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Sugarcane bagasse biochar functionalized with ZnO via zinc hydroxychloride thermal conversion for enhanced photocatalytic degradation of paracetamol

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ABSTRACT

The increasing contamination of water resources by pharmaceutical residues requires efficient and scalable advanced oxidation technologies. In this work, a zinc oxide-functionalized biochar (ZnO@BC) composite was synthesized via thermal conversion using sugarcane bagasse and zinc hydroxychloride (ZHC) as precursor materials. The synthesized photocatalyst was evaluated for the degradation of paracetamol (PCT) in aqueous solution under UV/Visible light irradiation. X-ray diffraction (XRD) and scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) confirmed the successful integration of crystalline ZnO nanoparticles onto the porous carbon matrix. Batch photocatalytic experiments demonstrated that ZnO@BC achieved over 78% PCT removal within 90 min, outperforming commercial ZnO nanoparticles. Non-linear pseudo-first-order kinetic modeling revealed a rate constant for ZnO@BC ($k_1 = 0.0207 \text{ min}^{-1}$) significantly higher than that of pristine ZnO ($k_1 = 0.0079 \text{ min}^{-1}$). Scavenging assays indicated that hydroxyl ($\text{HO}\cdot$) and superoxide ($\text{O}_2^{\cdot-}$) radicals, along with photogenerated holes (h^+), are the main reactive species involved in the degradation process. Overall, the ZnO@BC composite represents a promising, low-cost material derived from agro-industrial waste for application in advanced wastewater treatment

Keywords: *Pharmaceutical degradation, ZnO supported into biochar, Water decontamination, Paracetamol, Acetaminophen*

INTRODUCTION

The continuous discharge of pollutants into water bodies has become a critical environmental challenge, as conventional wastewater treatment plants (WWTPs) often fail to eliminate these substances effectively [1, 2]. Among

these, emerging contaminants (ECs) can be highlighted as recent detected contaminants, which have not been included in monitoring actions, and show eco-toxicologic effects in water bodies, fauna and in animal life, impacting different trophic levels [3, 4]. Beneath these substances, pharmaceuticals, personal care products, and pesticides can be listed as examples [5–7]. The persistence of ECs in the environment is primarily due to their diverse chemical structures and their occurrence at trace concentration levels (e.g., $\mu\text{g L}^{-1}$ or ng L^{-1}) which complicates their detection and necessitates the development of advanced removal technologies [3, 8].

Among the diverse classes of ECs, paracetamol (PCT) stands out due to its massive global consumption as an analgesic and antipyretic drug [9–11]. Since it is only partially metabolized by the human body, significant amounts of the compound and its metabolites are continuously discharged into municipal sewage. Because it is not fully degraded by biological wastewater treatments, PCT has been frequently detected in surface waters and even drinking water. Its persistence in the environment is concerning, as long-term exposure can lead to chronic toxicity in aquatic organisms and the potential formation of even more toxic byproducts during chlorination processes [9, 11].

Aiming the degradation of environmentally persistent pharmaceuticals, Advanced Oxidation Processes (AOPs), particularly heterogeneous photocatalysis, have emerged as highly efficient degradation strategies. Zinc oxide (ZnO) is widely utilized due to its low cost, non-toxicity, and high photosensitivity [12]. However, the practical application of pure ZnO is often hindered by rapid electron-hole recombination and its tendency to undergo photocorrosion in aqueous media, which reduces its catalytic stability. Furthermore, the recovery of fine ZnO particles after treatment remains a technical challenge [13, 14].

To overcome these limitations, ZnO can be combined with other materials, such as carbonaceous matrices. Carbonaceous materials, such as biochar, activated carbon, graphene, and carbon nanotubes can act as electron acceptors and conductive supports, promoting charge separation, suppressing electron-hole recombination, and increasing the availability of active sites for photocatalytic reactions [15, 16]. In addition, the porous structure and large specific surface area of biochar-based composites improve pollutant adsorption, bringing contaminants into closer contact with the photocatalyst and thereby facilitating their subsequent degradation.

The biomass valorization is also an advantage of biochar synthesis, once it can redirect the agricultural waste into this class applicable material. Sugarcane bagasse is a globally abundant agricultural residue, being produced over 1.9 billion tons worldwide, in 2020 [17]. Its ligno-cellulosic composition provides carbon and oxygen rich precursor that is viable into biochar conversion, promoting actions towards the agricultural waste management. Thus, the

functionalization of biochar and carbonaceous materials emerges as a strategic alternative, given that the biochar support not only increases surface area and provides synergistic adsorption but also acts as an electron trapper, suppressing charge recombination and enhancing the overall photocatalytic performance of the ZnO-based composite [18–20]. Also, it has been reported that the biochar produced from sugarcane bagasse can serve as support for functionalized materials [21].

Other strategic methodologic step is the synthetic process of ZnO through thermal transformation from ZHC, once its layered structure dismisses the use of organic templates, also providing crystalline structures and has the possibility of generating oxygen vacancy sites into ZnO framework [22, 23].

This work aims to obtain and characterize a ZnO supported in sugarcane bagasse composite (ZnO@BC) using ZHC as precursor, and study its application in the photocatalytic degradation of PCT in aqueous systems.

2 EXPERIMENTAL

2.1 MATERIALS

The sugarcane bagasse was collected from local market in Itajubá, Minas Gerais, Brazil. Zinc Chloride salt was purchased from Dinâmica Química Contemporânea® (purity >97%). P-benzoquinone was purchased from Sigma Aldrich® (purity >98%). Sodium Hydroxide (purity >97%) was purchased from Synth®. Methanol (LS Chemicals; purity >99,0%). EDTA was purchased from Synth® (purity>99,0%). PCT (purity >98%) was sourced from compounding pharmacy (Itajubá, Minas Gerais, Brazil) and used as received without any further purification.

