

Article

Preparation of Ho-Doped ZnO Powders by Sol–Gel and Hydrothermal Routes and Their Tribocatalytic Performance in Paracetamol Degradation

Stefani Petrova ¹ , Albena Bachvarova-Nedelcheva ^{1,2} , Ralitsa Mladenova ³ , Simona Delibaltova ³ ,
Hristo Kolev ³  and Nina Kaneva ^{4,*} 

- ¹ Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev, Str., bl. 11, 1113 Sofia, Bulgaria; stefany@svr.igic.bas.bg (S.P.); albenadb@svr.igic.bas.bg (A.B.-N.)
² National Centre of Excellence Mechatronics and Clean Technologies, 8 bul., Kl. Ohridski, 1756 Sofia, Bulgaria
³ Institute of Catalysis, Bulgarian Academy of Sciences, “Acad. G. Bonchev” Str., Bld. 11, 1113 Sofia, Bulgaria; ralitsa@ic.bas.bg (R.M.); delibaltova@ic.bas.bg (S.D.); hgkolev@ic.bas.bg (H.K.)
⁴ Laboratory of Nanoparticle Science and Technology, Department of General and Inorganic Chemistry, Faculty of Chemistry and Pharmacy, University of Sofia, 1164 Sofia, Bulgaria
 * Correspondence: nina_k@abv.bg

Abstract

In this study, pure ZnO and Ho-doped ZnO powders (1 and 2 mol % Ho) were synthesized via hydrothermal and sol–gel methods and evaluated for their tribocatalytic activity toward the degradation of paracetamol, an emerging pharmaceutical contaminant in aquatic environments. Structural, morphological, and optical properties of the obtained materials were investigated by X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDS), ultraviolet–visible (UV–Vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), and electron paramagnetic resonance (EPR) spectroscopy. SEM observations revealed pronounced morphology differences between the synthesis routes, with hydrothermally prepared samples exhibiting well-defined rod-like structures. XPS and EPR analyses provided evidence for successful Ho modification of ZnO and the presence of defect-related electronic states associated with Ho doping. The tribocatalytic performance was examined in distilled, tap, and mineral water using friction rods with different geometries in order to assess the influence of synthesis route, Ho concentration, and water composition. Among all the investigated materials, hydrothermally synthesized ZnO doped with 2 mol % Ho exhibited the highest tribocatalytic activity, achieving 96.91% degradation of paracetamol at an initial concentration of 15 mg/L within 24 h. The enhanced performance was attributed to improved charge separation induced by Ho modification, combined with the favorable rod-like morphology of the particles. Higher degradation efficiencies were observed in distilled water compared to tap and mineral water, indicating the important role of dissolved ions during the tribocatalytic process. These findings demonstrate that the synthesis route, Ho doping, and water composition collectively govern the tribocatalytic performance of ZnO-based materials, highlighting their potential for water purification.

Keywords: sol–gel and hydrothermal synthesis; tribocatalysis; Ho rare earth



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1. Introduction

Recent years have witnessed growing interest in tribocatalysis as an emerging advanced oxidation process that converts mechanical energy into chemical activity for envi-

ronmental remediation. In contrast to photocatalytic systems that rely on light irradiation, tribocatalysis utilizes friction-induced charge separation at the catalyst interface, enabling the generation of reactive oxygen species (ROS) under dark conditions [1,2]. Owing to its ability to operate through simple mechanical stimuli such as stirring, vibration, or frictional contact, tribocatalysis has attracted considerable attention as a sustainable and energy-efficient approach for wastewater treatment. The absence of external energy input further highlights its potential as a green alternative to conventional oxidation technologies, particularly in systems where irradiation efficiency is limited or energy consumption must be minimized.

The increasing occurrence of pharmaceutical residues in aquatic environments has intensified the demand for efficient catalytic remediation technologies [3,4]. Among these contaminants, paracetamol represents an appropriate probe molecule for tribocatalytic studies because its degradation proceeds through oxidative pathways involving ROS, allowing direct evaluation of the ability of mechanically activated catalysts to generate reactive species in the absence of light irradiation [5,6]. Furthermore, paracetamol is considered a suitable model pollutant for evaluating advanced oxidation processes due to its relatively high chemical stability and the formation of potentially toxic intermediates during degradation, allowing a reliable assessment of catalytic efficiency [7,8]. The persistence of paracetamol and its transformation products poses ecological risks associated with oxidative stress, enzymatic disruption, and toxic effects on aquatic organisms [9]. Moreover, its widespread consumption, frequent detection in surface and drinking waters, and incomplete removal by conventional wastewater treatment plants make paracetamol one of the most representative model pharmaceutical pollutants for evaluating advanced oxidation technologies. Consequently, the development of efficient catalytic systems capable of degrading pharmaceutical pollutants under mild and sustainable conditions remains an important research challenge.

Semiconductor-based materials have been extensively investigated for tribocatalytic applications because of their ability to facilitate interfacial charge generation and redox reactions. Among them, ZnO represents one of the most promising candidates owing to its non-toxicity, chemical stability, low cost, and favorable electronic structure [10,11]. Nevertheless, the practical tribocatalytic efficiency of pristine ZnO is frequently limited by rapid electron–hole recombination and insufficient surface-active sites, which suppress ROS generation and reduce catalytic performance [12]. Various modification strategies have therefore been proposed to improve the charge separation efficiency and defect chemistry of ZnO-based materials.

Rare-earth modification has emerged as an effective strategy for tailoring the electronic, surface, and defect-related properties of oxide semiconductors [13]. Among rare-earth elements, holmium is of particular interest due to its partially filled 4f electronic configuration and ability to introduce localized electronic states within oxide matrices. However, in semiconductor-based catalytic systems, the significance of Ho modification is primarily related to its influence on electronic structure and defect chemistry rather than its magnetic properties. The localized 4f states and charge compensation effects associated with Ho³⁺ substitution can modify defect chemistry, oxygen vacancy concentration, and interfacial charge-transfer processes, which are critical factors governing reactive oxygen species generation during tribocatalysis. Therefore, in the present study, Ho was selected primarily as a defect-engineering modifier rather than as a magnetic dopant [14]. Compared with more extensively studied rare-earth modifiers such as Ce, La, or Eu, Ho-based oxide semiconductor modifications remain relatively less explored, particularly in tribocatalytic systems. The unique electronic configuration of Ho³⁺, together with its ability to induce defect-related states, makes it a promising candidate for regulating charge transfer and reactive oxygen

species generation in ZnO-based catalysts [15]. In ZnO-based materials, Ho modification may therefore regulate oxygen vacancy formation and localized electronic states, thereby influencing charge separation and ROS generation [16–18]. In addition, incorporation of rare-earth ions into the ZnO wurtzite lattice may improve dopant stabilization and reduce the potential environmental mobility of free rare-earth species [19]. Previous studies on rare-earth-modified ZnO have mainly focused on photocatalytic applications, where dopant-induced band structure modification and improved charge separation are emphasized. In contrast, the role of rare-earth ions, particularly Ho^{3+} , in mechanically driven catalytic processes remains largely unexplored. Furthermore, most reported studies on Ho-modified ZnO have focused on optical or photocatalytic properties, while the relationship between Ho-induced defect states, synthesis-dependent morphology, and tribocatalytic activity remains insufficiently understood. Moreover, the influence of synthesis methodology on the defect structure and tribocatalytic behavior of Ho-modified ZnO has not been systematically investigated. Besides chemical composition, the synthesis route strongly influences the structural and morphological characteristics of ZnO-based catalysts, including crystallinity, particle size, defect density, and dopant distribution. Among the commonly employed preparation techniques, hydrothermal and sol–gel synthesis offer distinct advantages regarding morphology control and dopant incorporation [20,21]. Hydrothermal synthesis is frequently associated with the formation of anisotropic rod-like structures, whereas sol–gel methods provide enhanced compositional homogeneity and tunable particle dimensions. Comparative investigations of these synthesis approaches are therefore essential for understanding structure–activity relationships in tribocatalytic systems. Our research group has extensive experience in the development of rare-earth-modified oxide materials [22,23] and their application in tribocatalytic processes [24–26]. Building on our previous investigations of dopant-induced defect engineering for mechanically driven remediation, this study explores the synergistic effects of Ho^{3+} -doping on the tribocatalytic performance of ZnO. To the best of our knowledge, systematic studies correlating synthesis approach, defect engineering, and tribocatalytic performance of Ho-modified ZnO remain scarce.

In this work, pure and Ho-doped ZnO powders (1 and 2 mol % Ho) were synthesized via hydrothermal and sol–gel methods and evaluated for the tribocatalytic degradation of paracetamol in different aqueous media (distilled, tap, and mineral). The selection of Ho as the dopant was motivated by its expected ability to tailor the defect chemistry and charge-transfer characteristics of ZnO, thereby enhancing reactive oxygen species generation during tribocatalysis. The effects of synthesis methodology, dopant concentration, water composition, and friction interface geometry were systematically investigated. Structural, morphological, and optical properties were analyzed using XRD, SEM–EDS, and UV–Vis spectroscopy analysis, while XPS and EPR investigations were employed to confirm Ho incorporation and evaluate defect-related electronic states associated with the tribocatalytic mechanism. The obtained results provide insight into the relationship between synthesis strategy, defect engineering, and tribocatalytic activity, contributing to the development of efficient mechanically driven catalytic systems for pharmaceutical wastewater degradation.

2. Materials and Methods

2.1. Materials

Zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, >99.5%], holmium nitrate pentahydrate ($\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, >99.0%), and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$, >99.5%) were acquired from Merck (Rahway, NJ, USA). Deionized water was used to prepare the tribocatalysts.

Paracetamol (PCA, $\text{C}_8\text{H}_9\text{NO}_2$, $\lambda_{\text{max}} = 243 \text{ nm}$, purity $\geq 99.0\%$; Teva, Dupnitsa, Bulgaria) was employed as the target pharmaceutical pollutant in all tribocatalytic experiments

because of its frequent detection in surface and wastewater systems. To investigate the effect of the reaction medium on tribocatalytic performance, degradation experiments were conducted in distilled, tap, and mineral water. The use of these different water matrices enabled assessment of the influence of dissolved ions and other naturally occurring constituents on the efficiency of the tribocatalytic degradation process under conditions representative of practical water treatment applications.

Tap water collected in Sofia served as a representative water matrix for investigating the effect of naturally occurring inorganic constituents on the tribocatalytic degradation process. The water is characterized by relatively low mineralization and low total hardness (<0.75 mgeq/L), corresponding to freshwater conditions. According to the chemical analysis, the concentrations of the main dissolved ions were as follows: $\text{Na}^+ < 5.01$ mg L⁻¹, $\text{Ca}^{2+} < 10.74$ mg L⁻¹, $\text{Mn}^{2+} < 11$ µg L⁻¹, $\text{Fe}^{2+} < 123$ µg L⁻¹, $\text{Cl}^- = 5$ mg L⁻¹, $\text{SO}_4^{2-} = 11$ mg L⁻¹, and $\text{NO}_3^- = 0.94$ mg L⁻¹. The municipal water supply originates predominantly from the mountainous Beli Iskar Dam reservoir and undergoes purification and disinfection treatment prior to distribution in accordance with European drinking water regulations.

Mineral water from Bankya was used to evaluate the influence of dissolved inorganic ions and higher mineralization on the tribocatalytic degradation process. The water is characterized by low to moderate mineralization and slightly alkaline pH, containing naturally occurring ionic species that may influence charge-transfer processes and reactive oxygen species generation during tribocatalysis. According to the manufacturer's chemical composition, the predominant dissolved ions are HCO_3^- (≈ 280 – 320 mg L⁻¹), Na^+ (≈ 70 – 90 mg L⁻¹), Ca^{2+} (≈ 20 – 35 mg L⁻¹), Mg^{2+} (≈ 10 – 18 mg L⁻¹), SO_4^{2-} (<25 mg L⁻¹), and Cl^- (<10 mg L⁻¹). The mineral water originates from natural hydrothermal springs and therefore represents a more realistic aqueous matrix for assessing catalyst performance under environmentally relevant conditions.

