Solar-light-driven ZnO/biochar treatment of pesticides contaminated wastewater: A practical and computational study

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Abstract
Biochar (BC) was prepared by carbonizing sludge from agricultural lignocellulosic waste fermentation and then used to adsorb lambda-cyhalothrin (LM), malathion (MA), and oxamyl (OX) as potential pesticides in agrochemical industrial wastewater. Additionally, the photodegradation performance of ZnO and ZnO/Fe was evaluated using various catalyst doses in a constructed parabolic solar collector reactor. The optimal ZnO catalyst dose and reaction time was 1.0 g/L and 135 min. OX, MA, and LM removal increased from 38%, 30%, and 24% in pristine ZnO to 55%, 70%, and 46.9% in the case of the addition of BC with ZnO (ZnO/BC), respectively. The doping of ZnO with iron did not improve the photodegradation efficiency due to the reduction of crystallinity and catalyst affinity towards the pollutants after introducing those ions. The mechanism of degradation was proposed, and the by-products generated were identified. The total cost was estimated for pure ZnO, the addition of BC with ZnO (ZnO/BC), and the addition of BC with iron-doped ZnO (ZnO/Fe/BC). The highest binding energy of −44.74 was recorded for BC–OX complex, followed by BC–LM at −42.97. The adsorption of LM, MA, and OX by ZnO/BC is primarily due to the hydrophobic interaction, hydrogen bonding, and π–π interaction. After three cycles of recycling ZnO/BC, the degradation efficiency remained 55–52.5% for OX,
The increased demand for pesticides globally has accelerated the growth of agrochemical industries. The discharge of industrial effluents from agrochemical industries as well as the wastewater from agricultural activities into water sources without adequate treatment has serious consequences for humans, animals, and aquatic life. Pesticides have a high biopersistence and toxicity, making the treatment by biological processes such as activated sludge ineffective. Moreover, physical and chemical processes (e.g., electrocoagulation, adsorption, membrane filtration) have some drawbacks, such as generating secondary pollutants along with being energy-intensive processes. Due to pesticides' hazards, the researchers' motivation has been to develop low-cost, environmentally friendly, and effective techniques for treating industrial effluents containing bio-resistant pollutants (e.g., pesticides). Advanced oxidation processes (AOPs) have been widely recognized for decomposing bio-resistant micropollutants. The degradation of bio-resistant contaminants via AOPs is primarily based on the production of unselective radicals (e.g., hydroxyl radicals). In photocatalysis, radicals are produced after a semiconductor is excited by a light source (the energy of the light source must be greater than or equal to the bandgap of the semiconductor). In comparison to other AOPs, the photocatalysis process stands out due to its sustainability (use of solar light), green nature (no secondary pollutant), and high degradation performance. The wide bandgap and fast charge carriers recombination of commonly used semiconductors (TiO₂ and ZnO) are major limitations preventing the photocatalysis process from being used in practice.

Zinc oxide, on the other hand, is distinguished by its stability, low cost, and abundance. To overcome the limitations associated with ZnO, iron was doped in the lattice of ZnO to decrease the recombination rate, as iron could act as an electron trap. Chkirida et al. reported enhancing the photodegradation performance of ZnO doped with iron compared to pure ZnO for the degradation of MB. Despite the high level of interest in water contamination, the problem of solid waste management has intrigued much interest due to the serious environmental consequences. After anaerobic digestion of substrates, large amounts of sludge can be produced; thus, managing them is crucial. Converting waste bio-materials into biochar (BC) is also considered an effective negative emission technology for climate change mitigation (Osman, 2022; Fawzy, 2020). As a result, BC was prepared from the carbonization of anaerobic sludge generated from the fermentation of agricultural waste and employed in water purification. The addition of BC during the photodegradation process can improve the overall removal efficiency of target pollutants due to its ability to adsorb the pollutant molecules because of its high surface area, carbon content, and porosity. The modification by BC derived from such solid waste material promotes the circular bioeconomy while also lowering overall costs. Leichtweis et al. used BC prepared from pecan nutshells and ZnO to degrade acid red 97, while the synthesized composite showed higher performance than the pristine ZnO.

Recently, computational modeling has drawn researchers' attention to the physical and chemical interactions of pollutants adsorption studies using BC. However, few studies have been published on the computational modeling of BC-derived sludge combined with n-type semiconductors for pesticide removal in the wastewater industry.

Herein, the performance of pure ZnO, ZnO with adding BC (ZnO/BC), and ZnO doped with iron (ZnO/Fe) besides the addition of BC (ZnO/Fe/BC) for the degradation of three types of pesticides were evaluated. The influence of ZnO/BC loading and reaction time on the removal efficacy were investigated. Moreover, the degradation mechanism was suggested, and the intermediates produced were identified. Furthermore, an estimate of the expected cost of using photocatalysis in the presence of BC on a larger scale was performed. Computational modeling of solar-light-driven catalyst/
BC degrading pesticides containing wastewater was comprehensively presented.

