Efficient photo-adsorptive eradication of endocrine disrupting pesticides by chitosan co-decorated metal oxide bio-nanocomposite

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Abstract

Extensive consumption, toxicity, and bioaccumulation of malathion (MLT) and lindane (γ-HCH) pesticides collectively attract the world’s attention. Herein, the nanocomposite of chitosan wrapped NiO@ZnO was synthesized by a green methodology using Azadirachta indica leaves extract. Structural and morphological analysis of chitosan-NiO@ZnO showed hollow sphere-flake shaped image adsorbed on a solid chitosan surface with a large surface area of 73 m²g⁻¹. A decrease in values of lattice strain, dislocation density and crystallite size described the imperfection in crystal geometry and new peaks in FT-IR spectra at 698 cm⁻¹ and 448 cm⁻¹ of Ni-N and Zn-N, respectively confirms the coupling. The chitosan- NiO@ZnO nanocomposite with a reduced band gap due to the generation of new energy levels in the vicinity of of conduction and valence band. Chitosan-NiO@ZnO and individuals nanoparticles (NiO and ZnO) were well-characterized and utilized for degradation MLT and γ- HCH under direct sunlight and dark conditions. The highest degradation of pesticides (above 94%) resulted with 2 mg L⁻¹ and 10 mg L⁻¹ of MLT (π-π) and γ- HCH, respectively with a 20 mg catalyst dose, and pH of ~7 under daylight exposure (5 h). Chitosan-NiO@ZnO substantially suppressed the half-life of the targeted pesticides (MLT: 0.48 h; HCH 0.51 h) and demonstrated the first-order kinetics with a high adsorption capacity, Xₐ (MLT: 14.5 mg g⁻¹ and γ- HCH 20.7 mg g⁻¹), which also confirmed the strong binding with the pesticides, followed by their conversion into safer and smaller metabolites. The charge separation mechanism was elucidated by UV reflectance and photoluminescence data. Hydroxyl radicals were most frequently responsible for the degradation of pesticides as confirmed by scavenger analysis. The synthesized green-nano photocatalyst showed high reusability (up to 10th cycles), sensitivity, and stability within the degradation process, presumably making it suitable for industrial applications.

1. Introduction

Due to the widespread use of pesticides, their pollution of soil and water is inevitable (Kumar et al., 2018; Arisekar et al., 2019). Among pesticides, Malathion (MLT) and Lindane (γ-HCH) were consumed at the highest rate and most frequently found in ground-water (Kumar et al., 2018; Sankararamakrishnan et al., 2005). The respective maximum allowed MLT and γ- HCH concentration in water should not exceed 1 mgL⁻¹ and 8 mg L⁻¹ as per the World Health Organization (Li et al., 2020; Rani Because of their global utilization, wide distribution, bioaccumulation, high stability and extreme persistency, it is imperative to develop a promising technology to degrade or remove these dangerous pesticides (Sankararamakrishnan et al., 2005; Kassiri et al., 2021).

Current, nanomaterials-mediated advanced oxidation processes are considered the most effective approach for degradation of pesticides (including MLT and γ- HCH) because of their beneficial properties, such as applicable with a rapid single step, straightforward, sustainable, eco-friendly, cost effective and high photocatalytic efficiency. Kumar and Chand degraded 64% of MLT with a Bi₁₋ₓCeₓFeO₃ photocatalyst under visible light irradiation., but the cerium nitrate hexahydrate salt used is toxic (Kumar et al., 2022). TiO₂ immobilized on a continuous flowing rotating disc degraded 63% of lindane under UV light irradiation (Senthilnathan and Philip, 2010). Zaleska et al degraded 50% of lindane within 150 min using anatase supported on glass hollow microspheres (Zaleska et al., 2000). Table S1 summarizes the physico-chemical properties of targeted pesticides. These earlier studies focused on single component photocatalysts (ZnO, NiO), which often have low efficiency and poor stability due to the high recombination rate of the electron- hole pair and inefficient visible
light absorption (Thamri et al., 2017). Recently, composites of semiconductor materials with the synergistic effect of their properties such as adsorption and improved charge carrier migration have been developed (using chitosan polymer) NiO and ZnO-based photocatalyst. The organic-inorganic nanocomposite materials showed new combined properties material such as carrier life time, charge transfer ability, chemical stability, charge separation efficiency and optical properties (Zhang et al., 2020; Elumalai et al., 2015; Bhuyan et al., 2015). Among various metal oxides, zinc oxide (ZnO) an n-type semiconductor material with superior electrical and optical properties but is restricted to the UV region because of its wide band gap (Thamri et al., 2017). ZnO holds unique optical, chemical, semiconducting, electric conductivity and piezoelectric properties (Sirelkhatim et al., 2015). The excitonic emission can preserve higher at room temperature and the conductivity increases when ZnO doped with other metals (Djerdj et al., 2010; Ong et al., 2018). Nickel oxide (NiO) is a p-type semiconductor having a high band gap value. When coupled with ZnO, NiO promotes the interfacial charge transfer and finds extensive application in photocatalysis. The combination of metal oxides generates an interesting p-n heterojunction where different kinds of electronic transition (metal-metal or metal-oxygen-metal) occur in the NiO@ZnO nanocomposite due to the inner electric field generated, making it function in the visible range with improved characteristics (You et al., 2020; Mahajan et al., 2022).

Chitosan can have physical interactions with NiO@ZnO nanocomposites via hydroxyl and amino groups (Ali et al., 2018; Demirezen et al., 2021), provides wettability (hydrophilic-hydrophobic) to nanocomposite surface and also helps to control the size and dispersion of the nanocomposite as well due to its spreading out during the synthesis of photocatalyst (You et al., 2020; Hameed et al., 2009). Moreover, ionomeric polymeric interaction bearing strong chelating ionic groups might be used as an active layer to promote the binding of nanoparticles onto metallic surfaces (Hameed et al., 2021). To the best of our knowledge, no reports have been published on green synthesis of Chitosan-NiO@ZnO ternary nanocomposite and its further application in degradation of pesticides.