2.2 METHODS

2.2.1 Synthesis of sugarcane bagasse biochar functionalized with ZnO

Sugarcane bagasse collected from the local market in Itajubá, Minas Gerais, Brazil, were washed with distilled water. The impregnation of the 6,8164 g of biomass was approached with the co-precipitation of ZHC into the biomass, by the dropwise addition of a 100.0 mL of ZnCl₂ solution (0.5 mol L⁻¹). The management of pH value was adjusted by addition of NaOH (1.0 mol L⁻¹), to keep pH=8 in the synthetic process, for 2 hours of synthesis. The resulting biomass impregnated with ZHC was filtered, washed with distilled water and dried in oven furnace, at 60 °C for 24h.

After drying process, the resulting material was placed into a porcelain crucible and placed in a muffle furnace for the thermal treatment, at 500 °C for 5 h, to achieve the thermal conversion of ZHC into ZnO, as represented in previous reports [23, 24] . As result, the functionalized ZnO@BC was obtained, characterized and applied in photocatalytic degradation of PCT in aqueous solutions.

2.2.2 Characterization

The prepared biochar was characterized by Fourier Transform Infrared Spectroscopy, FT-IR with attenuated total reflectance module (Spectrum 100, PerkinElmer®) from 650 cm⁻¹ to 4000 cm⁻¹, with 16 scans; X-ray Diffraction, XRD (X'pert PRO, PANalytical®) from 10° to 80° of 2θ, 0.02° s⁻¹ (with Cu X-ray source), and Scanning Electron Microscopy with Energy Dispersive Spectroscopy, SEM-EDS (EVO-MA 15, Zeiss®). The Sherrer's Equation was applied to assess the average ZnO crystallite size, as represented below in Eq. 1:

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (1)$$

Where D is the crystallite size, K represents Scherrer constant (adopted as $K=0.90$ in this case); λ is the corresponding wavelength of X-ray source (0.15406 nm), β is the full width at half maximum in each crystallographic peak and θ is the Bragg's angle of each crystallographic peak.

The optical characterization of ZnO@BC was made in spectrophotometer K-37 (KASVI), using a dispersion of 5.0 mg of ZnO@BC in 30 mL of ethanol, previously suspended in ultrasonic bath (for 5 min). The resulting measurements were analyzed according tauc plot, considering the absorbance of material in ethanol, as represented in Eq 2:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

Where α is the molar absorptivity coefficient, h is the Planck constant, ν is the frequency of incident light, $h\nu$ is the energy of incident photon, A is the proportionality constant and E_g represents the energy of the bandgap. Also, the conduction band and valence band energy were estimated from Mulliken electronegativity theory, with Eqs. 3 and 4.

$$E_{VB} = X - E_e + \frac{1}{2}E_g \quad (3)$$

$$E_{CB} = E_{VB} - E_g \quad (4)$$

2.2.3 Photocatalytic removal of PCT from water

The PCT removal experiments were performed with the objective of assessing the different mechanisms in the contaminant removal from aqueous medium. In this scenario, the experiments were planned to approach the effects of the absence of light (and the contribution of sorption processes) and with the irradiation with near UV Hg light source (emission spectrum presented in Fig. S1, Supporting Information).

All the experiments, made in triplicates, were made with 0.25 g L^{-1} of the ZnO@BC catalyst in aqueous solution of PCT (1.0 mg L^{-1}) in a photoreactor with a magnetic stirrer, using a Hg vapor lamp at 15 cm from reaction beaker. Initially, samples were collected from the experimental sets before the addition of the catalyst, at an initial time (t_{30}). After the addition of the catalyst, the experiments considered an initial 30 minutes-adsorption experiment, by a sample after 15 and 30 minutes of experiment with absence of light (t_{15} and t_{30}). Then the light source was turned on for a 60-min experiment, which samples were collected in t_{35} , t_{40} , t_{60} , t_{75} and t_{60} .

The collected samples were analyzed in HPLC-DAD, using C₁₈ column (XRD-C18, Agilent[®]), with isocratic elution using methanol and water (proportion of 30:70 v/v), with chromatographic flow of 0.5 mL min^{-1} and injection with $20 \text{ } \mu\text{L}$. The maximum absorbance of PCT was set to 243 nm. Control experiments with commercial ZnO nanoparticles (ZnO NPs) were performed following the methods described above. To evaluate the kinetics of PCT removal, the experimental data obtained during the photocatalytic with ZnO NPs and ZnO@BC assays were fitted to the non-linear PFO model. The fitting was performed using the concentration values determined by HPLC at each sampling interval, and the kinetic rate (k_1) were compared with commercial ZnO NPs to assess the PCT degradation behavior under the investigated experimental conditions.

2.2.4 Scavenging Experiments

Photocatalytic experiments were conducted in the presence of scavengers to investigate the contribution of the main reactive species involved in PCT degradation. Methanol (10 mmol L^{-1}), *p*-benzoquinone (1.0 mmol L^{-1}), and ethylenediaminetetraacetic acid (EDTA, 1.0 mmol L^{-1}) were used as scavengers for hydroxyl radicals ($\text{HO}^\bullet$), superoxide radicals ($\text{O}_2^{\bullet-}$), and photogenerated holes (h^+), respectively [25–27].

The experiments were carried out under the same conditions described for the photocatalytic assays. A catalyst concentration of 0.25 g L^{-1} (ZnO@BC) was adopted in a 1.0 mg L^{-1} PCT solution. The specific scavenger was added to the reaction medium prior to the addition of the catalyst. The suspension was stirred magnetically in the dark for 30 min to establish adsorption-desorption equilibrium, and an initial aliquot was collected after adsorption-desorption

equilibrium (t_0), followed by irradiation with light source for 60 min. A final sample was taken after 60 minutes of light exposure in each quenching experiment. All collected the samples were filtered through 0.45 μm PTFE syringe filters (Millex-LCR) and analyzed by HPLC-DAD.