# MATERIALS AND METHODS

## 2.1 Chemicals

Hexamine (hexamethylenetetramine or methenamine) (C₆H₁₂N₄, 99%), zinc nitrate hexahydrate (Zn(NO₃)₂.6H₂O, 97%), and ferric nitrate nonahydrate (Fe(NO₃)₃.9H₂O, 95%) were purchased from Sigma Aldrich. Ethanol (C₂H₅OH, 96%), sulfuric acid (H₂SO₄, 99%), methanol (CH₃OH, 97%), acetic acid (CH₃COOH, 30%), and acetonitrile (C₂H₃N, 97%) were procured from Acros. The chemicals were used as received.

## 2.2 Preparation of zinc oxide (ZnO) and zinc oxide doped with iron (ZnO/Fe)

An amount of 3.36 g of hexamine was mixed with 2.142 g of zinc nitrate hexahydrate. Then, 60 ml distilled water and 180 ml ethanol were added to the mixture in a round flask (500 ml). The product was then vigorously stirred for 2.0 h at a temperature of 140°C using a hot plate. Subsequently, cooling and washing the mixture using ethanol and distilled water were conducted. After washing, the prepared mixture was dried at 50°C for 24 h. The ZnO powder was then calcinated at 350°C in an autoclave for 3 h. The same steps were repeated for the preparation of ZnO doped with Fe (ZnO/Fe) besides the addition of 0.5 g of ferric nitrate during the mixing between hexamine and zinc nitrate hexahydrate.²⁸

## 2.3 BC preparation and characterization

BC was synthesized from the carbonization of sludge generated during the fermentation of agricultural lignocellulosic wastes and employed for the photodegradation of pesticides.²⁶ Sludge samples were carefully withdrawn and placed in a pyrolysis stainless steel unit free from oxygen for carbonization at a temperature of 650°C for 1 h to have the BC. X-ray fluorescence (XRF) of the BC results is presented in Figure 1A,B. The SiO₂ was quite high in the BC (31.4 wt%). This high SiO₂ in the BC was due to the original sludge being mixed with lignocellulosic wastes. Incorporating 15% SiO₂ in TiO₂ films exhibited better photocatalytic activity with increased degradation efficiency.²⁹ TiO₂ was 1.2 wt% useful for photocatalytic degradation.³⁰ The Fe₂O₃, CaO, and ZnO, values were 12.7, 9.9, and 0.41 wt%, respectively, in the BC, which have a positive effect on the photocatalytic process and minimize the required catalyst concentration to accomplish the degradation process.¹⁸,³¹ The specific surface area, pore volume, and pore size of the BC were 88.7 m²/g, 0.09 cm³/g, and 3.32 nm, respectively.

## 2.4 Preparation of synthetic wastewater

Pesticide-containing synthetic wastewater was prepared to simulate real industrial effluents from agrochemical industries in the laboratory. The major contaminants in the end-off pipe effluents released by the industrial pesticide company are lambda-cyhalothrin (LM), malathion (MA), and oxamyl (OX). Table 1 displays the characterizations of synthetic pesticide wastewater.

## 2.5 Experimental procedures

A parabolic solar collector reactor was used to decompose LM, MA, and OX, as shown in Figure 1C. The full details of the reactor were previously described in our previous work.³² In brief, the reactor was situated in a sunny area (Latitude 30° 52′, Longitude 29° 35′). The photoreactor comprises six borosilicate transparent tubes having a length of 750 mm, a diameter of 28 mm, and a surface area of 0.36 m². The tubes mentioned above were placed on parabolic aluminum reflectors with a diameter of 18.4 cm.

The system was supplied with 4 L of the contaminated solution, and the flow was recirculated using a pump. Then, the catalyst dose was added. In the first 30 min of the reaction time, the catalyst was mixed with the contaminated solution in the tank without recirculation to achieve adsorption–desorption equilibrium and evaluate the adsorption performance of the synthesized materials. Then, the flow was recirculated till the end of reaction time, and samples were withdrawn for analysis.

The solar intensity was measured by a weather station located in the same reactor area, and it was 30 W/m². The normalized illumination time was calculated using the equations mentioned in Supporting Information: Text S1. In the case of adsorption by the prepared BC, the synthesized BC was added to the tank containing 4 L of the contaminated solution with continuous stirring and without flow recirculation for 300 min.

The effect of catalyst dose of ZnO (0.1–2 g/L), ZnO with 1.0 g of the prepared BC (ZnO/BC) (0.05–0.7 g/L),...
and ZnO doped with iron besides the addition of 1.0 g of BC ZnO/Fe/BC (0.05–0.7 g/L) on the degradation efficiency of pesticides was investigated. The adsorption performance of BC using different doses (0.1–2.5 g/L) was evaluated, along with the influence of contact time.

