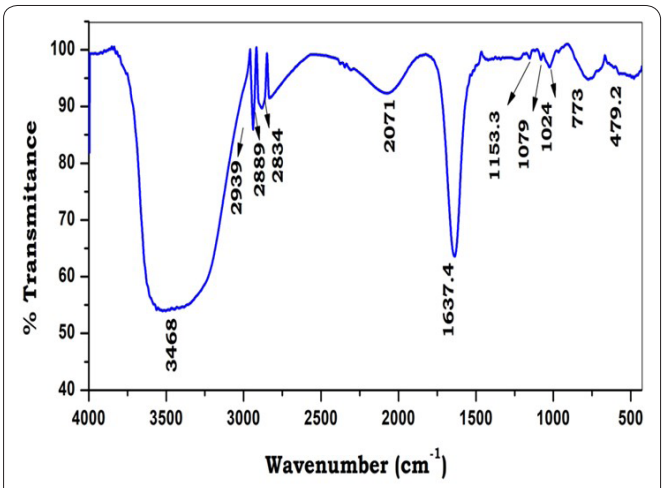


Figure 4: FTIR spectrum of nano-encapsulated pretilachlor.

TGA

The TGA analysis is performed to assess the resistance of the herbicide and encapsulating materials to raising temperatures. The TGA result of pretilachlor showed that double stage decomposition with high stable temperature at 180 °C with a weight loss of 46.97% and shown in figure 5. The thermal decomposition reaction is an endothermic reaction. The reaction then rapidly decreased from 200 °C to 600 °C with a final weight loss of 12.81% and followed a steady decomposition pattern.

According to the TGA results, the weight of the nano-encapsulated pretilachlor decreased gradually from room temperature and then quickly from 220 °C to 600 °C. The TGA result, which is depicted in figure 6, shows that the nano-encapsulated pretilachlor has good thermal stability up to 200 °C. The weight loss was recorded as a consistent breakdown pattern, with a gradual loss of 62.6% up to 200 °C and a final loss of 16.4% at 600 °C. These weight losses were attributed to the evaporation of volatile components, or the release of the solvent employed in the encapsulation process.

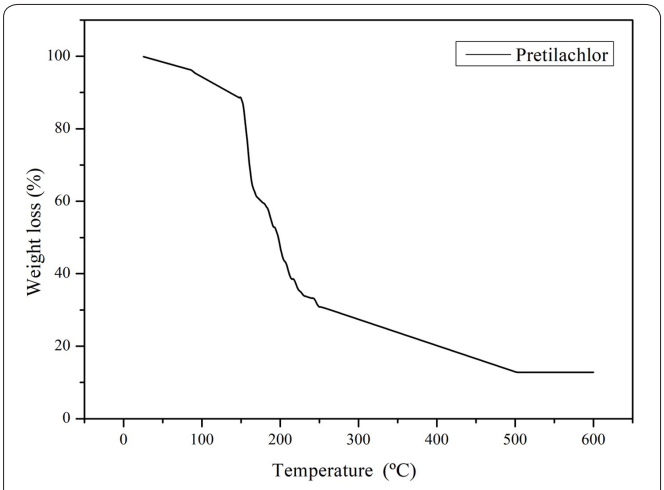


Figure 5: TGA thermogram of commercial pretilachlor.

GC-MS analysis

GC-MS analysis of different compounds of nano-encapsulated pretilachlor were detected representing 100% concentration, retention time (RT), with molecular formula and molecular weight are presented in table 1. The different compounds are detected in the GC-MS analysis of nano-encapsulated pretilachlor (Figure 7).

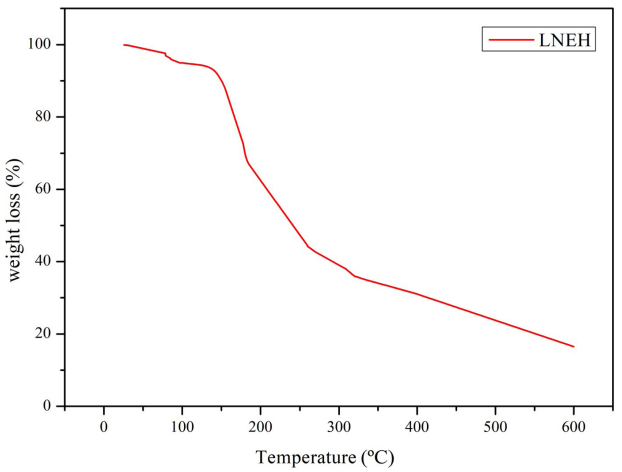


Figure 6: TGA thermogram of nano-encapsulated pretilachlor.

