

Research Article

Photocatalytic degradation and removal of type II pyrethroid pesticide (lambda-cyhalothrin) residue from wastewater using nanoceria for agricultural runoff application

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Abstract

Synthetic chemical pesticides' nature, mode of action, and persistence have brought about debates regarding whether the end justifies the means. Lambda-cyhalothrin is an important insecticide for farmers and households, with great accessibility and excellent action against pests and disease-carrying insects. Like other pyrethroid pesticides, Lambda-cyhalothrin targets the nervous system of insects or pests. However, its fate in the environment, especially in water and living systems, has made it crucial to explore methods of treating or degrading its residues in the environment. The present study aimed to develop a suitable method for the photocatalytic degradation and removal of Lambda-cyhalothrin (LCY) from wastewater and agricultural runoff. The nanoceria were used under natural solar irradiation without applying any scavenger chemical or buffer. This was synthesized using a simple co-precipitation method using cerium nitrate hexahydrate as a precursor. The synthesized nanoceria were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS), Fourier Transform Infrared spectroscopy (FTIR) and particle size analysis. The average size of the particle was 27 nm. The photocatalytic degradation was conducted in batches with various pesticide concentrations exposed to different amounts of nanoceria. The initial and final concentrations of the LCY at each level were determined using Shimadzu UV spectroscopy. At optimum conditions, nanoceria was found to degrade and remove more than 63% of the initial pesticide concentration. This method can be suitable for degrading and removing pesticide residue from agricultural runoff (at source) and industrial effluents from synthetic pesticide industries.

Keywords: Agricultural runoff, Lambda-cyhalothrin, Nanoceria, Photocatalytic degradation, Wastewater

INTRODUCTION

Some pesticides' destructive and hazardous impacts made them a global case for alarm and concern. Most synthetic chemical pesticides' nature, mode of action, and persistence have brought about debates regarding whether the end justifies the means. Several attempts have been made and more on the process of coming up with suitable alternatives to pesticides with little impact on the aim and goal of the processes that are

switching to an eco-friendly and economically viable solution. After the incidence of organochlorine pesticide pollution and their persistent nature, especially the issue of DDT effects on the ecosystem, which gave birth to silent spring, it was clear that a lot needs to be done in this regard (Nicolopoulou-Stamati *et al.*, 2016; Bai, *et al.*, 2018; Voltz *et al.*, 2021). Subsequently, less persistent synthetic pesticides were invented and put to use with great output. However, pesticides' hazardous effects are not limited to organochlorines because even

the less persistent pesticides were found to cause serious damage to the ecosystem (Mwila *et al.*, 2013; Zhang *et al.*, 2021).

Pyrethroid pesticides are a type of synthetic insecticides that are chemically similar to the natural insecticide pyrethrins, which are derived from chrysanthemum flowers (Alalibo *et al.*, 2019; Chatterjee *et al.*, 2021a). Pyrethroids are a type of recently developed synthetic insecticides/pesticides. They are commonly chosen over older insecticides, such as organophosphates and organochlorines, because they are highly effective against various insect pests through both ingestion and physical contact and are more potent (Alalibo *et al.*, 2019). Pyrethroids are advantageous over other pesticides for various reasons. They are highly effective at very low concentrations, can withstand sunlight exposure without breaking down, easily break down in the environment, and have low toxicity to birds and mammals (Alalibo *et al.*, 2019; Chatterjee *et al.*, 2021b; Al Malahi *et al.*, 2022). Lambda-cyhalothrin is an example of a pyrethroid pesticide that is classified as a type II pyrethroid pesticide. It is one of the most widely used pesticides with a different range of applications (He *et al.*, 2008; Aouey *et al.*, 2017, Aouey *et al.*, 2019).

Lambda-cyhalothrin (LCY), like other pyrethroid pesticides, targets the nervous system of insects or pests. Pyrethroids are toxins that specifically target nerve fibers by attaching to a protein that controls the sodium channel responsible for regulating nerve impulses (He *et al.*, 2008). In normal circumstances, the sodium channel stimulates the nerve impulse and then closes to halt the signal. These channels serve as conduits that allow ions to enter the nerve fiber, resulting in stimulation (He *et al.*, 2008). In addition, leaving the channels open causes the nerve cells to produce discharges repetitively, leading to paralysis (He *et al.*, 2008; Aouey *et al.*, 2017 Al-Amoudi, 2018; Chatterjee *et al.*, 2021a). LCY is an important pesticide and plays a significant role in agricultural activities and households.

