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Tribocatalytic Decolorization of Reactive Black 5 Using Pristine and La_2O_3-Modified ZnO Powders

Nina Kaneva*
University of Sofia, Faculty of Chemistry and Pharmacy, Department of General and Inorganic Chemistry, Laboratory of Nanoparticle Science and Technology, James Bourchier, Blvd., 1164, Sofia, Bulgaria

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Abstract

This study investigates the tribocatalytic decolorization of Reactive Black 5 using pristine zinc oxide and lanthanum oxide-modified ZnO powders prepared by ultrasound-assisted mixing followed by mild thermal drying at 100 °C. A series of seven samples with nominal La_2O_3 contents of 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mol% was prepared to systematically evaluate the influence of La_2O_3 modification on the structural, morphological, and tribocatalytic properties of zinc oxide. The prepared materials were characterized by X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. UV-Vis spectroscopy was employed to monitor the changes in RB5 concentration during tribocatalytic treatment. Tribocatalytic experiments were conducted in aqueous Reactive Black 5 solutions under mechanical stirring in the absence of light irradiation. The results revealed that Lanthanum oxide modification significantly influenced the tribocatalytic performance of ZnO, with the sample containing 2.0 mol% La_2O_3 exhibiting the highest activity, achieving 80% Reactive Black 5 decolorization within 6 h. The enhanced performance of the optimally modified catalyst highlights the beneficial role of lanthanum oxide in promoting mechanically driven catalytic processes. These findings demonstrate the potential of La_2O_3-modified ZnO powders as promising tribocatalysts for the decolorization of dye-containing aqueous solutions under mechanical excitation without external light irradiation.

Keywords: Tribocatalysis, Zinc oxide, Lanthanum oxide, Reactive Black 5, Rare-earth modification, Dye decolorization

1. Introduction

The contamination of aquatic environments by synthetic organic dyes remains a significant environmental concern, particularly due to their chemical stability, complex molecular structures, and resistance to conventional wastewater treatment processes. Reactive Black 5 (RB5), a widely used anionic azo dye, is characterized by high water solubility and a complex aromatic structure, making its removal from industrial effluents challenging. Consequently, advanced oxidation processes, particularly heterogeneous photocatalysis, have attracted considerable attention as effective approaches for the degradation of persistent organic pollutants [1,2]. Among semiconductor metal oxides, zinc oxide (ZnO) has been extensively investigated as a promising catalytic material owing to its favorable electronic properties, relatively low cost, and versatile synthesis methods. Previous studies have demonstrated the effectiveness of ZnO-based photocatalysts for the degradation of organic dyes, including RB5 [1-5]. In particular, lanthanum modification has been shown to influence the structural, optical, and photocatalytic properties of ZnO, improving its performance toward dye degradation [2,5]. However, the dependence of photocatalytic processes on light irradiation and limitations associated with charge-carrier recombination have stimulated increasing interest in alternative catalytic approaches. Tribocatalysis has recently emerged as a promising method for the decolorization of organic pollutants through the utilization of mechanical energy without external light irradiation [6-8]. The process involves friction-induced charge generation and transfer, promoting surface redox reactions and the formation of reactive oxygen species. Previous investigations have demonstrated effective tribocatalytic decolorization using different semiconductor and metal oxide materials [8-10]. Recent studies have further highlighted the importance of surface defects, interfacial charge transfer, and friction conditions in determining tribocatalytic performance [6,11]. ZnO is particularly attractive for such applications due to its polar crystal structure and semiconducting properties, which may facilitate mechanically induced charge separation. The influence of ZnO morphology, specific surface area,

***Corresponding author:** Nina Kaneva, nina_k@abv.bg

stirring speed, and reactor configuration on tribocatalytic activity has also been demonstrated [12-14]. Rare-earth modification represents a promising strategy for improving the tribocatalytic properties of ZnO by altering its surface characteristics, defect structure, and charge-transfer behavior. In particular, La-modified ZnO has demonstrated enhanced tribocatalytic activity toward Rhodamine B decolorization [15]. Similar improvements have been reported for ZnO modified with other rare-earth elements during the tribocatalytic decolorization of pharmaceutical pollutants [16-18]. These findings indicate that rare-earth modifiers can significantly influence the catalytic behavior of ZnO under mechanical activation. Nevertheless, the systematic influence of La_2O_3 concentration on the tribocatalytic decolorization of Reactive Black 5 remains insufficiently investigated.