2.6 | Computational method

The computational simulation was carried out for the experimental data. Statistics behavior of BC adsorption interactions with LM, MA, and OX was discussed. A graphene structure composed of 10 × 10 aromatic rings was employed as a BC model. In addition, a computational method was employed to simulate the interaction of zinc oxide nanoparticles (ZnO) and zinc oxide doped iron nanoparticles (ZnO/Fe) with the three pesticides, LM, MA, and OX.

2.7 | Molecule preparation

Three-dimensional structures of LM, MA, and OX were downloaded from PubChem and optimized with
The Geometry Optimization quality in BIOVIA Forcite was set to Fine and the Forcefield to BIOVIA COMPASSII. BIOVIA Forcite was also used to optimize the structure of graphene. The optimized LM, MA, and OX molecules are shown in Figure 1D. The nanoparticles’ structure was created using BIOVIA Material Studio 2017 based on its characterization. The size of zinc oxide nanoparticles (ZnO) is 20 nm, and the size of zinc oxide doped iron nanoparticles

| Parameters                                      | Value     |
|------------------------------------------------|-----------|
| pH                                             | 7.6 ± 0.3 |
| Chemical oxygen demand (COD sol.) (mg/L)       | 6000 ± 450|
| Total dissolved solids (TDS) (mg/L)            | 620 ± 50  |
| Oxamyl (mg/L)                                  | 200 ± 11  |
| Lambda-cyhalothrin (mg/L)                      | 145 ± 4.8 |
| Malathion (mg/L)                               | 100 ± 4.4 |
(ZnO/Fe) is 10 nm. The geometry optimization was carried out as previously mentioned.

2.8 | Interaction of LM, MA, and OX with BC

The BIOVIA adsorption locator module was used to gain insight into how LM, MA, and OX interact with BC surfaces. The BIOVIA adsorption locator calculation's simulating annealing task was set to a quality of Fine (energy cutoff of $1.0 \times 10^{-4}$ kcal/mol) using the Smart algorithm. The atom-based summation method was used for the electrostatic and Van der Waals with a cubic spline truncation and a cutoff distance of 1.55 nm. The forcefield selected was BIOVIA COMPASSII. The binding energy of BC with LM, MA, and OX adsorbed dodecane was determined using Equation (1).

$$\Delta E = E_{BC@x} - E_{BC} - E_x,$$  \hspace{1cm} (1)

where $\Delta E$ presents the binding energy, $E_{BC@x}$ is the total energy of BC@LM, MA, or OX complex, $E_{BC}$ is the energy of BC and $E_x$ is the energy of LM, MA, or OX.

2.9 | Interaction of ZnO and ZnO/Fe with LM, MA, and OX

The interaction of LM, MA, and OX with the ZnO and ZnO/Fe surfaces was investigated using the BIOVIA adsorption locator module, as shown in Figure 1E. The atom-based summation method was used for the electrostatic with a cubic spline truncation, a cutoff distance of 71 nm, Van der Waals with a cubic spline truncation and a cutoff distance of 1.55 nm in the BIOVIA adsorption locator calculation, and the forcefield selected was BIOVIA COMPASSII.

2.10 | Analytical methods

Concentrations of LM, MA, and OX were quantified by a Shimadzu HPLC. Syringe filters with a porosity of 0.2 µm were used to remove any suspended matter before the analysis. A mixture of ultrapure water (30%) and acetonitrile (70%) was used with a flow rate of 1 ml/min and a temperature of 30°C to measure the concentrations of MA and LM. The MA and LM absorption wavelengths were 202 and 230 nm, respectively. For the analysis of OX, ultra-pure water and methanol with a volume ratio of 80:20, respectively, were used as a mobile phase at a flow rate of 1 ml/min. The column temperature and detector wavelength were set at 30°C and 210 nm, respectively.

The generated intermediates were detected using gas chromatography-mass spectroscopy (GC-MS, Shimadzu). The helium flow rate was 1.2 ml/min. The initial temperature was 75°C for 1 min, and then it was raised at a rate of 20°C/min to reach 275°C and kept at this temperature for 7 min. The injection temperature was 45°C and remained at this value for 1 min, and then it went up to 255°C for 12 min with an increased rate of 42°C/min.

A scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectroscopy (EDS) (Jeol-JEM-611) analyzed the morphology and structure of the synthesized catalysts. Moreover, the functional groups were investigated by Fourier transform infrared spectroscopy (Shimadzu, FTIR-8400S). An X-ray diffraction apparatus (XRD 6100, Shimadzu) was used to specify the crystal structure of the prepared catalysts. Elemental analysis by wavelength dispersive XRF spectrometry was carried out by Axios advanced, sequential WD_XRF spectrometer, P Analytical 2005. Surface area and pore size volume Brunauer–Emmett–Teller (BET) were determined by ASAP2010, Micrometrics). The bandgap was estimated using UV-Vis diffuse reflectance spectroscopy (Hitachi U-3900).