However, pollution of the environment and water, particularly by these pesticides and specifically lambda-cyhalothrin is a concern. Research has shown that only a small proportion, specifically around 2-5%, of pesticides applied are effective in controlling the intended organisms, while the remaining amount is distributed throughout the surrounding environment (Sherrif and Madadi, 2017). Therefore, a larger amount of the chemicals end up in the environment and may lead to several effects and ecosystem disruption. One of the major environmental impacts of pesticides is harm or effect to non-target organisms or insects. The movement of pesticide residues from their intended application sites via mechanisms such as volatilization, spray drift, agricultural runoff, leaching, or crop removal, is a crucial factor in evaluating the overall environmental effects of pesticides (He *et al.*, 2008; Liu *et al.*, 2014; Sherrif, Madadi,

2017). A study has shown that when LCY molecules become adsorbed, their degradation rate often decreases because they are less accessible to degradation factors compared to free molecules in a water column (Alalibo *et al.*, 2019). As such, there may be a tendency to bioaccumulate LCY in aquatic life and subsequent movement to higher organisms through the food chain. A study conducted by Ceuppens *et al.* (2015) revealed the effects of dietary lambda-cyhalothrin exposure on a bumblebee. It was discovered that lambda-cyhalothrin poses reproductive and survival effects on the test organism. Ibrahim *et al.* (2018) revealed that LCY causes significant abnormal cell death in both male and female reproductive cells and severe damage to both digestive and secretory cells in snails.

Advanced Oxidation Processes, popularly known as AOPs are the techniques for the degradation of contaminants in the environment. These methods involve using oxidizing agents which usually form reactive oxygen species and break down the contaminant. AOPs refer to eco-friendly chemical methods that can break down organic pollutants into safe substances without transferring the pollutants from one phase to another or generating large quantities of sludge. Nanoparticles and nanocomposites, especially those with special and unique properties, have been used as adsorbents and photocatalytic agents for the degradation and removal of pesticides (Ahmad *et al.*, 2020; Miri *et al.*, 2021; Hannachi *et al.*, 2022; Keerthana *et al.*, 2022; Pra-deepa & Nayaka, 2022). These particles possess unique properties, including a large surface area to volume ratio and band gap energy, especially in nanocomposites and metal oxide nanoparticles. The statement "there is more room at the bottom" by (Feynman, 1959) regarding immense opportunities and possibilities from miniaturization was a great beginning in the exploration of the capabilities of smaller particles. Several metal oxide nanoparticles like zinc oxide and titanium dioxide have been used as a photocatalyst in heterogeneous photocatalysis for the treatment of wastewater.

Cerium oxide nanoparticles, also known as nanoceria a metal oxide of Rare Earth Elements REEs made using a lanthanide metal cerium (Keerthana *et al.*, 2021). These particles are gaining attention recently due to their wide application and their unique properties, including their oxidation and other properties. This oxidation state plays an important role in redox reactions and photocatalysis. The effective redox site of cerium Ce^{4+}/Ce^{3+} and its ability to exchange oxygen (Keerthana *et al.*, 2021) have made nanoceria a great material for various activities, including environmental remediation. Nanoceria was found to possess multiple applications in environmental remediation and wastewater treatment. Its application in the degradation of toxic 4-nitrophenol was reported by (Keerthana *et al.*, 2021) under

visible light irradiation. It was revealed that nanoceria could degrade 4-nitro phenol in 45 minutes faster than the control. Ederer *et al.* (2019) reported on the destructive capability of nanoceria in degrading triphenyl phosphate pesticide, which begins by converting TTP to diphenyl phosphate and the final product phenol. Other applications of nanoceria include; the degradation of organophosphate pesticide fenchlorphos where the NPs serve as a reactive sorbent (Janoš *et al.*, 2015), in-vitro skin decontamination of organophosphate pesticide (Salerno *et al.*, 2017), electrochemical investigation of pantoprazole in the presence of epinephrine (Pradeepa & Nayaka, 2022), antimicrobial activity (Eka Putri *et al.*, 2021), degradation of methylene blue dye (Kouser *et al.*, 2021), degradation of phenol (Ahmad *et al.*, 2020), degradation of rhodamine B dye, methyl orange dye and tetracycline (Li *et al.*, 2018), anti-cancer potential (Kermani *et al.*, 2022) and effective removal of uranium from aqueous solution (Kashyap *et al.*, 2022).

These and many other nanoceria applications attract researchers to explore the capabilities of cerium oxide nanoparticles (NPs). Therefore, the present study aimed to explore the capabilities of nanoceria in the degradation of a type II pyrethroid pesticide lambda-cyhalothrin. A suitable method was developed for photocatalytic degradation of LCY in wastewater using nanoceria under natural solar irradiation with no application of any scavenger chemical or buffer.

MATERIALS AND METHODS

Chemicals and reagents

Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), Potassium carbonate (K_2CO_3), acetonitrile HPLC grade and ethanol were all purchased from Merck company (India), Mumbai. All the chemicals used were of analytical reagent AR grade and were used without further purification. Lambda-cyhalothrin 10% WP, a TATA product, was obtained from Rallis India Limited, Mumbai, Maharashtra, India. Millipore water was used throughout the experiments and was obtained from the Environmental Biotechnology Laboratory, GITAM Institute of Science, GITAM University, Visakhapatnam, Andhra Pradesh.