3 RESULTS AND DISCUSSION

3.1 Material Structural and Optical Characterization

The crystallographic characterization of ZnO@BC composite agrees with ZnO commercial and ZnO ICSD chart, as shown in Fig. 1a. The identification of the (100), (002), and (101) crystallographic planes, typical of ZnO with a hexagonal wurtzite-type structure, along with secondary signals such as (102), (110), (103), (200), (112), and (201) found in ZnO-based materials, indicates the successful conversion of the precursor synthesized ZHC into ZnO [23]. The resulting ZnO aggregates can be associated to synthetic process, once the $\text{OH}^-/\text{Zn}^{2+}$ ratio seem to morphologically impact the ZHC particles. As reported by Cousy *et al.*, $\text{OH}^-/\text{Zn}^{2+}$ ratios over 2.0 lead to the formation of aggregates of of ZHC [22]. Once aggregated, the thermal conversion of ZHC into ZnO can be reached in temperatures above 400 $^{\circ}\text{C}$ [23, 24]. The crystallite sizes of ZnO@BC and pristine ZnO NPs, calculated via the Scherrer equation across the main crystallographic planes (100), (002), (101), (102), (110), and (103), presented remarkably similar values ranging between 20 and 30 nm (Fig. 1c). This similarity indicates that the thermal conversion of zinc hydroxychloride directly on the sugarcane bagasse biochar matrix did not hinder the crystallization process or induce excessive grain growth. The oxygenated functional groups on the biochar surface likely provided well-dispersed nucleation sites, confining the growth of ZnO crystallites and preventing sintering during calcination. Consequently, the composite retained nanoscale dimensions comparable to commercial nanoparticles, ensuring a high density of active catalytic sites while benefiting from the structural support and enhanced electron mobility provided by the biochar framework

The observed ZnO occurrences in Fig. 1d can be associated to nanometric rods, as previously reported in literature [28]. Furthermore, the characteristic pores of the BC, resulting from the pyrolysis process, can also be observed in Fig. 1c and in Fig. S2 (Supporting Information). The average particle size, according Sherrer's equation, resulted in average of 28.9 nm. Although, it is noticeable the aggregation of ZnO after thermal treatment, as seen in Fig. 1b, resulting in aggregates of rod-like structures, under the size of 1.0 μm . The semi quantification, represented in Fig.1 and Table S1, also agrees with the regions containing the BC and the anchored ZnO, representing the lightened portion in Fig. 1c, associated to Zn and O portions (Figs. 1h and 1f, respectively). Additionally, Fig. 1e refers to the region

containing C atoms derived from the pyrolyzed biomass, whereas Fig. 1g refers to a region containing a low amount of Chlorine atoms, possibly associated to remaining precursor anions atoms from the synthetic process.

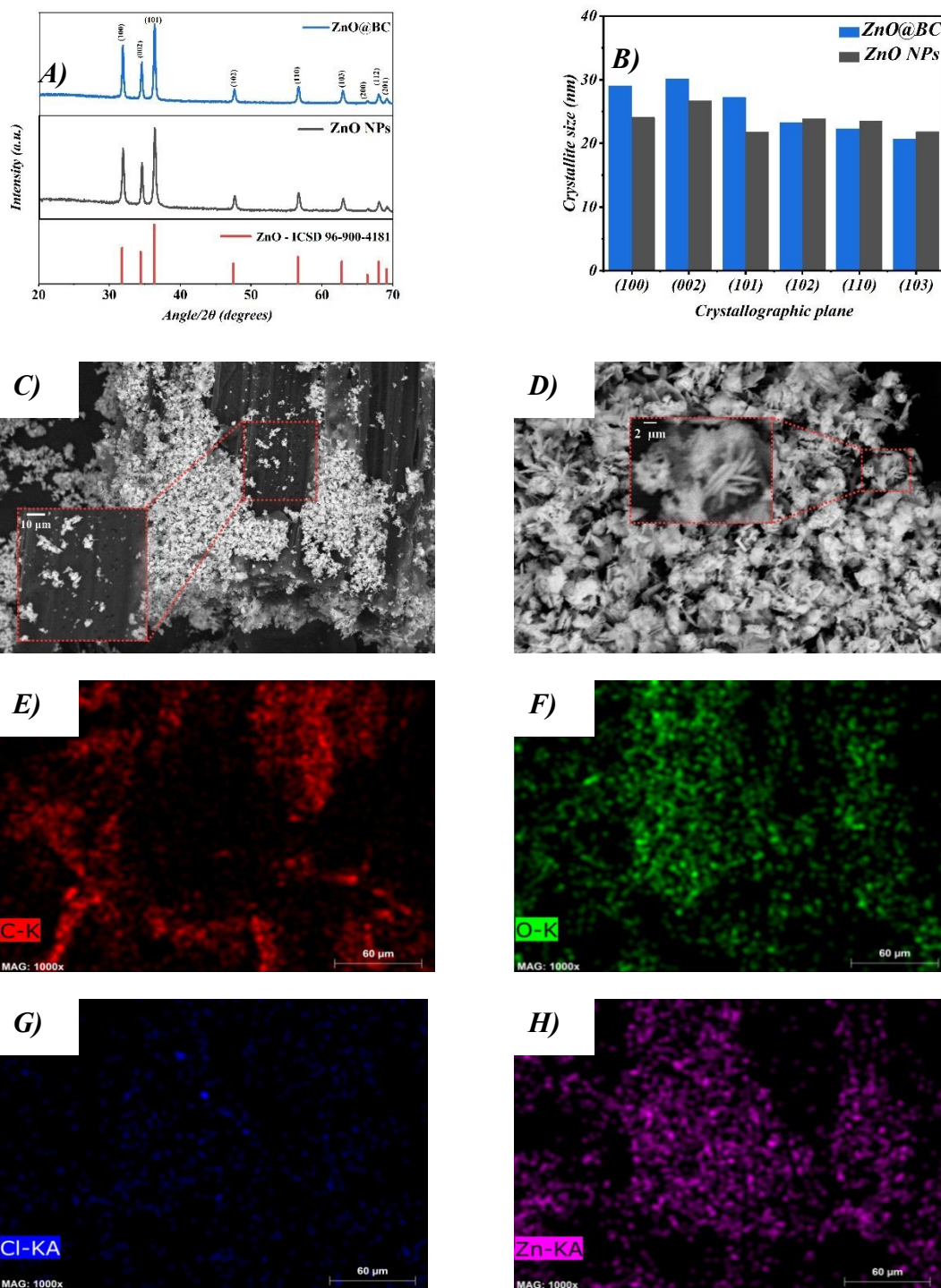


Fig. 1. ZnO@BC characterization: (A) XRD comparison between synthesized ZnO@BC, commercial ZnO and ICSD chard for ZnO (96-900-4181); (B) Crystalite comparative size between ZnO@BC and Commercial ZnO NPs; SEM micrograph at 1000x (C) and 5000x (D), EDS determination for carbon (E), for oxygen (F), for chlorine (G) and for zinc (H).