3 | RESULTS AND DISCUSSION

3.1 | Material characterizations

Figure 2A–C show the SEM images of pure ZnO, ZnO/Fe, and BC. The pure ZnO SEM images showed that the particle size ranged from 25.07 to 32.06 nm, while for ZnO/Fe, the particle size was less than 20 nm. The morphology of pristine ZnO was roughly hexagonal and turned to a spherical-like shape with some rod shapes after doping with iron. The decrease in particle size after Fe doping was due to the ability of iron ions to inhibit the crystal growth of ZnO. Figure 2C shows the irregular morphologies of BC, suggesting its high adsorption performance. The existence of Zn and O in the case of pure ZnO was confirmed, whereas the presence of Zn, O, and Fe was affirmed in the case of ZnO/Fe. Moreover, the BC sample contains different elements such as Na, C, Mg, Al, Si, P, and S. Additionally, the atomic and weight ratios of the chemical elements in the BC confirmed the high carbon content on the surface suggesting the high adsorption ability of BC. The diffraction peaks at 2θ of
31.7°, 34.39°, 36.33°, 47.55°, 56.58°, 62.88°, 66.36°, 67.88°, and 69.18° are attributed to the diffraction planes of ZnO (JCPDS 36–1451) as shown in Figure 2G. The other diffraction peaks may be for the precursors used in the synthesis process. The doping of iron into the lattice of ZnO resulted in the decrease of crystallinity, as shown in Figure 2H, as the replacement of zinc by iron ions in the lattice structure can result in the deformation of crystals. The diffraction peaks in the XRD pattern of the BC in Figure 2I are mainly ascribed to SiO2, MgO, KCl, and Al2O3. Figure 2J–L demonstrate the FTIR spectra of ZnO, ZnO/Fe, and BC. The bands at 437 and 988 cm⁻¹ suggested the existence of the Zn–O bond. The band at 3420 cm⁻¹ is ascribed to O–H bond vibrational stretching, while the band at 1568 cm⁻¹ is allocated to water molecules bending vibrations. The band at 2227 cm⁻¹ is imputed to C–H vibrational stretching. In the case of ZnO doped with iron, the same bands were observed with small shifts confirming the doping of iron ions into the lattice of ZnO.

Moreover, the band at 832 cm⁻¹ is imputed to Fe–O bond vibrations in the case of ZnO doped with iron. In the case of BC, the band at 3446.69 cm⁻¹ is due to O–H vibrational stretching, implying that the synthesized BC is hydrophilic, and the bands at 2925 and 2852 cm⁻¹ are due to the C–H bond stretching vibrations. The bands at 1638.86 and 1456.94 cm⁻¹ are imputed to water molecules adsorbed on the BC surface. The band at 1035 cm⁻¹ is ascribed to the vibration modes of the C–O group, whereas the peak at 468 cm⁻¹ is allocated to the stretching vibrations of the C–H group. Moreover, the FTIR pattern of the BC after the removal of the pollutants was provided in the Supporting Information File (Figure S1). No significant changes in the BC FTIR pattern after the removal of the pollutants affirmed the degradation of the adsorbed pollutant molecules on the BC surface by the
photocatalyst. The bandgap of ZnO/Fe was estimated using UV-Vis diffuse reflectance spectra as shown in Supporting Information: Figure S2 and the bandgap was around 3 eV compared to 3.3 eV in the case of pure ZnO as reported in the literature confirming the role of the dopant in the reduction of the bandgap.38

3.2 Adsorption performance of the prepared BC

Figure 3A depicts the adsorption performance of BC with time towards LM, MA, and OX at pH 7.6 ± 0.3, BC dose of 1.5 g/L, and initial OX, LM and MA concentrations of 200, 145 and 100 mg/L, respectively. The removal efficiencies were 36%, 19%, and 18.6% in the case of OX, LM, and MA, respectively, after a contact time of 135 min. The adsorption rate was quite good during the initial contact time due to the presence of high availability of active sites on the BC surface.42 This is linked to the adsorption of OX onto the BC was the highest where the binding energy was accounted for −44.74 BC/OX (BC–OX) complex. The binding energy was −42.97 for BC–LM and −38.8 for BC–MA complex compatible with the pesticide adsorption efficiency. Increasing the binding energy would highly improve the adsorption of the pesticides by BC application.43 By extending the time to 300 min, the removal efficiencies remained approximately the same in the case of the three pesticides. The BC surface may reach the equilibrium phase after 135 min; therefore, no improvement was observed after 135 min. Apparently, the active sites are occupied by LM, MA, and OX, which reduced the availability of further adsorption sites by increasing the contact time and subsequently decreasing the adsorption rate.42

