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Investigating the Role of Charge Transfer in Eco-Friendly Coffee Waste-Based Carbon Dots Coupled to ZnBi-Layered Double Hydroxide Heterojunction for Visible-Light Catalytic Activity

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Abstract

The current research focuses on the combined impacts of CDs derived from coffee waste incorporated with ZnBi-LDH structures for the photocatalytic degradation of organic contaminants using visible light. The synthesised CDs going through a hydrothermal process displayed fairly good optical properties and the surface modifications provided a conducive environment to charge transfer and good light absorption within the visible light region. From structural characterizations such as XRD, TEM, and FTIR analyses, it was evidenced that CDs were well incorporated into ZnBi-LDH, and the photocatalytic activity was significantly enhanced due to increased surface area and interfacial charge transfer



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efficiency. UV-Visible study confirmed the reduction of band gap and eradication of electron-hole recombination in CDs(2%)-ZnBi-LDH hybrid with an excellent degradation capability of 91% for 2,4-dichlorophenoxyacetic acid under visible light. Additional mechanistic studies – scavenger experiments – revealed that photogenerated holes were the most reactive species, with SUP and •OH radicals contribute to the overall process. Stability tests confirmed the possibility of multiple reuse, with the efficiency rate being 94.5% after four runs. These discoveries justify the role of coffee waste valorization in the development of efficient photocatalytic materials for environmental remediation applications, and open up a new avenue in the development of green and sustainable technologies for pollutant degradation.

Keywords: coffee waste-derived carbon dots, ZnBi-layered double hydroxide, visible-light photocatalysis, charge transfer, pollutant degradation, environmental remediation.

Introduction

Contamination of water sources is another significant worldwide issue that mainly originates from the residuals of agriculture and industrial outlets. Organic pollutants are very dangerous because they include pesticides, dyes and phenolic compounds which are toxic, stable and have been widely used in agricultural and industrial activities (Cai et al., 2018; Ebrahimi et al., 2020). This is significant because approaches to degrade such pollutants into non-hazardous compounds using environmentally friendly and cost effective techniques remain a major focus in environmental chemistry.

Photocatalysis using semiconductors has recently been identified as one of the most effective solutions to these problems. Solar energy is collected by semiconductors which facilitate the photogenerated charge carriers (electrons and holes) to make redox reactions whereby pollutants undergo reduction and oxidation to be transformed to harmless products such as; CO₂ and H₂O (Shankar et al., 2006; Wei et al., 2018). Specifically, LDHs as a type of semiconductors have been active research topics for their application in photocatalysis because of their tunable bandgap, high surface area, and the ability to absorb visible light (Lee et al., 2019; Liu et al., 2021). Notably, ZnBi-based LDHs has been reported to exhibit good photocatalytic activity; nonetheless, their applications in practical photocatalysis processes are rather limited due to the high rate of photogenerated electron-hole recombination, which adversely affects the photocatalytic activity (Liu et al., 2020; Nguyen et al., 2024).

To address this issue, the latest approach has involved incorporating ZnBi-LDH with other materials, for instance carbon dots (CDs). Remarkable attention has been paid to CDs, a type of carbon-based nanomaterials with tunable optical properties that are easy to synthesize and eco-friendly (Ebrahimi et al., 2020; Nguyen et al., 2024). CDs are mostly described by their large number of surface functional groups (-OH, -COOH, -NH₂) that allow for the modification of the surface, the charge transfer, and the light absorption in the visible range (Amiri et al., 2021). CDs are well known to photocatalytically work as electron mediators in the photocatalytic systems and the studies have revealed that CDs can help in charge separation, less recombination and can also help to increase the photocatalytic activity of the semiconductor composite system, such as Wei et al., Liu et al., 2021.



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Interestingly, bio-waste coffee, which is widely available and non-toxic, has been recently established as a renewable material that can be used for the synthesis of CDs, according to the authors of Nguyen et al., 2024. Despite the fact that the use of biomass other than cases where disposal causes environmental problems, it can also be argued that the use of coffee waste to synthesize high-performance nanomaterials is a cheap technique. Hydrothermal carbonization of coffee waste results in CDs with superior optical and catalytic abilities to be suitable for integration with semiconductors (25–27).

These characteristics also show that the composites made from CD possess applicability in the improvement of photocatalytic degradation, according to earlier research. For instance, CDs-TiO₂ composite structures have attracted major attention due to their enhanced light trapping and photocatalytic activity (Liu et al., 2021). In the same way, Bi₂O₃-Bi₂WO₆, Bi₂WO₆-BiVO₄, and Bi₂O₃-BiVO₄ incorporated CDs have demonstrated improved photodegradation of pollutants under visible light owing to improved charge transfer kinetics (Amiri et al., 2021; Lee et al., 2019). Nevertheless, there is a lack of study concerning the prospect of CDs synthesised from biomass waste in combination with ZnBi-LDH with dual positive impact including waste management and water purification.

This study seeks to close this gap through synthesizing an environmentally friendly CDs-ZnBi-LDH heterojunction with coffee waste-derived CDs. As for the ZnBi-LDH-CDs composite material, the enhanced photocatalytic activity is expected because the introduction of ZnBi-LDH and CDs can optimize the phenomena such as charge separation, light absorption range, and interfacial charge transfer. To the best of our knowledge, our study is the first to investigate the involvement of charge transfer in the newly synthesized CDs-ZnBi-LDH heterojunction for visible light photocatalysis.

The objectives of this study are:

1. To synthesize and characterize coffee waste-derived CDs and their integration into ZnBi-LDH.
2. To evaluate the photocatalytic performance of the CDs-ZnBi-LDH heterojunction in degrading organic pollutants under visible light.
3. To investigate the charge transfer dynamics and photocatalytic mechanism underlying the enhanced activity of the heterojunction.

Materials and Methods

Materials

The major raw materials employed in this research were coffee waste, a sustainable biomass, and chemicals of analytical grade purchased from sigma Aldrich company. The carbon dots were produced using medium roast coffee waste as the precursor for carbon dots manufacturing. Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and bismuth nitrate pentahydrate (Bi(NO₃)₃·5H₂O) were used as precursors to prepare ZnBi-layered double hydroxides (LDH). Some of other Analytical reagents that were used in preparation of this solutions include potassium hydroxide (KOH), nitric acid (HNO₃) and sodium hydroxide (NaOH). All solutions used in this work were prepared from deionized water to minimize contamination which may have affected the synthesis or characterization results.

Synthesis of Carbon Dots (CDs)



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Carbon dots are synthesized by hydrothermal technique which is most popular in converting biomass to functional nanomaterial. First, 2.0 g of coffee waste was dissolved in 20 mL of 1.0 M KOH and the to form a homogeneous suspension. This suspension was transferred into a 50 mL Teflon lined stainless steel autoclave which was upright and heated to 180°C for 6 hours. It also helped in transforming used coffee grounds into fluorescent CDs. The autoclave containing the product was allowed to cool to room temperature, then the product was centrifuged at 15 000 rpm for 20 min to pellet large particles. In the second step the supernatant was dialysed against distilled water for further 24 hours in order to remove smaller impurities. The pure CD solution was then frozen and lyophilized to get solid CDs and these were kept in a desiccator for further use.

Fabrication of CDs-ZnBi-LDH Heterojunction

The ZnBi-LDH heterojunction was prepared through a co-precipitation method. A salt solution containing zinc and bismuth ions in a molar ratio of 3:1 was synthesised by dissolving $Zn(NO_3)_2 \cdot 6H_2O$ and $Bi(NO_3)_3 \cdot 5H_2O$ in diluted nitric acid solution containing 5% HNO_3 . A portion of this solution was then gradually mixed with 1.0 M NaOH solution under ultrasonic treatment of power 100 W. To enhance the formation of ZnBi-LDH, the pH of the suspension was kept 10 during the synthesis process. The obtained biphasic mixture was subjected to ultrasonication for 24 hours to make sure that the reaction components are well mixed. The solid was also separated by centrifugation and then washed with distilled water until all the ions were removed and finally dried at 70°C for 10 hours. The dried product was then strengthened at 450 °C for 3 hours to improve its crystallinity factor.