Synthesis of nanoceria by coprecipitation method

Cerium oxide nanoparticles, also known as nanoceria were synthesized using a simple coprecipitation method as adopted from the work of (Farahmandjou *et al.*, 2016). 2 standard solutions of 0.02 M Cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 0.03 M Potassium carbonate (K_2CO_3) were separately and carefully prepared by dissolving 2.17 g ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) and 1.036 g (K_2CO_3) in a 250 ml millipore water/DI water in a volumetric flask as solution A and B respectively. 50 ml of solution A was weighed into a conical flask and 20 ml

of solution B into a burette. Solution A was placed on a magnetic stirrer and solution B in the burette was added into A in drops through the wall of the container. The pH of the solution was adjusted and maintained at pH 6 using DI water as a buffer. White precipitate particles of cerium carbonate were formed after an hour of stirring. The precipitates were allowed to settle, centrifuged at 3500 rpm and dried at 65° C for 2 hours. The resulting dried powder particles were cooled at room temperature and aged at 220° C for 2 hours and, later on, annealed at 600° C in a muffle furnace for 3 hours to obtain the nanoceria/cerium oxide nanoparticles.

Characterization

This was conducted to ascertain the specification of the size, structure, morphology, elemental composition and chemical composition of the synthesized particles. The particles' crystal structure and crystallite size were determined using powder X-Ray Diffraction (PXRD) through a Bruker D8 advanced instrument. The scan type used was coupled to two theta/theta, and the mode was continuous. The scanning process started at 10.000° and ended at 79.994°, with an interval of 0.020°, and was conducted at a temperature of 25° C/ room temperature. Fourier transform Infrared (FTIR) spectroscopy was employed to analyze the functional groups present. This was done using an FTIR spectrophotometer, Nicolet iS50, equipped with an IR source, DTGS KBr detector, and KBr beam splitter. A total of 32 scans were performed, with a collection length of 47.3 seconds and a resolution of 4.000. The FTIR range used for the analysis was from 500 to 4000 cm^{-1} wavenumber.

Surface morphology analysis was performed using Scanning Electron Microscopy (SEM) via an SEM-EDAX Jeol 6390 LA/OXFORD MXN instrument. The SEM was operated at an accelerating voltage range of 0.5 to 30 kv and a magnification of 300,000 times. A tungsten filament was used for this analysis. Energy Dispersive X-Ray Spectroscopy (EDAX) was used for elemental analysis with the same instrument. The EDAX had a resolution of 136 eV, and the detector area used was 30 mm^2 .

Photocatalytic degradation of Lambda-cyhalothrin

This was conducted in batches with 3 different concentrations of lambda-cyhalothrin prepared following standard procedure using millipore water and 2 quantities of nanoceria photocatalyst. Each concentration of the pesticide was exposed separately to 2 quantities of the photocatalyst and the sample setups were termed as follows;

100 ppm LCY and 10 mg nanoceria = LCe-1
 100 ppm LCY and 20 mg nanoceria = LCe-2
 50 ppm LCY and 10 mg nanoceria = LCe-3
 50 ppm LCY and 20 mg nanoceria = LCe-4

10 ppm LCY and 10 mg nanoceria = LCe-5

10 ppm LCY and 20 mg nanoceria = LCe-6

In this experiment, 10 and 20 mg nanoceria were weighed into a series of 100 ml of 10 ppm, 50 ppm and 100 ppm for the photocatalytic experiment. For each setup, the sample solutions were first kept in the dark for 30 minutes to achieve adsorption-desorption equilibrium before exposure to natural solar irradiation at normal environmental conditions. 10 ml of the solution from each setup was withdrawn at a particular time interval of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 hours after exposure to natural solar irradiation. The collected 10 ml samples were then centrifuged at 3500 rpm for 10 minutes to separate the supernatant liquid and the settled nanoceria. The collected supernatant liquids were further analyzed by Shimadzu UV spectrophotometer UV1800 for UV absorbance analysis and determination of the concentration. The UV absorbance of the supernatants or samples was determined at a 220-400 wavelength range. The final concentrations of the pesticide in the solutions were determined at the computed maximum wavelength of 227 nm λ_{max} . To establish the concentration in each measurement, a series of standards were meticulously created by employing the serial dilution technique. This allowed for the creation of a linear plot correlating concentration and absorbance. The samples' concentrations at time t /final concentrations were used to determine the degradation efficiency and reaction kinetics.

The separated nanoceria was later on washed 3 times with millipore water for further analysis of their activity. The same procedure was applied for the control with no nanoceria or photocatalyst during each round of the experiments with all the initial concentrations used.

Furthermore, some of the experimental conditions applicable to field application were optimized to obtain a better result. The optimization conditions considered in this research are as follows; initial concentration of lambda-cyhalothrin, the quantity of the nanoceria, irradiation time, and atmospheric conditions like UV index and temperature. All these conditions were found to play a crucial role in the degradation of lambda-cyhalothrin in wastewater using nanoceria.

The degradation efficiency of nanoceria or photocatalytic activity of the particle was determined using the following formula;

$$\% \text{ degradation/degradation efficiency} = \frac{L_{Co} - L_{Cf}}{L_{Co}} \times 100 \quad (\text{Eq. 1})$$

Where L_{Co} is the initial concentration of lambda-cyhalothrin pesticide and L_{Cf} is the final concentration of lambda-cyhalothrin pesticide.