The optical band gap energy of the synthesized photocatalysts was evaluated using the Tauc plot method (Fig. 2a). Pristine ZnO NPs exhibited a characteristic wide band gap of 3.21 eV, corresponding to its direct band-to-band electronic transition in the ultraviolet region. Notably, supporting ZnO onto the BC matrix induced a substantial redshift in the absorption edge, reducing the optical band gap to 2.72 eV ($\Delta E_g = 0.49$ eV). This pronounced narrowing is attributed to strong interfacial coupling between the ZnO particles and the carbonaceous matrix, which facilitates the formation of carbon-induced intermediate energy states within the band gap and effectively extends the material's light-harvesting capability into the visible-light region.

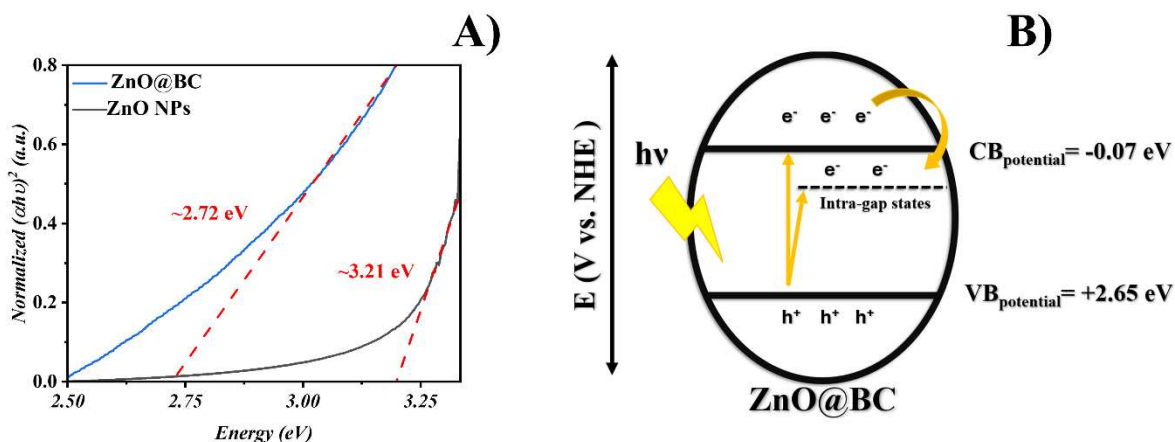


Fig. 2. Optical characterization: (a) normalized Tauc plot of ZnO NPs and ZnO@BC; (b) intragap structure of plausible effects of BC support in ZnO electronic structure.

To further elucidate the band alignment and charge transfer thermodynamics, the valence band (VB) and conduction band (E_{CB}) edge potentials were calculated via Mulliken's electronegativity theory, adopting an absolute electronegativity χ of 5.79 eV for ZnO. For pristine ZnONPs, the E_{VB} and E_{CB} values were estimated at +2.90 eV and -0.31 eV vs. NHE, respectively. For the ZnO@BC composite, the edge potentials shifted to 2.65 eV (E_{VB}) and -0.07 eV (E_{CB}) vs. NHE. Crucially, the E_{VB} of the composite (2.65 eV) remains substantially more positive than the standard redox potential required for hydroxyl radical generation ($H_2O/HO\cdot = +2.38$ eV vs. NHE). This confirms that photoinduced holes (h^+) retain adequate thermodynamic driving force to oxidize water and generate highly reactive oxygen species (ROS) under visible-light excitation.

3.2 PCT photocatalysis, reusability and mechanistic discussion

The application of ZnO@BC allowed the comparison with commercial ZnO in the photocatalytic degradation of PCT, with results represented in Fig. 3a. Firstly, the ZnO@BC composite showed a better adsorption-desorption yield until the equilibrium was reached, in comparison with the commercial ZnO NPs, being coherent with biochar's porous nature, which is represented in micrographs in Fig.S1, which improves the PCT interactions with the heterogenous solid phase.

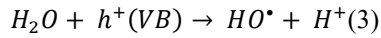
In photocatalysis, ZnO@BC showed a PCT degradation over 78% in 60 min of light exposed experiments, in comparison with 43% of commercial ZnO NPs. This contrast can be associated to biochar's synergic association with ZnO particles in ZnO@BC, which causes PCT molecules to concentrate on the material's surface, bringing it to a relative proximity with the ZnO active sites, potentially enhancing degradation [29].

The kinetic behavior of PCT photocatalytic degradation over ZnO@BC composite and commercial ZnO NPs was further evaluated using the non-linear pseudo-first-order kinetic model (Fig. 3b). As represented in Fig. 3b, the non-linear fitting demonstrated excellent agreement with the experimental data, yielding high determination coefficients ($R^2 = 0.99163$ for ZnO@BC and $R^2 = 0.89725$ for pristine ZnO NPs). The calculated apparent kinetic rate constant k_1 for ZnO@BC (0.0207min^{-1}) was noticeably higher than that obtained for commercial ZnO NPs (0.00791min^{-1}), indicating a significant enhancement in reaction kinetics. This accelerated degradation rate is primarily attributed to the synergistic effect between the sugarcane bagasse biochar framework and the anchored ZnO nanoparticles. The porous carbonaceous matrix not only provides an abundance of active surface sites for pollutant adsorption but also acts as an efficient electron acceptor, facilitating charge separation and reducing the recombination rate of photogenerated electron-hole pairs. Consequently, the non-linear kinetic analysis confirms that the functionalization of biochar with ZnO effectively boosts the photocatalytic degradation efficiency of recalcitrant pharmaceuticals like paracetamol in aqueous environments [30].