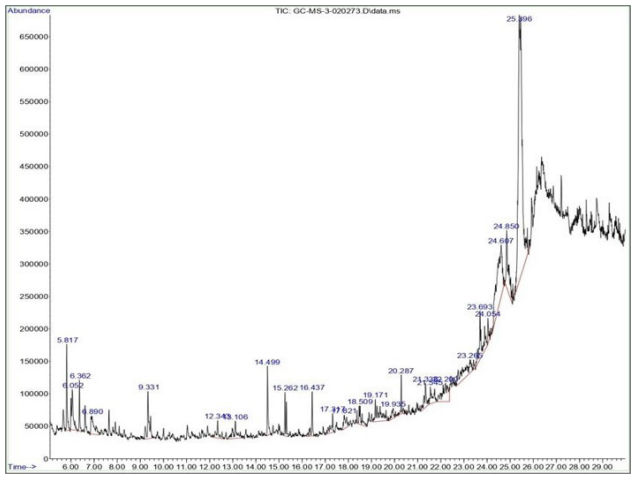


Figure 7: GC-MS spectrum of nano-encapsulated pretilachlor.

Table 1: GC-MS analysis of nano-encapsulated pretilachlor.

S. No.	Compound	RT (min)	Area %	Molecular formula	Molecular weight
1	Stigmastane-3,6-dione, (5.alpha.)-	25.396	37.87	$C_{29}H_{48}O_2$	428.7
2	Octadecane, 1-iodo-	24.607	11.25	$C_{18}H_{37}I$	380.4
3	4-Bromo-2-thiaadamantane	24.850	4.52	$C_9H_{13}BrS$	233.17
4	5-Amino-1-benzyl-1H-[1,2,3]triazole-4-carboxylic acid (4-trifluoromethoxy-phenyl)-	23.265	4.41	$C_{17}H_{14}F_3N_5O_2$	377.32
5	1,2,4-Oxadiazol-5(4H)-one, 4-phenyl-3-(3-pyridyl)-	23.693	4.13	$C_{13}H_9N_3O_2$	239.23
6	Benzenamine, 3-[2-(2-pyridinyl)ethyl]-	22.200	3.70	$C_{13}H_{14}N_2$	198.26
7	Sulfurous acid, isobutyl pentyl ester	9.331	3.07	$C_9H_{20}O_3S$	208.32
8	cis-Vaccenic acid	19.171	3.06	$C_{18}H_{34}O_2$	282.5
9	Nonane, 4-methyl	6.052	2.76	$C_{13}H_{28}$	184.36
10	Cyclopropanecarboxyllic acid, tridec-2-ynyl ester	6.890	2.33	$C_{17}H_{28}O_2$	264.4
11	2,2-Diethoxyacetophenone	5.817	2.22	$C_{12}H_{16}O_3$	208.25
12	4H-Pyran-4-one	14.499	2.09	$C_5H_4O_2$	96.08
13	Ethanone, 1-(4,5-dihydro-2-thiazolyl)	13.106	1.95	C_5H_7NOS	129.18
14	Phenol, 4,4'-methylenebis	21.336	1.87	$C_{29}H_{44}O_2$	424.7
15	Orcinol	15.262	1.83	$C_7H_8O_2$	124.14
16	1-Butene, 1-chloro-, (Z)-	18.509	1.66	C_4H_7Cl	90.55
17	3-Trifluoromethylbenzoic acid, 4-methylpentyl ester	16.437	1.65	$C_{14}H_{17}F_3O_2$	274.28
18	l-Alanine, N-octanoyl-, hexadecyl ester	21.545	1.57	$C_{27}H_{53}NO_3$	439.7
19	1-Decene	12.343	1.42	$C_{10}H_{20}$	140.27
20	Cyclopropane, 1-pentyl-2-propyl	17.821	1.31	$C_{11}H_{22}$	154.29
21	Cyclotrisiloxane, hexamethyl	6.362	1.20	$C_6H_{18}O_5Si_4$	282.54
22	Hexadecanoic acid, methyl ester	17.317	1.13	$C_{17}H_{34}O_2$	270.5
23	Fumaric acid, 2-ethylhexyl nonyl ester	20.287	1.06	$C_{21}H_{38}O_4$	354.5
24	Glutarimide, N-(5-chloro-2-methoxyphenyl)-	24.054	0.96	$C_{12}H_{12}ClNO_3$	253.68