Furthermore, this can be due to the binding energy between substrate and BC being decreased at increasing the contact time. Interactions of H-bonding and π–π reactivity between LM, MA, OX, and BC play the key factor in the adsorption process as well as the pore volume and surface area of BC.44 Fan et al.33 found similar results where the adsorption rate of sulfonamides on sludge-based BCs was rapidly increased in the first reaction 80 min and then slowed down until attaining the sorption equilibrium after a contacting time of 100 min.33

Figure 3B shows the influence of BC dose on the removal of LM, MA, and OX at pH 7.6 ± 0.3, contact time of 135 min, and initial OX, LM, and MA concentrations of 200, 145, and 100 mg/L, respectively. The increase of BC dose from 0.1 to 1.0 g/L improved the removal efficiencies from 6% to 33.5%, 9% to 18%, and 6.2% to 18.6% in the case of OX, MA, and LM, respectively at a contact time of 135 min. Raising the adsorbent dose increased the active adsorption sites, leading to improved removal efficiencies of OX, MA, and LM.45 However the removal of pesticides was not improved by a higher adsorbent dose above 1.0 g/L due to the agglomeration of BC particles which might reduce the surface area available for pollutants adsorption.46 Therefore, the optimum BC dose was considered 1.0 g/L. The maximum adsorption rate of organochlorine pesticides was 76–86% at a dose of zero-valent iron-doped BC (Fe0–BC) (0.45 g/L) of which was reduced at a level of 45% at a dose of 0.1 g/L.42 The efficiency of organochlorine pesticides remained at a level of 86–91%, with increasing the catalyst concentration from 0.45 to 0.7 g/L. This was related to the nonaccessibility of adsorption active sites

![Figure 3](image_url) (A) Effect of contact time after the addition of 1.5 g/L of biochar and (B) effect of biochar dose on the removal efficiency of oxamyl, lambda-cyhalothrin, and malathion.
on the Fe\textsuperscript{0}–BC and the equilibrium setting up between the substrate and BC. The BC derived from fruit peel waste at 350\degree C achieved a maximum cymoxanil (CM) adsorptive capacity of 161 mg CM/g BC.\textsuperscript{47} Chemical sorption of cymoxanil on the heterogeneous BC surface was the removal mechanism due to hydrophilic interaction between the substrate and the adsorbent. The removal of diazinon was increased up to 90\% at a BC dosage of 2.0 g/L. However, the removal efficiency remained at this level with increasing the BC up to 10 g/L.\textsuperscript{48}

### 3.3 Effect of ZnO dose on the photodegradation performance of pesticides

Figure 4A shows the effect of contact time on photodegradation efficiency of LM, MA, and OX at pH 7.6 ± 0.3, ZnO catalyst dose of 1.0 g/L, and initial OX, LM, and MA concentrations of 200, 145, and 100 mg/L, respectively. The degradation efficiencies of OX, LM, and MA were 37.5, 21.4, and 27\%, respectively, after a reaction time of 135 min. The extension of reaction time to 300 min did not show a meaningful change in the degradation ratios of pesticides due to the consumption of the catalyst. ZnO catalyst under irradiations of UVA and UVC for 120 min was conducted for photocatalytic degradation of pesticide (2,4-D).\textsuperscript{49} The maximum degradation efficiency of 2,4-D was achieved under UVC at 120 min. The mineralization of temephos pesticide was 55\% in the presence of ZnO film photocatalyst and reduced to 35\% using only photolysis. This indicates that photolysis greatly contributes to the mineralization of pesticides.\textsuperscript{50} The ZnO photocatalytic degradation mechanism of LM, MA, and OX can be explained as follows in Equations (2), (3), and (4).

\begin{equation}
\text{ZnO} + h\nu \rightarrow e^- + h^+ ,
\end{equation}

\begin{equation}
h^+ + \text{H}_2\text{O} \rightarrow \text{\textasciitilde{OH}} + \text{H}^+,\n\end{equation}

\begin{equation}
\text{\textasciitilde{OH}} + \text{Pesticides} \rightarrow \text{fragments} + \text{mineralization}.
\end{equation}

Photons excite ZnO semiconductor particles initially, so the electron-hole pairs are generated and migrate to the catalyst surface. Holes interact easily with the water molecule forming a hydroxyl radical that attacks and oxidizes the LM, MA, and OX into intermediate by-products. The separated electrons (e\textsuperscript{−}) are simultaneously interacting with the dissolved oxygen in the bulk liquid, producing more superoxide radicals, which contribute to the degradation of pesticides. Thus, ZnO catalyst can be applied to degrade pesticide-rich wastewater by natural sunlight irradiation.