RESULTS AND DISCUSSION

Cerium oxide nanoparticles (nanoceria) were success-

fully synthesized following the above-mentioned method. Initially, a white precipitate of cerium carbonate was obtained from the process, which was later converted to light brownish powder particles after hours of ageing. Fig. 1 reveals different stages of the synthesized nanoceria with aged and annealed NPs at 3 different temperatures. There was a slight change in color of the aged NPs at 220° C and annealed/calcinated NPs at 400° C. However, the annealed powder NPs at 600° C was found to be brighter than the former. As Henych *et al.* (2022) reported, the possible mechanism for creating nanoceria in a liquid phase involved the deliberate oxidation of a Ce^{3+} salt that was highly soluble to produce an insoluble precursor like cerium hydroxide or carbonate. This precursor can then be transformed into cerium (IV) oxide through processes like ageing, calcination, or hydrothermal treatment.

Characterization of the synthesized nanoceria

X-Ray Diffraction XRD analysis

The XRD pattern of the synthesized nanoceria obtained revealed the crystalline phase and crystallite size of the powder nanoceria. The pattern is shown in Fig. 2. The peaks were observed at angles of 28.507°, 33.032°, 47.446°, 56.214°, 58.994°, 69.327°, 76.598° and 79.54° are associated with the (111), (200), (220), (311), (222), (400), (311) and (420) crystal planes of the cubic fluorite structure found in nanoceria as identified in the standard JCPDS No 00-034-0394 (Keerthana *et al.*, 2022). The peaks of the crystal planes also agree with the findings of (Janos *et al.*, 2014; Farahmandjou *et al.*, 2016; Pujar *et al.*, 2020). The Debye-Scherrer equation was used to predict the average crystallite size based on the XRD peak broadening, and the obtained size was found to be 27 nm.

$$d = \frac{0.9 \lambda}{\beta \cos \theta} \quad (\text{Eq. 2})$$

where; d is the crystallite size, λ is the wavelength of $Cu K\alpha$ radiation, β is the full-width at half maximum (FWHM) of the diffraction peak and θ is the diffraction angle.

FTIR analysis

The Fourier transform Infrared FTIR pattern obtained from the synthesized nanoceria is shown in Fig. 3,

Table 1. Elemental composition of the synthesized nanoceria

Element	Line Type	Wt%	Atomic %
C	K series	25.09	50.69
O	K series	26.88	40.77
K	K series	0.51	0.32
Ce	L series	47.52	8.23



Fig. 1. Different stages of the synthesized powder nanoceria

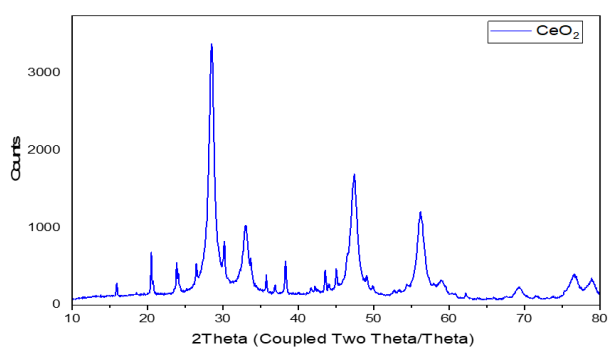


Fig. 2. XRD pattern of the calcinated nanoceria at 600 °C

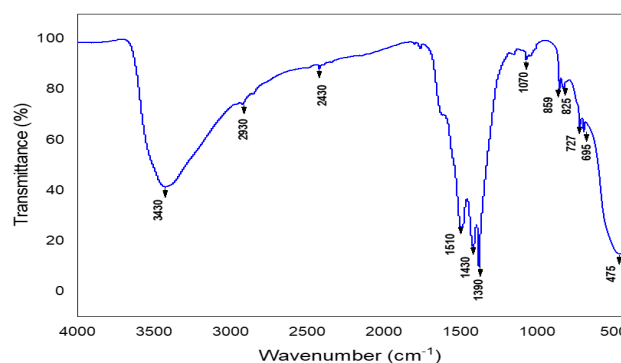


Fig. 3. FTIR spectrum of the synthesized nanoceria

which identifies the chemical bonds with the functional groups present. The spectrum has revealed various peaks relating to cerium-oxygen and water molecules used as solvents together with other peaks. From Fig. 3, it was observed that the peak at around 475-500 cm^{-1} corresponded to the stretching vibration of Ce-O₂ (Pujar *et al.*, 2020; Keerthana *et al.*, 2022). The broad peak at 3430 corresponds to the -O-H stretching vibration of OH⁻ in water molecules (Keerthana *et al.*, 2022). The other peaks at 2930, 2430, 1510, 1070 and 859 correspond to Methyl C-H asymmetric stretching, C-C

stretching, O-H stretching vibration, Ce-OH overtone and C-O-O stretching, respectively (Pujar *et al.*, 2020; Kaur *et al.*, 2022; Pradeepa and Nayaka, 2022).

Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy SEM-EDAX

Fig. 4 shows the SEM images and the EDAX spectrum showing the elemental composition of the synthesized nanoceria. As can be observed from the SEM images in Fig. 4, there exists an agglomeration at various points, which may have a significant effect on the deter-

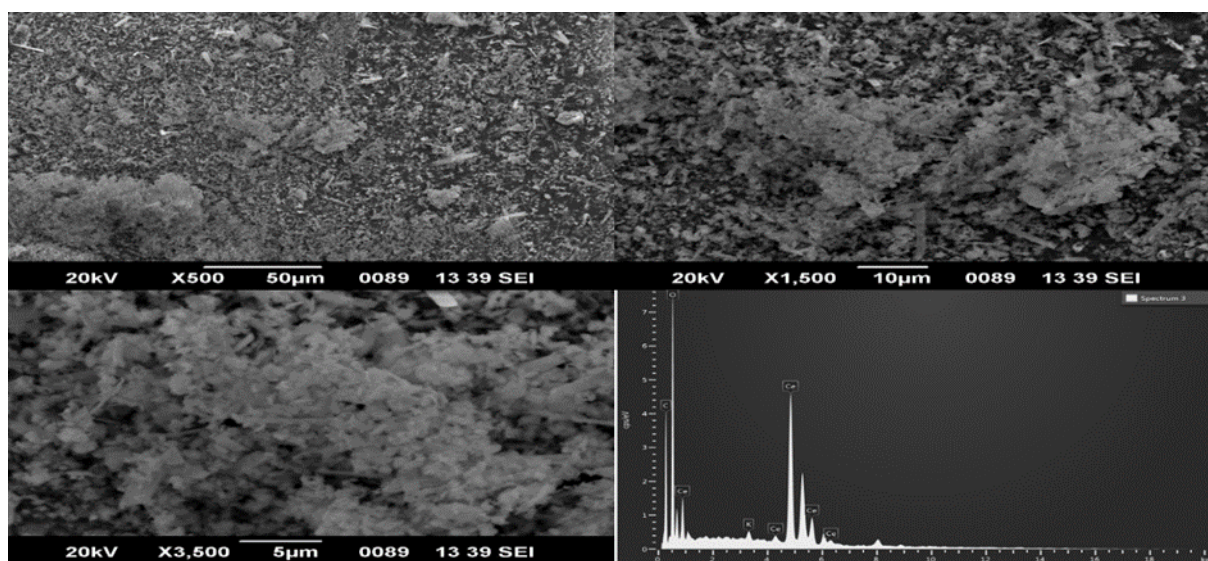


Fig. 4. FTIR spectrum of the synthesized nanoceria

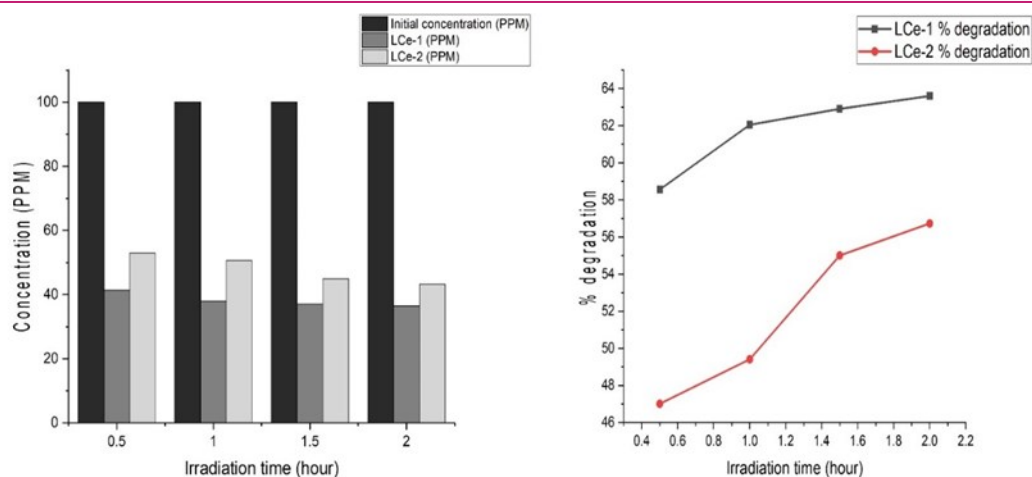


Fig. 5. Initial and subsequent/final concentrations and the percentage degradation over time LCe-1 and LCe-2