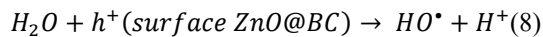
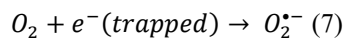
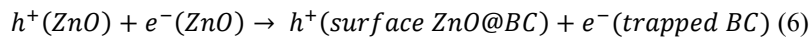
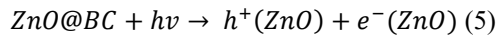
The reusability and operational stability of the ZnO@BC composite were evaluated over five consecutive photocatalytic cycles under identical experimental conditions, as illustrated in Fig. 3c. The photocatalytic degradation efficiency of paracetamol dropped from 68.5% in the initial cycle to 47.3% in the second run, gradually stabilizing at approximately 31–32% by the fourth and fifth cycles. This performance decay can be associated with the porous carbonaceous matrix of the biochar, which is susceptible to active site blockage through the strong accumulation of

recalcitrant degradation intermediates or unreacted contaminant molecules that are not completely desorbed during the water and ethanol washing protocol, thereby restricting light penetration to the anchored ZnO active sites. Also, the saturation of ZnO active sites can be associated to the degradation decline, once the association of BC matrix with ZnO can improve the adsorptive capacity of this material. Crucially, the stabilization of degradation rates around 31% after the third cycle indicates that the remaining active sites preserve their structural integrity and photoactivity without undergoing catastrophic degradation, confirming that ZnO@BC exhibits acceptable operational stability for repeated application in wastewater treatment.

The scavenging experiments showed an innovative result for ZnO application, represented in Fig. 3d. In the control system, the ZnO@BC composite displayed a notable PCT removal of 78.5 %. This superior performance is deeply tied to the structural role of biochar as an active support. When MeOH was added, the PCT degradation efficiency dropped sharply to 31.2 %, confirming that hydroxyl radicals ($\text{HO}^\bullet$) are heavily involved in the degradation pathway, as expected for ZnO photocatalytic application. Due its characteristic fast e^-/h^+ recombination, the major generation of $\bullet\text{OH}$ is viable through the reaction represented in Eq. 3.



However, when ZnO is supported in BC, the carbonaceous structures can affect directly the existing period of photogenerated holes (h^+), available to interact with reactive specimen and generate different type of ROS. For instance, the experiment with p-BQ showed a reduction in PCT degradation to 33.4 %, indicating that superoxide radicals ($\text{O}_2^{\bullet-}$) also show a co-dominance in PCT degradation. This observation puts the generated ROS in highlight in comparison with conventional ZnO systems, which shows $\text{HO}^\bullet$ and h^+ as predominant active species [31, 32]. Thus, the generation of $\text{O}_2^{\bullet-}$ can be associated with BC properties, as enhanced charge separators, by trapping e^- and h^+ being transferred to BC surface. These phenomena allow the reaction between trapped e^- and h^+ with adsorbed O_2 and H_2O molecules generating ROS, as represented in Eq. 5–8[30, 33].



The experiment with EDTA showed a moderate effect yet significant suppression, dropping the removal to 43.3%. This indicates that direct hole (h^+) oxidation also takes place. PCT molecules can interact directly with h^+ sites by charge transfer between photogenerated holes and the adsorbed organic structure of PCT, as represented by Eq. 9.