In the present study, mixed metal oxide systems of Chitosan-NiO@ZnO were synthesized with *Azadirachta indica* leaves extract to combine the n-type ZnO and the p-type NiO into a single photocatalyst. The chitosan-NiO@ZnO nanocomposites were then tested to: 1) degrade MLT and γ-HCH under sunlight and at different conditions (pesticide's concentration, pH and catalyst dosage); 2) analyze the reaction kinetics and mineralization processes; 3) elucidate the process mechanism and the role of free radicals under sunlight; and 4) determine the reusability of nanomaterials. Results of this study indicate that the innovative ternary nanocomposite has some advantageous over binary metal oxides, such as enhanced visible light absorption, electronic properties, and charge separation.

## 2. Experimental

### 2.1 Materials

Nickel chloride (99%), zinc chloride (99%), sodium hydroxide (<90%), and potassium dichromate were purchased from LOBA Chemie, India. Malathion and γ-HCH was purchased from Sigma Aldrich, Germany. From the local University campus, *Azadirachta indica* leaves were collected. The whole experimental process was performed with deionized water (aqua MAX-Barie 360 series; resistivity 18.2MΩcm⁻¹). A stock solution of MLT and γ-HCH having a concentration of 1000 mg L⁻¹ was also prepared.
2.2 Preparation Of Leaf Extract

Freshly collected *A. Indica* leaves (10 g) were washed (three times) with de-ionized water, crushed into fine pieces followed by centrifugation for 20 minutes at 200 rpm to get the aqueous solution of leaves which was placed at 4°C temperature until further use. Selected *A. indica* trees are easily available and have antibacterial and antifungal properties (Shankar et al., 2004; Ghosh et al., 2020; Manik et al., 2020). (Figure S1).

2.3 Green Preparation Of Nio, Zno, And Chitosan- Nio@zno Nanocomposite

NiCl$_2$ (0.05 M) containing *A. indica* extract (5 mL from 15 g leaves) were stirred continuously on a magnetic stirrer (1 h; 50°C) followed by dropwise addition of NaOH (saturated solution, 15–20 mL) till the pH of the solution becomes neutral. Abrupt precipitation of colorless Ni(OH)$_2$ occurred, and the solution was filtered and dried at 600°C for 4 h to get NiO (Rani et al., 2021). Similarly, ZnO nanoparticles were synthesized by their respective salt of zinc chloride (0.05) in a 100 mL solution (0.1 M ZnCl$_2$). After stirring, 5 mL of *A. indica* extract was added with continuous stirring for 30 minutes at room temperature, followed by drop-wise addition of 0.1 M NaOH solution till the neutral pH. Shiny white particles obtained were washed with deionized water several times, then muffled 200°C for 2 h and finally stored for further use (Yadav et al., 2022).

0.05 M NiCl$_2$ (100 mL) solution containing *A. indica* extract (5 mL) were continuously stirred (1 h; 50°C) followed by dropwise addition of ZnCl$_2$ (0.1 M, 100 mL). After this, add a 50 mL solution of 20% acetic acid by volume in 0.5 g chitosan into the beaker. Later then, after one-hour stirring, saturated solution of NaOH (50 mL) solution was dropwise added. Spruce blue colored Chitosan- NiO@ZnO nanocomposite (8.96 g) was collected (Fig. 1a).

The E-factor of synthesized nanoparticles was calculated by Eq. (1):

\[ \text{E-factor} = \frac{\text{Amount of waste}}{\text{Amount of product}} \]  

which is briefly explained in the supporting file S1 (Eckelman et al., 2008).

2.4 Calculation Of Photocatalytic Activity

Using UV-Vis NIR Spectrophotometer instrument (LAMBDA 750: Perkin Elmer; USA), the absorbance of samples was measured with quartz cuvette (medium scan-rate, baseline correction, and set data point interval of 1 nm). Stock solution of pesticides was simulated with methanol and was degraded with Chitosan-NiO@ZnO nanocomposite. Different sets with variable concentrations were used for the calibration curve. The highest peak area was observed at 2 mg L$^{-1}$ for MLT and 10 mg L$^{-1}$ for γ-HCH (used as a standard). The removal efficiency (%) of pesticides was calculated under daylight or dark irradiation as:

\[ \frac{C_i - C_t}{C_t} \times 100 \]  

(2)
Where the initial concentration (before source irradiation: Ci) and the final concentration (after degradation: Ct). A blank solution (10 mL) without any catalyst concentration was also made to understand the function of the catalyst. Different experimental parameters such as pollutant concentration (2-20 mg L\(^{-1}\) and 10-50 mg L\(^{-1}\)), catalyst amount (10-30 mg), and pH (5-9) were studied. The pH level was maintained using citrate buffer (0.1 M sodium citrate + 0.1M citric acid) and sodium metaboarate (0.1 M sodium hydroxide + 0.025M borax) buffer. Further, the acidic and basic pH were adjusted by adding sulphuric acid and ammonia solutions. Degradation studies were observed under solar irradiation having an Intensity; of 453 ± 182 W m\(^{-2}\) (151–813) and temperature; of 40.1 ± 1.7°C (range: 37.0–44.0) from 10:30 am to 3:30 pm at University campus, Rajasthan in April. Scavenger analysis was performed by adding 2 mL isopropanol, triethanolamine, and benzoquinone into the vial containing optimized parameters. All tests were conducted with triplicates, and the consistent results were obtained. The standard deviation was analyzed from the MS Excel program.

