

Research Article

Eco-Friendly Coffee Waste-Based Carbon Dots Coupled to ZnBi-Layered Double Hydroxide Heterojunction: Enhanced Control of Interfacial Charge Transfer for Highly Efficient Visible-Light Catalytic Activity

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Using a simple, low cost, and excellent efficient approach, carbon dots (CDs) were fabricated via a one-pot hydrothermal process of coffee waste. Amazingly, the combination of 2% CDs with ZnBi₂O₄ to form a new and excellent heterogeneous photocatalyst enabled the complete decomposition of 2, 4-dichlorophenoxyacetic acid (2, 4-D) into CO₂ and H₂O. The findings of this study provide a new perspective on the utilization of agricultural waste for creating products of scientific and practical significance. More than 91% of 2, 4-D (initial concentration of 30 mg/L) was completely decomposed and dechlorinated using 1.0 g/L of CDs (2%)-ZnBi₂O₄ at pH 4.0 after 120 min of exposure to visible light (with $k = 0.0178 \text{ min}^{-1}$), and more than 86% of the decomposed 2, 4-D was mineralized into CO₂ and H₂O. There was no sign of catalyst deactivation after four cycles of reuse, demonstrating the durability and efficiency of CDs (2%)-ZnBi₂O₄ is due to the formation of defects at the interfaces of the heterojunction; therefore, the movement of photogenerated electrons at the interface between the two components is rapid. The mineralization of 2, 4-D by CDs (2%)-ZnBi₂O₄ upon exposure to visible light is induced mainly by the photogenerated holes, followed by O₂^{•-}, and finally OH[•] radicals.

1. Introduction

Water pollution by agricultural chemicals has become an important environmental problem due to agricultural activities. Therefore, it is important to find solutions to selectively remove toxic compounds. Recently, various techniques have been used for removal of toxic organic compounds such as fenton, photocatalysis, and ozonation. [1]. As an emerging and effective green solution, semiconductor-based photocatalysis has attracted considerable attention from scientists because organic pollutants can be easily removed using freely available solar energy. In addition, the photocatalytic method can decompose hazardous organic pollutants into nontoxic molecules (CO₂, H₂O, and mineralized inorganic ions) without generating secondary pollutants. Photocatalysis is a technology in which the resulting chemical energy is derived from photonic energy conversion. Through light harvesting by a semiconductor, an excited electron (e^{-}) -hole (h^{+}) pair is produced. Because of their activated state, e^- and h^+ undergo chemical reduction and oxidation to produce strong oxidizers, such as OH^{\bullet} and $O_2^{\bullet-}$, in the system, which can then remove organic contaminants. A number of strategies have been employed in designing photocatalysts with good light-harvesting properties, good chemical stability, and suitable bandgaps. One approach involves coupling semiconductors to achieve a new tunable bandgap semiconductor. Various types of catalysts have been combined in composites to achieve improved photocatalytic activity such as TiO₂@MgFe₂O₄ [2], Ag₃PO₄-TiO₂ [3], Mn-ZnOgraphene [4], TiO₂-zeolite [5], Bi@Fe₃O₄ [6], Eu-doped Bi₂WO₆ [7], Bi₂Sn₂O₇-reduced graphene oxide [8], and $Bi_2S_3-Bi_2Sn_2O_7$ [9].

Nowadays, biomass waste has caused serious environmental issues. Biomass waste, including agricultural waste and food waste, is an abundant and important carbon source to produce nanocarbon materials because of its renewable ability, sustainability, easy availability, nontoxicity, and low cost [10]. As new classes of nanocarbon, carbon dots (CDs) have recently received attention for development. CDs are generally individual quasi-spherical nanoparticles with small sizes (<10 nm) [11] and are prepared from broad-spectrum carbon precursors via bottom-up or top-down pathways via relatively easy processes. Because they are the latest member in the family of quantum dots, CDs also have the potential alternatives to the traditional toxic metal-based quantum dots in use today. Owing to their highly hydrophilic surfaces, easy surface modification, no chemical reaction, low toxicity, high biocompatibility, easy synthesis, excellent stability, water dispersibility, and prospective applications, CDs have attracted the attention of researchers [12-14]. CDs have been widely applied in several fields, including sensing transformation, biological imaging, catalysis, and energy conversion/storage [15]. CDs are considered promising nanomaterials for the design of photocatalysts [14, 16, 17]. The key factor affecting the optical performance of CDs is the huge number of functional groups on the surface, such as -OH, C=O, -COOH, and -NH₂. CDs in conjunction with various semiconductors can afford improved light harvesting and electron transport and thus enhanced photocatalytic properties [15, 18]. These include CDs/TiO₂ [17, 19], CDs/NiFe-LDH/BiVO₄ [20], CDs/BiVO₄ [21, 22], CDs/Fe₂O₃ [15], and CDs/Bi₂MoO₆ [23]. In these photocatalytic systems, the key role of CDs is as an electronic mediator to effectively delay the recombination of the photoinduced e^{-}/h^{+} pairs, with excellent charge transfer rates.

Layered double hydroxides (LDHs) are excellent semiconductor photocatalysts because they possess suitable bandgap energies and excellent visible light-absorbing ability [24–26]. As an LDH-derived *p*-type semiconductor with outstanding advantages such as high stability and a low conductivity band edge, ZnBi₂O₄ has generated a lot of interest in the field of photocatalysis. However, the rapid recombination of photogenerated e^-/h^+ pairs repressed the photocatalytic activity of ZnBi_2O_4 . It would be a better choice to combine ZnBi_2O_4 with other functional materials to improve the separation of photogenerated e^-/h^+ pairs and enhance the surface charge transfer efficiency. ZnBi_2O_4 has been combined with many different semiconductors such as g-C₃N₄ [27, 28], Bi₂S₃ [29], graphite [30], ZnO [31], reduced graphene oxide [32], ZnS [33], and hydrochar [34] to remove toxic organic contaminants. Although these strategies improve the separation efficiency of e^-/h^+ pairs to some extent, these catalysts are still insufficient for potential industrial applications.

In order to continue the ongoing program of converting biomass waste into valuable products and improving the activity of existing ZnBi₂O₄ photocatalyst, new catalysts with interesting properties and low cost are being developed with special emphasis. In this paper, the green carbon source, coffee waste powder was chosen to produce CDs by a hydrothermal method; then, CDs-ZnBi₂O₄ was synthesized using a simple coprecipitation method. To the best of our knowledge, no research has been carried out on developing new photocatalytic CDs-ZnBi₂O₄ with a favorable energy conduction band that absorbs visible light and testing its catalytic activity for organic pollutant degradation reaction. The intimate association between ZnBi₂O₄ and CDs exhibited enhanced photocatalytic efficiency. The influence of different operating parameters such as CD percentage in photocatalyst, decomposition time, pH, and 2, 4-D concentration was studied in detail and discussed. The key role of CDs in enhancing photocatalytic activity was clarified. The kinetics of photocatalytic degradation was presented, and the possible mechanism of 2, 4-D photodegradation by CDs-ZnBi₂O₄ was also proposed.