The present study aims to evaluate the tribocatalytic decolorization of RB5 using pristine and La_2O_3-modified ZnO powders prepared by ultrasound-assisted mixing and subsequent drying at 100 °C. Seven samples containing nominal La_2O_3 amounts of 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mol% were prepared and characterized to assess the influence of lanthanum-containing modification on the physicochemical properties and tribocatalytic performance of ZnO. The tribocatalytic performance was investigated under mechanical stirring in the absence of light irradiation, with particular emphasis on the influence of La_2O_3 concentration on catalytic activity. The study seeks to establish relationships between material composition, physicochemical properties, and tribocatalytic performance, highlighting the potential of mechanically activated ZnO-based materials for the treatment of dye-contaminated wastewater.

2. Materials and Methods

Commercial zinc oxide (ZnO, purity >99.0%) and lanthanum oxide (La_2O_3, purity >99.0%) powders, together with absolute ethanol, were obtained from Fluka and used without further purification. Distilled water was employed throughout all experimental procedures. RB5, supplied by Sigma-Aldrich, was selected as a representative organic pollutant for evaluating the tribocatalytic performance of the synthesized materials. The dye has a molecular formula of $C_{26}H_{21}N_5Na_4O_{19}S_6$, a molecular weight of 991.82 g mol^{-1}, a maximum absorption wavelength (λ_{max}) of approximately 595 nm, and a nominal dye content of approximately 55%. RB5 is an anionic diazo dye containing four aromatic rings and two azo (–N=N–) linkages, which are responsible for its characteristic dark-blue coloration in aqueous solution. Its widespread industrial application, complex molecular structure, and potential adverse health effects, including allergic reactions and respiratory irritation, make it a relevant model contaminant for investigating dye removal from aqueous environments [1]. Pristine and La_2O_3-modified ZnO powders were prepared by ultrasound-assisted mixing followed by mild thermal treatment, based on a previously reported procedure [2]. Commercial ZnO and La_2O_3 powders were used as starting materials. Seven compositions, each with a total mass of 5 g and nominal La_2O_3 contents of 0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 mol%, were prepared by accurately weighing the corresponding amounts of the oxide precursors. The powders were thoroughly mixed in a ceramic vessel with the addition of 8-10 drops of absolute ethanol to facilitate homogenization. The resulting mixtures were subjected to ultrasonic treatment for 30 min using an IKEDA RIKA ultrasonic bath (100 V, 50/60 Hz, 110 W). Subsequently, all samples, including pristine ZnO, were thermally treated in a closed furnace at 100 °C for 1 h without the introduction of any additional gas. This treatment was intended to remove residual ethanol and adsorbed moisture. No high-temperature calcination step was performed. Although commercially available La_2O_3 was directly used as the modifying oxide, its partial interaction with atmospheric moisture and CO_2 during preparation and handling cannot be excluded. The thermal treatment at 100 °C does not ensure complete decomposition of possible lanthanum hydroxide or carbonate species. Therefore, the La_2O_3 contents reported in this study represent the nominal amounts of the starting modifier. The morphological, structural, and elemental characteristics of the prepared ZnO-based powders were investigated using complementary analytical techniques. Scanning electron microscopy (SEM) was performed using a JEOL JSM-5510 microscope operated at an accelerating voltage of 10 kV. Prior to examination, the powder samples were coated with a thin gold layer using a JEOL JFC-1200 fine coater to improve surface conductivity and image quality. The crystalline structure and phase composition of the pristine and La_2O_3-modified ZnO samples were examined by X-ray diffraction (XRD) using a Siemens D500 powder diffractometer equipped with Cu Kα radiation. Diffraction patterns were collected at room temperature over a 2θ range of 30–70°, with a step size of 0.05° and a counting time of 2 s per step. Elemental analysis was carried out by Energy-dispersive X-ray spectroscopy (EDS) using a Bruker Quantax 200 detector with an energy resolution of 126 eV, providing information on the elemental composition of the investigated materials. The tribocatalytic activity of pristine and La_2O_3-modified ZnO powders was evaluated through the removal of RB5 from aqueous solution. Experiments were performed in a 100 mL glass reactor containing 25 mL of RB5 solution (5 mg/L) and 25 mg of catalyst. All tests were conducted at room temperature (23 ± 2 °C) in the absence of light to exclude photocatalytic contributions. The reactor was kept closed throughout the 6 h experiments to minimize evaporation. The UV-Vis absorption spectra were recorded using a Thermo Scientific Evolution 300 spectrophotometer (Madison, WI, USA) at 23 ± 2 °C. Measurements were performed in quartz cuvettes with an optical path length of 1 cm. Prior to mechanical activation, the suspensions were maintained under static conditions for 30 min to establish adsorption–desorption equilibrium. The RB5 concentration measured after this equilibration period, immediately before mechanical stirring, was defined as the initial concentration (C_0) for the kinetic calculations. Tribocatalysis was subsequently initiated by magnetic stirring at 500 rpm using a PTFE-coated stirring bar (8 × 35 mm), providing the mechanical energy required for the process. At selected reaction intervals, 2 mL aliquots were withdrawn and centrifuged at 6000 rpm for 5 min to remove catalyst particles. The residual RB5 concentration was determined by UV-Vis spectroscopy by monitoring the characteristic absorption band at approximately 595 nm. To verify the tribocatalytic contribution to RB5 removal, control experiments