Figure 4B describes the effect of catalyst dose on the degradation efficiency of pesticides at pH 7.6 ± 0.3, reaction time of 135 min, and initial OX, LM, and MA concentrations of 200, 145, and 100 mg/L, respectively. The removal efficiencies increased from 8.5\% to 37.5\%,
12% to 27%, and 10.3% to 21.4% for OX, MA, and LM, respectively, by increasing the catalyst dose from 0.1 to 1 g/L after a contact time of 135 min. The rise of catalyst dosage increases the number of active sites leading to the raising of generated radicals and improvement of degradation efficiency. However, the excess doses (above 1.0 g/L) did not show any improvement in the degradation efficiencies of the pesticides due to the agglomeration of catalyst particles in the case of higher doses reducing the surface area available for photon absorption. Moreover, high catalyst doses increase the scattering of photons and reduce the number of photons reaching the catalysts' surface.

3.4 Effect of the addition of BC to ZnO and ZnO/Fe

The addition of 1.0 g of the BC to 0.4 g of ZnO resulted in the increase of the removal efficiencies to 55%, 70%, and 46.9% in the case of OX, MA, and LM, respectively, compared to 38%, 30% and 24% in the case of the addition of 1.0 g of ZnO only after a reaction time of 135 min as shown in Figure 5A. The introduction of BC ameliorates the removal performance of pesticides due to the adsorption of pollutant molecules on the BC besides the photodegradation by ZnO. Likely, the photocatalysis by BC–ZnO nanocomposite achieved a degradation efficiency of 83.5% for Safranin O (Saf) after irradiation for 60 min. The reduction of Mancozeb was 56.5% within 50 min in visible light, 27.5% in UV light, and 25.2% in dark conditions.

The influence of the catalyst dose of ZnO in the case of BC addition on the removal efficiencies of pesticides is depicted in Figure 5B. The removal percentages of OX, MA, and LM went up from 10% to 55%, 20% to 70%, and 13.7% to 46.9%, respectively, by raising the dose from 0.05 to 0.4 g/L after a reaction time of 135 min. The results showed that adding BC could improve the removal at a lower dose of ZnO (0.4 g/L, optimum catalyst dose). The reduction in catalyst dose, as well as the low cost and availability of BC, all contribute to lowering the overall cost of the treatment process.

To improve the optical properties of pristine ZnO, the pure ZnO was doped with iron to reduce the bandgap and recombination rate. However, the removal efficiencies of OX, MA, and LM reduced to 41%, 37%, and 21.4%, respectively, after a reaction time of 135 min at a BC dose of 1 g/L and ZnO/Fe dose of 0.4 g/L as shown in Figure 5C. The decrease in the removal efficiencies of pesticides may be due to the reduction of crystallinity of the ZnO after introducing iron, as shown in the XRD analysis. Moreover, the doping of Fe may reduce the surface area and the affinity of the photocatalyst toward the pollutant molecules. Paganini et al. reported a decrease in phenol degradation efficiency after doping ZnO with iron, and the pure ZnO showed higher performance.

The effect of the catalyst dose of ZnO/Fe in the case of the addition of 1 g/L was investigated. The results showed an increase in the removal efficiencies from 11.5% to 41%, 20% to 27%, and 13.1% to 21.4% in the case of OX, MA, and LM, respectively, by raising the catalyst dose from 0.05 to 0.4 g/L after a reaction time of 135 min as depicted in Figure 5D. The optimum catalyst dose was 0.4 g/L.

3.5 Mechanism of pesticides removal and generated intermediates

In the case of pure ZnO, the excitation of the nanoparticles by solar light results in electron transfer from the valence band to the conduction band; thereby, holes are generated in the valance band. The reaction between holes and hydroxyl ions along with electrons and oxygen forms hydroxyl and superoxide radicals, respectively. During the reaction, the catalyst particles might be impregnated on the BC's surface due to its high surface. Then, the BC-supported ZnO could accept electrons generated after the excitation of the catalyst, which retarded the recombination rate. Furthermore, the metal oxides (e.g., TiO2, SiO2, ZnO, Fe2O3) in the BC, as reported by XRF in Figure 1B, could act as photocatalysts which contributed to the improvement of removal efficiency. Additionally, the electrons generated after the excitation of the BC could transfer to the conduction band of the catalyst, which might increase the number of reactive species. Moreover, the pollutant molecules could be adsorbed on the BC's surface, which participated in the increase of the overall efficiency.

Iron doping of ZnO was achieved to reduce the bandgap and increase visible light absorption. The introduction of iron ions into the lattice of ZnO could contribute to the formation of new energy levels below the CB or above the VB, reducing the bandgap, as shown in Figure 6A. Moreover, iron ions could act as electron acceptors and reduce the recombination rate. The reduction of removal efficiencies of pesticides using ZnO/Fe might be due to reducing the surface area and crystallinity of ZnO after introducing Fe ions.