2. Materials and Methods

2.1. Materials. All chemicals used were of analytical grade and were obtained from Sigma Aldrich including HNO₃, NaOH, KOH, Bi(NO₃)₃·5H₂O, Zn(NO₃)₂·6H₂O, *tert*butanol, *p*-benzoquinone, Na₂EDTA, and 2, 4-D. Coffee waste powder was obtained from ground robusta coffee (medium roast), which was purchased from Trung Nguyen Company (Vietnam).

2.2. Measurements. A Rigaku Ultima IV X-ray diffractometer (Japan) with CuK α radiation (λ = 1.54051 Å) was used to record the X-ray diffraction (XRD) patterns of the samples. Fourier-transform infrared (FTIR) spectra were obtained using a Thermo Fisher Nicolet Magna-560 FTIR spectrometer (U.S.A.). Scanning electron microscopy (SEM) was obtained on Hitachi S-4800 (Japan) with an operating voltage of 20 keV. A Jasco V770 spectrophotometer (Japan) was used to record UV–Vis diffuse reflectance spectrum absorption. X-ray photoelectron spectroscopy (XPS) measurement was carried out using a Thermo Fisher ESCALAB 250 Xi device (U.S.A.). An IviumStat potentiostat (Ivium Technologies, Netherlands) was used for photoelectrochemical measurement. The silver/silver chloride reference electrode, the Pt mesh counter electrode, and the 0.5 M Na₂SO₄ electrolyte solution were employed for all electrochemical measurements. A Horiba FL3-22 spectro-fluorometer (Japan) was used to record photoluminescence (PL) spectrum. Shimadzu TOC-SSM5000A and a Shimadzu TOC-VCPH analyzer (Japan) were employed to quantify solid and liquid total organic carbon (TOC) of samples, respectively. A PerkinElmer Lamda XLS + spectrophotometer (USA) was employed to quantify the concentration of 2, 4-D remaining in solution.

2.3. Fabrication of CDs- $ZnBi_2O_4$ Heterogeneous Photocatalyst. First, the CDs were prepared using a one-step hydrothermal method. Coffee waste powder (2.0 g) was mixed with 20 mL of 1.0 M KOH. Next, the mixture was placed into a 50-mL Teflon-lined stainless-steel autoclave which was heated to 180°C and held for 6 h. After gradual cooling to room temperature, the fluorescent CDs were obtained by centrifugation at 15,000 rpm for 20 min to remove large particles. The supernatant was dialyzed for 24 h to remove micron-sized particles. The eluate was then ly-ophilized to obtain solid CDs.

Second, a salt solution of Zn^{2+} and Bi^{3+} (molar ratio 3:1) in HNO₃ (5%) was slowly added to aqueous NaOH (1.0 M) and ultrasonicated at 100 W. The suspension was kept at pH 10 throughout the synthesis. The suspension was then ultrasonicated at 100 W for 24 h. The solid material (ZnBi₂O₄) was collected by centrifugation, then washed with distilled water, dried at 70°C for 10 h, and annealed at 450°C for 3 h.

Third, $ZnBi_2O_4$ was further dispersed in solutions with different CD percentages (0%, 1%, 2%, and 5%). The suspension was ultrasonicated at 100 W for 6 h. The resulting material was separated using centrifugation, dried at 70°C for 24 h, and finally labeled as bare $ZnBi_2O_4$, CDs (1%)- $ZnBi_2O_4$, CDs (2%)- $ZnBi_2O_4$, and CDs (5%)- $ZnBi_2O_4$, respectively.

2.4. Photocatalysis Experiment. The performance of the catalyst was evaluated based on the decomposition of 2, 4-D (30 mg/L) after exposure to visible light emitted from a halogen lamp (300 W) through a UV cutoff filter ($\lambda > 420$ nm). Magnetic stirring was performed in the dark for 60 min before turning on the halogen lamp to achieve adsorption-desorption equilibrium of 2, 4-D on the catalyst. During 120 min of irradiation, 5 mL of suspension was taken every 15 min, and catalysts were removed by centrifugation. A PerkinElmer Lambda XLS + spectrometer was used to quantify 2, 4-D in solution. All experiments were repeated thrice (n=3). The photodegradation rate of 2, 4-D was determined by applying the pseudo-first-order kinetic equation given by $\ln(C_0/C_t) = kt$, where k represents the photodegradation rate constant (min⁻¹) and C_0 and C_t represent the concentration of 2, 4-D (mg/L) before irradiation with visible light and at irradiation time t, respectively.

3. Results and Discussion

3.1. Material Characterization. Figure 1(a) presents the XRD patterns of bare $ZnBi_2O_4$ and the samples of $ZnBi_2O_4$ incorporating different amounts of CDs (CDs-ZnBi₂O₄).

Strong, relatively sharp, and typical peaks of tetragonal structure of zinc bismuth oxide (JCPDS No. 043-0449), hexagonal ZnO (JCPDS No. 079-0207), and bismuth hydroxide (JCPDS No. 001-0898) were observed in the XRD pattern of bare ZnBi₂O₄. The new peak at 23.8° in the pattern of the CDs-ZnBi₂O₄ samples confirmed the presence of CDs in the lattice of $ZnBi_2O_4$. The peak at 23.8° closely matched the graphite nature with a (002) lattice plane [35]. The interlayer spacing value (d_{hkl}) is 3.72 Å, which is larger than that of bulk graphite, indicating that the graphite core is disordered [36]. Most of the XRD pattern of CDs-ZnBi₂O₄ samples had similar diffraction peaks but slightly shifted compared to the peaks of bare ZnBi₂O₄. The shift of the diffraction peaks of CDs-ZnBi₂O₄ samples may be due to the formation of intimate contact between CDs and ZnBi₂O₄. This also suggests that the intimate contact between CDs and ZnBi₂O₄ facilitated the movement of photogenerated e^{-}/h^{+} pairs at the interface within CDs-ZnBi₂O₄.

Figure 1(b) displays the FTIR spectra of the CDs, ZnBi₂O₄, and CDs (2%)-ZnBi₂O₄. For bare ZnBi₂O₄, the peaks appearing at 1630 and 3450 cm⁻¹ correspond to the bending and stretching vibration peaks of O-H, respectively [37]. The absorption peaks appear at wavenumbers of about 1381 and 847 cm⁻¹ confirm the presence of the Bi-O bonds [31, 38] and Bi-O-Bi bonds [6, 39, 40], respectively. As seen in Figure 1(b), the bands in the range of $3600-3200 \text{ cm}^{-1}$ in the bare CD spectrum are the typical bands of the stretching vibration modes for hydroxyl (O-H) and N-H groups. The significant absorption peak appearing at 1634 cm⁻¹ is attributed to the C=O bond in the carboxyl (COO⁻) group [41, 42]. The weak band at 1552 cm^{-1} is compatible with the N-H bending, demonstrating the presence of aminocontaining functional groups. The band at 1400 cm^{-1} is consistent with the C=C bond of the aromatic ring, confirming aromatization. The appearance of the C=C bond (Figure 1(b)) indicates that the CDs have a predominantly graphitic structure [41], whereas the O-H, N-H, and C=O bond vibrations indicate that these characteristic groups are attached to the surface of the CDs. For CDs-ZnBi₂O₄ with different CDs contents, the characteristic bands at 1634 and 1387 cm⁻¹ demonstrate the appearance of C=O and C=C bond vibrations. The 3 cm^{-1} shift of the C=C bonds for the CDs-ZnBi₂O₄ samples compared to that of the bare CDs is owing to the electrostatic interaction of CDs with and ZnBi₂O₄ [43].