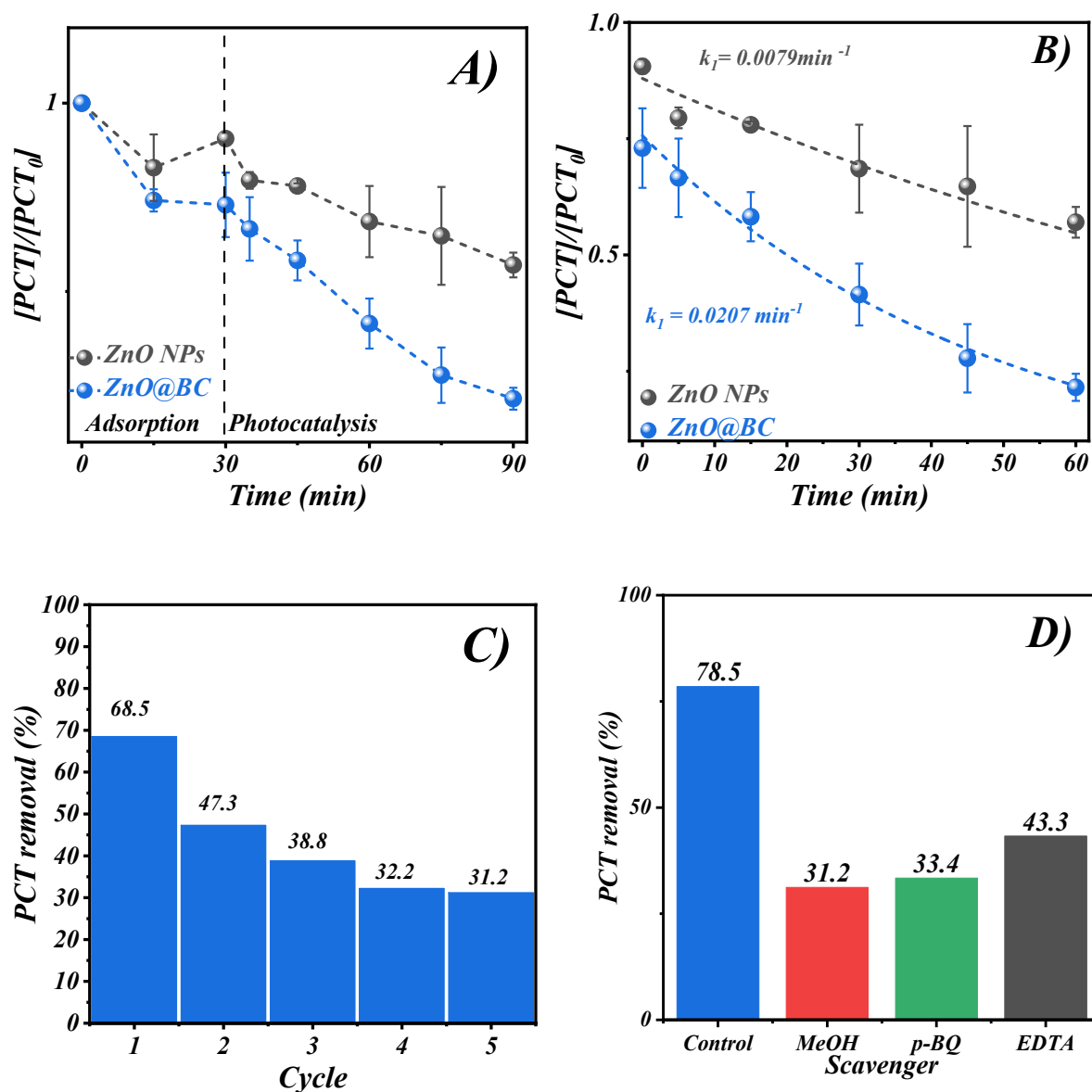


Fig. 3. Adsorption and photocatalytic degradation of PCT using commercial ZnO NPs (black line) and ZnO@BC (blue line) (A); Non-linear pseudo-first-order kinetic fitting for photocatalytic degradation ($R^2=0.89725$ for commercial ZnO NPs and 0.99163 for ZnO@BC) (B); Reusability of ZnO@BC catalyst in 5 cycles of photocatalysis (C); Effect of radical scavengers MeOH, *p*-BQ and EDTA on PCT removal efficiency by ZnO@BC (D). Experimental conditions: $[PCT]=1.0 \text{ mg L}^{-1}$, $[catalyst]=0.25 \text{ g L}^{-1}$.

Radical trapping experiments were performed using MeOH, *p*-benzoquinone and EDTA were used in scavenging agents for hydroxyl radicals ($\text{HO}^\bullet$), superoxide radicals ($\text{O}_2^{\bullet-}$) and photogenerated holes (h^+) scavenging (Fig. 3d). As depicted in Fig. 3d, the addition of both MeOH and *p*-BQ induced a drastic suppression of PCT removal efficiency from 78.5% (control) down to 31.2% and 33.4%, respectively, whereas EDTA caused a moderate inhibition (43.3 %). These quenching trends confirm that $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ function as the primary reactive oxygen species (ROS) driving the photocatalytic degradation, while h^+ plays a secondary supportive role. This synergistic ROS generation aligns seamlessly with the established electronic band structure: photogenerated holes residing in the valence band of ZnO ($E_{\text{VB}} = +2.65 \text{ eV}$ vs. NHE) possess a sufficiently positive potential to drive the direct oxidation of adsorbed $\text{H}_2\text{O}/\text{OH}^-$ into $\text{HO}^\bullet$ radicals ($+2.38 \text{ eV}$ vs. NHE). Concurrently, photoexcited electrons transferred via carbon-induced intra-gap states to the conductive π -conjugated network of the biochar matrix undergo efficient interfacial reaction with dissolved O_2 to yield $\text{O}_2^{\bullet-}$ radicals. The biochar matrix acts as an effective electron sink, hindering charge recombination and prolonging carrier lifetimes, which sustains the continuous, high-yield production of both $\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$ active species.

In summary, the scavenging profile demonstrates that the biochar support does not merely hold the semiconductor mechanically, but can participate in charge separation and transport, triggering an interconnected mechanism driven simultaneously by $\text{HO}^\bullet$, $\text{O}_2^{\bullet-}$ and h^+ [15, 33, 34]. The PCT molecules can primarily be adsorbed onto ZnO@BC surface (Fig. 3a) due to BC adsorptive properties. Secondly, PCT molecules can interact with both radicals ($\text{HO}^\bullet$ and $\text{O}_2^{\bullet-}$) or directly with the photogenerated holes (h^+) promotes its degradation, through advanced oxidation and reduction processes, as represented in Fig. 4.