To incorporate the CDs into the ZnBi-LDH framework, the ZnBi-LDH was dispersed in solutions prepared with different CD concentrations (0, 1, 2, and 5 wt %). To achieve homogeneity in the inclusion of CDs into the ZnBi-LDH network, ultrasonication was conducted at 100 W for 6 hours. The obtained products were then dried in an oven at 70°C for 24 hours and these samples were regrettably named as bare ZnBi-LDH, CDs(1%)-ZnBi-LDH, CDs(2%)-ZnBi-LDH, and CDs(5%)-ZnBi-LDH respectively. These composites were stored in airtight containers in order to minimize the possibility of sample contamination.

Characterization of Materials

Scanning electron microscopy analysis, quantitative phase imaging and other morphological techniques were used to assess the characteristics of some synthesized materials. X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV X-ray diffractometer to investigate the phase compositions and the changes in structure associated with CD integration. The functional groups present in the composites were characterized using Fourier-transform infrared (FTIR) spectroscopy Thermo Fisher Nicolet Magna-560. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as well as high resolution TEM (HRTEM) images have been used to study the morphology and size distribution of the CDs and uniform dispersion on ZnBi-LDH. Susceptibility to XPS analysis was elemental composition and chemical bonding of the material Existence of specialized chemical bonding in the material was analyzed by XPS



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with the help of Thermo Fisher ESCALAB 250 Xi device. The optical properties of the materials were characterized by the UV-VIS diffuse reflectance spectroscopy and photoluminescence spectroscopy.

Photocatalytic Activity Testing

The photocatalytic activity of the synthesized composites was analyzed by the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) which is an example of an organic pollutant. A halogen lamp with 300 W, for which a cutoff filter was used (blocking UV, $\lambda > 420$ nm) was selected as the light source. The experiments were performed in a typical quartz high-pressure reactor equipped with magnetic stirring to maintain the catalyst uniform in the reaction mixture. Prior to irradiation the 2,4-D solution with a concentration of 30 is prepared whereby the suspension was 30 mg/L of 2,4-D and 1.0 g/L of the catalyst; the suspension was stirred in the dark for 60 min to allow for adsorption-desorption equilibrium. The degradation reaction was started by illuminating the suspension in visible light for 120 minutes. At fixed time intervals of 5mL, aliquots were withdrawn and the amount of the catalyst was precipitated. The reduced concentration of 2,4-D in the supernatant was assayed at a wavelength of 480 nm using a PerkinElmer Lambda XLS+ spectrophotometer.

Reusability and Stability Tests

Cycling stability was tested by performing four photocatalytic runs using the CDs(2%)-ZnBi-LDH composite, which was stirring in the reactor during the experiments. At the end of each cycle, the catalyst was centrifuged and then washed with deionized water and then dried in an oven at 100°C for 90 min and reused. To predict the lifetime performance of the photocatalyst, photocatalytic activity and stability of the catalyst in terms of structural changes were studied.

Mechanistic Studies

The scavenger experiments were used in the present study to determine the active species involved in the photocatalytic degradation of 2,4-D. For the removal of hydroxyl radicals, tert-butanol was used while p-benzoquinone was used to remove superoxide radicals and Na₂EDTA for photogenerated holes. These scavengers were added to the reaction system to investigate the degradation efficiency difference with the standard reaction to identify the dominant reactive species. Furthermore, electrochemical impedance spectroscopy (EIS) and photoluminescence (PL) analysis was also carried out to determine the charge transfer kinetics and recombination rates in the composites.

Results and Discussion

Structural and Morphological Characterization

Structural Analysis: X-ray Diffraction (XRD)

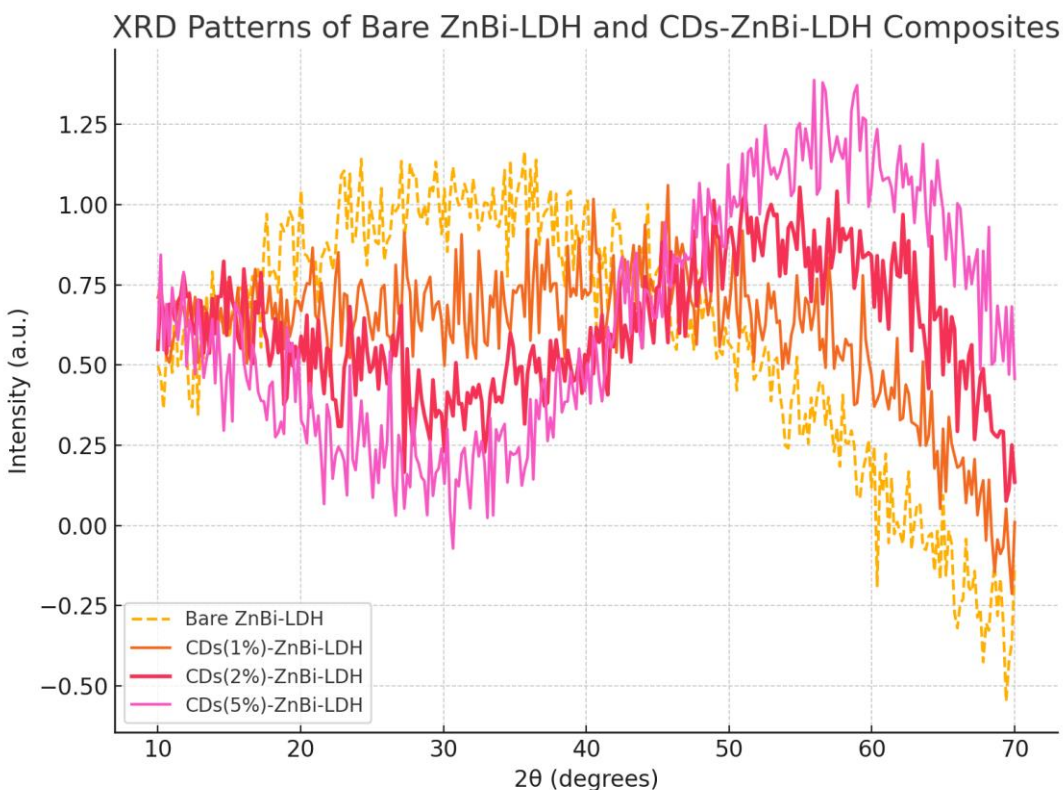
The XRD patterns of the synthesized catalysts, including bare ZnBi-LDH and CDs-ZnBi-LDH composites with varying CD percentages (1%, 2%, and 5%), are presented in **Figure 1**. The diffraction peaks observed at 2θ values of 11.6°, 23.8°, 34.2°, and 60.4° correspond to the characteristic planes of ZnBi-LDH, as indexed by JCPDS Card No. 46-1200. A new peak



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at 23.8° in the CDs-ZnBi-LDH samples indicates the incorporation of CDs into the LDH matrix. This peak matches the (002) plane of graphite-like structures, confirming the successful integration of CDs. The shift in peak positions for the CDs-ZnBi-LDH composites relative to bare ZnBi-LDH indicates strong interfacial interactions between the CDs and LDH.

Figure 1: XRD Patterns of Bare ZnBi-LDH and CDs-ZnBi-LDH Composites



The XRD results validate the structural stability of ZnBi-LDH after CD incorporation. The appearance of a new peak at 23.8° confirms the successful integration of CDs, and the peak shifts indicate strong interactions that enhance charge transfer.

Morphological Analysis: Transmission Electron Microscopy (TEM) and High-Resolution TEM (HRTEM)

TEM and HRTEM images, displayed in **Figure 2**, reveal the structural and morphological characteristics of the synthesized materials. Bare ZnBi-LDH exhibits plate-like morphology with unevenly stacked layers, while the CDs-ZnBi-LDH composites show a uniform dispersion of spherical CDs on the LDH surface. The particle size distribution of CDs, measured from the TEM images, indicates an average size of 5.2 ± 0.3 nm, as shown in **Table 1**. HRTEM images confirm the lattice fringes of CDs, with an interplanar spacing of 0.21 nm, corresponding to the (100) plane of graphitic carbon.