The three water matrices (distilled, tap, and mineral water) exhibited distinct pH values, ranging from near-neutral conditions in distilled water and tap water to slightly alkaline conditions in mineral water from Bankya.

2.2. Synthesis of Pristine and Ho-Doped ZnO by Hydrothermal and Sol–Gel Routes

Pure and Ho-doped ZnO powders were prepared using a modified hydrothermal method based on a previously reported procedure [27]. For the synthesis of undoped ZnO, 1.1 g of zinc acetate dihydrate was dissolved in 10 mL of deionized water. In the case of Ho-modified samples, the total precursor solution volume was kept constant at 10 mL by dissolving zinc acetate dihydrate in 5 mL of deionized water, while the required stoichiometric amount of holmium nitrate pentahydrate was dissolved separately in the remaining 5 mL before combining the two solutions. After mixing the precursor solutions and ensuring complete dissolution, 20 mL of ethylene glycol was added under constant stirring to maintain a consistent solvent-to-surfactant ratio and a total liquid volume of 30 mL. The prepared precursor solution was poured into a 50 mL Teflon-lined stainless-steel autoclave and subjected to hydrothermal treatment at 160 °C for 24 h [28]. After naturally cooling to room temperature, the resulting solid was separated by centrifugation, thoroughly rinsed several times with distilled water and ethanol to remove residual impurities, and dried. The dried material was then finely ground and calcined at 500 °C for 2 h, yielding the final ZnO-based powder.

For the sol–gel synthesis, zinc acetate was dissolved in 20 mL of ethylene glycol under continuous magnetic stirring. Ho-modified samples were prepared by introducing the appropriate stoichiometric amount of holmium nitrate hexahydrate into the precursor solution. Acetic acid was then added dropwise to regulate the hydrolysis process and suppress

premature precipitation, while stirring was maintained throughout the preparation. The resulting sol was poured into a Petri dish and left to age at room temperature for 24 h, allowing gelation to occur. The formed gel was subsequently dried to obtain a xerogel, which was finely ground and calcined at 500 °C for 2 h to produce the crystalline Ho-doped ZnO powders [29]. The obtained samples have been denoted as follows: Z-s, Z1H-s, Z2H-s for the sol-gel-derived materials and Z-h, Z1H-h, Z2H-h for the hydrothermally synthesized counterparts.

2.3. Structural and Physicochemical Characterization Methods

The crystal structure and phase composition of the synthesized materials were examined by X-ray diffraction (XRD). Diffraction patterns were recorded using a Bruker D8 Advance diffractometer (Bruker, Bremen, Germany) operating with Cu K α radiation ($\lambda = 1.5418$ Å). Measurements were carried out over a 2θ range of 10–80° using a step size of 0.05°. The average crystallite size (D) was determined from the XRD data using the Scherrer equation:

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

In the Scherrer equation, K is the shape factor, taken as 0.9, while λ corresponds to the wavelength of the Cu K α radiation (0.15418 nm). The parameter β represents the full width at half maximum (FWHM) of the selected diffraction peak, expressed in radians, and θ is the corresponding Bragg diffraction angle. The degree of crystallinity of the synthesized materials was further estimated using the following equation:

$$\% \text{ Crystallinity} = \frac{\text{Area of crystalline peaks}}{\text{Area of crystalline and amorphous peaks}} 100 \quad (2)$$

The optical properties of the synthesized powders were investigated by UV-Vis diffuse reflectance spectroscopy (DRS) using an Evolution 300 spectrophotometer (Thermo Electron Corporation, Madison, WI, USA). Diffuse reflectance spectra were collected over the wavelength range of 200–800 nm, with MgO employed as the reference material. The optical band gap energy (E_g) of each sample was estimated from Tauc plots according to the following equation:

$$\alpha h\nu = A(h\nu - E_g)^{\frac{n}{2}}. \quad (3)$$

In the Tauc equation, A is a proportionality constant independent of the photon energy ($h\nu$), whereas E_g denotes the optical band gap of the semiconductor. The band gap energies of the synthesized materials were determined using the Tauc method, as commonly reported for metal oxide photocatalysts [30]. The exponent n depends on the type of electronic transition involved, distinguishing between direct and indirect optical transitions.

The structural features and chemical bonding of the synthesized powders were further analyzed by Fourier-transform infrared (FTIR) spectroscopy. Infrared spectra were acquired in the 1600–400 cm^{-1} wavenumber range using the KBr pellet method on a Nicolet 320 FTIR spectrometer (Thermo Electron Corporation, Madison, WI, USA). Each spectrum was recorded with 64 accumulated scans at a spectral resolution of 1 cm^{-1} .

The morphology and microstructure of the prepared materials were examined by scanning electron microscopy (SEM) using a JSM-5510 microscope (JEOL, Tokyo, Japan) operated at an accelerating voltage of 10 kV. Before imaging, the powder samples were sputter-coated with a thin gold layer using a JFC-1200 fine coater (JEOL) to improve electrical conductivity. Elemental composition and microstructural features were further characterized with a Zeiss EVO 15 scanning electron microscope (Zeiss, Oberkochen, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector.

The textural characteristics of the synthesized powders were evaluated from nitrogen adsorption–desorption isotherms measured at 77 K using a Quantachrome Nova 1200e surface area analyzer (Boynton Beach, FL, USA). The specific surface area was calculated according to the Brunauer–Emmett–Teller (BET) method, while the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of $p/p_0 \approx 0.99$. The average pore diameter and pore size distribution were obtained using the non-local density functional theory (NLDFT) equilibrium model for slit-shaped pores.

Room-temperature photoluminescence (PL) spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) using an excitation wavelength of 325 nm [22].

The surface chemical composition and oxidation states of pure and Ho-modified ZnO powders were investigated by X-ray photoelectron spectroscopy (XPS) using an ESCALAB MkII electron spectrometer (VG Scientific, now Thermo Fisher Scientific, Waltham, MA, USA). Measurements were carried out under an ultrahigh vacuum with a base pressure of 5×10^{-10} mbar, increasing to approximately 4×10^{-9} mbar during spectral acquisition. Non-monochromated Mg K α radiation ($h\nu = 1253.6$ eV) served as the X-ray excitation source. High-resolution spectra of the Zn 2p and O 1s regions were collected with a pass energy of 20 eV, whereas a pass energy of 50 eV was employed for the Ho 4d region to improve signal acquisition from the relatively low Ho surface concentration. The overall energy resolution of the instrument, estimated from the full width at half maximum (FWHM) of the Ag 3d $_{5/2}$ reference peak, was approximately 1 eV.

Spectral processing and quantitative analysis were performed using SpecsLab2 and CasaXPS software (version 2.3.26PR1, Casa Software Ltd., Teignmouth, UK). Prior to peak fitting, the spectra were corrected for X-ray satellite contributions and a Shirley background was applied. Peak deconvolution was carried out using symmetric Gaussian–Lorentzian line shapes, while elemental concentrations were determined from peak areas corrected with Scofield photoionization sensitivity factors [31,32]. This analysis enabled the assessment of Ho incorporation and the identification of oxygen-related surface species in the ZnO samples.

Electron paramagnetic resonance (EPR) spectroscopy was carried out to identify defect-related paramagnetic centers and evaluate the formation of reactive species in Ho-modified ZnO. The measurements were conducted at room temperature using a JEOL JES-FA100 X-band EPR spectrometer (JEOL, Tokyo, Japan) fitted with a standard TE011 cylindrical resonator. Spectra were acquired under the following operating conditions: modulation frequency of 100 kHz, microwave power of 6 mW, modulation amplitude of 0.2 mT, time constant of 0.1 s, and a magnetic field sweep time of 2 min.

2.4. Experimental Procedure for Tribocatalytic Activity Evaluation

Tribocatalytic activity was evaluated in a 100 mL glass reactor, where mechanical energy was supplied by magnetic stirring. Each experiment was carried out with 50 mL of an aqueous paracetamol (PCA) solution (15 mg L^{-1}) prepared using distilled, tap, or mineral water as the reaction medium. All experiments were performed in the absence of light at room temperature (23 ± 2 °C) to exclude any contribution from photocatalytic reactions.

For each test, 50 mg of pure or Ho-modified ZnO powder was dispersed in the PCA solution. Before initiating tribocatalysis, the suspension was kept under static conditions for 30 min to establish adsorption–desorption equilibrium between the catalyst surface and paracetamol molecules. Mechanical activation was then induced using a PTFE-coated magnetic stirring bar (8 mm in diameter and 35 mm in length) rotating at 500 rpm.

Aliquots (2 mL) were withdrawn at selected reaction times and centrifuged at 6000 rpm to separate the catalyst particles from the solution. The residual concentration of paracetamol was determined by UV–Vis spectroscopy in the wavelength range of 200–450 nm. Quantitative analysis was based on the characteristic absorption band of paracetamol at $\lambda_{\text{max}} = 243$ nm, and the degradation efficiency was calculated from the corresponding changes in absorbance.

To investigate the influence of the friction interface and the intensity of mechanical contact on tribocatalytic activity, additional experiments were conducted using two and three PTFE-coated magnetic stirring bars instead of a single rod.

Additional control experiments were conducted both in the absence of the catalyst and without PTFE-induced mechanical activation to verify that paracetamol removal under these conditions was insignificant. The tribocatalytic degradation mechanism was further investigated by identifying the reactive species responsible for the oxidation process through scavenger experiments.

Selective radical quenchers were individually introduced into the reaction system to suppress specific reactive species. Isopropyl alcohol (IPA), ascorbic acid (AA), and sodium ethylenediaminetetraacetate (EDTA-Na) were used as scavengers for hydroxyl radicals ($\bullet\text{OH}$), superoxide radicals ($\bullet\text{O}_2^-$), and tribogenerated holes (h^+), respectively. In each experiment, 6 mg of the selected scavenger was added to the reaction mixture, enabling assessment of the contribution of each reactive species to the overall tribocatalytic degradation mechanism.

Chemical oxygen demand (COD) measurements were performed to evaluate the mineralization efficiency during paracetamol degradation. The analyses were carried out using a DR 1900 Vis spectrophotometer coupled with an LT200 thermostat (HACH GmbH, Berlin, Germany). Total organic carbon (TOC) analysis of the treated solutions was performed with a Shimadzu TOC-L instrument (Shimadzu Corporation, Kyoto, Japan). The accuracy of the ICP-MS analysis was verified using certified water reference materials, including NIST 1640a (Trace Elements in Natural Water, National Institute of Standards and Technology, Gaithersburg, MD, USA), SPS-SW2 (Reference Material for Measurement of Elements in Surface Waters, Spectrapure Standards, Norway), and NWTM-23.5 (Environmental Matrix Reference Material, Environment and Climate Change Canada, Gatineau, QC, Canada). The measured concentrations were in good agreement with the certified reference values, confirming the reliability of the analytical procedure. Method precision was evaluated by analyzing three independent replicates, each measured six times. Instrumental drift was monitored by recalibrating the instrument after every ten samples, while potential memory effects were minimized by rinsing the system with 3% HNO_3 for 60 s, followed by analysis of a blank solution.

3. Results and Discussion

3.1. Structural and Surface Characterization of Hydrothermal and Sol–Gel ZnO and Ho/ZnO Samples

The X-ray diffraction (XRD) pattern of prepared pure ZnO as well as ZnO doped with 1 and 2 mol % Ho, prepared by different methods hydrothermal and sol–gel are presented in Figure 1a,b. All diffraction patterns revealed that ZnO has sharp and well oriented peaks. The diffraction occurs at angles 31.7201° , 34.4701° , 36.2901° , 47.6001° , 56.6701° and 62.9801° matched with standard d-spacing of ZnO wurtzite hexagonal structure (JCPDS-36-1451). Presence of these planes confirms the formation of ZnO nanocrystals and specifically wurtzite structure [33]. The sharp peaks confirm that the ZnO are highly crystalline in nature. No additional peaks of any other phases were observed which clearly predicts the purity of ZnO.