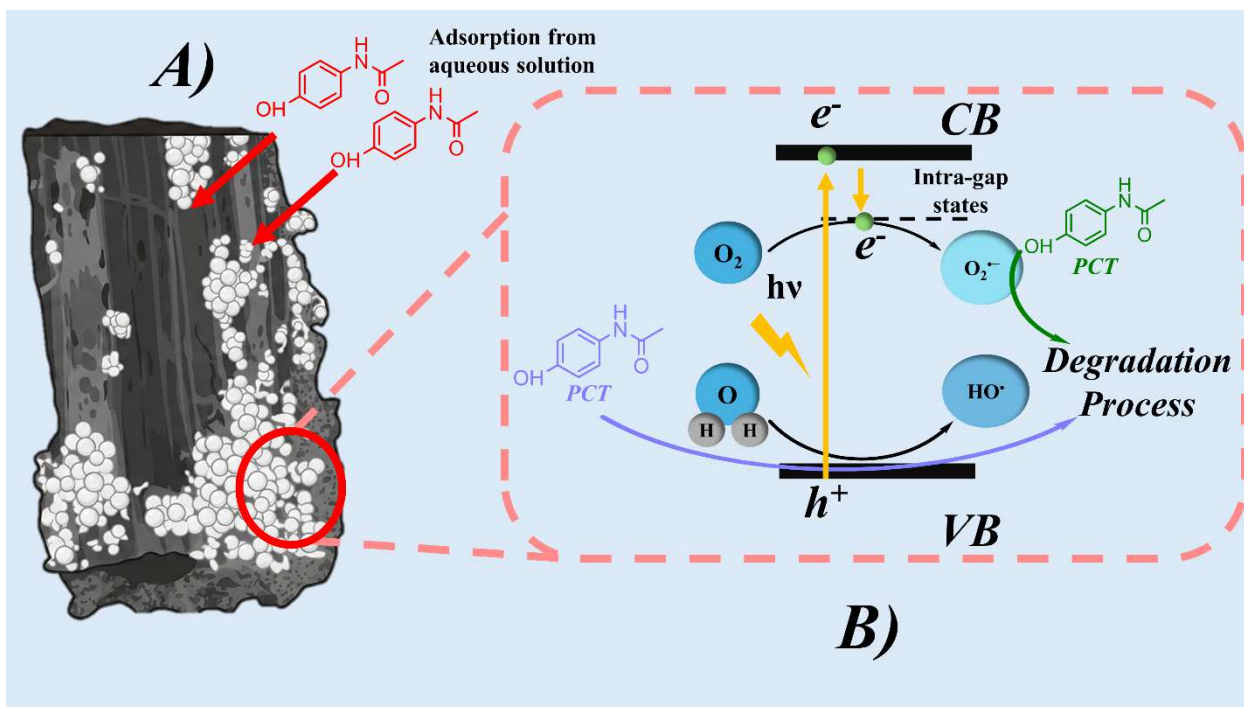


Fig 4. Proposed radicals generation steps and in plausible interactions between PCT and ZnO@BC: through adsorption processes (A) and in photocatalysis with PCT and ROS (green arrow) and PCT with h^+ (blue arrow) (B).

CONCLUSIONS

The contamination of aquatic environments by pharmaceuticals has sparked interest in developing efficient, sustainable materials for the removal and degradation of contaminants. In this study, the synthesized ZnO@BC material was successfully characterized and demonstrated excellent photocatalytic performance in removing paracetamol, achieving a degradation efficiency of 78.5%. Degradation kinetics were well described by a PFO model, indicating a process dependent on pollutant concentration. Radical scavenger experiments suggested that $HO^\bullet$, $O_2^{\bullet-}$ radicals and photogenerated electron-hole pairs were the primary reactive species involved under mercury-vapor lamp irradiation, leading to the proposal of a degradation mechanism.

Overall, these results demonstrate the potential of ZnO@BC as an effective and eco-friendly photocatalyst for water treatment. Future studies should focus on scaling up synthesis, identifying degradation by-products, and evaluating the material's performance and reusability in real wastewater systems.

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AUTHOR CONTRIBUTIONS

PEREIRA, E.S.: Conceptualization, data curation, formal analysis, investigation, methodology, validation, writing-original draft, writing-review and editing

conceptualized the study, developed the methodology, performed data curation, wrote, reviewed, and edited this article.

JUNIOR, R.R.R.: Formal analysis, data curation, investigation, methodology, validation, writing-original draft, conceptualized the study, developed the methodology, performed data curation, wrote, reviewed, and edited this article.

ANDRADE, S.J.: Funding acquisition, conceptualization, methodology, project administration, supervision, resources, writing-review and editing.

DATA AVAILABILITY STATEMENT

The data will be made available on request.

AI DISCLOSURE STATEMENT

During the preparation of this work, the authors used Grammarly (v.1.2.236.1843) in order to improve the readability and language of the text. After using this tool, the authors reviewed and edited the content as needed and take full responsibility for the content of the publication. Google Gemini was used in order to conceptualize the initial draft of Fig. 4.

CONFLICT OF INTEREST

The Authors declare that no competing financial interest or personal relationships is known.

REFERENCES

1. Kasonga TK, Coetzee MAA, Kamika I, et al (2021) Endocrine-disruptive chemicals as contaminants of emerging concern in wastewater and surface water: A review. *J. Environ. Manage.* 277
2. Pakharuddin NH, Fazly MN, Ahmad Sukari SH, et al (2021) Water treatment process using conventional and advanced methods: A comparative study of Malaysia and selected countries. In: *IOP Conference Series: Earth and Environmental Science*. IOP Publishing Ltd
3. Saidulu D, Gupta B, Gupta AK, Ghosal PS (2021) A review on occurrences, eco-toxic effects, and remediation of emerging contaminants from wastewater: Special emphasis on biological treatment based hybrid systems. *J Environ Chem Eng* 9:105282. <https://doi.org/10.1016/j.jece.2021.105282>
4. Yadav D, Rangabhashiyam S, Verma P, et al (2021) Environmental and health impacts of contaminants of emerging concerns: Recent treatment challenges and approaches. *Chemosphere* 272:. <https://doi.org/10.1016/j.chemosphere.2020.129492>
5. Taheran M, Naghdi M, Brar SK, et al (2018) Emerging contaminants: Here today, there tomorrow! *Environ. Nanotechnol. Monit. Manag.* 10:122–126
6. Morin-Crini N, Lichtfouse E, Liu G, et al (2022) Worldwide cases of water pollution by emerging contaminants: a review. *Environ. Chem. Lett.* 20:2311–2338
7. Khan S, Naushad M, Govarthan M, et al (2022) Emerging contaminants of high concern for the environment: Current trends and future research. *Environ Res* 207:. <https://doi.org/10.1016/j.envres.2021.112609>
8. Turk Sekulic M, Boskovic N, Slavkovic A, et al (2019) Surface functionalised adsorbent for emerging pharmaceutical removal: Adsorption performance and mechanisms. *Process Safety and Environmental Protection* 125:50–63. <https://doi.org/10.1016/j.psep.2019.03.007>