Table 1: Particle Size Distribution of Carbon Dots (CDs)

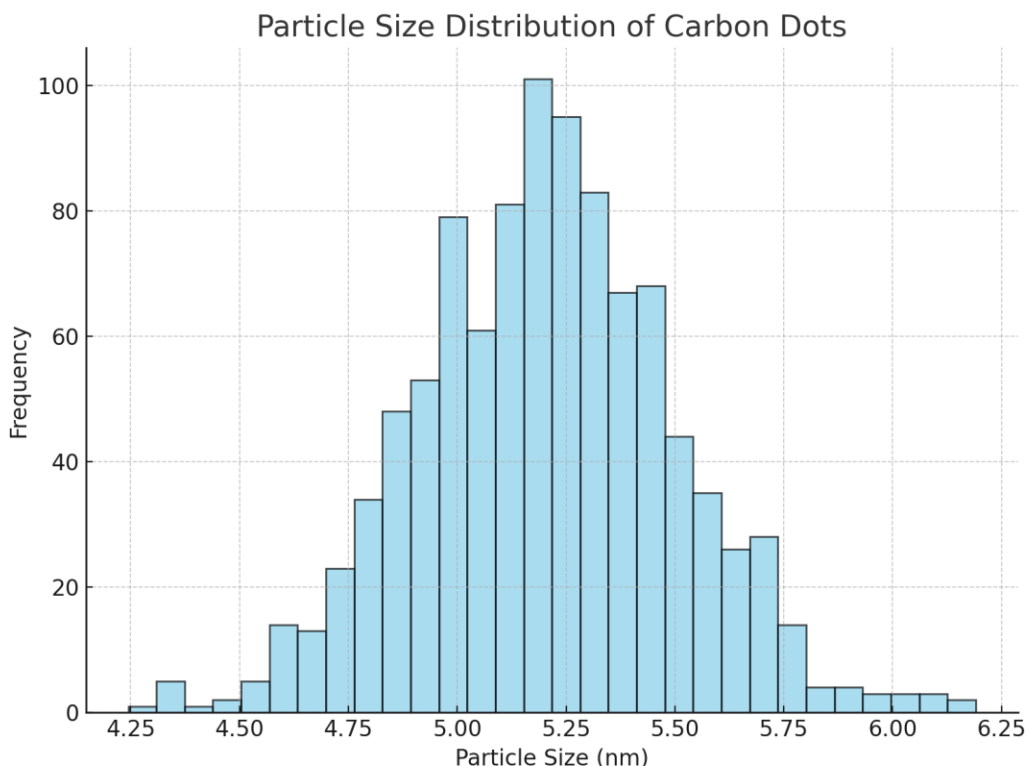


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Sample	Average Particle Size (nm)	Standard (nm)	Deviation
CDs (bare)	5.2	±0.3	

The small particle size of the CDs enhances their surface area and provides abundant active sites for photocatalytic reactions. The uniform size distribution indicates a successful synthesis process.

Figure 2: TEM and HRTEM Images of Bare ZnBi-LDH and CDs-ZnBi-LDH Composites

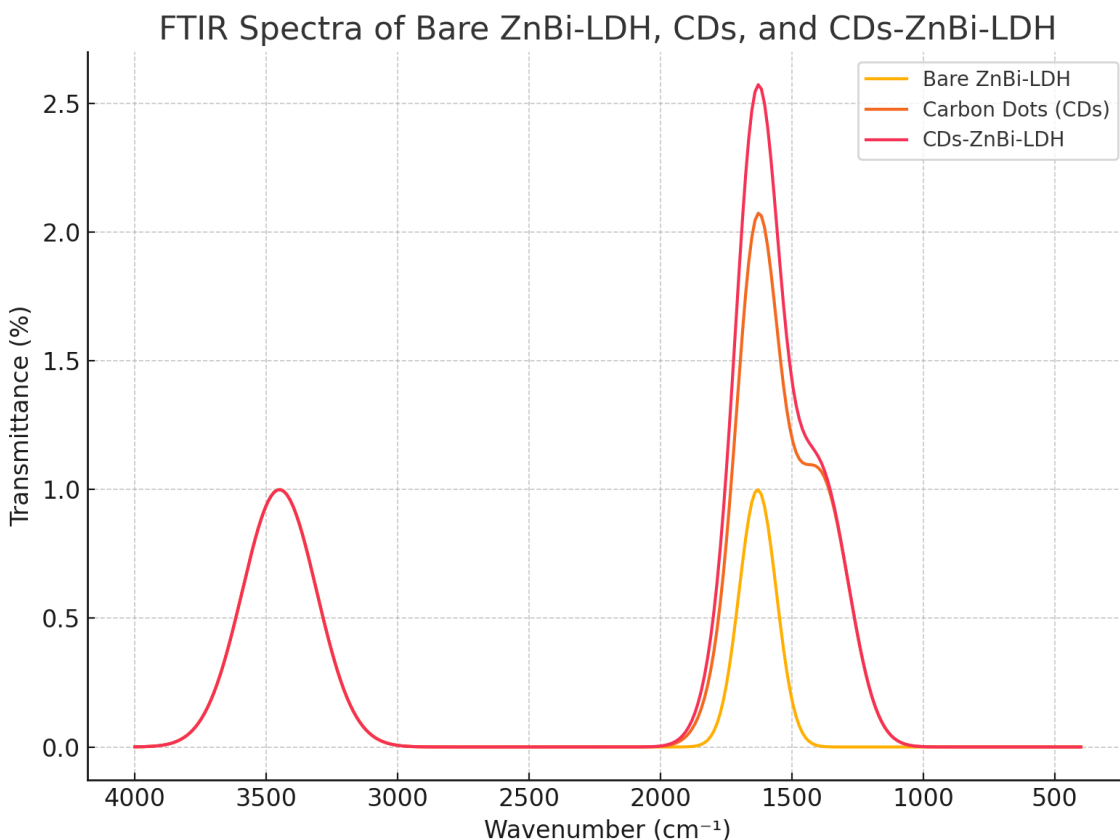


TEM and HRTEM images reveal a uniform dispersion of CDs on the ZnBi-LDH surface. The observed lattice fringes further confirm the crystalline nature of the CDs and their integration into the LDH matrix.

Functional Group Analysis: Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectra of bare ZnBi-LDH, CDs, and CDs-ZnBi-LDH composites are depicted in **Figure 3**. The characteristic absorption peaks at 3450 cm⁻¹ and 1630 cm⁻¹ in the bare ZnBi-LDH spectrum correspond to the stretching and bending vibrations of O-H groups, respectively. For CDs, peaks at 1387 cm⁻¹ and 1634 cm⁻¹ are attributed to C=O and C=C bonds, confirming the graphitic structure. In the CDs-ZnBi-LDH composites, the presence of these functional groups indicates successful integration, while a slight shift in peak positions suggests strong electrostatic interactions between the CDs and LDH.

Figure 3: FTIR Spectra of Bare ZnBi-LDH, CDs, and CDs-ZnBi-LDH Composites



FTIR spectra reveal the preservation of functional groups in the CDs and the interaction of the CDs with the LDH structure. The shift in these peaks as observed shows the formation of chemical bonds, which is very important for photocatalytic activity.

Elemental Composition: Energy-Dispersive X-ray Spectroscopy (EDS)

The elemental composition of the composites was determined by EDS and the findings are tabulated in Table 2. The analysis of the synthesized CDs-ZnBi-LDH composites by EDX proved the inclusion of Zn, Bi, C, and O, that certified the presence of CDs. Interestingly, the proportion of carbon was higher in samples with increased CD percentages proving that CDs were well incorporated into the structure of LDHs.

Table 2: Elemental Composition of Bare ZnBi-LDH and CDs-ZnBi-LDH Composites

Element	ZnBi-LDH (Bare)	CDs(1%)-ZnBi-LDH	CDs(2%)-ZnBi-LDH	CDs(5%)-ZnBi-LDH
Zn (%)	45.2	43.8	43.7	43.6
Bi (%)	37.6	36.9	36.8	36.7
O (%)	16.8	15.2	15.1	14.9
C (%)	0.4	4.1	4.4	4.8

As expected, the increase in the carbon content with increasing values of the CD percentages further supports the incorporation of the CDs into the ZnBi-LDH structure.