were conducted under dark conditions. These included RB5 solution without catalyst and mechanical stirring to assess its stability, RB5 solution subjected to magnetic stirring without catalyst to evaluate the effect of mechanical agitation, and RB5 suspension containing ZnO modified with 2 mol% La_2O_3 without stirring to determine the contribution of adsorption. The results of these control experiments were compared with those obtained in the simultaneous presence of the catalyst and mechanical stirring, allowing the effects of adsorption and stirring alone to be distinguished from the mechanically induced catalytic process. The reusability of pristine ZnO and ZnO modified with 2 mol% La_2O_3 was evaluated over three consecutive tribocatalytic decolorization cycles. After each cycle, the catalyst was separated from the reaction suspension by centrifugation (6000 rpm, 5 min), dried (60°C, 15 min), and subsequently reused in a fresh RB5 solution. The experiments were performed under the same tribocatalytic conditions as those applied in the initial activity measurements. The decolorization efficiency obtained after successive cycles was compared with that of the corresponding fresh catalyst to assess the retention of catalytic activity. To investigate the possible involvement of reactive species in the tribocatalytic decolorization of RB5, scavenger experiments were performed using pristine ZnO and ZnO modified with 2 mol% La_2O_3. Ascorbic acid (AA), isopropyl alcohol (IPA), and sodium ethylenediaminetetraacetate (EDTA-Na) were employed to probe the contributions of superoxide radicals ($\bullet O_2^-$), hydroxyl radicals (•OH), and mechanically generated positive charges (h^+), respectively. Each scavenger (6 mg) was introduced separately into the reaction suspension, and the resulting RB5 decolorization efficiency was compared with that obtained in the absence of scavengers.

