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PHOTOCATALYTIC DEGRADATION OF LAMBDA-CYHALOTHRIN (PYRETHROID) IN WASTEWATER USING ZINC OXIDE NANOPARTICLE

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ABSTRACT

Accumulating synthetic pesticides in the living system has brought about several critical alerts from researchers as it interferes with the essential processes in the body. Metal oxide nanoparticles possess suitable properties including band gap and have played an important role in the photocatalytic degradation of toxic chemicals in wastewater and the environment under natural solar radiation. This research aims at the photocatalytic degradation of Type II Pyrethroid Pesticide (Lambda-cyhalothrin) in wastewater and agricultural runoff using Zinc Oxide Nanoparticles. The synthesized ZnO Nanoparticle (NP) was ascertained by characterization using XRD for material crystallinity and crystallite size, SEM, and particle size analysis for surface morphology and size. The EDAX spectra confirmed the presence of Zinc elements and showed that the synthesized zinc oxide nanoparticles were pure. The degradation experiment was conducted under natural solar irradiation. The initial and final/equilibrium concentration of Lambda-cyhalothrin residue were determined using High-performance liquid chromatography (HPLC) followed by computation of degradation capacity. Photocatalytic degradation of LCY was successful following the application of Zinc oxide NPs as nanocatalysts with an efficiency of about 87% as compared to the control. The synthesized Nanoparticle was found to degrade a large percentage of Lambda-cyhalothrin residue in wastewater. Exploiting its application in the remediation of pesticides in agricultural runoff may be crucial at this point.

Keywords: Lambda-Cyhalothrin, Photocatalytic Degradation, Magnetic Nanoparticle, Wastewater, and Agricultural Runoff.

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INTRODUCTION

Continued application of synthetic or chemical pesticides in agriculture, households, and commercial activities made them a case of concern for society and human health. Pesticides are crucial to day in day out activities because they play an important role in food productivity and maintenance of livelihood. However, as a result of the wide application of pesticides in agricultural activities and households, residues of such particles are frequently found in water bodies which directly or indirectly affect the quality of water and disrupt the aquatic ecosystem. In other cases, such particles find their way into the food chain affecting various organisms at different levels. Accumulating synthetic pesticides in the living system has brought about several critical alerts from researchers as it interferes with the essential processes in the body. Studies have shown that the deposition of pesticides into non-target areas including water bodies is one of the major issues regarding pesticides.[1-4] Lambda-cyhalothrin (LCY) is a type II pyrethroid pesticide and is a synthetic insecticide made up of 2 stereoisomers of cyhalothrin with long-term action against pests.[5]

It is a neurotoxin that disrupts the functioning of the nervous system in insects, leading to paralysis and later death.[6] It has a wide application across several anthropogenic activities including; agricultural activities[7-9] households and public health and is also considered among the most widely used synthetic pesticides in the whole world as a result of its low persistency as compared to other classes of pesticides, in addition to low toxicity to humans, wide insecticidal activity and spectrum.[10] However, extensive use of LCY pesticide had made it another pollutant/contaminant in the environment. Residues of such synthetic chemical pesticides were found to be present in water bodies,[11-15] vegetables, food, and the living system.

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Although LCY was reported to pose lesser toxicity to humans as compared to other pesticides, this pesticide was reported to be toxic to aquatic life, essential insects, and other mammals. Reports have shown LCY to alter purine hydrolysis and nucleotide gene expression in rat liver and platelets.