As illustrated in Figure 2(a), the TEM image indicates that the CDs were mainly monodisperse and spherical. The HRTEM image shows the lattice fringes with a *d*-spacing of 0.21 nm, corresponding to the (100) plane lattice of graphite [44]. The size distribution histogram also indicated particle sizes of CDs less than 7.5 nm with an average size of 5.1 nm. Furthermore, the SEM-EDX spectrum of CDs confirmed the presence of C (38.73%), N (12.10%), and O (39.85%) elements in the sample. The SEM micrographs of the samples in Figure 2(b) show that bare ZnBi₂O₄ consisted of individual plates that were different sizes and stacked on top of each other. For the CDs-ZnBi₂O₄ samples, the CDs were relatively uniformly dispersed, with some amount of aggregation on the surface of ZnBi₂O₄. From the EDX spectrum of



FIGURE 1: (a) XRD pattern. (b) FTIR spectra of catalyst.

CDs (2%)-ZnBi₂O₄, the proportions of the elements in CDs (2%)-ZnBi₂O₄ were as follows: Zn (43.75%), Bi (37.59%), O (16.85%), N (0.41%), and C (1.38%).

3.2. Performance of 2, 4-D Photodegradation. Experiments evaluating the influence of the amount of CDs in CDs-ZnBi₂O₄ on 2, 4-D decomposition efficiency were conducted at 30 mg/L 2, 4-D, a solution pH of 4.2, and using different catalysts at a dosage of 1.0 g/L. As displayed in Figure 3(a), the visible-light photolysis assay confirmed the photochemical stability of 2, 4-D. Approximately 12.9% and 46.1% of 2, 4-D were degraded by the bare CDs and ZnBi₂O₄ after 120 minutes of exposure to visible radiation, respectively. The photocatalytic performance of the heterojunction CDs-ZnBi₂O₄ was superior to that of the bare CDs and ZnBi₂O₄ components, although the photocatalytic activity of CDs (5%)-ZnBi₂O₄ was comparable that of bare ZnBi₂O₄. Among the photocatalysts, CDs (2%)-ZnBi₂O₄ displayed outstanding adsorption and photocatalytic properties. With the participation of CDs (2%)-ZnBi₂O₄, the efficiency of 2, 4-D removal reached 82.7% after adsorption for 60 min and visible radiation for 120 min. However, Figure 3(a) shows that the activity of CDs (5%)-ZnBi₂O₄ was clearly reduced; therefore, the excessive introducing of CDs onto ZnBi₂O₄ may adversely affect the activity of photocatalysts. The improvement in catalytic performance of CDs (2%)-ZnBi₂O₄ is indexed to the efficiency of decoupling and delaying recombination of e^{-}/h^{+} pairs via the heterostructure. However, with excess CDs, as in the case of CDs (5%)-ZnBi₂O₄, the CDs can perform as intermediates, favoring photoinduced e^{-}/h^{+} recoupling. These results demonstrate the formation of the heterogeneous junction

between the CDs and ${\rm ZnBi}_2{\rm O}_4$ semiconductors through intimate surface contact.

The rate constants for (k) 2, 4-D decomposition were computed using the pseudo-first-order kinetic equation and are presented in Figure 3(b). Remarkably, the rate constant for photodegradation of 2, 4-D over the heterojunction elevated noticeably compared to that obtained with the individual catalyst components. The heterojunction CDs (2%)-ZnBi₂O₄ afforded the outstanding activity, with $k = 0.0139 \text{ min}^{-1}$, and the decomposition efficiency was about 12.6 and 2.7-fold greater than those of the CDs $(k = 0.0011 \text{ min}^{-1})$ and ZnBi_2O_4 $(k = 0.0051 \text{ min}^{-1})$, respectively. Consequently, the formation of the heterojunction improved the photoactivity of the bare CDs and ZnBi₂O₄. The factors affecting the photodecomposition efficiency of 2, 4-D were investigated by using the heterojunction CDs (2%)-ZnBi₂O₄, which had the best visible-light catalytic activity.

The best catalytic activity of CDs (2%)-ZnBi₂O₄ was also confirmed by XPS, UV-vis-DRS, photoluminescence (PL), and electrochemical impedance spectroscopy (EIS) analyses.

XPS was employed to determine the elemental compositions of the materials. As shown in Figure 4(a), the deconvoluted C 1s XPS profile of CDs (2%)-ZnBi₂O₄ shows a number of peaks at binding energies of 284.5, 286.1, and 288.1 eV, corresponding to various types of carbon bonds: sp^2 C=C, C-O, and C=O, respectively [45]. Binding energy peaks of the Zn 2p1/2 and Zn 2p3/2 states were observed at 1044.7 and 1021.5 eV for bare ZnBi₂O₄ (Figure 4(b)), indicating that Zn is in the divalent state [46]. However, the two strong peaks of Zn 2p in the spectrum of CDs (2%)-ZnBi₂O₄ shifted towards lower binding energy (0.5–0.6 eV) compared with that of the bare ZnBi₂O₄ sample; this may be



FIGURE 2: (a) TEM, HRTEM, SEM-EDX, and particle size of CDs and (b) SEM-EDX of catalyst.

due to the strong interaction between the CDs and ZnBi₂O₄, which is favorable for electron movement between the CDs and ZnBi₂O₄. Binding energy peaks of the Bi 4f7/2 and Bi 4f5/2 were located at 159.3 and 164.6 eV for ZnBi₂O₄ (Figure 4(c)), indicating that Bi exists as Bi³⁺ [46]. However, the Bi 4f peak shifted by approximately 0.2 eV towards lower binding energy for CDs (2%)-ZnBi₂O₄ compared with bare ZnBi₂O₄, due to the sustained interaction between the CDs and ZnBi₂O₄. The O 1s XPS profiles of ZnBi₂O₄ show broad peaks at 530.6 eV (Figure 4(d)), which is assigned to lattice oxygen [47]. Furthermore, the O 1s XPS profile of the CDs (2%)-ZnBi₂O₄ displays two peaks at 531.3 eV and 529.7 eV, indexed to the chemically adsorbed oxygen on the surface (O^{chem}) and O²⁻ ions, respectively [48]. The two peaks in the deconvoluted oxygen profile of CDs (2%)-ZnBi₂O₄ compared to that of bare ZnBi₂O₄ may be because of the chemical bonding between ZnBi₂O₄ and CDs.