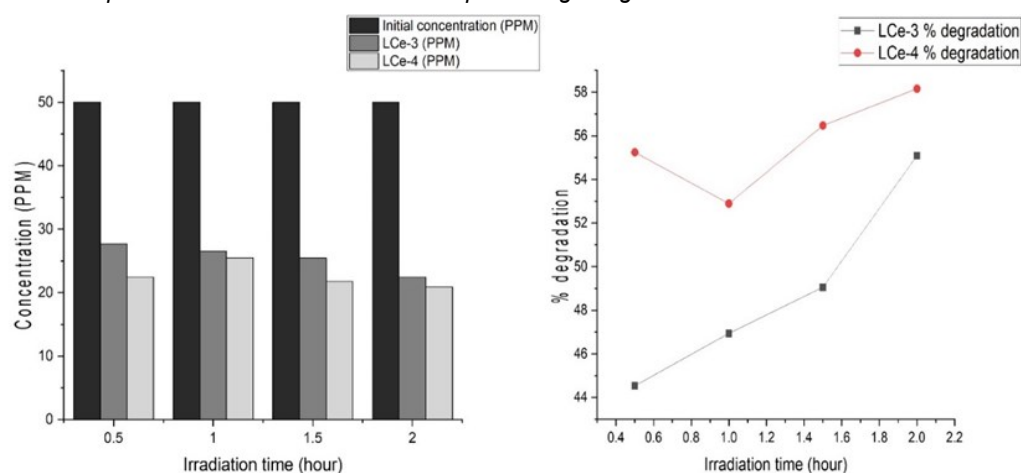


Fig. 6. Initial and subsequent/final concentrations and the percentage degradation over time LCe-3 and LCe-4

mination of the shape of the NPs. However, clusters of thin plate irregular shapes (Henych *et al.*, 2022) can be observed in the images depicting the synthesized nanoceria (Janos *et al.*, 2014). Other studies have reported spherical structure for nanoceria, which may have all to do with the method of synthesis and calcination temperature (Farahmandjou *et al.*, 2016; Jayakumar *et al.*, 2019).

The EDAX spectra in Fig. 4 revealed the elemental composition of the synthesized nanoceria, with elements cerium and oxygen accounting for the largest portion or percentage of the elements present. Table 1 provides the percentage of each of the elements present in the NPs.

Degradation of Lambda-cyhalothrin

The degradation of LCY pesticide using nanoceria in this study follows a unique pattern with the pesticide's initial concentration affecting the NPs' activity. Three different concentrations were studied with two quantities of the nanoceria. Fig. 5 shows the initial and subsequent/final concentrations change at different time intervals and the percentage degradation of Lce-1 and LCe-2. Looking at Fig. 5, it can be observed that there

was a decrease in the pesticide concentration with an increase in time until 2 hours. It was observed that after several runs of the experiment, the degradation significantly reduced and sometimes stopped at 2 hours, with few cases showing otherwise. Moreover, the quantity of the NPs in Lce-1, which is 10mg, was found to show more effect than the 20mg in the LCe-2. This may be attributed to photocatalytic degradation rather than just adsorption by the nanoceria, which agrees with the findings of Henych *et al.* (2022) where both substrates are degraded rather than just adsorbed. Fig 5. shows that 10mg nanoceria has an optimum percentage degradation of 63% LCY in a water solvent.

Fig. 6 and 7 show the degradation patterns in LCe-3, LCe-4, LCe-5 and LCe-6 with different pesticide and nanoceria quantities concentrations. Fig. 6 revealed the changes in the initial concentration over time, with the quantity of the nanoceria playing a significant role. LCe-3 and LCe-4 with 50 ppm concentration of LCY have shown that the decrease in the pesticide concentration may increase the chances for more adsorption rather than more degradation as in the previous case of 100 ppm. In this regard, LCe-4 with 50 ppm LCY and 20 mg nanoceria was found to possess high activity in remov-

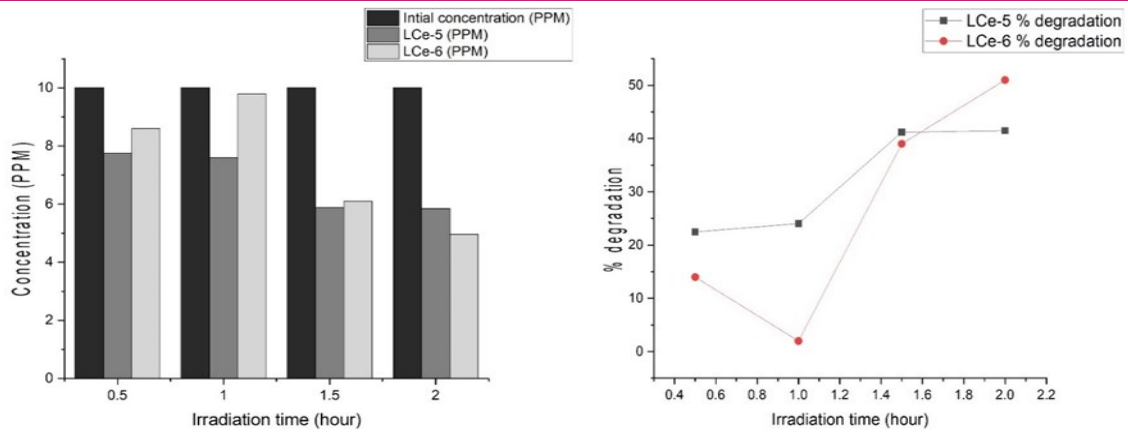


Fig. 7. Initial and subsequent/final concentrations and the percentage degradation over time LCe-1 and LCe-2