### 3. Results And Discussion

#### 3.1 Structural analysis

Powder X-ray diffraction (PXRD) analysis was performed to calculate the crystallinity, strain, composition, crystallite size, and crystal structure of nanomaterials. The nanocomposite of Chitosan-NiO@ZnO showed semi-crystalline behavior (broad peaks) due to polymer coating. No extra peaks or changes were observed in PXRD spectra on chitosan coating because the polymer does not alter the plane's position (Fig. 1b). The peak at different 2\(\theta\) positions were 32.15°, 34.81°, 36.71°, 47.99°, 57.13°, 63.31°, and 68.56° showing respective planes at (100), (002), (101), (111), (200), (102) and (110) confirming the purity of the sample. Maximum relative intensity was observed at 36.71° with d-spacing 3.2 A°. The broad peaks of NiO were observed at 18.20°, 33.06°, 38.77°, 51.80°, 59.91°, 62.70°, and 72.59° positions with the respective plane (002), (111), (022), (211), (113), (222) and (310) with a good match with ICSD card No. (98-064-6096). The broadness in peaks is due to oxygen vacancies and lattice disorder (Rani et al., 2021). The crystal system has face-centered cubical structure (\(a = b = 2.98\) A° c = 5.16 A° and \(\alpha = \beta = 90^\circ\) \(\gamma = 120^\circ\)) with an Fm-3m space group (Rani et al., 2021). Maximum relative intensity was observed at 33.06 positions having (111) miller indices and d-spacing 2.097A°. Along with this, ZnO nanomaterials showed variable planes (100), (002), (101), (102), (112), and (201) to their respective 2\(\theta\) position of 31.66°, 34.32°, 36.32°, 56.45°, 59.71° and 62.90° with a perfect match with ICSD card No. (01-079-2205). Tetragonal wurtzite crystal structure with \(a = b = 4.3\) A°, \(c = 9.9\) A° and \(\alpha = \beta = 90^\circ\), \(\gamma = 120^\circ\) was obtained with the P6-3mc space group (Yadav et al., 2022). The calculated crystallite size of Chitosan-NiO@ZnO (17.5 nm) followed by NiO (77.24 nm) and ZnO (96.2 nm) using Debye–Scherer’s equation (detailed in supporting information):–

\[
CrystalliteSize, D = \frac{k\lambda}{\beta\cos\theta} - - - - - - (3)
\]

Where, \(D\) is the size of crystallite; \(\lambda\) is the wavelength of CuK\(\alpha\); \(\beta\) is the half width of the peak and \(\theta\) is the Bragg’s angle.

The lattice strain of nanomaterials was calculated using Eq. 3
\[
Lattice Strain, \epsilon = \frac{\beta_{hkl}}{4 \tan \theta} - \cdots - \cdots \quad (4)
\]

\(\beta_{hkl}\) is the full width at half maximum of peaks (radian) and \(\theta\) is diffraction angle.

The dislocation density of nanomaterials was calculated using Eq. 5

\[
Dislocation\ density, \delta = \frac{1}{D^2} - \cdots - \cdots \quad (5)
\]

Where, \(D\) is the crystallite size.

The values of crystallinity parameters (lattice strain and dislocation density) were decreased upon coupling \(\text{ZnO}\) (0.32%; 0.18* 10^{-3}), \(\text{NiO}\) (0.18%; 0.16* 10^{-3}), and \(\text{Chitosan-NiO@ZnO}\) (0.11%, 3.2*10^{-3}), indicating the enhanced amorphous behavior and doping. These factors affect the structural defects (Thamri et al., 2017) which showed maximum loss of electrons from vacancies that occurred in chitosan-NiO@ZnO (Bulcha et al., 2021). All these parameters shifted the peaks towards a lower angle. The difference in crystallite size, lattice strain, and dislocation density showed the doping of parent materials in the nanocomposite. Both ZnO and NiO peaks can be found in the composites, indicating the ZnO-NiO nanocomposite was generated through robust interfacial interactions. This may be due to the existence of a constant strain (tension) that shifts the peaks and a non-uniform strain (compression) that broadens the peaks indicating structural change brought on by the incorporation of NiO into ZnO (Bulcha et al., 2021).

### 3.2 Spectral Analysis

Various biomolecules present in nanomaterials synthesized by plant extract were analyzed by FT-IR spectroscopy. FT-IR analysis was within 400−4000 cm\(^{-1}\), and pellets were mixed with a small amount of nanoparticles with KBr. NiO nanoparticles showed stretching frequencies at 3445 cm\(^{-1}\), 1619 cm\(^{-1}\), 1379 cm\(^{-1}\), and 581 cm\(^{-1}\) representing OH stretching (due to water molecules), H-O-H bending, Ni-O-H, and Ni-O vibrations, respectively. In ZnO spectra, a broad peak was observed at 3434 cm\(^{-1}\) due to hydroxyl stretching because of surface acidity. Extra peaks at 1635 cm\(^{-1}\), 1543 cm\(^{-1}\), and 1436 cm\(^{-1}\) were due to bending vibrations in the H-O-H bond, C-C, and C = C stretching. These peaks might be due to the presence of different kinds of insoluble biomolecules in \textit{A. indica} extract (Yadav et al., 2022; Devaraj et al., 2013). In Chitosan-NiO@ZnO nanocomposite, an OH stretching segment (a tiny peak) was observed at 3642 cm\(^{-1}\). Broad N-H stretching and bending vibrations were observed at 3451 cm\(^{-1}\), and 1070 cm\(^{-1}\) due to chitosan polymer, and wagging vibration of NH\(_2\) was observed at 1555 cm\(^{-1}\). Phytochemicals of plant extract showed sharp peak segments of C-N, C-C at 2177 cm\(^{-1}\) and 1438 cm\(^{-1}\). New peaks were indicated at 698 cm\(^{-1}\) and 448 cm\(^{-1}\) of Ni-N and Zn-N bonds, respectively, demonstrating that the chitosan overlapping on NiO@ZnO and \textit{H-bonding} prevents leaching of metal ions (Fig. 1c). These observations and peak pattern were in accordance to the similar reports available (Ramos-Delgado et al., 2013).