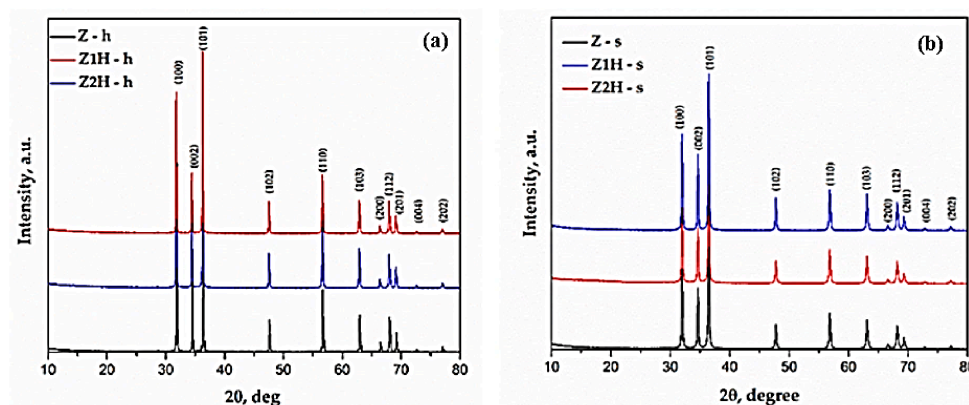


Figure 1. XRD patterns of pure ZnO and ZnO doped with 1 and 2 mol % Ho, prepared by different methods—hydrothermal (a) and sol-gel (b).

The particle size was calculated by employing the Scherer's equation [34] for pure and doped ZnO. The estimated crystallite size for sol-gel powders is about 40 nm while for the hydrothermal prepared samples—in the range 40–50 nm (Table 1). Obviously, the Ho doping reduces the crystallite sizes of the as-prepared powders. The obtained data are consistent with those reported in earlier studies [35].

Table 1. Calculated particles size and crystallinity of the prepared samples.

Sol-Gel Films	Particle Size, nm	Crystallinity (%)
Z-s	42.8	67.6
Z1H-s	40.8	68
Z2H-s	40.5	62
Z-h	56.3	79
Z1H-h	46.5	77
Z2H-h	35.7	75

The investigated materials, both pure and doped with 2 mol % Ho ZnO, were subjected to IR measurements in order to obtain structural information (Figure 2). The IR analysis of the sol-gel synthesized ZnO and 2 mol % Ho-doped ZnO (Figure 2a) confirms the formation of ZnO through the characteristic stretching Zn–O vibrations in the 400–600 cm^{-1} region. The bands at 1570 and 1430 cm^{-1} can be assigned to the vibrations of COO^- groups, indicating the presence of residual acetate species originating from the precursor. The band at 1350 cm^{-1} could be attributed to the vibrations of C–H bonds. The absorption bands at 1080, 1040 and 1020 cm^{-1} may be associated with the C–O and C–O–C stretching vibrations of residual alkoxide or alcohol species formed during the hydrolysis and condensation reactions of the sol-gel process. The bands in the range 950–860 cm^{-1} are commonly attributed to Zn–OH vibrations or hydroxylated zinc oxide species, indicating incomplete condensation and the presence of surface hydroxyl groups. The bands at 690, 620 and 510 cm^{-1} correspond to the vibrations of the Zn–O bond and confirm the formation of ZnO as observed by XRD analysis. After calcination at 500 °C (Figure 2a), the organic groups are significantly reduced or disappear. On the other hand, the Zn–O bands become more intense and better defined, indicating an increase in the crystallinity of the material. Ho doping does not lead to the appearance of new functional groups but causes slight changes in the position and intensity of the Zn–O vibrations, suggesting modifications in the ZnO local structural environment [36]. The IR spectra of the hydrothermally synthesized ZnO and 2 mol % Ho-doped ZnO (Figure 2b) are mainly characterized by Zn–O vibrations

in the 550–400 cm^{-1} region. The absence of absorption bands associated with organic groups confirms the high purity of the synthesized materials. After heat treatment at 500 °C, the Zn–O bands become more pronounced and better resolved, indicating improved crystallinity. Doping with 2 mol % Ho results (Figure 2b) leads to changes in the intensity and partial splitting of the Zn–O vibrations, which can be attributed to the local structural distortions induced by the incorporation of Ho^{3+} ions into the ZnO lattice, without the formation of new functional groups or a separate oxide phase as observed by XRD [37,38].

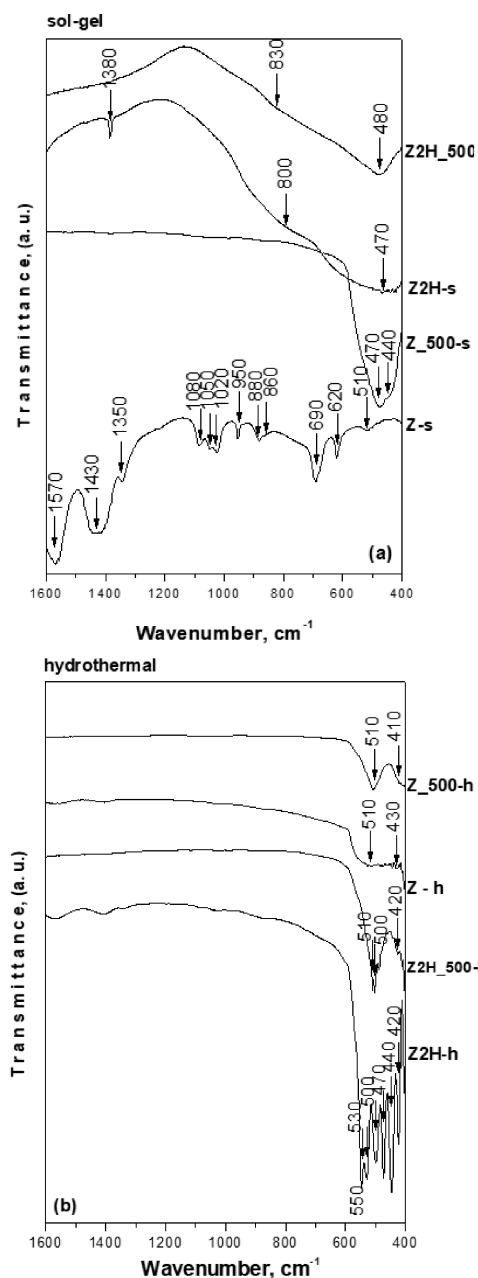


Figure 2. IR spectra of prepared pure and doped with 2 mol% Ho ZnO—by sol-gel method (a) and hydrothermally (b).

The textural properties of the investigated samples were assessed using low-temperature nitrogen adsorption. The adsorption–desorption isotherms of selected samples Z-h (a) and Z2H-h (b) are presented in Figure 3. The textural parameters of the above samples are shown in Table 2. The BET isotherms can be classified as Type II, characteristic of non-porous or macroporous materials according to IUPAC classification [39]. At higher

relative pressures ($p/p_0 > 0.5$), a distinct hysteresis loop is observed, which follows the H3 classification according to the IUPAC report. The H3-type loops are usually associated with non-rigid aggregates of plate-like particles or rod-like structures that form slit-shaped pores within the interstitial spaces, which is in good agreement with the obtained SEM data. The calculated specific surface areas (Table 2) are relatively low, consistent with the micrometer-scale dimensions observed by SEM analysis. The compact BET surface [40]. It can be concluded that the increase in crystallinity has occurred at the expense of the specific surface area.

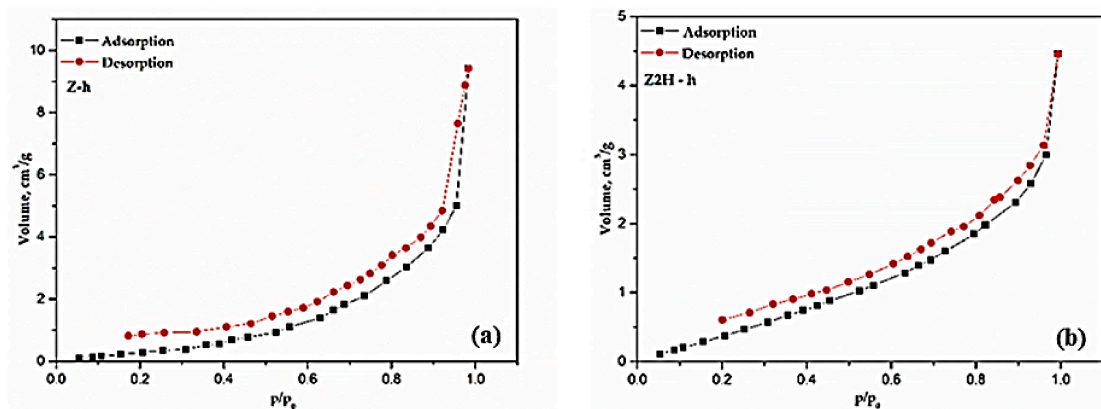


Figure 3. Adsorption-desorption BET isotherms of ZnO (a) and 2% Ho/ZnO (b).

Table 2. Textural characteristics of the selected powders.

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	D_{av} (nm)
Z2H-h	2.8	0.007	9.7
Z-h	1.7	0.015	33

It is evident that the modification of Ho^{3+} into the crystal lattice does not affect the isotherm type or the hysteresis loop classification, but it leads to an increase in the specific surface area and a decrease in the average pore diameter. Specifically, the BET surface area increased from $1.7 \text{ m}^2/\text{g}$ for pure ZnO to $2.8 \text{ m}^2/\text{g}$ for the ZnO/2Ho sample. This shift suggests that the holmium dopant acts as a grain growth inhibitor during the hydrothermal process influencing the ripening of the hexagonal rods which correlate well with the obtained XRD data [41]. This is further supported by the decrease in the average pore diameter (D_{av}) from 33 nm to 9.7 nm upon Ho doping. The significant reduction in D_{av} indicates that the voids between the rod-like structures have become smaller and more numerous probably due to the formation of more fragmented rods.

Figure 4a–f shows scanning electron micrographs (SEM) of ZnO nanoparticles prepared by hydrothermal (Figure 4a–c) and sol–gel approaches (Figure 4d–f). The obtained results revealed clear differences in the morphology of ZnO depending on the synthesis method and Ho doping concentration. The hydrothermally prepared samples (a–c) exhibit predominantly rod-like structures, where pure ZnO shows randomly oriented nanorods with some size variation, while Ho doping (b,c) leads to more uniform, well-defined rods and enhanced crystallinity, as well. In contrast, the sol–gel derived samples (d–f) display agglomerated nanoparticle clusters. Pure ZnO (d) appears densely packed, whereas increasing Ho content (Figure 4e,f) results in more porous and loosely arranged aggregates, suggesting that doping reduces particle agglomeration. The rod-like structures and agglomerated particles with dimensions are in the micro- and nanoscale range. The rod-shaped particles exhibit lengths of approximately 1–2.5 μm and diameters in the range of 150–400 nm. In addition, irregular agglomerates with overall sizes between 2 and 6 μm are

observed. These agglomerates appear to be composed of much smaller nanoparticles, with estimated sizes of about 50–120 nm. In summary, the hydrothermal method facilitates the growth of structurally uniform doped nanorods, while the sol–gel method produces high surface area nanoparticle aggregates whose morphology and degree of agglomeration are influenced by Ho modification. Bearing in mind the obtained results it could be suggested that the precursor of reactants, hydrothermal temperature and time were the key factors for preparing ZnO materials. This phenomenon has been reported by several authors [27,42], who have shown that the use of different alcohols as precursors leads to the formation of rod like ZnO.