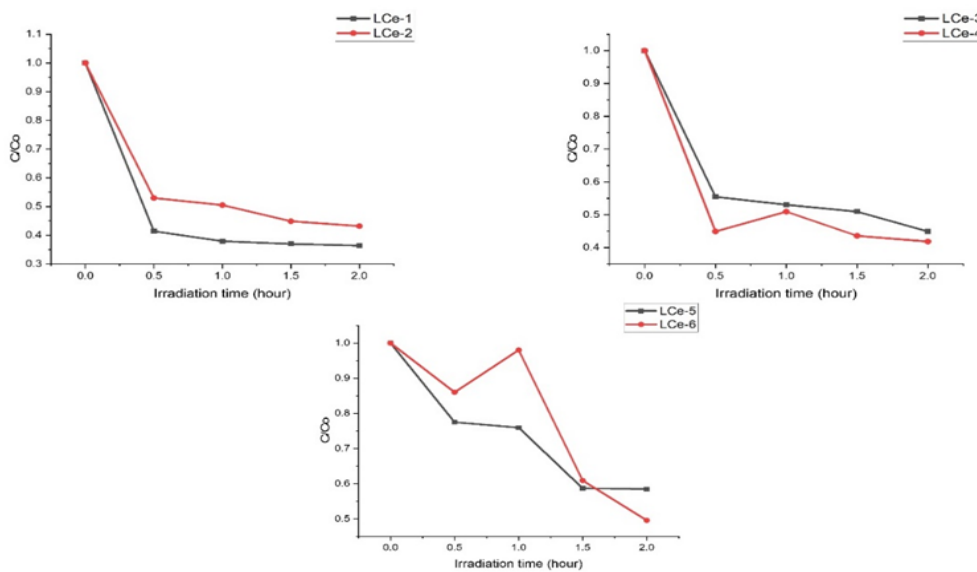


Fig. 8. Degradation rate of 3 different concentrations of lambda-cyhalothrin in water using two different quantities of 10 and 20 mg nanoceria

ing and degrading the pesticide. The large surface area of the NPs plays a significant role in this regard, where nanoceria acts as an active sorbent for removing contaminants (Janos *et al.*, 2014; Janoš *et al.*, 2022). However, LCe-5 and LCe-6 have shown yet another pattern with the 2 quantities of the nanoceria. Fig. 7 shows the degradation pattern where at the initial stage of the experiment, 10 mg nanoceria in LCe-5 shows better activity with 20 mg in LCe-6. But, after 2 hours of irradiation time, LCe-6 was found to possess better activity than the former. This shows that different concentrations of the pesticide may strongly affect the activity of the NPs.

Hence, the percentage degradation in LCe-4 and LCe-6 with 20 mg were found to be above 50% degradation efficiency, with LCe-4 showing very close to 60% efficiency at 2 hours. However, LCe-3 in Fig. 6 shows about 54% efficiency, with LCe-5 having less than 50% efficiency.

Fig. 8 shows the degradation rate of 100 ppm, 50 ppm

and 10 ppm lambda-cyhalothrin using 10 and 20 mg nanoceria. LCe-1, 2, 3 and 4 show a faster initial reaction at 30 minutes, followed by subsequent slower reactions until 2 hours or 120 minutes. A similar faster initial reaction rate was also reported by (Henych *et al.*, 2022; Janoš *et al.*, 2022), which was attributed to the availability of the active sites at the initial stage of the reaction, which further stabilized and decreased at a certain rate. However, the degradation rate for LCe-5 and 6 showed somehow a different degradation rate with an increase in the concentration at a certain point in time and followed by a faster rate between 1 hour of irradiation time and 1.5 hours or 90 minutes. This may be attributed to a variety of factors, including environmental factors or the issue of extraneous variables.

UV Absorbance

The UV absorbance of each of the samples has been determined at various time intervals between 0 and 3 hours, with six samples at an interval of 30 minutes