Discussion

TEM

A magnification of 15,000,000X was used. The spherical shape of the two polymer layers and the active component inside the hollow shell was seen under this magnification [11]. The presence of pretilachlor is visible inside the capsule as indicated by the dark color within the sphere in the TEM image, and similar findings were reported by [12].

XRD

In order to determine the atomic and molecular composition of a crystal, X-ray crystallography is a technique in which the crystal's atoms cause a beam of incoming X-rays to diffract in an array of varied directions [13]. An image of the density of electrons within the crystal may be created in three dimensions by measuring the angles and intensities of these diffracted beams. The average locations of the atoms in the crystal, their chemical bonds, their ailments, and several other details can potentially be calculated from this electron density. The XRD pattern of nano-encapsulated herbicide was shown from the X-ray diffractogram (Figure 3), the characteristic peaks are amorphous seen at an angle (2θ) of 17.3° and 25.7° with d spacing value of 0.51 and 0.35. The same XRD pattern

was observed consistent with JCPDS card no 00-003-0226 and 00-013-0686, respectively. The findings correspond with those of [14, 15], stated that herbicide release rates from nanocapsules are directly influenced by the surface to volume ratio.

FTIR

In parallel, an FTIR spectrometer gathers a wide range of spectral data. Contrasting this with a dispersive spectrometer, which measures intensity over a limited range of wavelengths at a time, offers a substantial advantage. In accordance with the alcohol group, peak shifting is observed at 3786 cm^{-1} and 3419 cm^{-1} (Figure 4). C-H stretching, which can be seen at 2877 cm^{-1}, confirmed the presence of alkanes. Similar FTIR spectrum data were drawn, indicating a substantial interaction between the hydrophobic chain and acetanilide based on the intensity of the absorption bands at 2850 cm^{-1} [16]. Pretilachlor is an amide group member that displays an absorption frequency of 1637 cm^{-1} and a C=O stretching vibration. Similar outcomes corroborate the findings of [17], who observed that the frequencies linked to the nanocapsules, and the herbicide's absorption frequencies typically overlap and spectrum of nanocapsules containing pretilachlor is nearly the same as that of free nanocapsules.

TGA

According to Khan et al. [18], TGA is a technique for thermal analysis in which the detrimental impact of temperature increase on the physical and chemical characteristics of materials are assessed. Physical processes including second-order phase transitions, such as vaporization, sublimation, absorption, adsorption, and desorption, may be studied using TGA. It is used to determine the herbicide and encapsulation material's resistance to steadily rising temperatures.

The thermogram of nano-encapsulated pretilachlor herbicide showed a double pattern of decomposition which is due to removal of solvents from surface of the polymer. Two stages of decomposition were observed at 200 °C and 300 °C (Figure 5 and figure 6). The results of thermogram indicated that nano-encapsulated pretilachlor had good thermal stability up to 300 °C, which is in agreement with previous studies that have shown that chitosan-based nano-encapsulated herbicide exhibit good thermal stability up to this temperature range [19]. The encapsulating substance was proven to have degraded and the active herbicide to have been released by the exothermic peak that was seen at 400 °C. The results of the study concur with [20] findings, which stated that the steady weight loss seen at higher temperatures can be related to the evaporation of volatile components or the release of the solvent used in the encapsulation process.

GC-MS analysis

GC enables the separation and identification of various components present in the sample. This determines the quality and efficacy of nano-encapsulated herbicide [21].

The GC-MS analysis of nano-encapsulated pretilachlor confirmed the presence of 24 compounds as indicated in figure 7. The results showed that the presence of 2,2-diethoxyacetophenone with retention time of 5.817, area 2.22% and 4-trifluromthoxy-phenyl with retention time of 23.2, area 4.41% in the nano-encapsulated pretilachlor sample is comparable with peak profile noticed in the chromatogram. The findings are in line with those of [22, 23], concluded that existence of 1-(+) ascorbic acid 2, n-hexadecanoic acid confirms the presence of a fatty acid peak in the chromatogram. The results of the nano-encapsulated pretilachlor release efficiency were below the MRL of 0.05 µg/g defined by FSSAI [24]. The findings resonate with the conclusions made by [25, 26].