### 3.3 Morphological Study
Scanning electron microscopic analysis of synthesized nanomaterials showed formation of uniformly distributed nanoflowers of ZnO with particle size of ~ 100 nm. NiO was observed spherical shaped nanomaterials with a particle size of ~ 100 nm. However, the composite of NiO@ZnO with chitosan showed particles were embedded in the chitosan pores (Fig. 2 (i)). Energy dispersive spectroscopy was also performed, showing the elemental composition of Zn (48%), Ni (23%), O (13%), N (12%), and C (4%), respectively. Thus, these results confirmed that the chitosan merged around metal oxides moiety.

The internal morphology and crystallinity of synthesized nanoparticles were revealed from TEM analysis. The coming out of opaque concentric dots in circular shadow of selected area electron diffraction data of the Chitosan-NiO@ZnO nano-framework confirms its semi-crystalline behavior (Fig. 2 (ii)). Calculated size histograms of synthesized nanoparticles with J image software were Chitosan-NiO@ZnO (50_70 nm), ZnO (70_125 nm), and NiO (100_150 nm), which showed a good match with the size obtained from SEM analysis (Figure S2). The morphological variation is due to the polarity, molecular structure, and size of the alcohols, which significantly influence the processes of aggregation, crystal growth, pre-nucleation, and nucleation.

### 3.4 Elemental And Surface Analysis

XPS is a potential technique used to confirm the valence state and composition of the synthesized product because it can easily detect and distinguish the electron lines (Appu et al., 2021). An Al Kα (1486.6 eV) radiation source with a 0.8 eV resolution power was used to study the XPS spectra. XPS spectra confirmed the interaction between metal oxide nanoparticles and chitosan and identified the adsorption sites. The XPS peak of Chitosan-NiO@ZnO photocatalyst at 398 eV is attributed to the amino group of chitosan that ensures the contribution of protonated amine, which is involved in hydrogen bond (NH-O) (Appu et al., 2021; Unsoy et al., 2012). The spectral analysis was conducted by CASA-XPS software. Likewise, the O1s spectrum showed binding energies at 531 eV and 529 eV of C-O and M-O (M = Zn/Ni), respectively (AbuTalib et al., 2021). Two deconvoluted carbon peaks with binding energies at 287.2 eV (H-NH$_2$) and 284 eV (C-NH$_2$) were observed. The Zn 2p spectra of ZnO is split into two major photoelectron component, 1021 eV and 1044 eV, attributed to Zn 2p 3/2 and Zn 2p ½, respectively. However, the observed spin orbit splitting of Zn 2p is about 23 eV, which is consistent with the corresponding value of pure ZnO nanofillers, indicating a normal state of Zn$^{2+}$ in the ZnO. The binding energy of Ni 2p spectra was calculated as 20 eV, i.e., Ni 2p 3/2 was observed at 853 eV, and its satellite function at 860 eV and Ni 2p ½ showed a broad spectrum at 873 eV. Since the Ni$^{2+}$ ion's electronegativity was roughly 1.91, 0.26 more than Zn$^{2+}$ ions, the Ni$^{2+}$ ion's screening impact on electrons would be greater than Zn$^{2+}$s. The Ni-O-Zn bond and chelation between amino groups of chitosan and metals (NH$_2$-M), respectively, are attributed to the shifted and new peaks in the XPS spectrum (AbuTalib et al., 2021) (Fig. 3a). From the XPS spectrum, it was calculated that the atomic percentage of Zn, Ni, O, N, and C is 43.44%, 27.8%, 15.54%, 9.83%, 1.94%, respectively.

The gas sorption analysis was performed to calculate the surface properties of synthesized nanocomposites. The study summarizes the surface areas, pore size, and pore volume of all synthesized nanomaterials calculated by the N$_2$ adsorption/ desorption isotherm method. The mesoporous structure of nanocomposite with maximum surface area (73 m$^2$g$^{-1}$) followed by NiO@ZnO (68 m$^2$g$^{-1}$), ZnO (16 m$^2$g$^{-1}$), and NiO (15 m$^2$g$^{-1}$) was confirmed by type IV isotherm and H3 hysteresis ring with a relative pressure = 0.05–0.25 (Fig. 3b).
Furthermore, the adsorption isotherm was calculated by the BJH model (Yadav et al., 2022). Mesoporous morphology of synthesized nanoparticles was confirmed by the BJH model and the average pore size followed the order of CS/NiO@ZnO (8.36 nm) > NiO@ZnO (3.51 nm) > ZnO (3.059 nm) and NiO (2.98) which was reliable to the particle size observed from TEM analysis. The enhancement of results is due to volume buffering nature of chitosan. Furthermore, it also prevents the aggregation and clumping of nanoparticles (Sabir et al., 2022). Second, large total surface area obtained by chitosan provided additional surface to the nanocomposite NiO@ZnO (Meenu et al., 2022). Greater surface area means more light harvesting on the surface leading high photocatalytic performance.