The identification of transformation products generated after the photodegradation of OX, MA, and LM was performed using GC-MS analysis. The generated
intermediates of MA (m/z: 331) were naloxone, diethyl malate, diethyl maleate, ethyl 2-hydroxysuccinate, and D-malate with m/z values of 315, 163, 173, 191, and 135, respectively. Phenol, 2,4-bis(1,1-dimethyl ethyl) (m/z: 206), 2,6-Di-t-butyl-4-methyl phenol acetate (ester) (m/z: 262), diethyl Phthalate (m/z: 222), octanal, 2-(phenyl methylene) (m/z: 216), phthalic acid, butyl 2-methyl butyl ester (m/z: 306), phthalic acid, 6-ethyloct-3-yl 2-ethylhexyl ester (m/z: 418), and phthalic acid, isobutyl 4-octyl ester (m/z: 334) were the major intermediates generated during LM (m/z: 449.85) photodegradation.

Regarding the generated intermediates during OX photodegradation, few studies investigated the generated intermediates of this pesticide, and the generated by-products are still unknown. However, the intermediate (2-dimethylamino-N-hydroxy-2-oxo-thioacetamide acid methyl ester-R-OH derivative) was detected. Table 2 shows the generated by-products in the case of the three pesticides. Supporting Information: Figure S3a–f show the graphical mass spectra of the target pollutants and their detected by-products, as well as the degradation pathways of OX, MA, and LM.
**Figure 6**

(A) Photodegradation mechanism of oxamyl (OX), lambda-cyhalothrin (LM), and malathion (MA). (B) Recyclability of ZnO/biochar for the OX, LM, and MA degradation. (C) Binding energy values of LM, MA, and OX adsorption on biochar. (D) The interaction between ZnO nanoparticles with LM (a1), the interaction between ZnO and MA (a2), the interaction between ZnO and OX (a3), and the interaction between LM, MA, and OX with same ZnO particles (a4). (E) The interaction between ZnO/Fe nanoparticles with LM (a1), the interaction between ZnO/Fe and MA (a2), the interaction between ZnO/Fe and OX (a3) and the interaction between LM, MA, and OX with same ZnO/Fe particles (a4).
TABLE 2 Transformation products of oxamyl, malathion, and lambda-cyhalothrin

| Transformation products                                      | m/z  |
|-------------------------------------------------------------|------|
| Malathion                                                   | 331  |
| Malaoxon                                                    | 315  |
| Diethyl maleate                                             | 163  |
| Diethyl maleate                                             | 173  |
| Ethyl 2-hydroxysuccinate                                    | 191  |
| D-malate                                                    | 135  |
| Lambda-cyhalothrin                                          | 135  |
| Phenol, 2,4-bis(1,1-dimethylethyl)                          | 206  |
| 2,6-Di-t-butyl-4-methylphenol acetate                       | 262  |
| Diethyl Phthalate                                           | 222  |
| Octanal, 2-(phenylimethylene)                               | 216  |
| Phthalic acid, butyl 2-ethylbutyl ester                     | 306  |
| Phthalic acid, 6-ethyloct-3-yl 2-ethylhexyl ester           | 418  |
| Phthalic acid, isobutyl 4-octyl ester                       | 334  |
| Oxamyl                                                      | 219.3|
| 2-dimethylamino-N-hydroxy-2-oxo-thioacetimidic acid methyl ester-R-OH derivative | 163  |

Secondary pollution risks are significantly reduced through catalyst regeneration and recycling. The reusability of the ZnO/BC was determined by repeating the degradation process three times. After three cycles, the performance efficiency of ZnO/BC in removing OX, LM, and MA remained nearly unchanged, as shown in Figure 6B. The degradation efficiency has remained at a level of 55–52.5% for OX, 70–65% for MA, and 46.9–42.8% for LM after the recyclability of ZnO/BC three times. This indicates that the ZnO/BC has excellent stability for real application. Similar results were observed for ZnO nano-flowers catalytically oxidizing pesticides. The degradation rates of 2,4-dichlorophenol in five cycles using sulfur/titanium dioxide (S-TiO₂) were kept at a level of 98%, 96%, 90%, 86%, and 80.4%, respectively. The accumulation and/or deposition of pollutants on active S-TiO₂ surface area was minor, and hence, hydroxyl radicals were still generated in the reaction medium resulting in high removal efficiency. The degradation efficiency was reduced in the third, fourth, and fifth cycles due to the surface scouring of S-TiO₂ induced by the friction and shear forces. Nevertheless, tetracycline removal by BC from rice straw remained at 69% after five cycles.
3.7 Computational modeling analysis