9. Agarwal N (2022) Paracetamol - A Contaminant of High Concern: Existence in Environment and Adverse Effect. *Pharmaceutical Drug Regulatory Affairs Journal* 5:. <https://doi.org/10.23880/pdraj-16000128>
10. Lee WJ, Goh PS, Lau WJ, Ismail AF (2020) Removal of Pharmaceutical Contaminants from Aqueous Medium: A State-of-the-Art Review Based on Paracetamol. *Arab. J. Sci. Eng.* 45:7109–7135
11. Audino F, Conte LO, Schenone AV, et al (2019) A kinetic study for the Fenton and photo-Fenton paracetamol degradation in an annular photoreactor. *Environmental Science and Pollution Research* 26:4312–4323. <https://doi.org/10.1007/s11356-018-3098-4>
12. Zhu C, Wang X (2025) Nanomaterial ZnO Synthesis and Its Photocatalytic Applications: A Review. *Nanomaterials* 15
13. Hu H, Sun L, Gao Y, et al (2020) Synthesis of ZnO nanoparticle-anchored biochar composites for the selective removal of perhenate, a surrogate for pertechnetate, from radioactive effluents. *J Hazard Mater* 387:. <https://doi.org/10.1016/j.jhazmat.2019.121670>
14. Tharayil JM, Chinnaiyan P, Ramasamy B, Sathasivan A (2025) Biogenic synthesis of Cu/ZnO functionalized biochar composite: A sustainable approach for visible light-photocatalytic degradation. *Environ Technol Innov* 39:. <https://doi.org/10.1016/j.eti.2025.104337>
15. Weidner E, Karbassiyazdi E, Altaee A, et al (2022) Hybrid Metal Oxide/Biochar Materials for Wastewater Treatment Technology: A Review. *ACS Omega* 7:27062–27078. <https://doi.org/10.1021/acsomega.2c02909>
16. Li X fang, Li R xian, Wang K xin, Feng X qiang (2023) Highly synergic adsorption and photocatalytic degradation of walnut shell biochar/NiCr-layered double hydroxides composite for Methyl orange. *Journal of Industrial and Engineering Chemistry* 126:270–282. <https://doi.org/10.1016/j.jiec.2023.06.017>
17. Saenthornsinn K, Hunt AJ, Limtragool OA, Noppawan P (2025) Mesoporous SBA-16/SO₃H from waste sugarcane bagasse ash for efficient Biginelli reactions. *Sci Rep* 15:. <https://doi.org/10.1038/s41598-025-99670-w>
18. Song Q, Kong F, Liu BF, et al (2024) Biochar-based composites for removing chlorinated organic pollutants: Applications, mechanisms, and perspectives. *Environmental Science and Ecotechnology* 21:. <https://doi.org/10.1016/j.ese.2024.100420>
19. Han M, Liu Z, Huang S, et al (2024) Application of Biochar-Based Materials for Effective Pollutant Removal in Wastewater Treatment. *Nanomaterials* 14
20. Lodhi N, Chadar SN, Singh Thakur D, Raikwar A (2024) A Comprehensive Study on Biochar-Based Nanocomposites in Removal of Organic Pollutants from Wastewater. *Journal of Water and Environmental Nanotechnology* 9:302–317
21. Iwuzor KO, Chizitere Emenike E, Ighalo JO, et al (2022) A Review on the thermochemical conversion of sugarcane bagasse into biochar. *Cleaner Materials* 6
22. Cousy S, Gorodylova N, Svoboda L, Zelenka J (2017) Influence of synthesis conditions over simonkolleite/ZnO precipitation. *Chemical Papers* 71:2325–2334. <https://doi.org/10.1007/s11696-017-0226-4>
23. Moezzi A, Cortie M, McDonagh A (2016) Transformation of zinc hydroxide chloride monohydrate to crystalline zinc oxide. *Dalton Transactions* 45:7385–7390. <https://doi.org/10.1039/c5dt04864h>
24. Kozawa T, Onda A, Yanagisawa K, et al (2011) Effect of water vapor on the thermal decomposition process of zinc hydroxide chloride and crystal growth of zinc oxide. *J Solid State Chem* 184:589–596. <https://doi.org/10.1016/j.jssc.2011.01.015>

25. Liu Z, Liu L, He S, et al (2025) Quenching should be used with caution to evaluate the role of reactive oxygen species in the degradation of pollutants by electro-advanced oxidation technology. *Process Safety and Environmental Protection* 195:. <https://doi.org/10.1016/j.psep.2025.106823>
26. Carlsson C, Fégeant B, Svensson E, et al (2022) On the Selectivity of Radical Scavengers Used To Probe Hydroxyl Radical Formation in Heterogeneous Systems. *Journal of Physical Chemistry C* 126:12435–12440. <https://doi.org/10.1021/acs.jpcc.2c01834>
27. Azizi S, Shahri MM, Mohamad R (2017) Green synthesis of zinc oxide nanoparticles for enhanced adsorption of lead Ions from aqueous solutions: Equilibrium, kinetic and thermodynamic studies. *Molecules* 22:. <https://doi.org/10.3390/molecules22060831>
28. Perillo PM, Atia MN, Rodríguez DF (2018) Studies on the growth control of ZnO nanostructures synthesized by the chemical method. *Revista Materia* 23:. <https://doi.org/10.1590/S1517-707620180002.0467>
29. Mohan D, Sarswat A, Ok YS, Pittman CU (2014) Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent - A critical review. *Bioresour Technol* 160:191–202. <https://doi.org/10.1016/j.biortech.2014.01.120>
30. Mian MM, Liu G (2018) Recent progress in biochar-supported photocatalysts: Synthesis, role of biochar, and applications. *RSC Adv.* 8:14237–14248
31. Mahajan M, Kumar S, Gaur J, et al (2025) Green synthesis of ZnO nanoparticles using *Justicia adhatoda* for photocatalytic degradation of malachite green and reduction of 4-nitrophenol. *RSC Adv* 15:2958–2980. <https://doi.org/10.1039/d4ra08632e>
32. Ahmed ZM, Allam AA, El-Sayed MI, et al (2026) Visible-light photocatalytic mineralization of 4-Chlorophenol over ZnO-loaded sulfonated carbonaceous bentonite: kinetic analysis, pathway elucidation, and catalyst reusability. *Sci Rep.* <https://doi.org/10.1038/s41598-026-35956-x>
33. Cui J, Zhang F, Li H, et al (2020) Recent progress in biochar-based photocatalysts for wastewater treatment: Synthesis, mechanisms, and applications. *Applied Sciences (Switzerland)* 10
34. Lu Y, Cai Y, Zhang S, et al (2022) Application of biochar-based photocatalysts for adsorption-(photo)degradation/reduction of environmental contaminants: mechanism, challenges and perspective. *Biochar* 4:. <https://doi.org/10.1007/s42773-022-00173-y>

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