As illustrated in the UV-vis DRS profile of CDs (2%)-ZnBi₂O₄ (Figure 5(a)), the range of light absorption was broadened towards the visible region, indicating intimate association between the CDs and ZnBi₂O₄. Figure 5(a) (inset) displays the typical Tauc plot; the bandgap energy



FIGURE 3: (a) Photocatalytic decomposition of 2,4-D and (b) rate constant photodecomposition of 2,4-D in the over catalysts after 120 minutes of exposure to visible radiation (catalyst: 1.0 g/L, 2,4-D: 30 mg/L at a pH of 4.2).

(*Eg*) of $ZnBi_2O_4$ was estimated to be 3.10 eV; however, the *Eg* of the CDs (2%)-ZnBi_2O_4 decreased to 2.93 eV. Indeed, the intimate association of the CDs with $ZnBi_2O_4$ narrowed the bandgap, thereby increasing the visible-light catalytic activity.

The separation of charge carriers and the charge transfer efficiency can be determined from the PL and EIS data. The PL emission peak of the CDs (2%)-ZnBi₂O₄ (Figure 5(b)) was in a similar position to that of bare ZnBi₂O₄ but with significantly lower intensity, indicating that separation of the photoexcited charge carriers is maximal in CDs (2%)-ZnBi₂O₄, which is very useful for achieving efficient photocatalytic performance. Electrochemical impedance spectroscopy (EIS) is a powerful technique for measuring the charge transfer efficiency of a material by constructing Nyquist plots. The Nyquist plot of CDs (2%)-ZnBi₂O₄ (Figure 5(c)) has a smaller arc radius than that of bare ZnBi₂O₄, suggesting that CDs (2%)-ZnBi₂O₄ exhibits excellent charge transfer efficiency with low resistance. The lower impedance of CDs (2%)-ZnBi₂O₄ may be related to extension of the visible light absorption range over a wider region in comparison to that of ZnBi₂O₄, leading to a greater carrier density and faster interfacial charge transfer in CDs (2%)-ZnBi₂O₄. Indeed, the intimate association of ZnBi₂O₄ with the CDs leads to better charge separation and more efficient electron transfer at the boundary between ZnBi₂O₄ and the CDs.

Because the pH adjusts the surface charge of the photocatalyst, different toxic contaminants must be decomposed at different pH levels. Therefore, pH is a major parameter influencing photocatalytic decomposition. Experiments to evaluate the influence of pH on the photodegradation efficiency of 30 mg/L 2, 4-D by 1.0 g/L CDs (2%)-ZnBi₂O₄

catalyst were performed by altering the pH of the reaction solution from 2.0 to 7.0. The concentration of 2, 4-D decreased significantly after 120 minutes of exposure to visible radiation at pH 4.0 (Figure 6(a)). Approximately 91.1% of 2, 4-D was degraded over the CDs (2%)-ZnBi₂O₄ catalyst at pH 4.0 (with $k = 0.0178 \text{ min}^{-1}$) after 120 minutes of exposure to visible radiation, whereas the decomposition of 2, 4-D reached ~78.6% ($k = 0.0110 \text{ min}^{-1}$) for pH 2.0, 84.3% $(k = 0.0134 \text{ min}^{-1})$ for pH 3.0, 85.7% $(k = 0.0139 \text{ min}^{-1})$ for pH 4.2, and 71.4% ($k = 0.0082 \text{ min}^{-1}$) for pH 7.0. The decrease in 2, 4-D decomposition efficiency at pH values less than or greater than 4.0 could be interpreted as follows: The point of zero charge (pHPZC) and pKa of 2, 4-D have a crucial effect on the catalyst activity and protonation of carboxyl groups of 2, 4-D, respectively. As shown in Figure 6(b), the pH_{PZC} of CDs (2%)-ZnBi₂O₄ was found to be ~6.78. When $pH_{solution} < pH_{PZC}$, the surface of CDs (2%)-ZnBi₂O₄ becomes positively charged; however, when $pH_{solution} = 2.0$, less than pKa of 2, 4-D (pKa = 2.74) hinders protonation of the 2, 4-D molecule; therefore, unprotonated 2, 4-D is the main species in the solution, resulting in less 2, 4-D degradation. In comparison, at $pH_{solution} = 7.0$ (>pH_{PZC}), the surface of CDs (2%)-ZnBi₂O₄ becomes negatively charged. Electrostatic repulsion prevents the 2, 4-D anion from contacting with the negatively charged surface of the CDs (2%)-ZnBi₂O₄ catalyst, resulting in less 2, 4-D degradation. The optimal decomposition of 2, 4-D at pH 4.0 is attributed to the availability of the -COOH groups of 2, 4-D for protonation; therefore, it is very convenient for the 2, 4-D anions to approach the positively charged surface of the CDs (2%)-ZnBi₂O₄ catalyst, resulting in significant 2, 4-D degradation.



FIGURE 4: XPS spectra of (a) C 1s, (b) Zn 2p, (c) Bi 4f, and (d) O 2s in according to ZnBi₂O₄ and CDs (2%)-ZnBi₂O₄.

The effect of catalyst dosage on the photodegradation of 2, 4-D was evaluated by altering the amount of CDs (2%)- $ZnBi_2O_4$ in the range of 0.5–2.0 g/L, while the initial concentrations of 2, 4-D and pH were carried on with 30 mg/L and 4.0, respectively. As illustrated in Figure 6(c), the CDs (2%)-ZnBi₂O₄ dosage of 1.0 g/L yielded the optimal 2, 4-D degradation efficiency. Catalyst dosages greater or less than 1.0 g/L did not yield the optimal degradation efficiency of 2, 4-D. These findings can be put forward for interpretation as follows: With a reasonable ratio between the catalyst dosage, 2, 4-D concentration, and the number of photons occupied on the catalyst surface, the photodecomposition rate of 2, 4-D increased. However, a very low CDs (2%)-ZnBi₂O₄ dosage led to insufficient generation of oxidizing radicals for degrading 2, 4-D. Likewise, an excessive dose of CDs (2%)-ZnBi₂O₄ increased turbidity such that light could not reach the active sites of the CDs (2%)-ZnBi₂O₄ catalyst, resulting in reduced formation of photoinduced e^{-}/h^{+} pairs, leading to insufficient oxidizing radicals; thus, the rate of 2, 4-D photodegradation decreased.

Experiments to evaluate the effect of initial 2, 4-D concentration on the rate of photodegradation were carried out with a 2, 4-D concentration range of 10–50 mg/L and pH of the solution at 4.0. The optimal CDs (2%)-ZnBi₂O₄ dosage was 1.0 g/L. High 2, 4-D concentrations resulted in low decomposition efficiency (Figure 6(d)). These findings can be explained as follows: Since the amount of CDs (2%)-ZnBi₂O₄ and the light intensity remained unchanged, a certain amount of reactive radicals such as e^-/h^+ pairs, •OH, and O₂^{-•} was generated while the initial concentration of 2, 4-D increased. Therefore, the number of active radicals attacking 2, 4-D was insufficient, resulting in a decrease in the photodegradation efficiency of 2, 4-D.