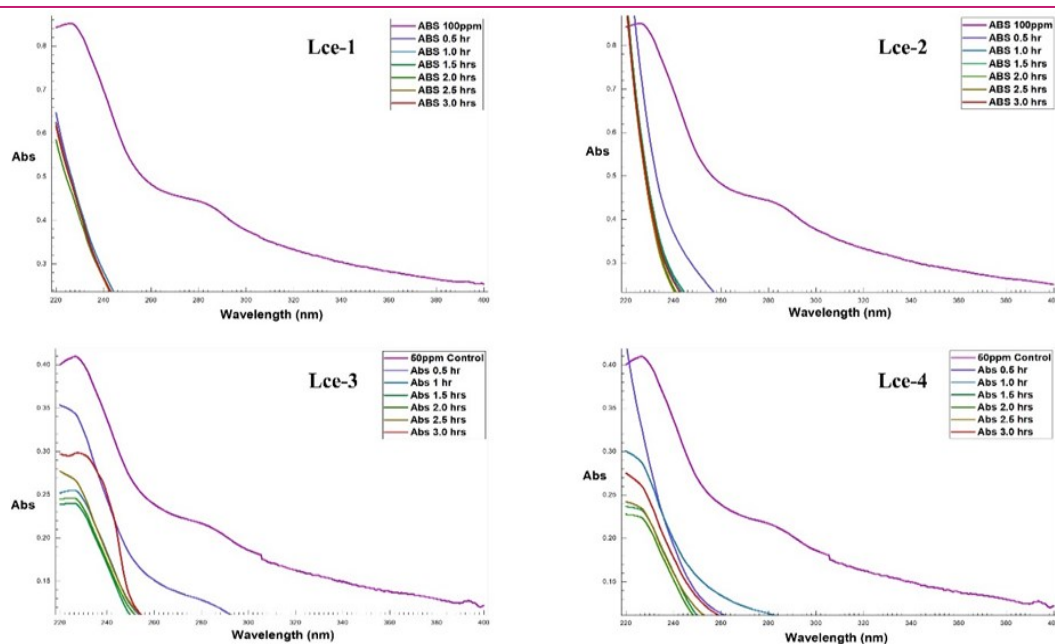


Fig. 9. Decrease in the UV absorbance for LCe-1, 2, 3 and 4 together with control with

each. Fig. 9 shows the decrease in the UV absorbance over time for LCe-1, 2, 3, and 4 with the control experiment with no nanoceria. The peak/maximum absorbance was observed at a wavelength of 227, as seen in the figure. There was a disappearance of the peak at λ_{max} in LCe-1 and 2, as observed on the UV spectrum, which may be attributed to the sharp reduction in the concentration after exposure to natural solar irradiation. However, LCe-3 and 4 shows yet another reduction or decrease in the absorbance but not its disappearance. Hence, all the samples have shown a decrease in UV absorbance over time until 2 hours of solar irradiation exposure, where either the process stops/slowed down or begins to be unstable as in the case of LCe-3. (Keerthana *et al.*, 2022) reported on the heterogeneous catalytic activity of nanoceria which causes a decrease in the absorbance of 4-nitro phenol over time/irradiation time and a shift of the peak to form another compound. Nanoceria has shown a significant activity towards degradation of lambda-cyhalothrin under natural solar irradiation at a very faster rate than the control experiment.

Optimization of the experimental conditions

Conditions that may be feasible to control in the field, together with the initial concentration of LCY were optimized to obtain a better activity of the nanoceria against LCY. The conditions include the quantity of the nanoceria/cerium oxide nanoparticles, irradiation time and atmospheric conditions, UV index, and temperature. The effects of the initial concentration of the pesticide and the quantity of nanoceria are discussed in the previous sections of the present study. However, the atmospheric conditions, especially the UV index, were also significant in lambda-cyhalothrin degradation. As

reported in numerous research articles, for photocatalysis to occur or begin, the applied energy must be greater than or equal to the band gap energy of the photocatalyst (Andronic *et al.*, 2022; Barzagan, 2022; Irfan *et al.*, 2022; Sraw *et al.*, 2022). Therefore, for holes and electrons to be generated at the valence and conduction band, respectively, there must be radiation greater than the bandgap energy (Andronic *et al.*, 2022). Hence, the intensity of UV radiation or solar radiation is crucial. During this study, it was observed that only a UV index above 8 which is categorized as a very high UV index, was found to initiate the process of photocatalytic degradation of LCY over time. At a moderate UV index of 6-7, there was no/or slight difference between the sample and control. Hence, the radiation source or energy is crucial for catalytic degradation using nanoceria (Bruckmann *et al.*, 2022; Goel & Arora, 2022). Moreover, any change recorded at a lower UV index situation may result from adsorption but not photocatalysis. In regards to temperature, it was observed that an increase in temperature together with the UV index increases the photocatalyst's activity, which agrees with the finding of (Bruckmann *et al.*, 2022).

Conclusion

The present study successfully synthesized cerium oxide nanoparticles/nanoceria using a simple coprecipitation method with special features for photocatalytic degradation of lambda-cyhalothrin. The synthesized nanoceria was investigated for the degradation of LCY under natural environmental conditions with no employment of any acid scavenger or chemical. The activity of the nanoceria was due to the synthesised particle's

great nature, including its sized distribution, surface area and purity. Hence, under optimal conditions observed in this research, 10 mg nanoceria was found to successfully degrade more than 63% of the initial 100 ppm concentration of lambda-cyhalothrin under natural solar irradiation with a UV index of 9, denoting very high UVI after 2 hours. Although other important adjustments could have improved the activity of the photocatalyst, this study focused only on the intrinsic capacity of the nanoceria in the degradation of LCY for field application on agricultural runoff from farmlands. Therefore, improving the purity of the particle and considering active dopants that may reduce the bandgap energy will play a significant role in the photocatalytic degradation of pollutants in agricultural runoff. Reducing the concentration of pesticides in the agric runoff before reaching water bodies/tributaries may halt the menace of pesticide pollution. As such, researchers and scientists need to focus more on optimizing conditions applicable in the field for better outcomes in the degradation of pollutants using nanoparticles.

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Conflict of interest

The authors declare that they have no conflict of interest.

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