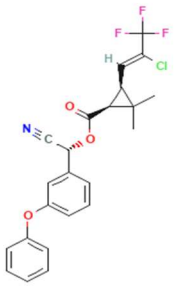

Fig.-1: Structure of LCY

Other toxic effects include; the cytotoxic effect on *Apis mellifera* honey bee,[16] lethal to guppy fish, induced oxidative stress in the kidney of rats,[17] induced behavioral and histopathological effects on gills of Blackchin tilapia fish,[18] alterations of hematological activity, plasma biochemical, enzymological and stress parameters in gills and liver of common carp fish,[19] induced thyroid toxicity on Albino rat,[20] abnormal necrosis in snails,[21] induced injury to the liver by activation of oxidative stress and inflammation in the rat liver and affects reproduction and foraging in bumble bee.[22] These made this synthetic pesticide a case of concern in the environment. Zinc oxide nanoparticle was revealed to be an effective photocatalytic agent in the degradation of contaminants in wastewater and agricultural runoff. Some of the applications include; photocatalytic degradation of methylene blue and methyl orange under natural sunlight.[23-24] Despite the wide acceptance of ZnO nanoparticles as a photocatalytic agent and the success recorded using several nanocomposites, little attention is given to the intrinsic capacity of zinc oxide nanoparticles, not in combination with any other particle. This may be a result of its lapses which include wide band gap energy that results in issues concerning light absorption and fast recombination of charge carriers. The present work aims to explore the intrinsic capacity of ZnO nanoparticles in the degradation and removal of LCY pesticide residue in water.

EXPERIMENTAL

Chemicals

All chemicals used for this study are of analytical grade and obtained from Himedia company in India. LCY 10% WP pesticide was obtained from the market (product of TATA Company) which is mostly used by farmers and households. All the chemicals were used without further purification.

Preparation of ZnO Nanoparticle

Zinc oxide nanoparticles were synthesized using the co-precipitation method using sodium hydroxide as precipitating agent and starch as stabilizing agent. 9.648g zinc nitrate hexahydrate was dissolved in 500 ml of DI water, 2g of sodium hydroxide dissolved in 250 ml DI water, and 1% starch solution. 90ml of 1% starch was added into 150ml zinc nitrate hexahydrate on a magnetic stirrer. Drops of sodium hydroxide solution were added to the solution while stirring until white precipitates are formed in the solution. The stirring was continued for 6 hours and the solution was allowed to settle overnight. It was then centrifuged at 4000 rpm for 15 minutes to obtain the precipitate. The precipitates were, later on, washed 3 times using ethanol and DI water, oven-dried overnight at 80° C in an oven, and calcinated at 600° C. The white ZnO nanoparticles powder was obtained and properly stored until further analysis.

Characterization

To ascertain and confirm the formation of zinc oxide nanoparticles, the sample was characterized using an X-Ray Diffraction (powder XRD) for the crystal structure of the particle and particle size, scanning electron microscope (SEM) for surface morphology, Energy Dispersion X-ray spectrometry (EDX) for chemical and elemental composition.

Preconcentration and Photodegradation

LCY obtained from the market was carefully preconcentrated using DI water to a concentration of 100 ppm. The photodegradation experiment was conducted for 2 sets of solutions with the tag LCY 1 and LCY 2. LCY 1 contains 5ml of 100ppm pesticide, photocatalyst (50ppm ZnO), and DI water while LCY 2 contains 20ml of 100ppm pesticide, photocatalyst (100ppm ZnO), and DI water. Both LCY 1 and LCY 2 were first kept in the dark to achieve the absorption-desorption equilibrium of the pesticide on the catalyst surface for 30 minutes. The solutions were then brought out to natural solar irradiation at room temperature (31^{o}C) for 60 minutes before separation. The 2 solutions LCY 1 and LCY 2 were then centrifuged at 4000 rpm for 10 minutes to separate the supernatant liquid and the photocatalyst. The concentration of LCY pesticide in the supernatant liquid was determined using HPLC analysis in triplicate. The experiments were repeated multiple times to observe the efficiency of the nanocatalyst after several runs. The degradation efficiency was estimated using the following formula:

$$\text{Degradation efficiency} = \text{Co-Ce/m x V}$$

Where, Co is the initial concentration of LCY, Ce is the concentration at equilibrium, m is the mass of the adsorbent, and V is the volume of the solution containing the solute.