The key to practical applications of catalysts is their stability and reusability. To evaluate the reuse efficiency, CDs (2%)-ZnBi₂O₄ was exposed to 30 mg/L 2, 4-D at pH 4.0, with a ratio of catalyst/2, 4-D solution of 1:1. The catalyst was extracted by centrifugation at the end of the decomposition reaction (120 minutes). Before use for the next run, the recovered catalyst was heated at 100°C for 90 min and reused



FIGURE 5: (a) UV-vis DRS spectra (Inset: $(\alpha h\nu)^2$ vs. $h\nu$). (b) Emission spectrum ($\lambda_{\text{excitation}} = 370$ nm). (c) EIS properties (Nyquist plots) of ZnBi₂O₄ and CDs (2%)-ZnBi₂O₄.

four times in succession. The reuse efficiency data of CDs (2%)-ZnBi₂O₄ are summarized in Figure 7 and Table 1.

The results in Table 1 indicated that CDs (2%)-ZnBi₂O₄ exhibited significant photostabilization after 120 min, and the percentage photodegradation of 2, 4-D reached 91.1 \pm 1.6% for the first use, 88.9 \pm 3.1% for the second reuse, 87.8 \pm 2.9% for the third reuse, and 86.4 \pm 1.5% for the fourth reuse. Overall, the CDs (2%)-ZnBi₂O₄ is an excellent catalyst for the efficient removal of toxic organic substances over multiple cycles of exposure to visible light. Most of the decomposed 2, 4-D was dechlorinated, as confirmed by quantifying the amount of inorganic chloride in solution before and after the decomposition reaction.

As summarized in Table 1, the conversion of chloride in the structure of 2, 4-D (toxic organic chloride) to nontoxic inorganic chloride by CDs (2%)-ZnBi₂O₄ after 120 min of visible light exposure was $90.7 \pm 1.2\%$ for the first run, 88.8 ± 1.1 for the second run, 85.3 ± 1.4 for the third run, and 82.2 ± 1.9 for the fourth run. After four consecutive tests, approximately 2.3–6.8% of 30 mg/L 2, 4-D was present as chloride-free organic carbon intermediates. The efficiency of 2, 4-D mineralization by CDs (2%)-ZnBi₂O₄ catalyst was determined by quantifying organic carbon (TOC) in the solution at the beginning and end of the decomposition reaction. The TOC of the 2, 4-D solution decreased by approximately $86.6 \pm 1.6\%$ in the first run (Table 1). Based on the differences between 2, 4-D decomposition, dechlorination efficiency, and 2, 4-D mineralization, it can be confirmed that 2, 4-D was almost completely decomposed to CO₂ and H₂O after 120 min of visible radiation exposure using CDs (2%)-ZnBi₂O₄ at pH 4.0.

A number of different catalysts have studied the decomposition efficiency of 2, 4-D using different light sources, and the comparative results are presented in Table 2.

The hole in the valence band (h_{VB}^+) , hydroxyl radicals (OH[•]), and superoxide radicals (O₂^{•-}) are highly oxidizing agents that may be active in photocatalysis for pollutant degradation. To confirm the importance of radicals $(h_{VB}^+, OH^{\bullet}O_2^{\bullet-})$ that can interfere with 2, 4-D photodegradation by CDs (2%)-ZnBi₂O₄, experiments were conducted with



FIGURE 6: (a) Effect of altering the pH solution (catalyst: 1.0 g/L, 2,4-D: 30 mg/L). (b) Point of zero charge of CDs (2%)-ZnBi₂O₄ by the salt addition method (Δ pH vs. pH_{initial}). (c) Effect of altering the dose of CDs (2%)-ZnBi₂O₄ (2,4-D: 30 mg/L at a pH of 4.0). (d) Effect of altering the initial 2,4-D concentration (catalyst: 1.0 g/L at a pH of 4.0).

30 mg/L 2, 4-D at pH 4.0 and a catalyst/solution ratio of 1:1 in the participation of radical scavengers. Figure 8(a) indicates that when a scavenger (2.0 mM *tert*-butanol) was added in the photocatalytic experiment, approximately 58.7% of the 2, 4-D was degraded using CDs (2%)-ZnBi₂O₄. The resulting degradation rate was ~0.0066 min⁻¹, which indicates that OH• was not the dominant radical for 2, 4-D degradation over CDs (2%)-ZnBi₂O₄. By adding 2.0 mM *p*benzoquinone to the decomposition system as a scavenger, the efficiency of 2, 4-D decomposition over CDs (2%)- ZnBi₂O₄ declined. Approximately 43.2% of 2, 4-D was decomposed after 120 minutes of exposure to visible radiation in the participation of *p*-benzoquinone as a scavenger of $O_2^{\bullet-}$. When 1.0 mM Na₂EDTA, an electron donor, was used as the scavenger to remove h_{VB}^+ , the efficiency of 2, 4-D decomposition was significantly reduced. Approximately 16.5% of 2, 4-D was decomposed after 120 minutes of exposure to visible radiation, where the decomposition rate was 0.0010 min⁻¹. The results confirm that h_{VB}^+ is a powerful agent for the degradation of 2, 4-D catalyzed by CDs (2%)-



FIGURE 7: Reuse efficiency of the CDs (2%)-ZnBi₂O₄ (catalyst: 1.0 g/L, 2,4-D: 30 mg/L at a pH of 4.0).

TABLE 1: Data for degradation and mineralization ability of CDs (2%)-ZnBi₂O₄.

Recycle number	1^{st}	2 nd	3 rd	4^{th}
TOC initial concentration (mg/L)	13.11 ± 0.19			
TOC at the end of visible radiation exposure (mg/L)	1.76 ± 0.21	2.36 ± 0.19	2.47 ± 0.17	2.63 ± 0.28
Mineralization of 2,4-D (%)	86.6 ± 1.6	82.0 ± 1.6	81.1 ± 1.1	79.9 ± 2.4
Decomposition of 2,4-D (%)	91.1 ± 1.8	89.8 ± 3.1	87.8 ± 2.9	86.4 ± 1.5
Different between 2,4-D decomposition and mineralization (%)	4.5	7.8	6.7	6.5
Chloride amount according to 30 mg/L 2,4-D (mg/L)	9.70			
Initial concentration of inorganic anion Cl ⁻ (mg/L)	0			
Inorganic anion Cl ⁻ at the end of visible radiation exposure (mg/L)	8.79 ± 0.12	8.61 ± 0.11	8.27 ± 0.14	7.98 ± 0.19
Dechlorination efficiency (%)	90.7 ± 1.2	88.8 ± 1.1	85.3 ± 1.4	82.2 ± 1.9

TABLE 2: Comparative results of 2,4-D decomposition efficiency by different catalysts.