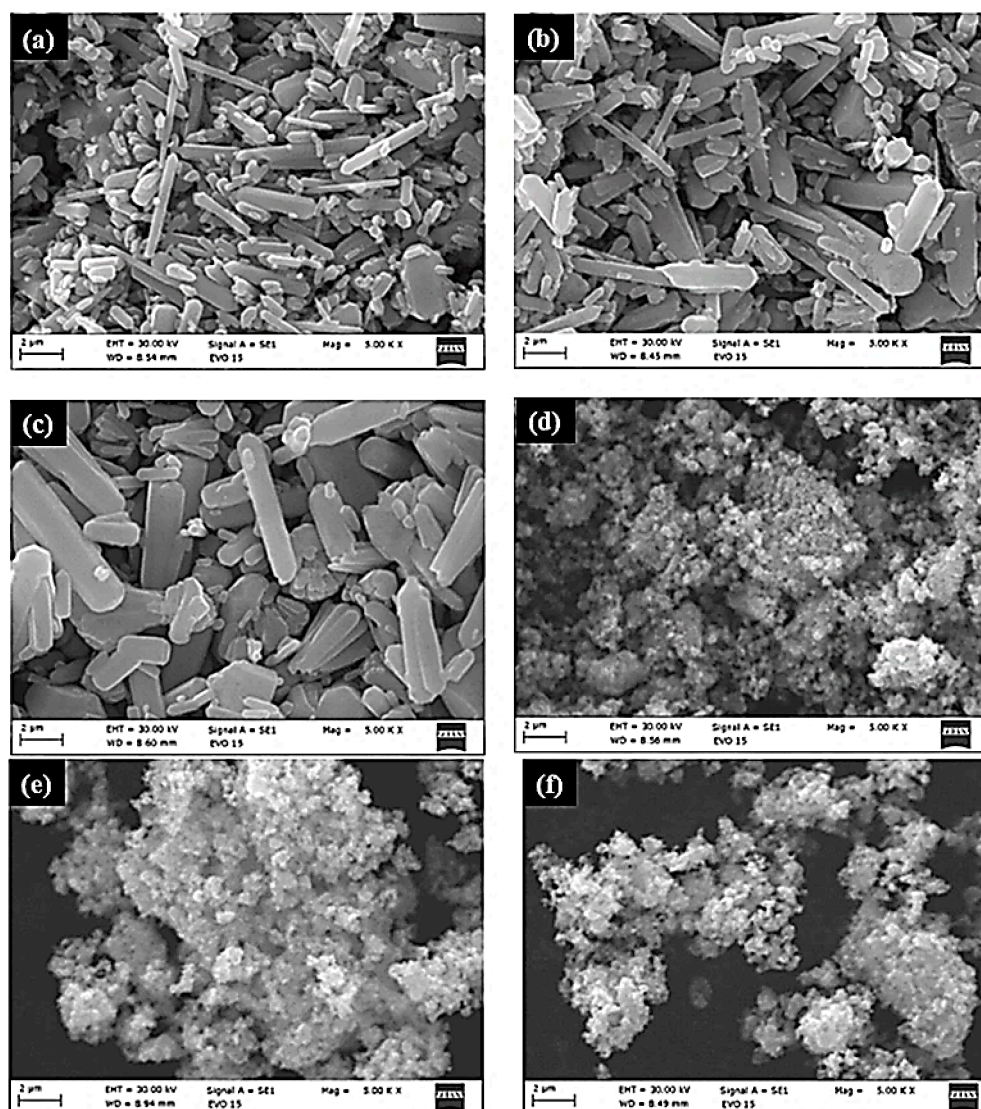
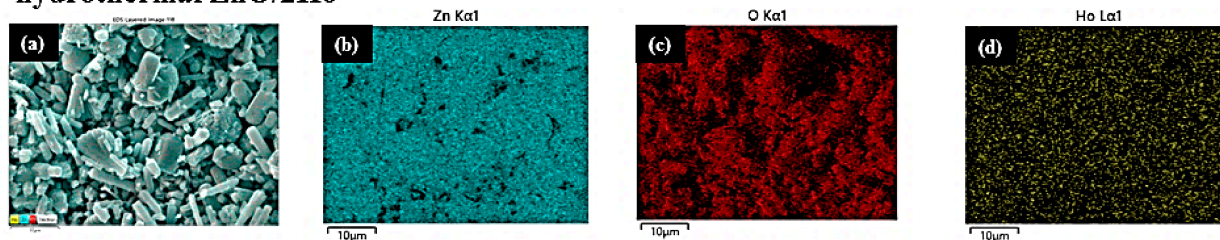


Figure 4. SEMs of ZnO prepared by hydrothermal (a–c) and sol–gel method (d–f) heat treated at 500 °C—hydrothermally obtained ZnO (a), 1Ho/ZnO (b), 2Ho/ZnO; sol–gel obtained ZnO (c), 1Ho/ZnO (d), 2Ho/ZnO (f).

The SEM–EDS elemental mapping confirms the presence and distribution of all elements Zn, O and Ho within the samples (Figure 5). The elemental maps exhibited a relatively uniform distribution of both elements across the analyzed areas, indicating successful formation of pure ZnO without significant phase segregation. In the hydrothermal sample, Zn, O and Ho showed a more homogeneous spatial distribution, suggesting better compositional uniformity. In contrast, the sol–gel sample shows slight inhomogeneity with localized regions of higher intensity, which can be attributed to particle agglomeration.

hydrothermal ZnO/2Ho



sol-gel ZnO/2Ho, 500°C

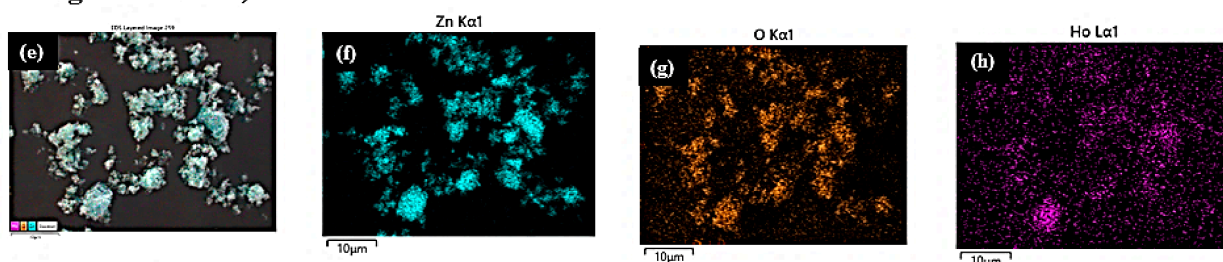


Figure 5. SEM image elemental mapping of ZnO doped with 2% Ho obtained by hydrothermal (a) and sol-gel (e) method heat treated at 500 °C; composition map of Zn (b,f); composition map of O (c,g); composition map of Ho (d,h).

Figure 6 presents the room-temperature photoluminescence (PL) spectra of pristine ZnO and Ho-modified ZnO prepared by the hydrothermal and sol-gel methods. All samples exhibit a broad visible emission band commonly associated with intrinsic defect-related luminescence arising from native defects, including oxygen vacancies, zinc interstitials, and other lattice imperfections in ZnO. The emission intensity strongly depends on both the synthesis route and Ho modification.

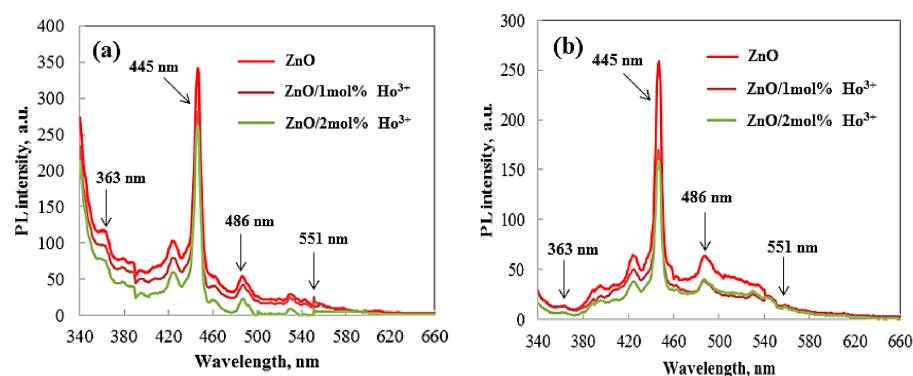


Figure 6. Photoluminescence (PL) spectra of pristine and Ho-modified ZnO prepared by (a) sol-gel synthesis and (b) hydrothermal synthesis.

For both synthesis methods, Ho modification leads to a pronounced decrease in PL intensity relative to pristine ZnO, indicating a reduced recombination rate of tribogenerated electron-hole pairs. The reduced PL emission is consistent with the formation of localized electronic states associated with Ho modification, which may act as charge-trapping centers, thereby facilitating charge separation and prolonging the lifetime of charge carriers. Consequently, a larger fraction of tribogenerated charge carriers is expected to participate in surface redox reactions, thereby promoting the generation of reactive oxygen species (ROS). Among all investigated samples, the hydrothermally prepared ZnO/2Ho catalyst exhibits the lowest PL intensity, indicating the most efficient suppression of charge-carrier recombination. This observation correlates well with its superior tribocatalytic performance

toward paracetamol degradation, supporting the proposed role of Ho incorporation in suppressing charge-carrier recombination and promoting ROS-mediated oxidation. This interpretation is consistent with the radical scavenging experiments, which identify $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ as the predominant reactive species involved in the tribocatalytic degradation of paracetamol.

3.2. Electronic Structure Characterization of Pure and Ho-Doped ZnO Powders

EPR and XPS analyses were performed to investigate the surface chemical composition, electronic structure, and defect-related properties of pure and Ho-doped ZnO samples, as well as to evaluate the influence of Ho modification on oxygen vacancy formation and reactive species generation. The EPR spectra of the investigated samples are presented in Figure 7, while the extracted spectroscopic parameters are summarized in Table 3. All spectra exhibit two well-defined sharp signals, denoted as S1 and S2.

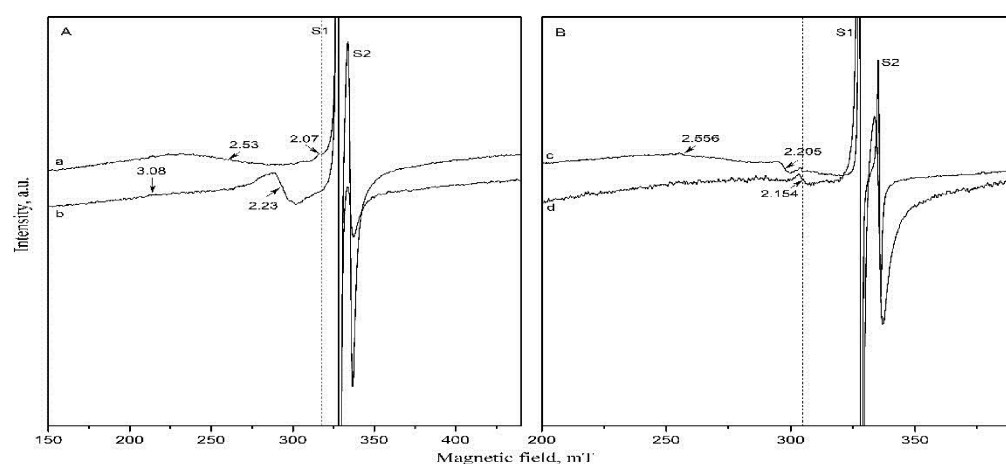


Figure 7. X-band EPR spectra of: (A)—(a) ZnO and (b) 2 mol % Ho-doped ZnO synthesized via sol-gel; (B)—(c) ZnO and (d) 2 mol % Ho-doped ZnO synthesized via hydrothermal methods.