3.5 Uv-vis Spectroscopy For Band Gap Calculation

The bandgap of synthesized nanoparticles Chitosan-NiO@ZnO, NiO@ZnO and ZnO, and NiO was determined by absorption spectra between 200 nm and 750 nm. The electronic transition occurred from valence band to conduction band. Tauc equation ((αhv)^2 vs. hv) calculated band gap energy of Chitosan-NiO@ZnO, NiO@ZnO, ZnO, and NiO was found to be 2.3 eV, 2.8 eV, 3.4 eV and, 3.6 eV respectively (Figure S3) (Meenu et al., 2022). This variation could be attributed to the appearance of energy levels in the vicinity of conduction band and valence band (Thamri et al., 2017). Chitosan doping caused shifts in the absorption edge value to a lower wavelength, indicating a blue shift in bandgap energy from 2.8 to 2.3 eV and can be attributed to the quantum confinement effects and loss of crystalline order (Vasseghian et al., 2022). Therefore, quantum confinement and small crystallite size are the two factors responsible for variation in band gap energy (Al-Ghamdi et al., 2022).

3.6 Photocatalytic Performance Studies

The photocatalytic performances of synthesized nanoparticles were monitored at different concentrations of respective pesticides under sunlight illumination. Before irradiation, the adsorption was also carried out under dark conditions (Moghni et al., 2022). Furthermore, for measurement of efficiency, all the optimized parameters (pollutant concentration, catalyst dose, pH, and temperature) were kept constant except the performing one. The wide range of attention was selected based on their environmental concern and the UV spectrophotometer’s limit of detection or linear absorbance.

The concentration of pesticides in water is one of the most promising parameters to investigate photocatalytic performance. Different concentrations (2-10 mgL^{-1}) of MLT and (10-50 mg L^{-1}) of γ-HCH were studied to evaluate photocatalytic performance (Figure S4). With an increase in the concentration of targeted pesticides, limited interaction was observed on the surface of catalyst active sites, leading to deficiency of hydroxyl radicals and reduction in the degradation rate (Yadav et al., 2022; Majumdar et al., 2022). Escalating the initial concentration decreases the path length of the photon that falls on the surface of the photo-active catalyst (the Beer-lambert law) and reduces the excitation of electrons from lower energy band to higher energy band. The better degradation was observed at 2 mg L^{-1} and 10 mg L^{-1} of MLT and γ-HCH.

In the photocatalytic process, the dosage of photocatalyst (Chitosan-NiO@ZnO) influences degradation efficiency. The amount of catalyst varied from 10 to 30 mg with a constant concentration of pesticides (Figure
Initially, it was observed that with an increase in the amount of catalyst, the degradation efficiency increases, but after 20 mg, it started slightly decreasing (Hunge et al., 2022). It is possible that the availability of more active sites enhanced redox reaction, and irradiation generated charge carriers that helped the degradation of targeted pesticides (Rani et al., 2021; Al-Musawi et al., 2021; Balarak et al., 2020). Moreover, beyond 20 mg catalyst dose the efficiency has been decreased due to turbidity in the solution, aggregation, and screening effect, which reduces the light absorption capacity of the catalyst and slows down the degradation rate (Reza et al., 2017).

Solution pH is one of the influential factors in heterogeneous photocatalysis by creating surface particle charge and catalyst agglomeration. It was observed that degradation decreases in acidic and basic mediums whereas highest degradation observed at natural pH due to the measured pH\textsubscript{pzc} \approx 7.2 for photocatalyst. Under acidic condition the amine group of chitosan-NiO@ZnO moiety get protonated (Chitosan: NH\textsuperscript{3+}). Moreover, it starts repelling into the solution and reduces the associated interaction between chains (Ramanery et al., 2013; Miri et al., 2022). Under basic conditions, the repulsive force between chain molecules decreases and favors H-bonding and hydrophobic interaction (Miri et al., 2022). Both the conditions resulted in a reduction in photocatalytic activity at these pH ranges. The surface charge was calculated by zeta potential at neutral pH because of the estimated pH\textsubscript{pzc} value (~ 7.2). Chitosan-NiO@ZnO nanocomposite showed the highest value of zeta potential (29 mV), followed by NiO@ZnO (19 mV), ZnO (11 mV), and NiO (10 mV) (Figure S5).

### 3.7 Irradiation Source

The photodegradation of targeted pesticides from an aqueous solution showed the photocatalytic activity of Chitosan-NiO@ZnO. It was studied under visible and dark conditions with initial pollutant concentrations of 2 mg L\textsuperscript{-1} and 10 mg L\textsuperscript{-1} of MLT and γ- HCH respectively, for 5 h exposure. Maximum efficiency (≥ 94%) was observed under a visible light irradiation source due to the generation of photoinduced charge carriers (Rout et al., 2021) (Fig. 4a). They show that there is no appreciable difference between the absorption before and after stirring in the dark, suggesting that the dye degradation process starts right away after exposure to light. In photocatalytic mechanism Π-Π stacking interaction for MLT and simple adsorption for lindane was found to be predominant (Park et al., 2019). The lower photoluminescence intensity of photocatalyst showed that photoexcited e\textsuperscript{-}/h\textsuperscript{+} pairs have higher separation and lower recombination rate (Fig. 4b). Additionally, chitosan behaves as electron sinks and restricts the charge carrier's recombination by trapping the delocalized electrons (Park et al., 2019).

Charge migration between two semiconductors can be predicted by a number of charge migration theories, including type II heterojunctions and direct Z-scheme mechanisms (Ghosh et al., 2020; Manik et al., 2020). The type-II heterojunction mechanism, which exhibits a double charge-transfer channel, is a frequently reported mechanism for photocatalytic degradation. Although type-II heterojunction photocatalysts make it easier to separate photogenerated electron-hole pairs, they have some drawbacks from kinetic and thermodynamic standpoints. The constraints of traditional type-II heterojunction photocatalysts have recently been overcome by the revolutionary S-scheme (step-scheme) heterojunction of semiconductors (Elumalai and Velmurugan, 2015; Bhuyan et al., 2015). ZnO has a lower conduction band maximum (CBM) and a higher valence band minimum (VBM) than NiO and serves as an oxidation photocatalyst. NiO serves as a reduction photocatalyst.
because of its significantly higher CBM and lower VBM. Therefore, the compatibility of ZnO and NiO in terms of bandgap energies enables charge migration through the step S-scheme mechanism, which involves the removal of superfluous electrons and holes with low potential and the preservation of charge carriers with high potential for effective redox reactions.