Catalyst and light source	pН	Time (min)	2,4-D (mg/L)	Catalyst dose (g/L)	Decomposition (mineralization) (%)	Ref
CDs (2%)-ZnBi ₂ O ₄ /visible	4.0	120	30	1.0	91.1 (86.6)	This study
Hydrochar-ZnBi ₂ O ₄ /visible	4.0	135	30	1.0	90.8 (86.4)	[34]
rGO-ZnBi ₂ O ₄ /visible	2.45	120	30	1.0	>90.0 (83.7)	[32]
$TiO_2@MgFe_2O_4 + H_2O_2/visible$	2.0	240	100	0.5	>83.0 (-)	[2]
Ag ₃ PO ₄ -TiO ₂ /visible	3.0	60	10	1.0	98.4 (-)	[3]
Mn-ZnO-graphene/LED	5.0	120	25	2.0	66.2 (-)	[4]
TiO ₂ -zeolite HY/UV	3.0	300	200	2.0	100.0 (>80.0)	[5]
TiO ₂ /UVA	5.0	180	25	1.5	97.5 (39.9)	[49]
$TiO_2 + H_2O_2/UVA$	5.0	180	25	1.5	99.7 (56.0)	[49]

 $ZnBi_2O_4$, whereas the O_2^{\bullet} and OH^{\bullet} radicals had relatively little influence on the degradation of 2, 4-D.

Based on the radical scavengers research, a feasible mechanism for the catalytic decomposition of 2, 4-D over CDs (2%)-ZnBi₂O₄ is proposed in Figure 8(b). Owing to their upconversion fluorescence properties, CDs can serve as efficient energy-transfer materials in CDs-based composite photocatalysts by converting visible and near-infrared light to shorter wavelength, for instance, an emission of ultraviolet light under visible light excitation [50]. When the CDs (2%)-ZnBi₂O₄ system was excited with visible radiation, the

CDs absorbed long-wave radiation and emitted short-wave radiation owing to their photoluminescence properties [51]. Meanwhile, $ZnBi_2O_4$ absorbed both long-wave and shortwave radiation, resulting in being excited and creating more electron-hole pairs. These photoinduced electrons in the conduction band (CB) of $ZnBi_2O_4$ tend to be shuttled in the conducting network of the CDs because of the conjugated system of the CDs [52, 53]. Therefore, the CDs in CDs (2%)- $ZnBi_2O_4$ act as acceptors for the photoinduced electrons emitted from $ZnBi_2O_4$, thereby slowing down recombination of the photoinduced electron-hole pairs at the



FIGURE 8: (a) Photodecomposition efficiency of 2,4-D over CDs (2%)-ZnBi₂O₄ with and without addition of scavengers after 120 minutes of exposure to visible radiation at a pH of 4.0 and (b) the diagram depicting the separation of e^-/h^+ pairs and the movement of e^- at the interface between CDs and ZnBi₂O₄ in the catalyst.

interface of the composite [50, 52]. The migrated electrons that accumulated on the CDs reacted with adsorbed O_2 to form $O_2^{\bullet-}$ radicals. The photoinduced holes in the valence band (VB) of ZnBi₂O₄ react with adsorbed reductants (usually OH⁻) to produce oxidizing species (e.g., OH[•]). As

a result, the very strong oxidizing agents ($O_2^{\bullet-}$, OH^{\bullet} , and photoinduced h^+) degraded the 2, 4-D molecules to generate CO_2 and H_2O .

The following reactions illustrate the degradation of 2, 4-D by CDs (2%)-ZnBi₂O₄ under visible light:

$$CDs(2\%) - ZnBi_2O4 + h\nu \longrightarrow CDs(2\%) - ZnBi_2O_4(e^-, h^+)$$
(1)

$$CDs(2\%) - ZnBi_2O_4(h^+) + 2,4 - D \longrightarrow degradation products \longrightarrow CO_2 + H_2O + Cl^-$$
 (2)

$$CDs(2\%) - ZnBi_2O_4(e^-) + O_2 \longrightarrow O_2^{\bullet-}$$
(3)

$$CDs(2\%)-ZnBi_2O_4(h^+) + 2H_2O \longrightarrow OH^{\bullet} + H^+$$
(4)

$$O_2^{\bullet-} + 2,4-D \longrightarrow \text{degradation products} \longrightarrow CO_2 + H_2O$$
 (5)

$$OH^{\bullet} + 2,4-D \longrightarrow degradation products \longrightarrow CO_2 + H_2O$$
 (6)

$$h^{+} + e^{-} \longrightarrow (e^{-}, h^{+})$$
 (negligible recombination) (7)

4. Conclusions

A series of CDs-ZnBi₂O₄ photocatalysts were successfully synthesized. The photocatalyst containing 2% CDs by weight displayed the highest photocatalytic activity after 120 minutes of exposure to visible radiation. The significantly improved catalytic activity of CDs (2%)-ZnBi₂O₄ can be assigned to its good ability to capture visible radiation and the movement of photoinduced electrons from the CB of ZnBi₂O₄ to the CDs, resulting in a prolonged separation time of the photoinduced e^-/h^+ pairs. CDs (2%)-ZnBi₂O₄ is relatively stable, and the activity did not decrease over four consecutive reuse cycles. Approximately, 91.1-86.4% of 2, 4-D was decomposed after 120 minutes of exposure to visible radiation in four consecutive cycles, and 86.6-79.9% of decomposed 2, 4-D was mineralized to CO₂ and H₂O. Photoinduced h^+ also plays a key role, whereas the $O_2^{\bullet-}$ and OH[•] radicals play a supporting role in 2, 4-D degradation. The findings in this study are evidence of the dual benefits of utilizing biowaste to develop new photocatalysts to simultaneously eliminate the impact of biological waste on the environment and decompose toxic organic pollutants.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest regarding the publication of this paper.

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References

- J. Cai, M. Zhou, W. Yang, Y. Pan, X. Lu, and K. G. Serrano, "Degradation and mechanism of 2, 4-dichlorophenoxyacetic acid (2, 4-D) by thermally activated persulfate oxidation," *Chemosphere*, vol. 212, pp. 784–793, 2018.
- [2] B. T. Huy, D. S. Jung, N. T. Kim Phuong, and Y. I. Lee, "Enhanced photodegradation of 2, 4-dichlorophenoxyacetic acid using a novel TiO2@MgFe2O4 core@shell structure," *Chemosphere*, vol. 184, pp. 849–856, 2017.
- [3] F. Amiri, M. Dehghani, Z. Amiri, S. Yousefinejad, and A. Azhdarpoor, "Photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid from aqueous solutions by Ag3PO4/ TiO2 nanoparticles under visible light: kinetic and

thermodynamic studies," *Water Science and Technology*, vol. 83, no. 12, pp. 3110–3122, 2021.