RESULTS AND DISCUSSION

Formation of ZnO Nanoparticles

The crystalline white powder of zinc oxide nanoparticles was successfully synthesized using a simple and friendly coprecipitation method as shown in Fig.-2.

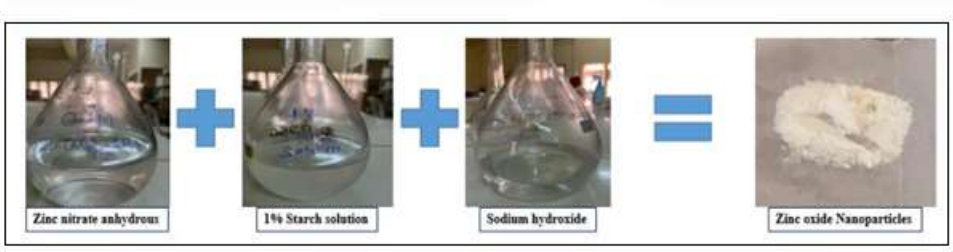

Fig.- 2: Formation of ZnO Nanoparticle

After adding 1% starch into zinc nitrate hexahydrate solution, a cloudy solution was formed which changes after adding drops of sodium hydroxide while stirring to white precipitate particles. The stirring was continued for 6 hours until the white precipitates were completely formed. The collected white ppt was then centrifuged, washed, oven dried, and calcinated to form the crystalline powder of ZnO nanoparticles. The synthesized ZnO nanoparticle was later confirmed by characterization.

XRD Analysis

XRD analysis provides an insight into the crystalline structure of the synthesized nanoparticles with peaks at suitable positions depicting the crystalline nature of ZnO nanoparticles. Figure-3 shows the XRD peaks obtained at 2Ɵ are as follows; 31.640^{o}, 34.291^{o}, 36.083^{o}, 47.380^{o}, 56.537^{o}, 62.679^{o}, 67.949^{o}, 68.871^{o}, and 72.297^{o}. The peaks at 31.640^{o}, 34.291^{o}, and 36.083^{o} corresponds to (100), (002), and (101) planes of hexagonal crystal patterns of ZnO respectively, and are in agreement with JCPDS card no. 89–0510.[24] The intensity of the peaks describes the quality of the ZnO nanoparticles synthesized.

SEM Analysis

Scanning Electron Microscopy was used to determine the surface morphology and the particle size. The SEM images were obtained at various ranges as shown in Fig.-4 with 1µm, 500 nm, 300 nm, and 100 nm as A, B, C, and D respectively at different magnifications. The spherical and hexagonal structure of the synthesized nanoparticles can be observed in the SEM images with agglomeration at some particular points. The nanocrystalline structure can be seen from the images which confirm the formation of ZnO nanoparticles and agrees with reported literature.[23]

EDS Analysis

EDAX spectra of synthesized ZnO nanoparticles present the elemental composition of the synthesized ZnO nanoparticle as shown in Fig.-5 with peaks at around 1.0 eV, 1.2 eV, and 8.8 eV for zinc and oxygen

in the sample. Other peaks were small and minute which indicates the purity of the synthesized particle. This result is in agreement with the work of [24] on green synthesized zinc oxide nanoparticles. The atomic mass of oxygen and zinc in ZnO nanoparticles was found to be 69.62 and 30.38% respectively.