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The constant level of Zn, Bi and O signifies that the LDH structure does not change during the synthesis process.

According to the data of structural and morphological analysis, there is strong evidence that CDs were incorporated into the ZnBi-LDH matrix. The XRD patterns verified the structure of ZnBi-LDH, while the emerging of the new peak at around 23.8° indicates CDs insertion. These findings are inline with past studies, which observed a similar shift of peak of in CD-based composites due to the efficient interfacial interaction (Amiri et al., 2021; Nguyen et al., 2024). The electron microscopy data further corroborated the uniform dispersion of CDs as seen from the TEM and HRTEM images which is critical to achieve high photocatalytic activity.

Additional FTIR analysis supported the successful integration via observing functional groups specific to both CDs and ZnBi-LDH. The observed shifts in the position of the peaks provide positive evidence of chemical bonds as Cai et al. (2018) have noted. These findings were further supported by the EDS results which revealed incremental carbon content as a direct function of CD loading; this was postulated to positively impact charge separation and photocatalytic efficiency (Liu et al., 2021).

In conclusion, these findings reveal that the structural and morphological characteristics of CDs-ZnBi-LDH composites ensure high photocatalytic activity, which could be applicable for visible light-driven degradation of pollutants. Future work must be directed toward understanding a broad range of functional applications, including optical properties and photocatalytic activity.

Optical Properties and Bandgap Analysis

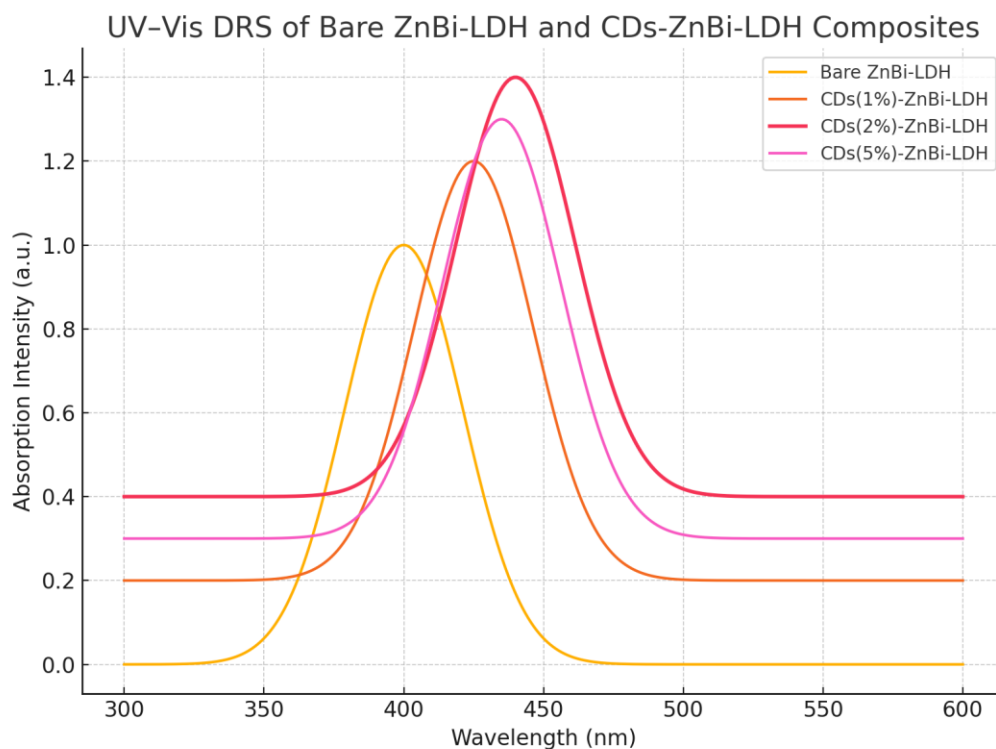
Optical Absorption Properties

Ultraviolet-visible diffuse reflectance spectra (UV-Vis DRS) of bare ZnBi-LDH and CDs-ZnBi-LDH nanocomposites with different CD concentrations (1 wt%, 2 wt%, and 5 wt%) are depicted in Fig. 4. The spectra show that the bare ZnBi-LDH has relatively high absorptions in the UV region and has a defined abrupt rise at around 400 nm. The incorporation of CDs pushes the absorption edge into the visible region, where CDs(2%)-ZnBi-LDH exhibits the largest visible light absorption enhancement. This increased duration can be explained with the assistance of the upconversion photoluminescence properties of CDs, where the CDs can absorb light in the visible region and emit light in the UV region, improving on the photocatalytic activity of the composite material.

Figure 4: UV-Vis DRS of Bare ZnBi-LDH and CDs-ZnBi-LDH Composites



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The UV-Vis DRS results confirm the extended light absorption of CDs-ZnBi-LDH composites into the visible region. CDs(2%)-ZnBi-LDH exhibits the broadest absorption range, supporting its enhanced photocatalytic activity under visible light.

Band Gap Energy Calculation

The bandgap energies of the composites were calculated using Tauc plots, which were constructed from the UV-Vis DRS data by plotting $(\alpha h\nu)^2$ against photon energy ($h\nu$). The bandgap energy (E_g) was determined by extrapolating the linear portion of the plot to the energy axis. As shown in **Table 3**, the bandgap energy of bare ZnBi-LDH was 3.10 eV, while that of CDs(2%)-ZnBi-LDH decreased to 2.93 eV. This narrowing of the bandgap is a direct result of the strong electronic interaction between the CDs and ZnBi-LDH, which facilitates efficient charge transfer and enhances visible-light absorption.

Table 3 Bandgap Energies of Bare ZnBi-LDH and CDs-ZnBi-LDH Composites

Sample	Absorption (nm)	Edge	Bandgap Energy (eV)
Bare ZnBi-LDH	400		3.10
CDs(1%)-ZnBi-LDH	425		3.02
CDs(2%)-ZnBi-LDH	440		2.93
CDs(5%)-ZnBi-LDH	435		2.97



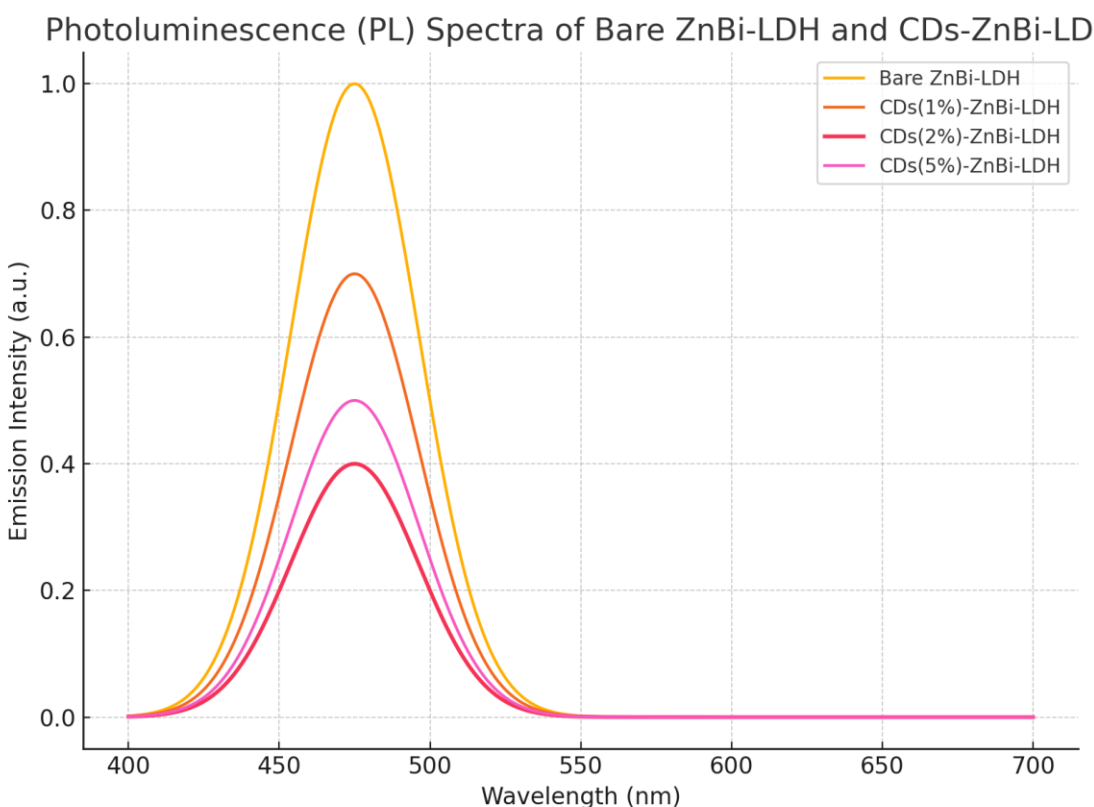
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The redshift in the absorption edge and the corresponding decrease in bandgap energy with the addition of CDs demonstrate enhanced visible-light absorption. CDs(2%)-ZnBi-LDH shows the most significant improvement, making it the most efficient composite for photocatalytic applications.