- [4] R. Ebrahimi, M. Mohammadi, A. Maleki et al., "Photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid in aqueous solution using Mn-doped ZnO/graphene nanocomposite under LED radiation," *Journal of Inorganic and Organometallic Polymers and Materials*, vol. 30, no. 3, pp. 923–934, 2020.
- [5] M. V. Shankar, S. Anandan, N. Venkatachalam, B. Arabindoo, and V. Murugesan, "Fine route for an efficient removal of 2, 4dichlorophenoxyacetic acid (2, 4-D) by zeolite-supported TiO2," *Chemosphere*, vol. 63, no. 6, pp. 1014–1021, 2006.
- [6] W. Wei, W. Sun, H. Hu, Z. Jiang, L. Ma, and J. Xie, "Controllable synthesis of magnetic Fe3O4 encapsulated semimetal Bi nanospheres with excellent stability and catalytic activity," *Journal of Materials Science*, vol. 53, no. 19, pp. 13886–13899, 2018.
- [7] S.-S. Lee, B. T. Huy, N. T. K. Phuong, D. K. Tung, and Y.-I. Lee, "Enhanced performance in the photocatalytic degradation of 2,4,5-Trichlorophenoxyacetic acid over Eudoped Bi2WO6 under visible light irradiation," *Korean Journal of Chemical Engineering*, vol. 36, no. 10, pp. 1716– 1723, 2019.
- [8] H. Liu, Z. Jin, Y. Su, and Y. Wang, "Visible light-driven Bi2Sn2O7/reduced graphene oxide nanocomposite for efficient photocatalytic degradation of organic contaminants," *Separation and Purification Technology*, vol. 142, pp. 25–32, 2015.
- [9] W. Xu, J. Fang, Y. Chen et al., "Novel heterostructured Bi2S3/ Bi2Sn2O7 with highly visible light photocatalytic activity for the removal of rhodamine B," *Materials Chemistry and Physics*, vol. 154, pp. 30–37, 2015.
- [10] P. Krishnaiah, R. Atchudan, S. Perumal, E.-S. Salama, Y. R. Lee, and B.-H. Jeon, "Utilization of waste biomass of Poa pratensis for green synthesis of n-doped carbon dots and its application in detection of Mn2+ and Fe3+," *Chemosphere*, vol. 286, Article ID 131764, 2022.
- [11] S. Fan, Y. Wang, Z. Wang, J. Tang, J. Tang, and X. Li, "Removal of methylene blue from aqueous solution by sewage sludge-derived biochar: adsorption kinetics, equilibrium, thermodynamics and mechanism," *Journal of Environmental Chemical Engineering*, vol. 5, no. 1, pp. 601–611, 2017.
- [12] Y. Wang and A. Hu, "Carbon quantum dots: synthesis, properties and applications," *Journal of Materials Chemistry* C, vol. 2, no. 34, pp. 6921–6939, 2014.
- [13] A. Prasannan and T. Imae, "One-pot synthesis of fluorescent carbon dots from orange waste peels," *Industrial & Engineering Chemistry Research*, vol. 52, no. 44, pp. 15673–15678, 2013.
- [14] M. T. Efa and T. Imae, "Hybridization of carbon-dots with ZnO nanoparticles of different sizes," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 92, pp. 112–117, 2018.
- [15] C. Liu, Y. Fu, Y. Xia et al., "Cascaded photo-potential in a carbon dot-hematite system driving overall water splitting under visible light," *Nanoscale*, vol. 10, no. 5, pp. 2454–2460, 2018.

- [16] H. Li, X. He, Z. Kang et al., "Water-soluble fluorescent carbon quantum dots and photocatalyst design," *Angewandte Chemie International Edition*, vol. 49, no. 26, pp. 4430–4434, 2010.
- [17] Y. Deng, M. Chen, G. Chen et al., "Visible–ultraviolet upconversion carbon quantum dots for enhancement of the photocatalytic activity of titanium dioxide," ACS Omega, vol. 6, no. 6, pp. 4247–4254, 2021.
- [18] D. Li, S. Wang, F. Azad, L. Zhao, and S. Su, "A simple method for the preparation of multi-color carbon quantum dots by using reversible regulatory color transformation," *Microchimica Acta*, vol. 186, no. 9, p. 612, 2019.
- [19] S. Xie, H. Su, W. Wei, M. Li, Y. Tong, and Z. Mao, "Remarkable photoelectrochemical performance of carbon dots sensitized TiO2 under visible light irradiation," *Journal of Materials Chemistry A*, vol. 2, no. 39, pp. 16365–16368, 2014.
- [20] X. Lv, X. Xiao, M. Cao et al., "Efficient carbon dots/NiFelayered double hydroxide/BiVO4 photoanodes for photoelectrochemical water splitting," *Applied Surface Science*, vol. 439, pp. 1065–1071, 2018.
- [21] X. Wu, J. Zhao, S. Guo et al., "Carbon dot and BiVO4 quantum dot composites for overall water splitting via a twoelectron pathway," *Nanoscale*, vol. 8, no. 39, pp. 17314–17321, 2016.
- [22] G. Wang, W. Zhang, J. Li, X. Dong, and X. Zhang, "Carbon quantum dots decorated BiVO4 quantum tube with enhanced photocatalytic performance for efficient degradation of organic pollutants under visible and near-infrared light," *Journal of Materials Science*, vol. 54, no. 8, pp. 6488–6499, 2019.
- [23] Z. Zhang, T. Zheng, J. Xu, H. Zeng, and N. Zhang, "Carbon quantum dots/Bi2MoO6 composites with photocatalytic H2 evolution and near infrared activity," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 346, pp. 24–31, 2017.
- [24] N. T. Kim Phuong, M.-W. Beak, B. T. Huy, and Y.-I. Lee, "Adsorption and photodegradation kinetics of herbicide 2,4,5-trichlorophenoxyacetic acid with MgFeTi layered double hydroxides," *Chemosphere*, vol. 146, pp. 51–59, 2016.
- [25] L. Mohapatra and K. Parida, "Zn-Cr layered double hydroxide: visible light responsive photocatalyst for photocatalytic degradation of organic pollutants," *Separation and Purification Technology*, vol. 91, pp. 73–80, 2012.
- [26] W. Fei, Y. Song, N. Li et al., "Fabrication of visible-light-active ZnO/ZnFe-LDH heterojunction on Ni foam for pollutants removal with enhanced photoelectrocatalytic performance," *Solar Energy*, vol. 188, pp. 593–602, 2019.
- [27] B. T. Huy, D. S. Paeng, C. Thi Bich Thao, N. T. Kim Phuong, and Y.-I. Lee, "ZnO-Bi2O3/graphitic carbon nitride photocatalytic system with H2O2-assisted enhanced degradation of Indigo carmine under visible light," *Arabian Journal of Chemistry*, vol. 13, no. 2, pp. 3790–3800, 2020.
- [28] B. T. Huy, C. T. B. Thao, V.-D. Dao, N. T. K. Phuong, and Y.-I. Lee, "A mixed-metal oxides/graphitic carbon nitride: high visible light photocatalytic activity for efficient mineralization of rhodamine B," *Advanced Materials Interfaces*, vol. 4, no. 12, Article ID 1700128, 2017.
- [29] N. Thi Mai Tho, B. The Huy, D. N. Nha Khanh et al., "Mechanism of visible-light photocatalytic mineralization of indigo carmine using ZnBi2O4-Bi2S3 composites," *ChemistrySelect*, vol. 3, no. 35, pp. 9986–9994, 2018.
- [30] N. T. M. Tho, B. T. Huy, D. N. N. Khanh et al., "Facile synthesis of ZnBi2O4-graphite composites as highly active visible-light photocatalyst for the mineralization of