Table 3. EPR parameters of ZnO and 2 mol % Ho-doped ZnO synthesized via sol-gel and hydrothermal methods.

Sample	Synthesis Method	I (S1), a.u.	ΔH (mT)	N_s (S1)	I (S2), a.u.	ΔH (mT)	N_s (S2)
ZnO	Sol-gel	5820	0.64	23 839	263	3.033	2419
Ho-doped ZnO	Sol-gel	3543	0.64	1451	42	3.59	541
ZnO	hydrothermal	1697	0.48	391	118	1.117	147
Ho-doped ZnO	hydrothermal	2656	0.48	612	37	3.59	477

Notes: Where I is the signal intensity, ΔH is the peak-to-peak linewidth, and N_s is the relative spin concentration ($I \times \Delta H^2$).

The most intense low-field signal S1, centered at $g = 2.000$, often assigned to unpaired electron trapped at an oxygen vacancy site, in agreement with previous reports [43–45]. The high-field signal S2, located at $g = 1.955$, is assigned to shallow donor (SD) centers. These centers are typically associated with zinc-related defects, most likely zinc interstitials (Zn_i), although contributions from oxygen-vacancy-related donor states cannot be excluded [42,43,46–48]. The higher relative intensity of S1 compared to S2 in all samples indicates that oxygen vacancies are the dominant paramagnetic defects.

In addition to the primary signals, weak contributions at $g \approx 2.07$ and a broad resonance centered at $g \approx 2.53$ are observed in undoped ZnO synthesized via the sol-gel

method. The signal at $g \approx 2.07$ is attributed to surface-related oxygen radical species such as O_2^- or $OH\bullet$, while the broad feature at higher g -values likely originates from defect complexes or structurally disordered regions [49,50].

The modification of 2 mol % Ho^{3+} into ZnO leads to a substantial modification of the EPR response (Figure 7A, b). A pronounced decrease in the intensities of both S1 and S2 signals is observed, indicating a strong reduction in both oxygen vacancies and shallow donor centers.

The linewidth of S1 remains unchanged ($\Delta H \approx 0.64$ mT), suggesting that the local environment of the remaining oxygen vacancies is not significantly altered. In contrast, the linewidth of S2 increases from 3.03 mT to 3.59 mT, indicating enhanced disorder or increased distribution of donor environments after Ho modification. These results suggest that Ho^{3+} ions act as compensating centers, suppressing the formation of intrinsic donor-like defects, likely through defect-complex formation. Furthermore, an additional anisotropic signal with $g_{\perp} = 2.23$ and $g_{\parallel} = 2.83$ appears in the Ho-doped sample (Figure 7A, b). This signal probably is attributed to Ho^{3+} -related centers, in agreement with the results reported by Kabongo et al. [45]. Although Ho^{3+} (4f10) is a non-Kramers ion and thus expected to be EPR silent in an ideal crystal field, the observed anisotropic signals indicate that Ho^{3+} ions occupy low-symmetry sites in the ZnO lattice. This suggests the formation of defect-associated Ho centers, where crystal field distortions give rise to an effective spin doublet, enabling EPR activity. A significant modification of the EPR spectra is observed when comparing samples prepared by the sol-gel and hydrothermal methods (Figure 7B, c,d), reflecting the different defect formation mechanisms associated with the two synthesis routes.

Hydrothermally synthesized ZnO exhibits a pronounced decrease in the intensity of the S1 signal (from 5820 to 1697 a.u.), indicating a substantially lower concentration of singly ionized oxygen vacancies (V_O^+). Similarly, the S2 signal decreases (from 263 to 118 a.u.), indicating suppression of shallow donor defects, such as Zni under hydrothermal conditions. The narrowing of the linewidth (ΔH from 3.03 mT to 1.12 mT) suggests a more homogeneous defect environment, consistent with improved crystallinity and reduced structural disorder. The disappearance of the signal at $g \approx 2.07$ suggests a reduced contribution from surface-related oxygen radical species, which is likely due to differences in surface chemistry and lower surface defect density. New signals observed at $g = 2.154$, 2.205, and 2.556 are attributed to defect centers characteristic of the hydrothermal growth environment. Signals in this g -range are commonly associated with strongly distorted oxygen-related surface species and defect complexes in oxide materials [51]. A similar but less pronounced trend is observed for Ho-doped ZnO samples (Figure 7, b,d). The S1 intensity decreases from 3543 to 2656 a.u., indicating a reduction in oxygen vacancy concentration; however, the effect is weaker compared to undoped ZnO. This suggests that Ho^{3+} ions partially stabilize oxygen-related defects even under hydrothermal conditions. The higher concentration of oxygen vacancies in hydrothermally synthesized Ho-doped ZnO compared to undoped ZnO is clearly evidenced by the S1 signal intensities (Table 3). This behavior can be attributed to charge compensation effects induced by Ho^{3+} modification. Substitution of Zn^{2+} by Ho^{3+} introduces excess positive charge, which is compensated by the formation of oxygen vacancies. Additionally, the larger ionic radius of Ho^{3+} induces local lattice distortions, facilitating the formation and stabilization of V_O -related defects. The formation of Ho- V_O complexes likely contributes to the persistence of oxygen vacancies even under conditions favoring improved stoichiometry.

More notably, the S2 signal shows only a minor decrease in SD relative concentration (from 541 to 477 a.u.), in contrast to the pronounced reduction observed in undoped ZnO. This indicates that shallow donor centers in Ho-doped ZnO are more stable with

respect to changes in synthesis conditions. The presence of Ho^{3+} likely promotes the formation of defect complexes (e.g., Ho-Zn_i or Ho-V_O), which are energetically more stable and less sensitive to synthesis-induced variations. The linewidth of S2 remains unchanged ($\Delta H \approx 3.59$ mT), further supporting the presence of stable and structurally complex defect configurations in the doped samples. A key observation is the disappearance of the anisotropic Ho-related signal ($g_{\perp} = 2.23$, $g_{\parallel} = 2.83$) in the hydrothermally synthesized sample. This suggests a modification of the local environment of Ho^{3+} ions, possibly due to increased symmetry or modification into more ordered lattice sites, which suppresses EPR-active states. Additionally, only a weak signal at $g = 2.154$ is observed, indicating that the paramagnetic response is dominated by residual defect centers rather than Ho-related contributions.

The EPR results are consistent with the PL analysis, which revealed a reduced recombination rate after Ho modification. Together, these findings indicate that Ho-induced defect centers act as effective charge-trapping sites, thereby promoting charge separation and facilitating ROS generation during tribocatalysis.

Figure 8 and Table 4 summarize the surface chemical composition and oxidation-state analysis derived from XPS measurements. Figure 8a presents the fitting procedure of the O1s spectra recorded for the investigated samples. From top to bottom, the oxygen core-level spectra of Z-s, Z2H-s, Z-h, and Z2H-h are compared. All O1s spectra were deconvoluted into three components. The first component, centered at approximately 530.7 eV (green line), is assigned to lattice oxygen associated with Zn–O bonds and, to a significantly smaller extent, Ho–O bonds [25]. It should be noted that the calculated surface concentration of Ho is relatively low, amounting to 1.49 and 0.46 at % for the Z2H-s and Z2H-h samples, respectively. Consequently, the contribution of oxygen species directly bonded to Ho is expected to be minor relative to the dominant Zn–O contribution.

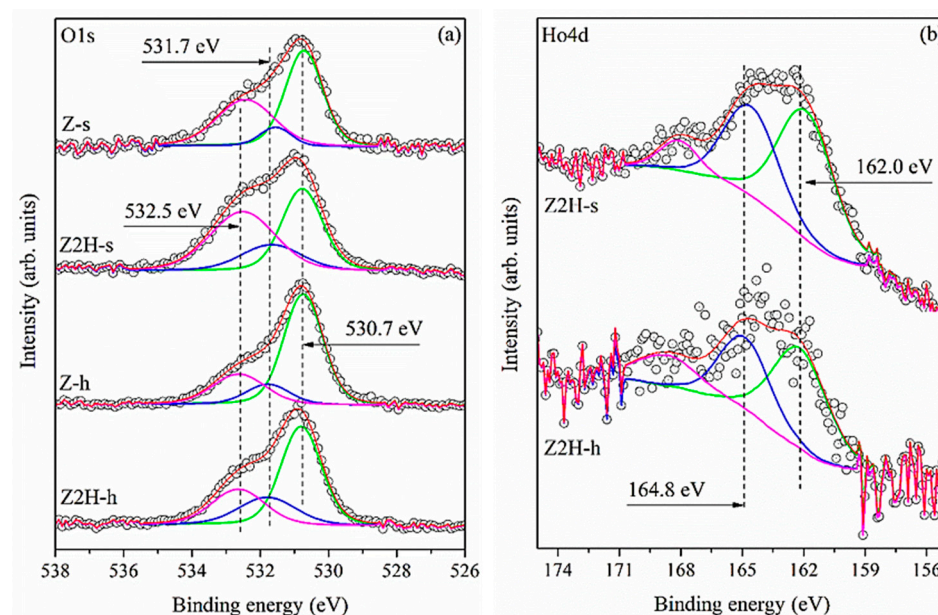


Figure 8. High-resolution XPS spectra of (a) O1s and (b) Ho4d regions recorded for the investigated samples. Open circles represent the experimental data, while the red line corresponds to the fitted envelope. In the O1s spectra, the green component is assigned to lattice oxygen related to Zn–O/Ho–O bonds, the blue component corresponds to defect-associated non-lattice oxygen species, and the magenta component is attributed to adsorbed hydroxyl-containing species and surface adsorbates. The Ho4d spectra were fitted using components associated with Ho^{3+} species incorporated into the ZnO matrix.

Table 4. Surface atomic concentrations (at %) derived from XPS analysis of the investigated ZnO and Ho-doped ZnO samples.

	O1s (Lattice)	O1s (Non-Lattice)	O1s (OH Groups)	Zn2p (Zn–O)	Ho4d (Ho ³⁺)
Z–s	30.86	5.01	22.65	41.48	0.00
Z2H–s	21.71	10.19	24.91	41.69	1.49
Z–h	31.80	6.40	11.59	50.20	0.00
Z2H–h	27.44	10.81	12.88	48.42	0.46

The second component, centered at approximately 531.7 eV (blue line), is attributed to defect-associated non-lattice oxygen species, including surface hydroxyl groups, chemisorbed oxygen species, and oxygen located in defective or oxygen-deficient surface regions. According to recent critical analyses by Idriss and Easton et al., this component should not be directly assigned to isolated oxygen vacancies, since such sites are rapidly hydroxylated or occupied by adsorbed oxygen species under ambient atmospheric conditions [52,53]. Nevertheless, the increased relative intensity of this component after Ho modification suggests an increase in defect-associated oxygen species and defective oxygen regions, which is consistent with the EPR results.

The third component (magenta line), located at higher binding energies, is attributed to adsorbed hydroxyl-containing compounds, residual organic species, and molecularly adsorbed surface contaminants originating from the synthesis and ambient exposure of the samples.

Figure 8b presents the Ho4d core-level spectra recorded for the Ho-doped Z2H–s and Z2H–h samples. Due to the relatively low surface concentration of Ho and the overlap with Zn3s-related loss features, the spectra were obtained after subtraction of the corresponding energy region recorded for pure ZnO. The resulting spectra were fitted using components associated with Ho4d_{5/2}, Ho4d_{3/2}, and a broad satellite contribution characteristic of rare-earth elements. The Ho4d spectra exhibit intrinsically broad features due to multiplet splitting and final-state effects characteristic of Ho³⁺ species in oxide environments. The Ho4d_{5/2} component centered at approximately 162.0 eV confirms the presence of oxidized Ho³⁺ species incorporated into the ZnO matrix. The obtained binding energies are in good agreement with previously reported values for Ho³⁺ incorporated into oxide matrices and Ho-doped ZnO systems [45,54–56].