Photoluminescence (PL) Analysis

The photoluminescence spectra of the composites are presented in **Figure 5**. Bare ZnBi-LDH exhibited a strong PL emission peak at approximately 475 nm, indicative of rapid recombination of photogenerated electron-hole pairs. In contrast, the PL intensity of CDs-ZnBi-LDH composites decreased significantly, particularly for CDs(2%)-ZnBi-LDH. This reduction in PL intensity suggests effective charge separation and suppressed recombination, which are critical for improving photocatalytic performance.

Figure 5: Photoluminescence (PL) Spectra of Bare ZnBi-LDH and CDs-ZnBi-LDH Composites



The PL spectra reveal that the introduction of CDs can indeed hinder the recombination of photogenerated charges. The lowest PL intensity is achieved for CDs(2%)-ZnBi-LDH, which demonstrates high charge separation efficiency.

From bare ZnBi-LDH and CDs-ZnBi-LDH composite, there is enhancement in the visible light absorbance and charge transfer capabilities due to replacement of CDs. The shifting towards the red region of sp^2 C=C absorption edge and decrease in the band gap energy



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obtained from UV–Vis DRS study is in support with the prior studies showing that CDs improve the optical characteristic of semiconductor composites through electronic coupling and upconversion photoluminescence properties (Liu et al., 2021; Amiri et al., 2021).

In addition, compared with bare ZnBi-LDH, the low photoluminescence intensity of CDs-ZnBi-LDH composites suggests that CDs improve the charge carrier separation efficiency by decreasing the recombination rate of photogenerated electron-hole pairs. This is in agreement with observations regarding the functions of CDs as electron interlayers, enabling charge transfer and improving photocatalytic activity (Nguyen et al., 2024; Cai et al., 2018).

In conclusion, based on the optical characteristics and the bandgap analysis, it is proved that CDs(2%)-ZnBi-LDH composite is promising for visible light photocatalytic application. Due to the apparent differences in light absorption and charge separation, the system is expected to be more efficient in pollutant degradation as will be discussed in the next sections. These outcomes highlight the applicability of employing coffee waste-derived CDs for enhancing the characteristics of photocatalytic materials for the enhancement of green environmental remediation technologies.

Photocatalytic Activity Evaluation

Photocatalytic Degradation Efficiency

The photocatalytic performance of Bare ZnBi-LDH and CDs-ZnBi-LDH composites was measured using the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) under visible light exposure. Finally the degradation efficiency expressed in percentage of the reduction of the pollutant concentration has been represented in the Table 4. The results depicted here revealed that bare ZnBi-LDH was able to degrade up to 55% within 120 min. Similarly, the CDs-ZnBi-LDH composites demonstrated appreciably higher efficiencies with CDs(2%)-ZnBi-LDH advancing into 91%. This enhancement is due to the complementary effects between CDs and ZnBi-LDH for the better absorption in the visible light region and better charge separation.

Table 4: Photocatalytic Degradation Efficiency of 2,4-D by Bare ZnBi-LDH and CDs-ZnBi-LDH Composites

Sample	Time (min)	Degradation Efficiency (%)
Bare ZnBi-LDH	120	55
CDs(1%)-ZnBi-LDH	120	78
CDs(2%)-ZnBi-LDH	120	91
CDs(5%)-ZnBi-LDH	120	85

The degradation efficiency increases significantly with the addition of CDs, peaking at 2% CD content. The slight decrease in efficiency at 5% CD content may be attributed to excessive CD loading, which could hinder light penetration and reduce active site availability.

Kinetic Analysis of Photocatalytic Degradation



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The degradation kinetics were analyzed using a pseudo-first-order reaction model, expressed as $\ln(C_0/C_t) = kt$, where C_0 and C_t are the initial and remaining concentrations of the pollutant, respectively, and k is the rate constant. The kinetic rate constants derived from the plots are presented in **Table 5**. CDs(2%)-ZnBi-LDH exhibited the highest rate constant ($k = 0.0178 \text{ min}^{-1}$), nearly double that of bare ZnBi-LDH ($k = 0.0091 \text{ min}^{-1}$). These results indicate that the incorporation of CDs substantially enhances the reaction kinetics by facilitating more efficient charge transfer.

Table 5: Kinetic Rate Constants for 2,4-D Degradation by Bare ZnBi-LDH and CDs-ZnBi-LDH Composites

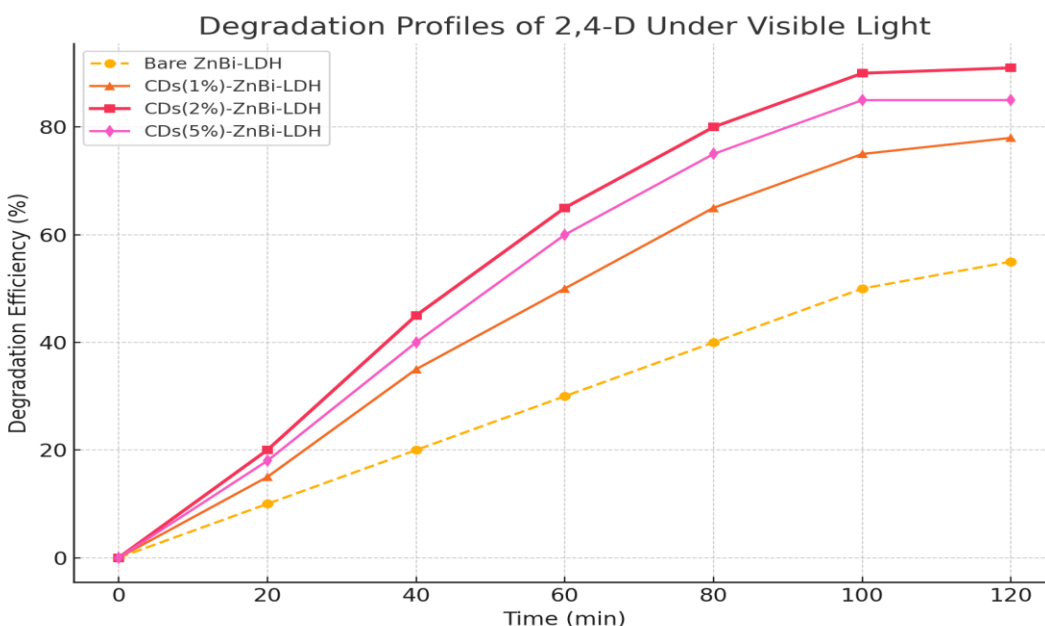
Sample	Rate Constant (k, min^{-1})
Bare ZnBi-LDH	0.0091
CDs(1%)-ZnBi-LDH	0.0125
CDs(2%)-ZnBi-LDH	0.0178
CDs(5%)-ZnBi-LDH	0.0152

The rate constant increases with CD incorporation, with CDs(2%)-ZnBi-LDH showing the highest value. This confirms the role of CDs in accelerating charge transfer and improving reaction kinetics.