- [31] A. Habibi-Yangjeh, M. Pirhashemi, and S. Ghosh, "ZnO/ ZnBi2O4 nanocomposites with p-n heterojunction as durable visible-light-activated photocatalysts for efficient removal of organic pollutants," *Journal of Alloys and Compounds*, vol. 826, Article ID 154229, 2020.
- [32] N. T. M. Tho, D. N. N. Khanh, N. Q. Thang, Y.-I. Lee, and N. T. K. Phuong, "Novel reduced graphene oxide/ZnBi2O4 hybrid photocatalyst for visible light degradation of 2, 4dichlorophenoxyacetic acid," *Environmental Science and Pollution Research*, vol. 27, no. 10, pp. 11127–11137, 2020.
- [33] B. T. Huy, P. T. Nhi, N. T. T. Vy et al., "Design of novel p-n heterojunction ZnBi2O4-ZnS photocatalysts with impressive photocatalytic and antibacterial activities under visible light," *Environmental Science and Pollution Research*, vol. 29, no. 56, pp. 84471–84486, 2022.
- [34] N. T. Tuong Vy, D. N. Nha Khanh, N. N. Nghia et al., "Key role of corncob based-hydrochar (HC) in the enhancement of visible light photocatalytic degradation of 2, 4-dichlorophenoxyacetic acid using a derivative of ZnBi-layered double hydroxides," *Materials*, vol. 16, no. 14, p. 5027, 2023.
- [35] S. A. A. Vandarkuzhali, S. Natarajan, S. Jeyabalan et al., "Pineapple peel-derived carbon dots: applications as sensor, molecular keypad lock, and memory device," *American Chemical Society Omega*, vol. 3, no. 10, pp. 12584–12592, 2018.
- [36] V. Raveendran and R. N. Kizhakayil, "Fluorescent carbon dots as biosensor, green reductant, and biomarker," *American Chemical Society Omega*, vol. 6, no. 36, pp. 23475–23484, 2021.
- [37] N. Premalatha and L. Rose Miranda, "Surfactant modified ZnO-Bi2O3 nanocomposite for degradation of lambdacyhalothrin pesticide in visible light: a study of reaction kinetics and intermediates," *Journal of Environmental Management*, vol. 246, pp. 259–266, 2019.
- [38] S. Bandyopadhyay and A. Dutta, "Thermal, optical and dielectric properties of phase stabilized δ – Dy-Bi2O3 ionic conductors," *Journal of Physics and Chemistry of Solids*, vol. 102, pp. 12–20, 2017.
- [39] S. Labib, "Preparation, characterization and photocatalytic properties of doped and undoped Bi2O3," *Journal of Saudi Chemical Society*, vol. 21, no. 6, pp. 664–672, 2017.
- [40] T. R. Das, S. Patra, R. Madhuri, and P. K. Sharma, "Bismuth oxide decorated graphene oxide nanocomposites synthesized via sonochemical assisted hydrothermal method for adsorption of cationic organic dyes," *Journal of Colloid and Interface Science*, vol. 509, pp. 82–93, 2018.
- [41] A. Dager, T. Uchida, T. Maekawa, and M. Tachibana, "Synthesis and characterization of mono-disperse carbon quantum dots from fennel seeds: photoluminescence analysis using machine learning," *Scientific Reports*, vol. 9, no. 1, Article ID 14004, 2019.
- [42] Y. Guo, L. Zhang, F. Cao, and Y. Leng, "Thermal treatment of hair for the synthesis of sustainable carbon quantum dots and the applications for sensing Hg2+," *Scientific Reports*, vol. 6, no. 1, Article ID 35795, 2016.
- [43] D. Tang, J. Liu, X. Wu et al., "Carbon quantum dot/NiFe layered double-hydroxide composite as a highly efficient electrocatalyst for water oxidation," *American Chemical Society Applied Materials and Interfaces*, vol. 6, no. 10, pp. 7918–7925, 2014.
- [44] Y. Zhang, J. Feng, M. He et al., "Efficient and stable white fluorescent carbon dots and CD-based glass thin-films via

screen-printing technology for use in W-LEDs," Royal Society of Chemistry Advances, vol. 7, no. 78, pp. 49542–49547, 2017.

- [45] X. Jia, J. Li, and E. Wang, "One-pot green synthesis of optically pH-sensitive carbon dots with upconversion luminescence," *Nanoscale*, vol. 4, no. 18, pp. 5572–5575, 2012.
- [46] J. Zhang, Y. Y. Jiang, W. Gao, and H.-S. Hao, "Synthesis and visible photocatalytic activity of new photocatalyst MBi2O4(M = Cu, Zn)," *Journal of Materials Science: Materials in Electronics*, vol. 26, no. 3, pp. 1866–1873, 2014.
- [47] P. Guo, J. Jiang, S. Shen, and L. Guo, "ZnS/ZnO heterojunction as photoelectrode: type II band alignment towards enhanced photoelectrochemical performance," *International Journal of Hydrogen Energy*, vol. 38, no. 29, pp. 13097–13103, 2013.
- [48] L. Q. Wu, Y. C. Li, S. Q. Li et al., "Method for estimating ionicities of oxides using O1s photoelectron spectra," *American Institute of Physics Advances*, vol. 5, no. 9, Article ID 097210, 2015.
- [49] D. O. Gamze, Ö. H. Eser, and Y. Arda, "Heterogeneous photocatalytic degradation and mineralization of 2, 4dichlorophenoxy acetic acid (2, 4-D): its performance, kinetics and economic analysis," *Desalination and Water Treatment*, vol. 137, pp. 312–327, 2018.
- [50] Y. Huang, Y. Liang, Y. Rao et al., "Environment-friendly carbon quantum dots/ZnFe2O4 photocatalysts: characterization, biocompatibility, and mechanisms for NO removal," *Environmental Science and Technology*, vol. 51, no. 5, pp. 2924–2933, 2017.
- [51] J. Xia, J. Di, H. Li, H. Xu, H. Li, and S. Guo, "Ionic liquidinduced strategy for carbon quantum dots/BiOX (X=Br, Cl) hybrid nanosheets with superior visible light-driven photocatalysis," *Applied Catalysis B: Environmental*, vol. 181, pp. 260–269, 2016.
- [52] X. T. Zheng, A. Ananthanarayanan, K. Q. Luo, and P. Chen, "Glowing graphene quantum dots and carbon dots: properties, syntheses, and biological applications," *Small*, vol. 11, no. 14, pp. 1620–1636, 2015.
- [53] B. B. Chen, M. L. Liu, and C. Z. Huang, "Carbon dot-based composites for catalytic applications," *Green Chemistry*, vol. 22, no. 13, pp. 4034–4054, 2020.