The computational modeling of the adsorption interaction between BC and OX, LM, and MA is presented in Figure 6C. The BC provided a high ability to adsorb LM, MA, and OX on its surface, which is compatible with removal efficiency performance. The highest binding energy of $-44.74$ was recorded for the BC-OX complex, followed by $-42.97$ for BC-LM. The lowest binding energy of $-38.8$ was obtained for of BC-MA complex (Figure 6C). The adsorption of LM, MA, and OX by BC is mainly due to the hydrophobic interaction, hydrogen bonding, and pores-filling. Furthermore, electrostatic and $\pi-\pi$ interaction between LM, MA, and OX, and BC is a removal mechanism.$^{27}$ The synthesized BC has $-\text{OH}$ and $-\text{COOH}$ functional groups, where the hydroxyls and carboxylate groups on the BC are mainly responsible for pesticide interactions.$^{59}$ The LM, MA, and OX molecule has electronegative atoms such as O, N, Cl, and S, and BC has $-\text{OH}$ groups that can form hydrogen bonding. The magnetic BC derived from rice straw was highly efficient for tetracycline adsorption.$^{58}$ Kaladeris et al. removed 2,4-dichlorophenol using BC synthesized from paper sludge and wheat husk.$^{50}$ The maximum adsorption capacity of tetracycline (26 mg/g) was attained by clay-BC composites.$^{59}$ This was due to the adsorption interactions between hydroxyl and amide tetracycline groups with carboxylate and hydroxyl functional BC groups. The graphite-like BCs with a surface area of 871.5 and 1065 m$^2$/g containing O-containing functional groups exhibited removal efficiency of 85% for imidacloprid and sulfadiazine after five successive recycling processes.$^{61}$

ZnO and ZnO/Fe had a high adsorption capacity of LM, MA, and OX on their surfaces and established hydrogen bonds between substrates and the catalyst. LM, MA, and OX act as hydrogen donors, and ZnO and ZnO/Fe are hydrogen acceptors, as shown in Figure 6D,E. $\pi-\pi$ interaction between ZnO and ZnO/Fe and LM, MA, and OX has occurred.$^{62}$ BC with a surface area of 88.7 m$^2$/g has a large number of active adsorption sites where ZnO or ZnO/Fe can be dispersed, resulting in high adsorption, photodegradation capacity of pesticides, and high electronic mobility between the catalyst and BC. Yin et al.$^{63}$ found that the BC modification structure by embedding Mg/Ca exhibited better phosphate adsorption from contaminated water than the crude BC structure.$^{63}$ The Mg/Ca addition added extra electrostatic adsorption sites with BC edge adsorption activity. Hu et al.$^{64}$ successfully used ZnO-anchored BC synthesized from bamboo shoot wastes to remove perренenate from wastewater where the sorption mechanism was dominant.$^{64}$

3.8 Cost estimation of the large-scale application

Cost estimation is a necessary step before implementing the photocatalysis process, which is highly dependent on reaction time, chemical cost, and reactor capacity. We calculated the amortization and operating costs using the assumptions listed in the Supporting Information File. The amortization cost comprises construction costs, mixers, pumps, connections, reflective surfaces, and other permanent facilities. The proposed reactor is assumed to treat 25 m$^3$/day and 7500 m$^3$/year. The reactor volume and amortization cost are estimated using Equations (3) and (4) in the Supporting Information File. Moreover, the annual amortization cost based on an interest rate (6%) is quantified using Equation (5) in the Supporting Information File. So, the amortization cost (AC) per cubic meter of the treated water is nearly 1.1 $/m^3$.

The operating costs include the chemicals (pH adjustment and photocatalyst synthesis chemicals), energy, and maintenance costs (2% AC). The commercial prices of chemicals were collected based on the recent international prices. The estimation of energy consumption cost is performed using Equation (6) in the Supporting Information. The operating costs were estimated to be 0.77, 0.6, and 0.65 $/m^3$ in the case of pure ZnO (1 g/L), ZnO/BC, and ZnO/Fe/BC, respectively (BC dose: 1 g/L; ZnO and ZnO/Fe dose: 0.4 g/L). The total cost is the summation of amortization and operating costs. So, the total costs are 1.87, 1.7, and 1.76 $/m^3$, respectively, in the case of the three materials. The results confirmed that the total cost was reduced after adding BC due to the decrease in catalyst dose. As a result, integrating the adsorption and photocatalysis processes can support full-scale photocatalysis applications.

4 CONCLUSIONS

In the case of LM, MA, and OX, the optimal adsorbent dose was 1 g/L, and the equilibrium time was 135 min. After 135 min of reaction, increasing the ZnO dose from 0.1 to 1 g/L increased the removal efficiencies of OX, MA, and LM from 8.5% to 37.5%, 12% to 27%, and 10.3% to 21.4%, respectively. The optimal ZnO catalyst dose was 1 g/L. After a 135 min reaction time, the removal efficiency of OX, MA, and LM increased to 55%, 70%, and 46.9% with the addition of 1 g/L of ZnO, respectively, compared to 38, 30, and 24% with the addition of only 1.0 g/L of ZnO. The degradation mechanism was proposed, and the generated by-products were identified. Total costs
for pure ZnO, ZnO/BC, and ZnO/Fe/BC were estimated to be 1.87, 1.7, and 1.76 $/m^3, respectively. The cost estimation study confirmed the BC's role in reducing total costs. Thus, effectively utilizing BC derived from lignocellulosic waste biomass in water remediation has the potential to be a significant carbon sink for BC use in climate change mitigation.

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SUPPORTING INFORMATION
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