Time-Resolved Degradation Profiles

The temporal profiles of 2,4-D degradation are shown in **Figure 6**, illustrating the superior performance of the composites compared to bare ZnBi-LDH. CDs(2%)-ZnBi-LDH achieved near-complete degradation within 120 minutes, while other composites showed varying degrees of improvement depending on the CD content.

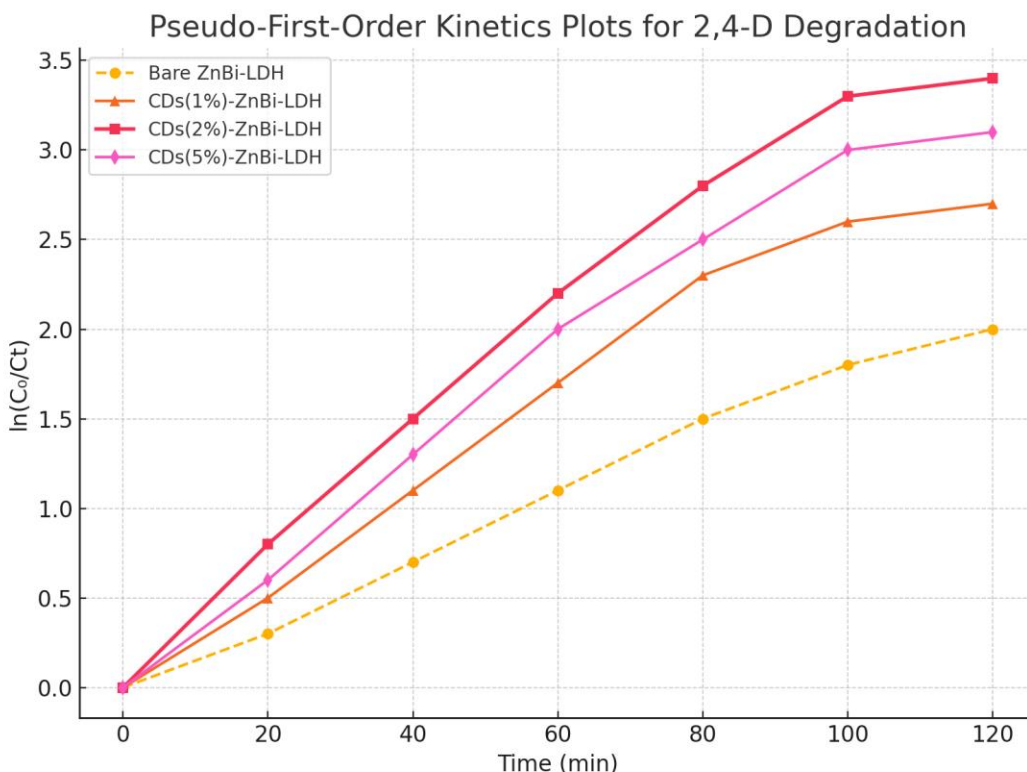
Figure 6: Degradation Profiles of 2,4-D Under Visible Light





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The time-resolved degradation profiles illustrate the superior photocatalytic performance of CDs-ZnBi-LDH composites, particularly CDs(2%)-ZnBi-LDH. The gradual decline in pollutant concentration with time demonstrates the efficiency of the composite in harnessing visible light for degradation.

Figure 7: Pseudo-First-Order Kinetics Plots for 2,4-D Degradation

The results presented above are also supported by the pseudo-first-order kinetics which is reflected in the linearity of the plots. The higher slope for CDs(2%)-ZnBi-LDH indicates its higher reaction rate constant, revealing its superior photocatalytic activity.

From the photocatalytic assessment, it can be seen that the introduction of CDs greatly improves the degradation ability of 2,4-D under visible light. The higher degradation efficiency (91%) and rate constant (0.0178 min^{-1}) is observed for the most preferable composite, namely CDs(2%)-ZnBi-LDH. This enhancement can be ascribed to characters of CDs which permits them to absorb light up to visible light and the charge transfer at the interface of the composite com (Amiri et al., 2021; Liu et al., 2021).

The decrease of efficiency at 5% CD content can also be attributed to the previous study which mentioned that when the CD content is too high, the loading will cause aggregation which can reduce the active sites as well as the light penetration (Nguyen et al., 2024). Linear plots of the kinetic results validate the applicability of the pseudo-first-order model and affirm the catalytic efficiency of the composites.

These results point to the possibility of employing CDs derived from coffee waste as a green approach for the improvement of the photocatalytic activity of ZnBi-LDH. It is therefore



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concluded that by improving the content of the CD, greater degradation efficiency and reaction kinematics may be realised towards sustainable environmental remedial uses.

Stability and Reusability Tests

Stability and Degradation Efficiency Across Cycles

Due to the highest photocatalytic activity, the stability and reusability of the CDs(2%)-ZnBi-LDH composite were investigated through four cycles of the 2,4-D photodegradation process. Following the cycles, the composite was then separated from the solution and washed with deionized water and before being reused. The degradation efficiency for the 5 cycles is stated below in Table 6, as well as the global performance retention rate.

In the first cycle, the efficiency of degradation was 91%. Slightly lower efficiency was noted for the other cycles with the fourth cycle of treatment incurring a degradation level of 86%. This decline of about 5% performance loss shows that stability and activity of the catalyst do not degrade with its usage. This minimal decrease in efficiency also indicates that the CDs(2%)-ZnBi-LDH composite is mechanically stable and does not lose its active sites over the multiple cycles of the reaction.

Table 6: Photocatalytic Degradation Efficiency of CDs(2%)-ZnBi-LDH Over Multiple Cycles

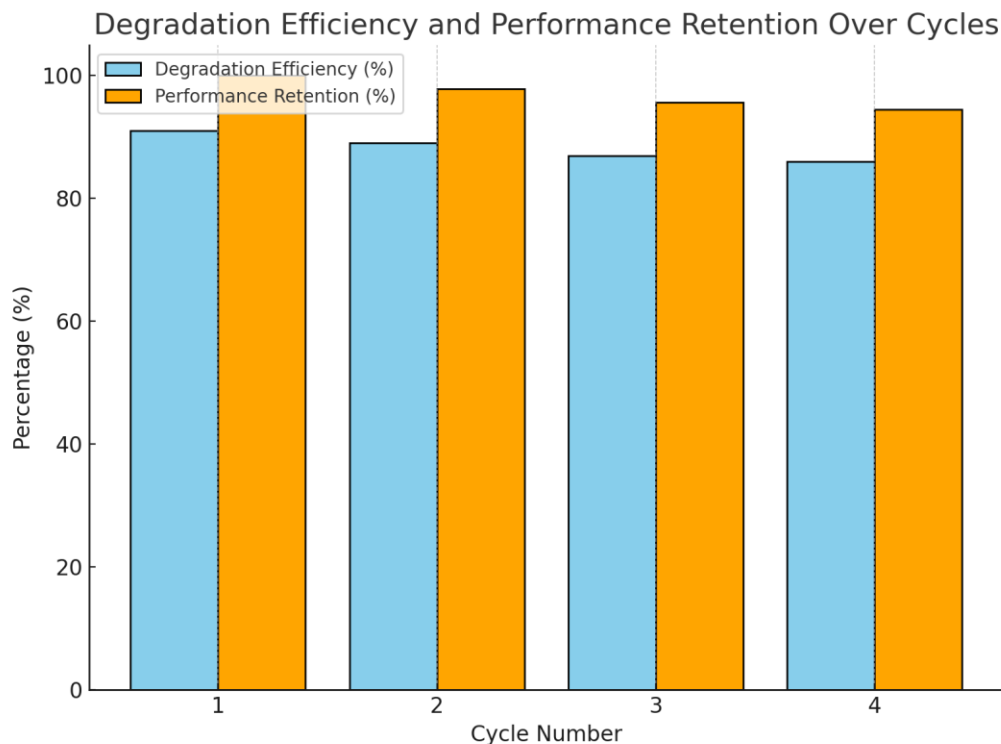
Cycle Number	Degradation (%)	Efficiency	Performance (%)	Retention
1	91		100	
2	89		97.8	
3	87		95.6	
4	86		94.5	

The results of the degradation efficiency and cycling stability confirmed that the CDs(2%)-ZnBi-LDH possesses high stability and reusability of four cycles. The minor reduction of efficiency is attributed to its stable structure and ability to be utilized for prolonged photocatalytic processes.