The overall XPS results confirm the formation of Ho³⁺-containing ZnO materials and demonstrate that Ho modification significantly modifies the surface defect chemistry of ZnO. In particular, Ho doping increases the relative concentration of defect-associated non-lattice oxygen species by approximately a factor of two, which correlates with the modified defect structure and enhanced tribocatalytic activity. Furthermore, the sol–gel synthesis route promotes the formation of hydroxyl-containing surface species and residual adsorbates, whose concentration is approximately two times higher compared to the hydrothermally synthesized samples. These observations are consistent with the results obtained from the complementary EPR and tribocatalytic investigations.

The combined PL, EPR, and XPS results consistently support the proposed mechanism that Ho modification modifies the defect chemistry and electronic structure of ZnO, suppresses charge-carrier recombination, and enhances ROS generation, thereby leading to improved tribocatalytic activity.

3.3. UV–Vis Spectroscopic Investigation of the Optical Band Gap

The optical band gap E_g of the pure and Ho³⁺-doped ZnO samples was determined using Tauc's relation by plotting $(\alpha h\nu)^2$ versus photon energy $h\nu$, as shown in Figure 9a,b.

By extrapolating the linear portion of the curve to the abscissa, the direct band gap values were obtained. A comparison between the two synthesis routes reveals that the sol–gel prepared samples generally exhibit slightly higher band gap energies compared to those prepared via the hydrothermal method. Analysis of the spectra reveals that the synthesis method slightly influences the optical properties, as the sol–gel prepared pure ZnO (Z–s) exhibited a slightly higher band gap of 3.22 eV compared to the 3.19 eV observed for the hydrothermally prepared counterpart Z–h (Figure 7, a,b). Upon introducing holmium ions, a consistent redshift in the absorption edge is observed across both preparation techniques, indicating a slight narrowing of the band gap. For the sol–gel series, Ho^{3+} modification at both 1 mol % and 2 mol % (Z1H–s and Z2H–s) reduces the E_g to 3.20 eV. In contrast, the hydrothermal series shows a more progressive decline, with Z2H–h sample reaching the lowest band gap value of 3.17 eV. This band gap narrowing probably attributed to the creation of sub-band gap defect levels or structural distortions induced by the larger holmium ions replacing Zn^{2+} in the crystal lattice [57].

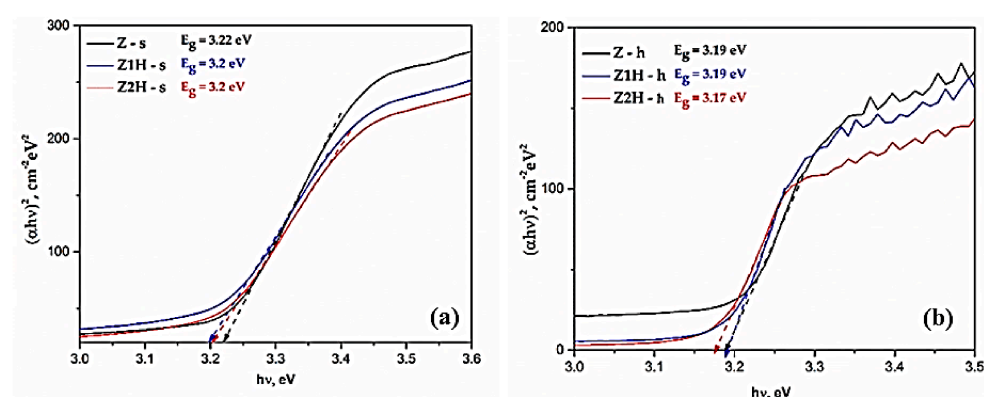


Figure 9. UV–Vis spectra of the investigated samples prepared by the sol–gel (a) and hydrothermal synthesis (b).

3.4. Tribocatalysis of Paracetamol Using Sol–Gel ZnO and $\text{ZnO}/\text{Ho}^{3+}$ Powders—Effect of Number of Rods

The tribocatalytic performance of pristine and Ho^{3+} -modified ZnO was systematically evaluated via paracetamol degradation under dark conditions employing a magnetic stirring system equipped with PTFE stirring rods operating at 500 rpm. To ensure direct comparability among the investigated systems, the initial paracetamol concentration was maintained at 15 ppm in all experiments, while the residual concentration was monitored spectrophotometrically at $\lambda_{\text{max}} = 243$ nm. As presented in Figure 10a, both pristine and Ho^{3+} -modified ZnO samples exhibited distinct tribocatalytic activity, which was further, assessed using one, two, and three magnetic stirring rods. The degradation kinetics was satisfactorily described by a pseudo-first-order kinetic model, according to $\ln(C/C_0) = -kt$, and the corresponding apparent rate constants are summarized in Figure 10b. The $\text{ZnO}/1\text{mol \% Ho}^{3+}$ sample exhibited an enhanced apparent rate constant ($k = 0.0333 \text{ h}^{-1}$) relative to pristine ZnO ($k = 0.0265 \text{ h}^{-1}$), indicating that Ho modification effectively promotes tribocatalytic performance.

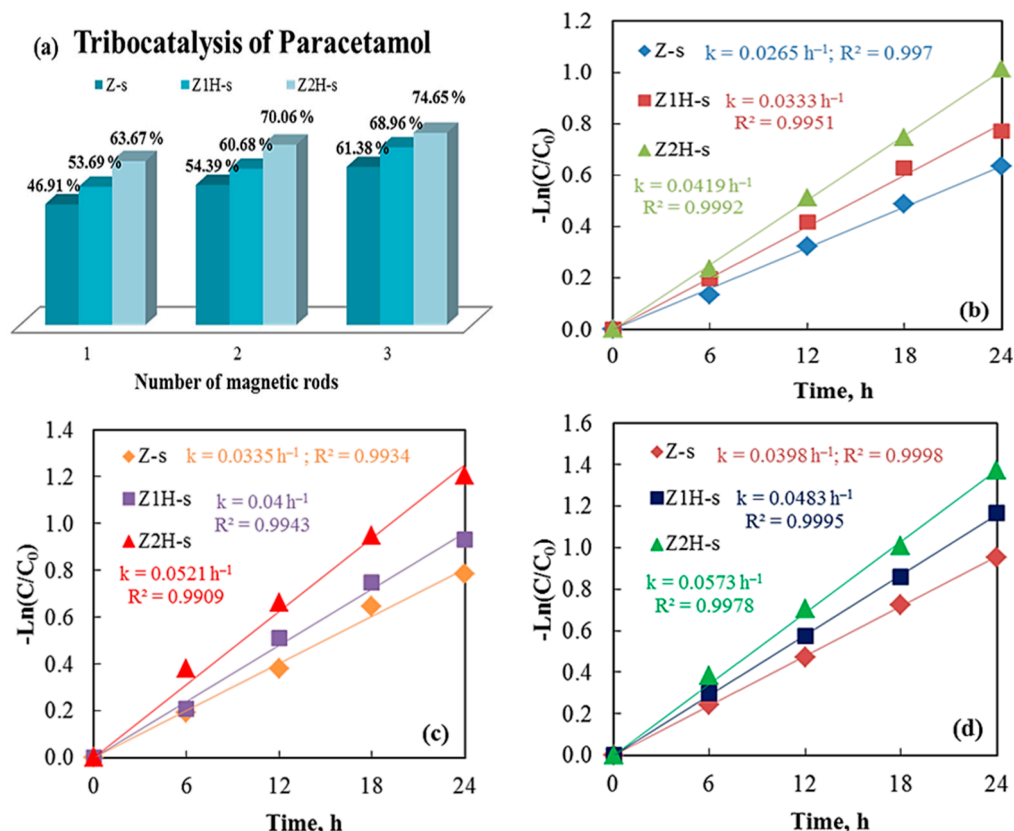


Figure 10. (a) Degrees of Paracetamol degradation versus number of magnetic rods. Tribocatalysis of analgesic at 500 rpm stirring speed using sol-gel powders with (b) one, (c) two and (d) three magnetic rods.

The improved activity of the Ho-modified sol-gel ZnO materials can be correlated with their altered microstructural characteristics, as evidenced by XRD and SEM analyses. Specifically, Ho modification resulted in reduced crystallite dimensions and diminished particle agglomeration, thereby enhancing interfacial contact efficiency and facilitating friction-induced charge transfer processes. Moreover, SEM observations revealed the formation of more porous aggregates upon Ho modification, providing an increased density of accessible triboactive sites for the generation of reactive oxygen species during paracetamol degradation. Notably, the sample containing the highest Ho concentration displayed the largest apparent rate constant ($k = 0.0419 \text{ h}^{-1}$), further confirming that rare-earth modification enhances charge separation efficiency and surface redox reactivity. To elucidate the mechanistic parameters governing the tribocatalytic process, additional experiments were performed by varying the number of magnetic stirring rods, thereby modulating the intensity of frictional interactions within the reactor. The lowest degradation efficiency was observed in the presence of a single PTFE rod, whereas the highest activity was achieved using three rods, demonstrating that increasing the number of stirring elements enlarges the effective solid–solid contact area and intensifies friction-induced interfacial interactions. Since tribocatalysis fundamentally relies on the conversion of mechanical energy into surface charge separation, both the magnitude and frequency of contact events among the stirring rods, catalyst particles, and reactor surface critically influence catalytic efficiency.

The role of direct mechanical contact was further examined by introducing two 1 mm thick PVC belt rings around a stirring rod to minimize direct contact with the reactor bottom. Under these conditions, the degradation efficiency decreased markedly to approximately 21.3%, confirming that effective tribocatalytic activity is governed predominantly by interfacial friction rather than bulk hydrodynamic agitation. Increasing the

number of stirring rods enhances (i) the total contact area between the rods and catalyst particles, (ii) the frequency of particle–particle collisions, and (iii) the extent of mechanical interactions with the reactor surface. Consequently, intensified friction promotes the generation of a higher density of surface defects and catalytically active sites, facilitating efficient separation of tribogenerated charge carriers, suppressing electron–hole recombination, and promoting charge migration toward the catalyst surface, where redox reactions occur [58].

As illustrated in Figure 10c,d, the use of two stirring rods significantly enhanced the degradation efficiency compared to a single rod, while the introduction of three rods further improved catalytic performance. The enlarged effective contact area and increased number of activated surface sites promote enhanced adsorption of paracetamol molecules and facilitate interfacial charge transfer processes. Simultaneously, the increased density of tribogenerated charge carriers favors the formation of reactive oxygen species, particularly $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals, which are primarily responsible for the oxidative degradation pathway. These findings demonstrate that tribocatalytic efficiency is strongly dependent on the dynamics of mechanical contact, whereby increased friction intensity enhances charge separation and accelerates paracetamol degradation. Although the sol–gel-derived samples exhibited relatively compact morphologies, Ho modification contributed to improved defect-assisted charge trapping and enhanced interfacial redox activity, ultimately resulting in superior tribocatalytic performance.

Mechanical friction during magnetic stirring induces triboelectric charge generation on both ZnO particles and the PTFE stirring rod, leading to the formation of positive (q^+) and negative (q^-) surface charges [59,60]. Similar to photocatalysis, these tribogenerated charges initiate redox reactions responsible for paracetamol degradation. Positive charges react with adsorbed water or hydroxide ions to produce hydroxyl radicals ($\bullet\text{OH}$), whereas negative charges reduce dissolved oxygen to superoxide radicals ($\bullet\text{O}_2^-$), which subsequently participate in oxidative degradation processes.