Furthermore, the more free radicals that reacted with the pesticides on the surface of the photocatalyst, the more robust photocatalytic activity. Whereas, only adsorption of targeted polluted molecules was observed under dark conditions. The following equations could explain a plausible photodegradation mechanism:

\[
\textit{Chitosan - NiO}@\text{ZnO} \rightarrow e^- + h^+ \quad \text{................. \(6\)}
\]

\[
h^+ + \text{Pesticides} \rightarrow \text{Degradation Products} \quad \text{................. \(7\)}
\]

\[
h^+ + H_2O \rightarrow H^+ + OH^- \quad \text{................. \(8\)}
\]

\[
OH^- + \text{Pesticides} \rightarrow \text{Degradation Products} \quad \text{................. \(9\)}
\]

\[
e^- + O_2 \rightarrow \cdot O_2^- \quad \text{................. \(10\)}
\]

\[
e^- + \text{Pesticides} \rightarrow \text{Degradation Product} \quad \text{................. \(11\)}
\]

\[
O_2^- + H_2O \rightarrow OH^- + OH^- + \frac{1}{2}O_2 \quad \text{................. \(12\)}
\]

\[
O_2^- + \text{Pesticides} \rightarrow \text{Degradation Products} \quad \text{................. \(13\)}
\]

Since in photocatalytic mechanism, ZnO is an n-type semiconductor and can easily donate electrons, whereas NiO is a p-type semiconductor. Their coupling caused a decrease in the n-type donor carrier’s concentration and increased resistivity with suppressing charge recombination capability (Fig. 4c). H₂O/O₂ molecules get interact with the generated e⁻/h⁺ charge carriers to create the hydroxyl (OH⁻), hydroperoxyl (HO₂⁻), and superoxide (O₂⁻) radical species and degraded or reduced pollutant into non-toxic products as confirmed by scavenger analysis (Taheran et al., 2016). Figures (4d) shows that the generated charge species have negative impact on reduction/ degradation of pollutant. The surface photoactive capability of photocatalyst has been enhanced with being less recombination of charge carriers.

3. 8. Kinetics

The photodegradation and kinetics of selected organic contaminants were studied at the optimized pollutant concentration, pH of ~ 7, and 20 mg catalytic dose. Selected pesticides showed measured decline in
degradation, and followed 1\textsuperscript{st}-order kinetics. With time, the photocatalytic activity of electrons (Chitosan-NiO@ZnO) enhanced under daylight irradiation. Enormous generated hydroxide and superoxide radicals may oxidize targeted pesticides with instantaneous action (Rani et al., 2021). Maximum degradation of MLT (97\%) and γ-HCH (94\%) were observed with the photocatalyst within 5 h exposure to daylight. High degradation of MLT is due to π-π stacking interactions. Furthermore, the rate constant and half-life value of synthesized nanoparticles were summarized in Table S2. The highest k-value and the lowest t_{1/2} showed faster degradation of targeted pesticides with the innovative nanocomposite. Initially, pesticides get absorbed over the surface of nanocomposite as justified with different adsorption isotherms. Langmuir isotherm adsorption was pleasantly followed in the photocatalysis process of pesticides and merited with the highest R\textsuperscript{2} values (Fig. 5i). Besides this, Freundlich (log X_{e} V/s log C_{e}) and D-RK Slips (InX_{e} v/s ε\textsuperscript{2}) models were not accepted statistically. In contrast, the Temkin model was also not acceptable due to the negative ln C_{e} values (Figure S6).

The obtained X_{m} (the maximum sorption capacity for pollutant; mg g\textsuperscript{-1}), K_{L} (dm\textsuperscript{3} mol\textsuperscript{-1}) and R\textsuperscript{2} standards for MLT and γ-HCH were found in the following array: Chitosan-NiO@ZnO (14.51; 0.925; 0.94) > NiO@ZnO (11.15; 1.83; 0.95) > ZnO (7.42; 2.66; 0.93) and NiO (8.22; 2.89; 0.93) and Chitosan-NiO@ZnO (20.73; 0.21; 0.97) > NiO@ZnO (18.54; 0.75; 0.99) > ZnO (6.16; 6.8; 0.97) and NiO (9.22; 2.9; 0.98) respectively. The highest removal of MLT and γ-HCH was observed with the nanocomposite rather than with native nanoparticles.

### 3.9 Lc-ms Analysis For Mlt And γ-hch

LC-MS Spectrometer Model Xevo G2-S Q Tof (Waters, USA) was used to analyze the degradation profile of pesticide. The degraded metabolites and byproducts of MLT using Chitosan-NiO@ZnO nanocomposite were recognized with optimized pesticide concentration; 20 mg catalyst dose and at neutral pH. The observed mass spectrum was operated with the reflection of electrospray spectrum number of basic sites on a molecule that can be protonated at low pH. The mass spectra were identified through the in-built NIST library and literature survey.