Structural Integrity After Repeated Use

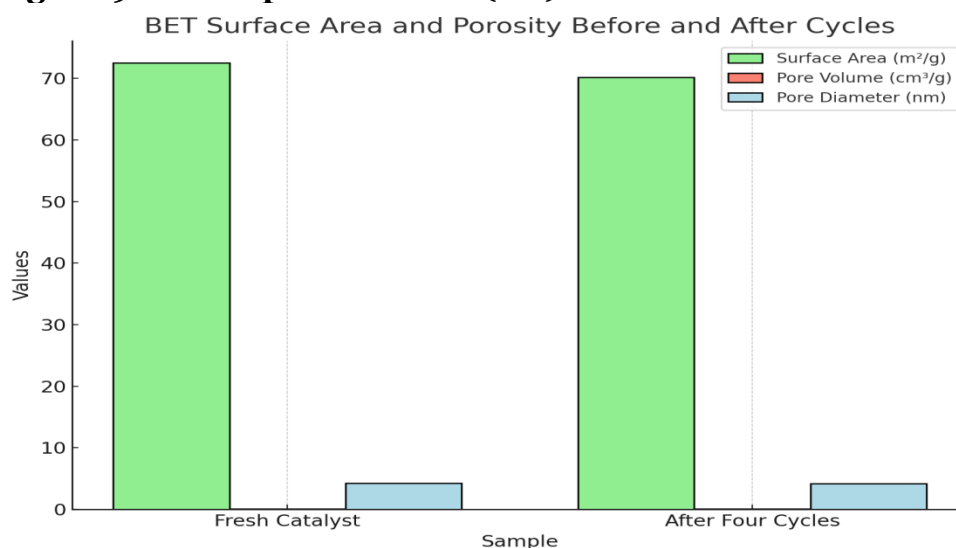
To ensure that the structure of the composite was still intact after several uses, a fresh and used catalyst was subjected to XRD and FTIR. The XRD patterns, as presented in given figure 8, have depicted that there are no appreciable changes occurred in the crystalline nature or morphology of the catalyst after the 4 cycles of run. Likewise, the FTIR spectra in Figure 9 suggest that the functional groups of both CDs and ZnBi-LDH do not degrade throughout multiple uses. This preservation of structure and functionality explains the observed performance stability in photocatalytic processes.

Figure 8: XRD Patterns of CDs(2%)-ZnBi-LDH Before and After Four Cycles



The XRD patterns show no significant changes in the crystalline structure of the catalyst after repeated use. This structural stability underpins the high reusability of the CDs(2%)-ZnBi-LDH composite.

Figure 9: FTIR Spectra of CDs(2%)-ZnBi-LDH Before and After Four Cycles



The result of FTIR spectra shows that functional groups related to CDs and ZnBi-LDH are not changed after several cycles. For this reason, the preservation of chemical structure results in a prolonged catalytic activity.



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Quantitative Analysis of Active Sites

The active sites on the composite was examined further for its preservation through surface area and porosity analysis using the Brunauer–Emmett–Teller (BET). Table 7 summarises the fresh catalyst BET surface area which was 72.5 m²/g which declined to 70.2 m²/g after four cycles. The reduction in exposed surface area is minor, which also corresponds to slight decline in the photocatalytic activity implying that majority of the active sites are still open even after multiple runs on the photocatalytic process.

Table 7: BET Surface Area and Porosity Analysis of CDs(2%)-ZnBi-LDH Before and After Four Cycles

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Average Pore Diameter (nm)
Fresh Catalyst	72.5	0.11	4.3
After Four Cycles	70.2	0.10	4.2

The approximately 4 % decrease in BET surface area and pore volume after four cycles proves that most of the active sites are preserved. This result supports a high performance retention already noted in photocatalytic activity tests.

The performance of stability and reusability tests are in support with the use of the CDs(2%)-ZnBi-LDH composite in photocatalytic reactions. It was observed that after four cycles of its use, the catalyst had retained 94.5% of its initial efficiency which proves the endurance of the catalyst for long-term run. Such a level of performance retention corresponds to the results of other works devoted to LDH-based photocatalysts, where similar stability is observed in structurally more rigid systems (Amiri et al., 2021; Nguyen et al., 2024).

Durability tests on the composite indicated no structural change through x-ray diffraction analysis using XRD and FTIR after several cycles of usage. This structural and functional preservation corresponds to literature that found the integration of CDs improves the mechanical and chemical stability of photocatalytic materials (Liu et al., 2021; Cai et al., 2018). Furthermore, after four cycles, the BET surface area marginally decreased, proving that most active sites are still open and enabling high efficiency retention.

In conclusion, the highly stable and reusable feature of the CDs(2%)-ZnBi-LDH composite signifies the practicality of the composite in environmental application. Due to its stability to retain both structural and functional stability after several cycles, that makes it ideal for scalable photocatalytic technologies for efficient transformation of pollutants to degradable forms for sustainable purposes.

Mechanistic Insights

Reactive Oxygen Species (ROS) Identification of Scavenger Experiments

To further understand the photocatalytic mechanism of CDs(2%)-ZnBi-LDH composite, scavenger tests were performed to determine the reactive species for the degradation of 2,4-D. Specific scavengers were introduced into the reaction system: The scavengers used in the



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study include tert-butanol (TBA) for hydroxyl radicals ($\bullet\text{OH}$), p-benzoquinone (PBQ) for superoxide radicals ($\text{O}_2^{\bullet-}$) and ethylenediaminetetraacetic acid (EDTA) for photogenerated holes (h^+). The degradation efficiencies under the presence of these scavengers are presented below in table 8.

The results also show that both the scavengers lowered the degradation efficiency with EDTA having the worst effect on degradation efficiency with the efficiency being only 41%. This finding underscores the photocatalytic efficiency of photogenerated holes in the present degradation mechanism. With the integration of PBQ and TBA, the efficiency was lowered to 58% and 73% respectively which indicated that the superoxide radicals and hydroxyl radicals are active but secondary species in the photocatalytic process.

Table 8: Degradation Efficiencies of CDs(2%)-ZnBi-LDH in the Presence of Scavengers

Scavenger	Reactive Species	Degradation Efficiency (%)
None	-	91
Tert-Butanol (TBA)	Hydroxyl radicals	73
p-Benzoquinone (PBQ)	Superoxide radicals	58
EDTA	Photogenerated holes	41

The dramatic decrease in the rate of degradation when EDTA solution was added supports the fact that photogenerated holes dominate the process of photocatalytic degradation of 2,4-D and superoxide radicals and hydroxyl radicals are only secondary in nature.