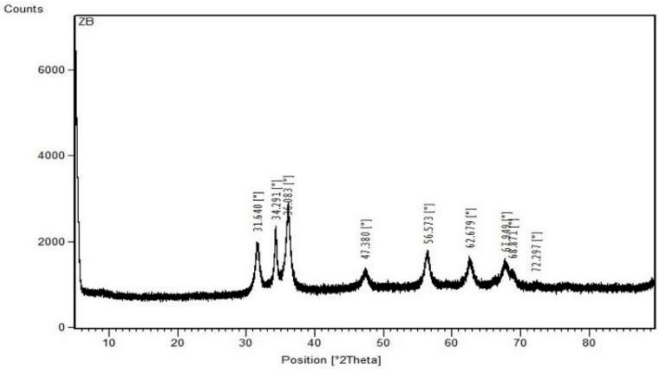

Fig.-3: XRD Profile of Synthesized ZnO Nanoparticle

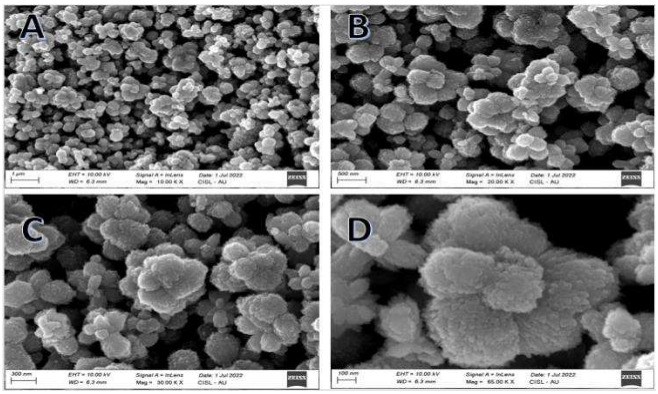

Fig.-4: SEM Images Showing Size and Surface Morphology of Synthesized ZnO Nanoparticle

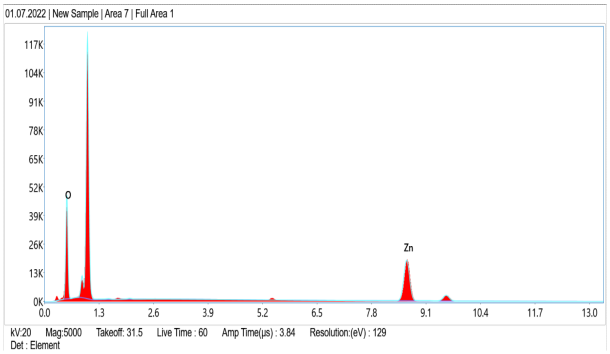

Fig.-5:EDS Spectrum Showing the Elemental Composition of the Synthesized Nanoparticle

Photocatalytic Degradation of LCY

Preconcentration

LCY was carefully preconcentrated to form 100ppm concentration using deionized water for photodegradation. 25mg of 10% WP LCY insecticide was dissolved in 250 ml deionized water to form 100 mg/L or 100ppm.

Photocatalytic Activity

The photocatalytic activity of ZnO nanoparticles on LCY was determined by employing batch reactions with different amounts of 100ppm LCY (5ml and 20ml) and ZnO nanoparticles as shown in Fig.-6. In the beginning, the photoreactivity or sensitivity of the preconcentrated pesticide was tested and after 2 hours in the dark and under natural solar irradiation, no significant change was observed.

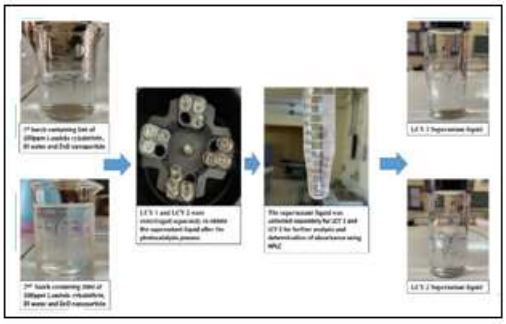

Fig.-6: Batch-Wise Photocatalytic Degradation Process

The whole process was carefully conducted following standard protocols. The 2 batches were carefully prepared and allowed to stay in the dark for adsorption-desorption equilibrium to be attained. Later on, there were brought to natural solar irradiation at a temperature range of 30-32ºC for an hour under constant stirring. The solutions were then centrifuged separately to get the supernatant liquid which was weight and stored carefully for HPLC analysis. The whole process was conducted in triplicate for clarity.