The enhanced tribocatalytic activity of Ho^{3+} -modified ZnO is mainly attributed to improved charge separation at the $\text{ZnO}/\text{Ho}^{3+}$ interface, which suppresses charge recombination and promotes reactive oxygen species (ROS) generation. In addition, Ho modification introduces oxygen vacancies and modifies the ZnO surface, enhancing the adsorption of paracetamol and reactive species. Ho-related trapping sites prolong charge carrier lifetime, enabling more efficient formation of $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ radicals. Consequently, Ho doping improves tribocatalytic performance through enhanced charge separation, increased ROS generation, and higher surface reactivity.

Scavenger experiments further clarified the dominant reactive species involved in the tribocatalytic degradation of paracetamol. In the absence of scavengers, the degradation efficiency increased from 61.38% for pristine ZnO to 68.96% and 74.65% for the 1 mol% and 2 mol% Ho-doped samples, respectively, confirming the beneficial effect of Ho modification on tribocatalytic activity. The addition of ascorbic acid (AA, $\bullet\text{O}_2^-$ scavenger) significantly reduced the degradation efficiency to 48.25%, 55.38%, and 61.13% for ZnO, ZnO/1Ho, and ZnO/2Ho, respectively, demonstrating that superoxide radicals are the predominant reactive species involved in the oxidation process. A less pronounced decrease was observed in the presence of isopropanol (IPA, $\bullet\text{OH}$ scavenger), indicating that hydroxyl radicals also contribute substantially to paracetamol degradation. In contrast, the addition of EDTA-Na (h^+ scavenger) resulted in only a slight decrease in degradation efficiency to 57.65%, 63.65%, and 67.47% for ZnO, ZnO/1Ho, and ZnO/2Ho, respectively, indicating that tribogenerated holes participate in the oxidation process but play a less significant role than $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals. In all scavenger experiments, the Ho-modified catalysts retained higher activity than pristine ZnO, supporting that Ho modification improves charge separation, thereby favoring ROS generation. Overall, these results demonstrate that

the tribocatalytic degradation of paracetamol proceeds predominantly via ROS-mediated oxidation, with $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ acting as the principal oxidative species, whereas the direct contribution of tribogenerated holes is comparatively minor. The enhanced activity of the Ho-modified samples is attributed to improved charge-carrier dynamics and more efficient ROS generation induced by Ho incorporation.

3.5. Tribocatalysis of Paracetamol Using Hydrothermal ZnO and ZnO/Ho³⁺ Powders—Effect of Type Catalysts

The morphology of ZnO and ZnO/Ho³⁺ strongly influences tribocatalytic performance, since friction-induced charge generation and reactive oxygen species (ROS) formation depend on surface structure and contact interactions [61]. Hydrothermally synthesized samples exhibited well-defined rod-like morphologies with higher aspect ratios and preferentially exposed crystal facets, promoting localized stress concentration and more efficient separation of tribogenerated charge carriers. Accordingly, the enhanced tribocatalytic activity of the hydrothermal ZnO/Ho³⁺ samples can be directly correlated with their anisotropic nanorod morphology observed by SEM analysis.

The degradation results further confirmed the combined effect of morphology and Ho³⁺ modification (Figure 11a,b). For sol–gel-derived ZnO, degradation efficiency increased from 61.38% for pristine ZnO to 89.02% and 96.91% after 1 and 2 mol % Ho³⁺ modifying, respectively. Hydrothermally synthesized samples exhibited even higher activity, consistent with their improved crystallinity (XRD) and enhanced surface accessibility (BET). BET analysis also showed that Ho modification increased the specific surface area and reduced the average pore diameter, indicating a higher density of accessible triboreactive sites. The superior activity of the hydrothermal Ho-doped samples was further supported by EPR analysis, which confirmed oxygen-vacancy-related defect centers acting as charge trapping sites and prolonging charge carrier lifetime. In particular, ZnO/2Ho exhibited the highest activity, demonstrating the synergistic effect between anisotropic morphology and defect-assisted charge separation, which together enhance ROS generation and accelerate paracetamol degradation.

Figure 11c shows the effect of radical scavengers on the tribocatalytic degradation of paracetamol over pristine and Ho-modified ZnO prepared via the hydrothermal method. In the absence of scavengers, all samples exhibit high tribocatalytic activity, which increases with Ho³⁺ content and reaches a maximum for ZnO/2Ho, indicating enhanced charge separation and reactive oxygen species (ROS) generation upon rare-earth modification. The addition of ascorbic acid (AA, $\bullet\text{O}_2^-$ scavenger) markedly suppresses the degradation efficiency, demonstrating that superoxide radicals are the predominant reactive species involved in the tribocatalytic process. A noticeable decrease in degradation is also observed in the presence of isopropanol (IPA, $\bullet\text{OH}$ scavenger), confirming the important contribution of hydroxyl radicals. In contrast, the addition of EDTA-Na (h⁺ scavenger) results in only a slight reduction in tribocatalytic activity, indicating that tribogenerated holes participate in the oxidation process but play a less significant role than $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ radicals. In all scavenger tests, the Ho-modified catalysts retain higher activity than pristine ZnO, suggesting that Ho incorporation promotes more efficient generation and utilization of reactive oxygen species through defect engineering and improved charge separation. These findings demonstrate that the tribocatalytic degradation of paracetamol proceeds predominantly via ROS-mediated oxidation, with $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ acting as the principal oxidative species, while the direct contribution of tribogenerated holes is comparatively minor. The superior performance of the ZnO/2Ho sample is attributed to the optimal balance between defect density, charge-carrier dynamics, and ROS generation.

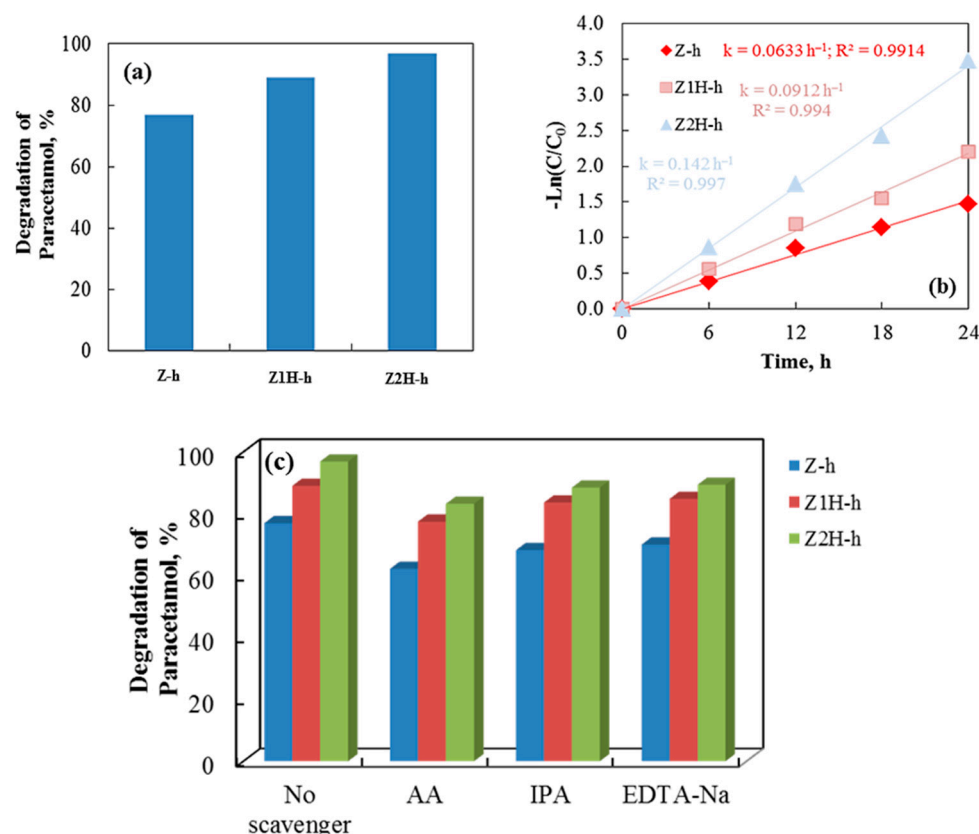


Figure 11. (a) Degradation efficiency and (b) pseudo-first-order kinetics of paracetamol using sol-gel and hydrothermal ZnO with varying Ho^{3+} content; (c) Effect of radical scavengers on tribocatalytic degradation of paracetamol using pristine and Ho-modified ZnO catalysts. AA: ascorbic acid ($\bullet\text{O}_2^-$ scavenger); IPA: isopropanol ($\bullet\text{OH}$ scavenger).

3.6. Control Experiments to Elucidate the Individual Contributions of Mechanical Activation and Catalyst-Dependent Factors

Control experiments were performed to elucidate the role of mechanical activation in the tribocatalytic degradation of paracetamol. In the absence of a catalyst, no degradation of paracetamol was detected, confirming the stability of the pollutant under the experimental conditions. When pure and Ho-modified ZnO catalysts were introduced without mechanical agitation, only limited degradation was observed, indicating that adsorption and intrinsic catalytic activity contribute negligibly to the overall process. For the sol-gel-derived ZnO samples, the degradation efficiencies in the absence of mechanical stimulation were approximately 8%, 10%, and 12% for pristine ZnO, ZnO/1Ho, and ZnO/2Ho, respectively. Similarly, the hydrothermally synthesized catalysts exhibited slightly higher degradation efficiencies of approximately 9%, 12%, and 14% for pristine ZnO, ZnO/1Ho, and ZnO/2Ho, respectively. In contrast, under tribocatalytic conditions, the degradation efficiencies increased markedly to 61%, 69%, and 75% for the sol-gel samples and to 77%, 89%, and 97% for the hydrothermal samples. These results demonstrate that mechanical stress is the dominant driving force for paracetamol degradation, while Ho^{3+} modification enhances the tribo-catalytic response by improving the generation and utilization of reactive species through defect engineering of the ZnO lattice.

3.7. Tribocatalysis of Paracetamol—Effect of Aqueous Medium

Water plays a critical role in tribocatalytic systems, serving not only as a solvent but also as an important component influencing interfacial charge transfer, reactive species generation, and degradation efficiency [62,63]. Parameters such as pH, ionic strength,

and dissolved mineral content can significantly affect surface reactivity and interactions between the catalyst and reactive species [25,64]. Therefore, the composition of the aqueous medium is an important factor governing tribocatalytic degradation processes.

To further evaluate whether pH changes during tribocatalysis could influence the degradation process, the pH of the filtered reaction solutions was measured before and after treatment. The highest degradation efficiency obtained in distilled water can be attributed to the absence of dissolved ionic species, which minimizes competitive surface interactions and facilitates pollutant adsorption and catalytic oxidation [65,66]. In contrast, the moderate decrease observed in Sofia tap water is likely associated with dissolved ions such as Ca^{2+} , Mg^{2+} , and bicarbonates, which can interact with the ZnO surface and partially suppress catalytic activity [67]. The lowest activity was detected in Bankya mineral water, where the higher concentration of bicarbonates and dissolved minerals likely reduced surface reactivity and hindered catalyst–pollutant interactions despite the slightly alkaline pH [68]. Ho modification further enhanced tribocatalytic activity by modifying the electronic structure of ZnO and facilitating tribo-induced charge transfer processes and enhancing the generation of reactive species under mechanical stirring [8]. Nevertheless, the relative degradation trend remained unchanged for all investigated media, indicating that the ionic composition of the aqueous environment exerts a stronger influence on tribocatalytic efficiency than pH alone. Overall, the results demonstrate that minimizing dissolved ionic species provides the most favorable conditions for efficient tribocatalytic degradation of paracetamol.