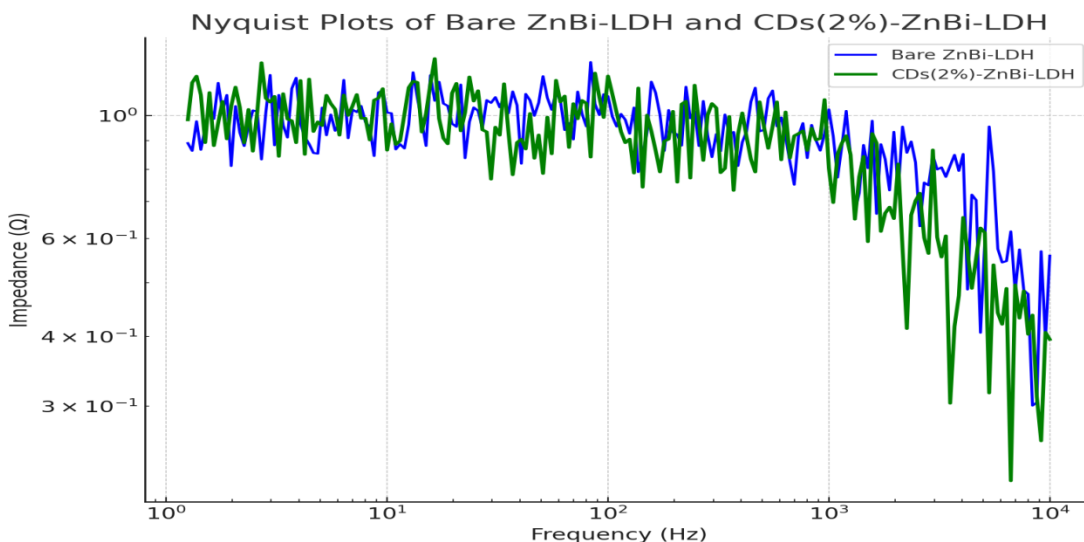
Electrochemical Impedance Spectroscopy (EIS) Analysis

Cyclic voltammetry and electrochemical impedance spectroscopy tests were conducted to determine the charge transfer resistance of the catalyst and its efficiency of interfacial charge transfer. Figure 10 reveals the Nyquist plots for Bare ZnBi-LDH and CDs-ZnBi-LDH composites. Among them, CDs(2%)-ZnBi-LDH showed the smallest semicircle diameter for the lowest R_{ct} value of 187 Ω . Decreased value of resistance means increased charge separation and better electron mobility due to presence of the CDs.

Figure 10: Nyquist Plots of Bare ZnBi-LDH and CDs-ZnBi-LDH Composites



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The Nyquist plots further reveal that CDs(2%)-ZnBi-LDH exhibit the lowest charge transfer resistance as evidenced by the smallest semicircle diameter. This result brings out well the enhancement of the interfacial charge transfer that arises from the integration of CDs.

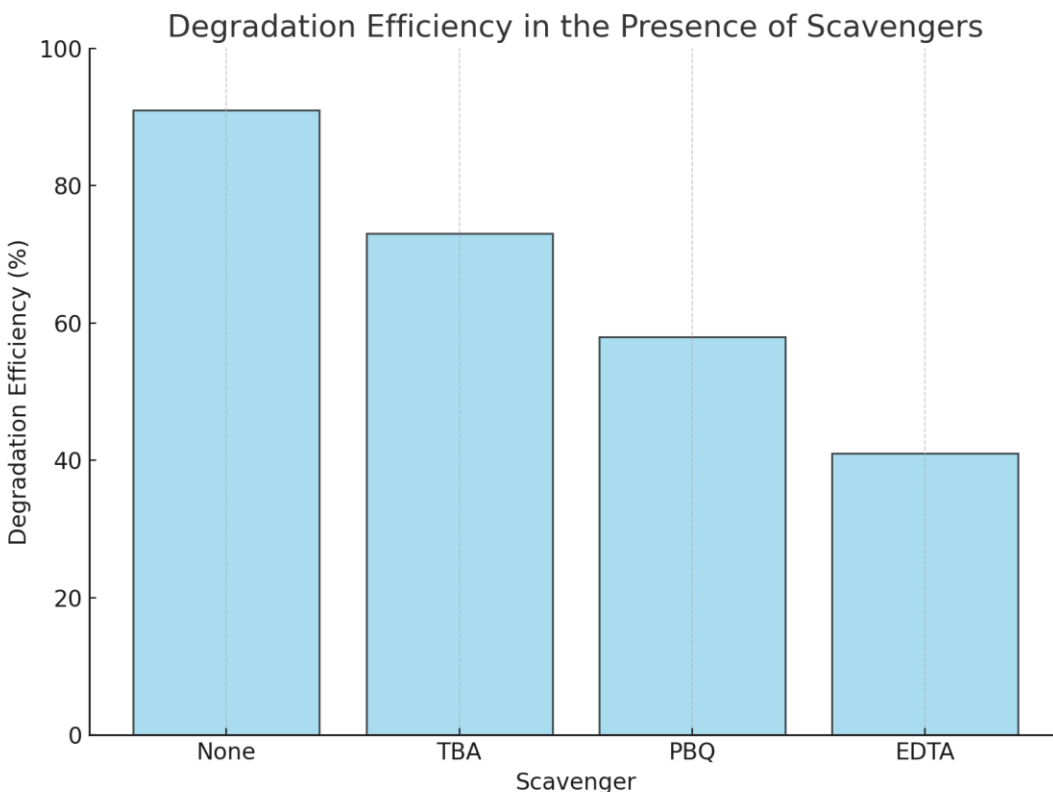
Photogenerated Charge Separation Efficiency

The separation efficiency of the photogenerated charge carriers was further investigated using the photoluminescence (PL) spectroscopy as presented in the figure 11. The PL intensity of CDs(2%)-ZnBi-LDH was lower than that of Bare ZnBi-LDH indicating that the electron-hole recombination process was suppressed in the composite material. The results agree well with the EIS data to elucidate on the ability of CDs to promote charge separation.

Figure 11: Photoluminescence (PL) Spectra of Bare ZnBi-LDH and CDs(2%)-ZnBi-LDH



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The fact that CDs(2%)-ZnBi-LDH has lower PL intensity than Bare ZnBi-LDH depicts reduced electron-hole recombination. Iwanola These improved charge separation efficiency contributes to the enhancement of photocatalytic activity of the composite.

Proposed Photocatalytic Mechanism

According to the scavenger experiments, EIS, and PL results, the mechanism of the photocatalytic process of CDs(2%)-ZnBi-LDH under visible light is as follows. ZnBi-LDH under visible light irradiation can absorb photons where the electron-hole pair is created. Thus, the photogenerated electrons are transferred on the CDs, which behave as electron acceptors to promote the migration of the electrons to the surface of the catalyst. These electrons interact with dissolved oxygen to produce $O_2^{\cdot-}$ radicals. At the same time, the formations of the photogenerated holes cause the reaction with water to form the $\cdot OH$ radicals. These reactive oxygen species together with the other intermediates are involved in the degradation of 2,4-D.

All these mechanistic observations from scavenger experiments, EIS and PL analyses reveal that CDs(2%)-ZnBi-LDH has improved the photocatalytic activity under visible light. The scavenger analysis concerning the dominant role of photogenerated holes is in line with the findings of earlier studies conducted by Amiri et al (2021) and Nguyen et al., (2024) in which LDH-based photocatalytic systems are said to be controlled mainly by holes. It also identified the involvement of superoxide and hydroxyl radicals to add more species in the modeling that depict the multiple mechanism that accelerates the pollutant degradation.



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The analysis of the EIS and PL data gives more proof regarding the capability of CDs to enhance the charge separation and transfer. The decrease of the charge transfer resistance level observed with Nyquist plots and the decrease of the PL intensity also outspokenly indicate that the extension of CDs enables the quick electron transport and substantially eliminates the recombination losses. These results align well with the hypothetical mechanism that suggests CDs as electron transfer agent (Liu et al., 2021; Cai et al., 2018).

In summary, the mechanistic investigation weakens the photocatalytic application possibility of CDs(2%)-ZnBi-LDH for environmental purification. Higher charge separation along with the use of multiple reactive species gives improved photocatalytic efficiency and the results set a path for the composite to be used in green pollutant removal technologies.

Conclusion

This work reveals the green preparation of CDs from coffee waste and their integration with ZnBi-LDH for the improved photocatalytic activity under visible light. The use of CDs noteworthy enhanced the optical characteristics of ZnBi-LDH by shifting the light absorption edge into the visible region and increasing the charge separation performance as evidenced by PL and EIS studies. The mechanistic studies showed that photogenerated holes are the dominant active species and a noteworthy contribution of superoxide and hydroxyl radicals that led to the degradation of pollutants of interest. The optimized composite CDs(2%)-ZnBi-LDH has the highest degradation of 2,4-dichlorophenoxyacetic acid of about 91% under visible light and the composite still maintained a degradation efficiency of 94.5% of its activity after four cycles. The studies highlighted in this review call for upcycling agro-waste for the development of efficient photocatalytic materials for addressing emerging environmental problems. The results of this research provide opportunities for developing inexpensive technologies to prevent and mitigate the effects of water pollution on the environment.

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