HPLC Analysis

Chromatographic Conditions

LCY determination was performed using a mobile phase (600 mL of acetonitrile and 400 mL of ultrapure water is taken in a reagent bottle and filter with 0.45 micrometers of filter paper) with a 1.0 mL/min flow rate. Ten microliters of the sample were injected, and LCY was detected at 275 nm under 25°C. Under the previously described conditions, the retention time (RT) for LCY was approximately 1.556 min. The HPLC chromatograms of LCY were shown in Fig.-7 and the results were shown in Table-2.

Table-1: HPLC Conditions

Instrument	Agilent HPLC (1290 Infinity II)
Detector	UV
Column	C18 -RP column (5.0 µm, 150 × 4.60 mm, i.d.)(Zodiac)
Flow rate	1.0 mL/min
Mobile phase	Acetonitrile and water
Software used	Agilent 2D- LC-solution software

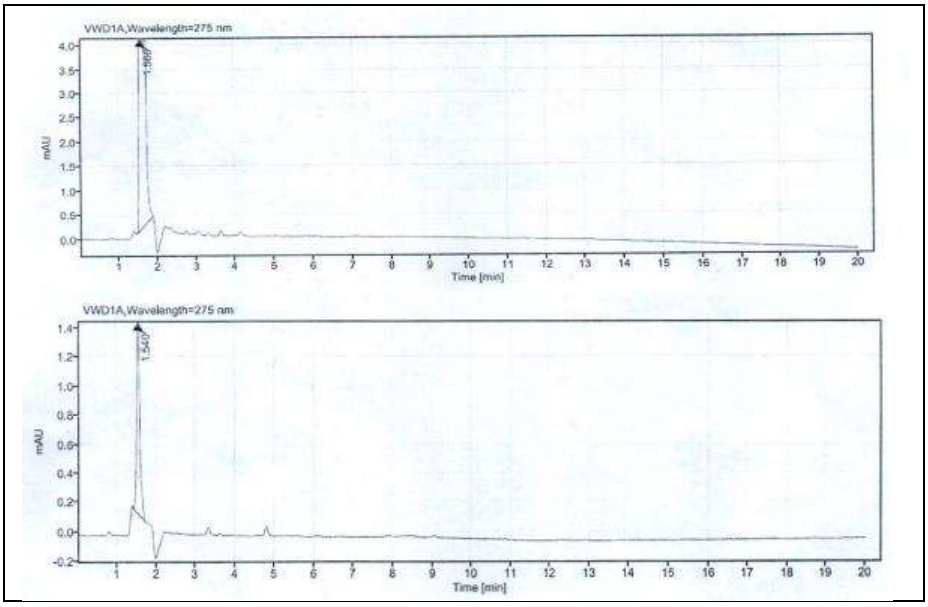

Fig.-7: HPLC LCY Chromatograms

Table-2: Confirmation of LCY Concentration

Sample	Concentration in ppm	Degradation efficiency %
LCY-1	1.229	87.79
LCY-2	1.338	87.72

CONCLUSION

A suitable method was established for the Photocatalytic degradation of Lambda-cyhalothrin (Pyrethroid) in wastewater using Zinc Oxide Nanoparticles. From various analytical techniques, zinc oxide nanoparticles were confirmed. The XRD spectra and SEM studies show that zinc oxide nanoparticles are Rhombohedral in structure. The EDAX spectra confirmed the presence of Zinc elements and showed that the synthesized zinc oxide nanoparticles were pure. Photocatalytic degradation of LCY using ZnO nanoparticles was found to be successful with an efficiency of 87%. This is a great sign that the intrinsic capabilities of semiconductor nanomaterials in the degradation of pollutants are yet to be completely explored. It may be crucial to alter other experimental conditions for better efficiency.

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CONFLICT OF INTERESTS

The authors declare that no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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