Conclusion

Based on the current research, it can be concluded that nano-encapsulated pretilachlor particles have a spherical form with well formed internal structure confirmed by TEM analysis. The functional group of pretilachlor is validated by FTIR spectrum. The XRD pattern of nano-encapsulated pretilachlor has an amorphous characteristic peak and exhibited thermal degradation at 200 °C and the releasing efficiency was analyzed by GC which validates the loading of herbicide in nanoparticles. Thus, it infers as herbicide that endured inside the starch polymer was effectively concealed from external factors and released gradually to control the weeds.

Acknowledgements

The authors wish to express their gratitude to the RUSA 2.0 for financial support and Department of Agronomy, Faculty of Agriculture, Annamalai University for providing necessary facilities to carry out the field research and Centre of Agricultural Nanotechnology, Coimbatore for providing laboratory facilities to carry out the research work.

Conflict of Interest

None.

References

1. Derakhshan Z, Ehrampoush MH, Mahvi AH, Ghaneian MT, Mazloomi SM, et al. 2018. Biodegradation of atrazine from wastewater using moving bed biofilm reactor under nitrate-reducing conditions: a kinetic study. *J Environ Manage* 212: 506-513. https://doi.org/10.1016/j.jenvman.2018.02.043
2. Marchiol L, Iafisco M, Fellet G, Adamiano A. 2020. Nanotechnology Support the Next Agricultural Revolution: Perspectives to Enhancement of Nutrient Use Efficiency. In Sparks DL (ed) Advances in Agronomy. Academic Press, Cambridge, pp 27-116.
3. Kah M, Hofmann T. 2014. Nanopesticide research: current trends and future priorities. *Environ Int* 63: 224-235. https://doi.org/10.1016/j.envint.2013.11.015
4. Khandbahale SV. 2020. Microencapsulation - a novel approach in drug delivery: a review. *Asian J Res Pharm Sci* 10(1): 39-50. https://doi.org/10.5958/2231-5659.2020.00009.0
5. Adisa IO, Pullagurala VLR, Peralta-Videa JR, Dimkpa CO, Elmer WH, et al. 2019. Recent advances in nano-enabled fertilizers and pesticides: a critical review of mechanisms of action. *Environ Sci Nano* 6(7): 2002-2030. https://doi.org/10.1039/c9en00265k
6. Reis CP, Neufeld RJ, Ribeiro AJ, Veiga F. 2006. Nanoencapsulation I. Methods for preparation of drug-loaded polymeric nanoparticles. *Nanomedicine* 2(1): 8-21. https://doi.org/10.1016/j.nano.2005.12.003