To evaluate the influence of the specific surface area on the tribocatalytic activity, the apparent rate constants were normalized by the BET surface area of the catalysts. The obtained BET-normalized rate constants (k/S_{BET}) are summarized in Table 5. Although ZnO/1Ho and ZnO/2Ho exhibited higher apparent rate constants compared with pristine ZnO, the normalization procedure revealed the contribution of the increased surface area to the overall catalytic performance. ZnO/2Ho retained the highest normalized rate constant in all investigated water matrices, indicating that its enhanced tribocatalytic activity is not solely related to the larger specific surface area, but also to Ho-induced modifications of the ZnO structure, including changes in defect characteristics and the formation of additional active sites. The comparable k/S_{BET} values of ZnO and ZnO/1Ho suggest that the improved degradation efficiency of the 1 mol% Ho-modified sample results from the combined effects of increased surface accessibility and structural modification introduced by Ho modification. The discussion has also been expanded to compare the BET-normalized activity of the prepared catalysts with previously reported rare-earth-modified ZnO systems [13,69].

Table 5. Tribocatalytic performance and BET-normalized kinetic parameters of ZnO and Ho-modified ZnO catalysts for paracetamol degradation in different water matrices.

Type of Water	ZnO			ZnO/1Ho			ZnO/2Ho		
	k, h^{-1}	$k/S_{\text{BET}} (\text{h}^{-1} \cdot \text{g} \cdot \text{m}^{-2})$	$D, \%$	k, h^{-1}	$k/S_{\text{BET}} (\text{h}^{-1} \cdot \text{g} \cdot \text{m}^{-2})$	$D, \%$	k, h^{-1}	$k/S_{\text{BET}} (\text{h}^{-1} \cdot \text{g} \cdot \text{m}^{-2})$	$D, \%$
Distilled	0.0633	0.0372	76.95	0.0912	0.0365	89.02	0.142	0.0507	96.91
Tap	0.0472	0.0278	68.56	0.0667	0.0267	80.74	0.0857	0.0306	86.63
Mineral	0.0348	0.0205	55.89	0.0451	0.0180	66.67	0.0535	0.0191	71.26

Notes: The apparent rate constants were normalized by the BET surface area of the catalysts (k/S_{BET}) to evaluate the intrinsic tribocatalytic activity of the materials.

Chemical oxygen demand (COD) measurements were used to evaluate the overall oxidation efficiency of the tribocatalytic process and to assess the changes in the concentration of oxidizable organic species after paracetamol treatment. The residual COD values

strongly depended on both the aqueous medium and catalyst composition. For pristine ZnO, residual COD values of 23.05%, 31.44%, and 44.11% were obtained in distilled, tap, and mineral water, respectively, demonstrating the significant influence of dissolved ions on catalytic efficiency. In contrast, ZnO/2Ho exhibited substantially lower residual COD values of 3.09%, 13.37%, and 28.74%, indicating the beneficial effect of Ho modification on the oxidative performance. The enhanced activity of Ho-modified ZnO can be attributed to more efficient separation of tribogenerated charge carriers and promoted reactive oxygen species (ROS) generation, which accelerate the oxidation of paracetamol and its intermediate products. However, COD analysis alone does not provide direct evidence of complete mineralization, since partially oxidized organic intermediates may still contribute to the measured values. Therefore, total organic carbon (TOC) analysis was additionally performed to determine the extent of organic carbon removal and to provide further insight into the mineralization efficiency of the tribocatalytic process.

To further evaluate the mineralization efficiency of the tribocatalytic process, total organic carbon (TOC) analysis was performed and compared with the paracetamol degradation results presented in Table 5. The TOC removal efficiencies were lower than the corresponding degradation values, indicating that the disappearance of paracetamol molecules was accompanied by the formation of partially oxidized organic intermediates remaining in the aqueous phase. Similar differences between pollutant degradation and mineralization efficiency have been reported for ZnO-based catalytic systems, where high paracetamol removal was achieved while TOC reduction remained lower due to the presence of oxidation intermediates [62]. For pristine ZnO, TOC removal efficiencies of 61.3%, 49.2%, and 39.5% were obtained in distilled, tap, and mineral water, respectively. In comparison, ZnO/2Ho exhibited significantly enhanced mineralization efficiency, achieving TOC removal values of 87.4%, 76.5%, and 61.8% in the respective media. The improved mineralization ability of the Ho-modified catalyst can be associated with enhanced charge carrier separation and more efficient reactive oxygen species generation, which facilitates the oxidation of paracetamol and its intermediate products. Similar effects of rare-earth modification on improving ZnO-based photocatalytic activity and TOC removal have been previously demonstrated. The lower TOC removal observed in mineral water is consistent with the reduced catalytic efficiency in complex aqueous matrices, where dissolved inorganic ions may compete for surface active sites and affect reactive species availability. Such matrix effects have also been reported for paracetamol removal processes performed in natural water systems [70].

Since the formation and subsequent oxidation of intermediate products may also influence the acid-base equilibrium of the reaction medium, the pH values of the solutions before and after tribocatalytic treatment were additionally determined. The pH values of the reaction solutions were measured before and after 24 h of tribocatalytic treatment to evaluate changes in the acid–base properties of the aqueous media. The initial pH values of distilled water, tap water, and Bankya mineral water were 6.8, 7.2, and 8.73, respectively. After tribocatalytic treatment with pristine ZnO, the pH decreased to 6.0, 6.5, and 7.8, respectively. In comparison, the corresponding pH values obtained using the ZnO/2Ho catalyst were 6.3, 6.8, and 8.3, indicating a less pronounced decrease in pH for the Ho-modified catalyst irrespective of the water matrix.

The observed decrease in pH is consistent with the oxidative degradation pathway of paracetamol during tribocatalysis. Friction-induced charge separation in ZnO promotes the formation of reactive oxygen species (ROS), which oxidize paracetamol through successive hydroxylation, aromatic ring-opening, and oxidation reactions, yielding low-molecular-weight oxygenated intermediates before complete mineralization. Previous studies on advanced oxidation processes have demonstrated that these transformation pathways

involve the transient formation of short-chain carboxylic acids, which may contribute to a slight acidification of the reaction medium [71,72]. This interpretation is supported by the COD and TOC results obtained in the present study. Although substantial reductions in COD confirm extensive oxidation of organic species, the lower TOC removal relative to paracetamol degradation indicates that partially oxidized intermediates are formed before being completely mineralized to CO_2 and H_2O .

The consistently higher final pH values observed for ZnO/2Ho correlate well with its superior tribocatalytic performance. Compared with pristine ZnO, the Ho-modified catalyst exhibited considerably lower residual COD values and significantly higher TOC removal efficiencies in all investigated aqueous media, demonstrating more efficient oxidation and mineralization of both paracetamol and its oxidation intermediates. Consequently, the residence time of acidic intermediate products in the reaction solution is expected to be shorter, resulting in a less pronounced decrease in pH. These results further support the beneficial role of Ho incorporation in enhancing the tribocatalytic efficiency of ZnO through improved utilization of tribogenerated charge carriers and more effective ROS-mediated oxidation.

Because changes in the pH of the reaction medium may affect the chemical stability of oxide catalysts during tribocatalytic treatment, the potential release of Zn and Ho species into the aqueous phase was further evaluated by ICP-OES analysis of the optimized ZnO/2Ho catalyst after 24 h of tribocatalysis. Trace amounts of dissolved metals were detected in all investigated water matrices. The concentrations of dissolved Zn were 4.34, 6.86, and 7.13 ng mL^{-1} in distilled, tap, and mineral water, respectively, whereas the corresponding Ho concentrations were only 0.004, 0.008, and 0.009 ng mL^{-1} . The slightly higher concentrations observed in tap and mineral water are likely associated with their higher ionic strength and dissolved mineral constituents compared with distilled water. Nevertheless, Ho concentrations remained below 0.01 ng mL^{-1} in all cases, demonstrating negligible dopant leaching during tribocatalytic operation. These findings confirm the excellent chemical stability of the Ho-modified ZnO catalyst under prolonged tribocatalytic conditions and indicate that the enhanced degradation performance originates from heterogeneous tribocatalytic reactions rather than from dissolved catalytically active species.

The demonstrated chemical stability of the ZnO/2Ho catalyst under tribocatalytic conditions prompted further evaluation of its long-term operational stability and reusability. Therefore, the recyclability of the optimized hydrothermally synthesized ZnO/2Ho tribocatalyst was investigated through consecutive tribocatalytic degradation cycles for paracetamol removal in distilled, tap, and mineral water (Figure 12). A gradual decrease in degradation efficiency was observed after repeated use, with an overall reduction of approximately 4% for all investigated water matrices. This minor loss of activity may be associated with partial occupation of surface-active sites by reaction intermediates or adsorbed species generated during the degradation process. Despite this slight decrease, the ZnO/2Ho catalyst maintained high degradation efficiency throughout the recycling experiments, demonstrating good stability under different aqueous conditions. The retained catalytic performance indicates that the hydrothermally synthesized ZnO/2Ho structure preserves its active sites and structural integrity during prolonged tribocatalytic operation. These results confirm the excellent reusability of the catalyst and highlight its potential for repeated application in sustainable paracetamol removal from various water environments.

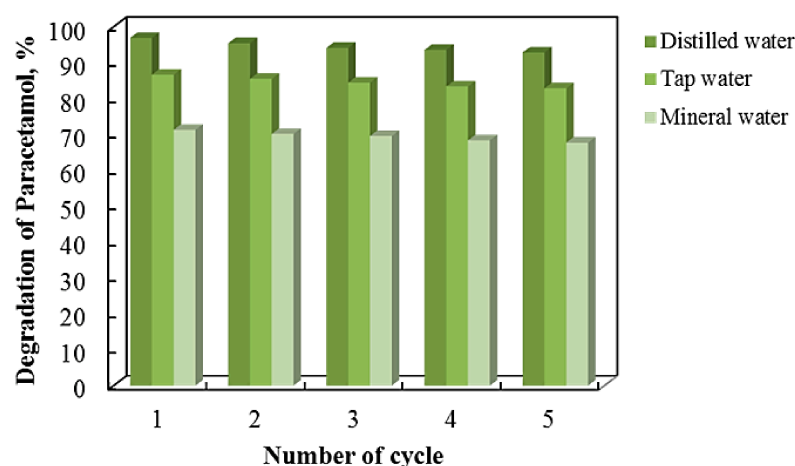


Figure 12. Five-cycle recyclability test of the hydrothermally synthesized ZnO/2Ho tribocatalyst for paracetamol removal in different water matrices.

4. Conclusions

Pure and Ho-doped ZnO powders were successfully synthesized via sol–gel and hydrothermal methods and evaluated for tribocatalytic paracetamol degradation under dark conditions. Structural analyses confirmed the formation of single-phase wurtzite ZnO, while SEM observations revealed significant morphology differences depending on the synthesis route. Hydrothermal synthesis produced highly crystalline rod-like structures, whereas sol–gel synthesis resulted in agglomerated nanoparticles. Ho modification increased the specific surface area, modified the defect structure, and promoted oxygen-vacancy-related electronic states, as confirmed by BET, XPS, and EPR analyses. The tribocatalytic activity was strongly affected by both the synthesis method and Ho concentration. Hydrothermally synthesized ZnO/2 mol% Ho³⁺ exhibited the highest activity, achieving 96.91% paracetamol degradation. The enhanced performance was attributed to the combined effect of anisotropic morphology, improved charge separation, defect-assisted carrier trapping, and enhanced reactive oxygen species generation. Radical trapping experiments identified $\bullet\text{O}_2^-$ radicals as the dominant reactive species, while $\cdot\text{OH}$ radicals played a secondary role. The catalytic efficiency was additionally influenced by mechanical activation and the aqueous medium. Increasing the number of PTFE stirring rods enhanced friction-induced interactions and accelerated degradation kinetics, confirming the key role of mechanical contact in tribogenerated charge separation. Distilled water provided the highest activity, whereas dissolved ions in tap and mineral water partially suppressed catalytic performance through competitive surface interactions and reduced ROS utilization. These findings demonstrate that Ho-doped ZnO, particularly hydrothermally synthesized materials, represents an efficient tribocatalyst for the degradation of pharmaceutical pollutants under environmentally relevant conditions.

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