According to the reports, the P=S bond of an organophosphate (Malathion: m/z: 330) is the main target of the OH radical's attack, which results in the production of a P=O bond by an oxidative desulfurization reaction (Vasseghian et al., 2022). Resulted diethyl-2-(di-methoxyphosphoryl)thio)succinate gives eliminated product diethyl maleate compound with ethane (1:1), and on hydroxyl attack it gives di-ethyl-2-hydroxysuccinate (He et al., 2014). The reduction of diethyl maleate generates diethyl succinate which on dealkylation produces succinic acid (Yang et al., 2009). This succinic acid is also produced on hydrolysis of di-ethyl-2-hydroxysuccinate, and degraded into smaller and safer mineralized products (CO\textsubscript{2} and H\textsubscript{2}O) as well (Isgoren et al., 2021) (Fig. 5ii (a)).

Under solar irradiation, lindane molecule (m/z: 289.86) shows dechlorination and produced chlorobenzene via 3,4,5,6- tetrachlorocyclohex-1-ene and 5,6- dichlorocyclohex-1,3-diene (Gad-Allah et al., 2011; Naqvi et al., 2018). On hydrolysis of chlorobenzene gives phenol which on hydroxyl attack produces pyrocatechol (Rani et al., 2018). The pyrocatechol get mineralized into safer small products (Fig. 5ii (b)).

### 3.10. Reusability And Leaching Analysis Of Photocatalyst
The loss of catalyst and leaching of metals during the reaction may affect the reusability of metal oxide nanostructure and reduce its photocatalytic activity (Rani et al., 2021). Reusability of synthesized nanocomposite was checked after reaction studies (photocatalyst washed with acetone and de-ionized water) for up to ten cycles at the optimized initial concentration of 2 mg L\(^{-1}\) and 10 mg L\(^{-1}\) of MLT and \(\gamma\)-HCH. The Chitosan-NiO@ZnO nanocomposite material (10 g) maintains its properties with the relative removal efficiency being reduced slightly from 100 to 95% after cycle 10 (Figure. 6a), presumably due to the loss of weight during recovery and the blocking of some active sites after several applications. This was supported by P-XRD data of the photocatalyst (1st and 10th cycle) showing no significant change in a model (Figure. 6b). The strong interaction of metal oxides with chitosan (H-bonding) prevents the leaching of ions (Fig. 9c). UV absorbance spectrum shows only the pollutant peak, which means metals (Ni and Zn) present in the nanocomposites no leached out.

### 3.11. Implications

In comparison with the literature survey, different synthesis approaches, metal catalyst, and irradiation source (UV light, microwave-assisted) were used to fabricate nanocatalyst Table 1 shows many studies on the basis of semiconductor materials or their coupled nanomaterials. In general, removal of targeted pesticides makes the process expensive and different nanocatalysts may have limited applications (e.g. UV irradiation, under ultrasonic conditions, visible light irradiation). It addition, various degradation types (Physical, Chemical and Microbiological) have been were used for the removal of pharmaceuticals.
<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Nanocomposite</th>
<th>Characterization</th>
<th>Summery</th>
<th>Mechanism</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-HCH</td>
<td>Zn@ZnO (Pulsed laser ablation)</td>
<td>XRD, SEM, TEM, UV-Vis, PL</td>
<td>Follows pseudo first order kinetics; k: 0.0352 min$^{-1}$</td>
<td>UV irradiation using Xe lamp; 40 min.</td>
<td>(Jung et al., 2018)</td>
</tr>
<tr>
<td>Malathion</td>
<td>Zn$_3$V$_2$O$_8$/g C$_3$N$_4$</td>
<td>PXRD, SEM, TEM, UV-Vis</td>
<td>10 mg L$^{-1}$ pesticide concentration; pH: 6; catalyst dose: 0.35 g L$^{-1}$</td>
<td>90% degradation under visible light irradiation (180 mW cm$^{-2}$)</td>
<td>(Thakur et al., 2022)</td>
</tr>
<tr>
<td>Malathion</td>
<td>US/UV/Fe$^{2+}$/H$_2$O$_2$:SPF</td>
<td>GC-MS analysis</td>
<td>20 mg L$^{-1}$ pollutant concentration; pH: 3</td>
<td>99% degradation; ultra sonic irradiation</td>
<td>(Vasheghian et al., 2022)</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>Ag@ZnO (Pulsed laser ablation)</td>
<td>XRD, UV-Vis, PL, SEM, TEM,</td>
<td>Follows pseudo first order kinetics; k: 0.035 min$^{-1}$</td>
<td>UV irradiation using Xe lamp; 40 min.</td>
<td>(Jung et al., 2018)</td>
</tr>
<tr>
<td>Malathion</td>
<td>ZnO-SiO$_2$@Fe$_3$O$_4$</td>
<td>FE-SEM, EDS, TEM, XRD, XPS, PL, BET, UV-Vis-DRS, pH$_{pzc}$</td>
<td>Neutral pH; 0.3 g L$^{-1}$ catalyst dose; 20 mg L$^{-1}$ pollutant concentration</td>
<td>80% degradation; ultraviolet irradiation</td>
<td>(Singh et al., 2013)</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>Hydrogen peroxide assisted</td>
<td>-</td>
<td>K: 9.7*10$^{-3}$ s$^{-1}$; pH: 7; [H$_2$O$_2$]: 1 mM; initial conc: 0.26µM</td>
<td>90% degradation in 4 min.</td>
<td>(Nienow et al., 2008)</td>
</tr>
<tr>
<td>γ-HCH</td>
<td>Al(OH)$_3$</td>
<td>XRD, FT-IR, SEM, BET, Zeta potential</td>
<td>25 mg mL$^{-1}$ catalyst dose; 60 min. pH: 6</td>
<td>93.66% degradation</td>
<td>(Nguyen et al., 2020)</td>
</tr>
<tr>
<td>Malathion</td>
<td>Prussian blue analog (FeHCF)</td>
<td>XRD, BET, UV-Vis, FE-SEM, TEM, Zeta potential; GC-MS analysis</td>
<td>50 mg L$^{-1}$ catalyst dose; 25 mg catalyst dose; neutral pH; $t_{1/2}$ -2.3 h</td>
<td>95% degradation under solar irradiation</td>
<td>(Rani et al., 2018)</td>
</tr>
<tr>
<td>Malathion</td>
<td>Bi$_{1-x}$Ce$_x$FeO$_3$</td>
<td>XRD, FE-SEM, EDS, BET, UV-Vis, Impedance analyzer, VSM</td>
<td>-</td>
<td>Visible irradiation; 64% degradation</td>
<td>(Kumar et al., 2018)</td>
</tr>
</tbody>
</table>
In the present study, the innovative Chitosan-wrapped NiO@ZnO photocatalyst has been synthesized by leave extract that are widely available and the method that are relatively simple and eco- friendly method that other conventional methods (Co-precipitation, spray pyrolysis, soft chemical root method, electro spinning and hydrothermal). The synthesized nanocomposite is 10 times reusable and having large scale utilization. All the reaction parameters were observed under natural daylight, making it a simple and efficient favorable process. Results of this indicate that the innovative ternary nanocomposite has some advantageous over binary metal oxides, such as enhanced visible light adsorption, electronic properties, and charge separation. Due to its hydrophobic nature and many functional groups, chitosan exhibits a range of properties, including non-toxicity and biodegradability. By forming hydrogen bonds with nanoparticles, the NH$_2$ and OH groups of chitosan produce nanocomposites with unique characteristics. Chitosan have chelating properties allow interactions with doped metal oxides to affect the removal of drugs. No literature has been provided for the synthesis of Chitosan-NiO@ZnO nanocomposite for degradation of endocrine disrupting pesticides.