7. Soppimath KS, Aminabhavi TM, Kulkarni AR, Rudzinski WE. 2001. Biodegradable polymeric nanoparticles as drug delivery devices. *J Control Release* 70(1-2): 1-20. https://doi.org/10.1016/S0168-3659(00)00339-4
8. Brown WH, Poon T. 2014. Introduction to Organic Chemistry. John Wiley & Sons, Hoboken, NJ.
9. Lu DR, Xiao CM, Xu SJ. 2009. Starch-based completely biodegradable polymer materials. *Express Polym Lett* 3(6): 366-375. https://doi.org/10.3144/expresspolymlett.2009.46
10. Sousa GF, Gomes DG, Campos EV, Oliveira JL, Fraceto LF, et al. 2018. Post-emergence herbicidal activity of nanoatrazine against susceptible weeds. *Front Environ Sci* 6: 12. https://doi.org/10.3389/fenvs.2018.00012
11. Kanimozhi V, Chinnamuthu CR. 2012. Engineering core/hallow shell nanomaterials to load herbicide active ingredient for controlled release. *Res J Nanosci Nanotechnol* 2(2): 58-69.
12. Diyanat M, Saeidian H, Baziar S, Mirjafary Z. 2019. Preparation and characterization of polycaprolactone nanocapsules containing pretilachlor as a herbicide nanocarrier. *Environ Sci Pollut Res* 26: 21579-21588. https://doi.org/10.1007/s11356-019-05257-0
13. Wu C, Lou X, Huang A, Zhang M, Ma L. 2020. Thermodynamics and kinetics of pretilachlor adsorption: implication to controlled release from organobentonites. *Appl Clay Sci* 190: 105566. https://doi.org/10.1016/j.clay.2020.105566
14. Tong W, Gao C. 2007. Selective removal of particle cores to fabricate manganese carbonate hollow spheres and composite microcapsules. *Colloids Surf A Physicochem Eng Aspects* 295(1-3): 233-238. https://doi.org/10.1016/j.colsurfa.2006.09.005
15. Wang X, Zhao J. 2013. Encapsulation of the herbicide picloram by using polyelectrolyte biopolymers as layer-by-layer materials. *J Agric Food Chem* 61(16): 3789-3796. https://doi.org/10.1021/jf4004658
16. Ghaderpoori M, Jafari A, Nazari E, Rashidipour M, Nazari A, et al. 2020. Preparation and characterization of loaded paraquat-polymeric chitosan/xantan/tripolyphosphate nanocapsules and evaluation for controlled release. *J Environ Health Sci Eng* 18: 1057-1066. https://doi.org/10.1007/s40201-020-00527-3
17. Diyanat M, Saeidian H. 2019. The metribuzin herbicide in polycaprolactone nanocapsules shows less plant chromosome aberration than non-encapsulated metribuzin. *Environ Chem Lett* 17: 1881-1888. https://doi.org/10.1007/s10311-019-00912-x
18. Khan BA, Nadeem MA, Javaid MM, Maqbool R, Ikram M, et al. 2022. Chemical synthesis, characterization, and dose optimization of chitosan-based nanoparticles of clodinofop propargyl and fenoxaprop-p-ethyl for management of *Phalaris minor* (little seed canary grass): first report. *Green Process Synthesis* 11(1): 1118-1127. https://doi.org/10.1515/gps-2022-0096
19. Huang B, Chen F, Shen Y, Qian K, Wang Y, et al. 2018. Advances in targeted pesticides with environmentally responsive controlled release by nanotechnology. *Nanomaterials* 8(2): 102. https://doi.org/10.3390/nano8020102
20. Zhang A, Xu C, Liu W. 2008. Influence of toxicity and dissipation of racemic fenoxaprop and its R-enantiomer in *Scenedesmus obliquus* suspension by cyclodextrins. *J Environ Sci Health Part B* 43(3): 231-236. https://doi.org/10.1080/03601230701771149
21. Nuruzzaman MD, Rahman MM, Liu Y, Naidu R. 2016. Nanoencapsulation, nano-guard for pesticides: a new window for safe application. *J Agric Food Chem* 64(7): 1447-1483. https://doi.org/10.1021/acs.jafc.5b05214
22. Abirami S, Priyalakshmi M, Soundariya A, Samrot AV, Saigeetha S, et al. 2021. Antimicrobial activity, antiproliferative activity, amylase inhibitory activity and phytochemical analysis of ethanol extract of corn (*Zea mays* L.) silk. *Curr Res Green Sustain Chem* 4: 100089. https://doi.org/10.1016/j.crgsc.2021.100089
23. Sujitha V, Murugan K, Panneerselvam C, Aziz AT, Alatawi FA, et al. 2022. Fabrication of green nanoinsecticides from agri-waste of corn silk and its larvicidal and antibiofilm properties. *Green Process Synthesis* 11(1): 810-822. https://doi.org/10.1515/gps-2022-0062
24. Food Safety and Standards (Contaminants, Toxins and Residues) Regulations, 2011.
25. Carvalho LB, Godoy IS, Preisler AC, de Freitas Proença PL, Saraiva-Santos T, et al. 2023. Pre-emergence herbicidal efficiency and uptake of atrazine-loaded zein nanoparticles: a sustainable alternative to weed control. *Environ Sci Nano* 10(6): 1629-1643. https://doi.org/10.1039/d2en01064j
26. Kaur P, Kaur P, Duhan A, Bhullar MS. 2017. Effect of long-term application of pretilachlor on its persistence and residues in paddy crop. *Environ Technol* 38(19): 2410-2415. https://doi.org/10.1080/09593330.2016.1263684