### 4. Conclusions

Chitosan-wrapped NiO@ZnO photocatalyst was synthesized via leaves extract of *A. indica* species with a cheap, simple, and practical approach. Shifting peaks in PXRD and new vibrations (Ni-N and Zn-N) in FT-IR spectra showed the bonding between NiO@ZnO and chitosan. The morphology of spherical shaped NiO and flake shaped ZnO adsorbed on chitosan surface showed by FE-SEM analysis and HR-TEM analysis revealed the particles size of the photocatalyst ranging from 50 to 70 nm. The high elemental composition of Zn in XPS spectra confirmed that NiO behaves as the dopant in NiO@ZnO nanocomposite. Under solar light exposure, degradation of pesticides followed by the 1st-order kinetics and the sorption behavior can be fitted with the Langmuir adsorption model. The chitosan-NiO@ZnO nanocatalysts dominated over the parent NiO and ZnO particles, depending on the surface charge (29 mV), area (73 m$^2$g$^{-1}$), and bandgap (2.3eV) of the nanocomposite. Chitosan-NiO@ZnO nanocomposite may enhance the optical properties and avoid the possible combination possibilities of generated charge carriers under solar light irradiation. Furthermore, they react with H$_2$O and O$_2$ molecule and produce OH, h$^+$, and O$_2^-$ which degraded the targeted pesticides. Metabolites of pesticides were examined by LC-MS analysis the photocatalytic degradation. The reusability of the nanocatalysts (10 g) was studied up to the 10th cycle. All these results showed the innovative photocatalysts may warrant a green technology with industrial applicability.

### Declarations
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Declaration of Competing Interest

“The authors have no relevant financial or non-financial interests to disclose.”

Author Contributions

Jyoti Yadav: Data curation, Formatting, Data curation, Software, Validation.

Manviri Rani: investigation, writing - original draft,.

Uma Shanker: Supervision, Writing – review & editing,

Tian Zhang: quality assurance/ quality control (QA/QC), writing_ review & editing.

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-Consent to Participate: All authors have given their consent to participate
-Consent to Publish: All authors have given their consent to publish
-Availability of data and materials: The data will be made available on genuine request

References


Figures

(a) Schematic representation of synthesis of Chitosan-NiO@ZnO nanocomposite using A.indica extract; (b) PXRD spectrum and; (c) FT-IR analysis of synthesized nanoparticles
Figure 2

(i) FE-SEM image and EDX spectra of (a) NiO (b) ZnO (c) NiO@ZnO (d) Chitosan-NiO@ZnO nanocomposites; (ii) (a-c) NiO; (d-f) ZnO; (g-i) NiO@ZnO (j-l) Chitosan-NiO@ZnO describes TEM image, HR- fringes and SAED pattern.
Figure 3

(a) XPS survey scan and elemental composition of CS-NiO@ZnO nanocomposite; (b) Surface area and pore width analysis of (i) CS-NiO@ZnO and (ii) NiO@ZnO.

Note: Data derived from N₂-sorption isotherms. Taking all error sources (measurement setup, fit, etc.) into account, the relative error of the values given is \( \leq 5\% \).

Figure 4
(a) Role of irradiation source; (b) Photoluminescence spectra with relative intensity; (c) photo catalytic mechanism of nanocomposite; (d) Effect of scavengers on photocatalytic activity.

**Figure 5**

(i) Reaction kinetics and Langmuir adsorption model for degradation of pollutants i.e. (a and c) MLT; and (b and d) γ-HCH over photo catalysts respectively and (ii) Proposed degradation pathway analyzed from LC-MS analysis of (a) MLT; and (b) γ-HCH.

*Note: Triplicate experiments (n=3) were evaluated for estimation of error bar (error 0.007 to 0.009).
Figure 6

Reusability analysis of Chitosan-NiO@ZnO nanocomposite up to 10\textsuperscript{th} cycles supported; (b) P-XRD data; and (c) Amount of catalyst loss (10 mg after 10\textsuperscript{th} cycle).

Supplementary Files

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