3. Results

The X-ray diffraction patterns of pristine ZnO and ZnO modified with 2 mol% La_2O_3 exhibited the characteristic reflections of hexagonal wurtzite ZnO (space group $P6_3mc$). The prominent diffraction peaks were indexed to the (100), (002), (101), (102), (110), and (103) crystallographic planes, indicating that the wurtzite ZnO phase remained dominant following La_2O_3 modification (**Figure 1**). The lattice parameters estimated from the XRD peak positions were a = 3.24540 ± 0.00052 Å and c = 5.19866 ± 0.00134 Å for pristine ZnO, compared with a = 3.24388 ± 0.00063 Å and c = 5.19574 ± 0.00157 Å for ZnO modified with 2 mol% La_2O_3. The reported uncertainties represent approximate standard errors obtained from peak fitting and do not include systematic instrumental contributions. Although both samples were measured under identical experimental conditions, the observed differences are small and cannot be regarded as conclusive evidence of lattice contraction, particularly in the absence of an internal standard. Furthermore, considering the larger ionic radius of La^{3+} compared with Zn^{2+}, substitutional incorporation of La^{3+} into the ZnO lattice cannot be inferred from these results. The XRD data are consistent with La-containing species predominantly located at the ZnO surface or present as minor secondary phases, although their precise distribution and possible limited lattice incorporation cannot be established conclusively.

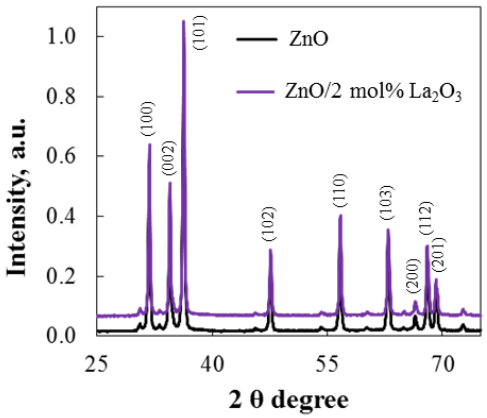


Figure 1 | X-ray diffraction patterns of pristine ZnO and 2 mol% La_2O_3-modified ZnO powders, showing the characteristic diffraction reflections of the hexagonal wurtzite ZnO structure.

The apparent average crystallite sizes, estimated using the Scherrer equation from six characteristic diffraction reflections, were 29.22 nm for pristine ZnO and 32.12 nm for the La_2O_3-modified sample. Thus, the modified material exhibited an approximately 9.9% larger apparent crystallite size. A preliminary Williamson–Hall analysis yielded apparent microstrain values of 5.93×10^{-4} and 9.05×10^{-4} for pristine and La_2O_3-modified ZnO, respectively, with corresponding coefficients of determination (R^2) of 0.8075 and 0.9209. The relatively low R^2 value for pristine ZnO indicates considerable scatter in the Williamson–Hall fit, limiting the reliability of the corresponding microstrain estimate. Furthermore, since instrumental broadening was not independently corrected, the calculated crystallite sizes and microstrain values should be regarded as approximate estimates. No distinct diffraction peaks attributable to La-containing secondary phases were identified within the investigated 2θ range. However, due to the low nominal La_2O_3 content (2 mol%) and the detection limitations of conventional XRD, the presence of minor La-containing phases, including possible hydroxide or carbonate species, cannot be excluded. **Figure 2** presents the SEM micrographs of pristine ZnO (a) and ZnO modified with 2 mol% La_2O_3 (b). Both samples exhibit an irregular, highly agglomerated morphology composed of fine particles forming larger, porous aggregates. Pristine ZnO displays relatively small, loosely interconnected particle agglomerates with a heterogeneous surface texture. Following La_2O_3 modification, the aggregates appear more compact and coarser, with a more pronounced granular morphology. These observations suggest that La_2O_3 modification influences particle aggregation and surface morphology while preserving the overall particulate structure of ZnO. The elemental composition of the samples was further investigated by EDS. The EDS analysis of pristine ZnO confirmed the presence of zinc and oxygen, with normalized weight percentages of 67.09 and 32.91 wt.%, respectively, corresponding to atomic concentrations of 35.10 at.% Zn and 64.90 at.% O.

Following modification with 2 mol% La_2O_3, the EDS analysis revealed the presence of zinc, oxygen, and lanthanum, with normalized weight percentages of 65.95, 27.36, and 6.68 wt.%, respectively. The corresponding atomic concentrations were 36.45 at.% Zn, 61.81 at.% O, and 1.74 at.% La.

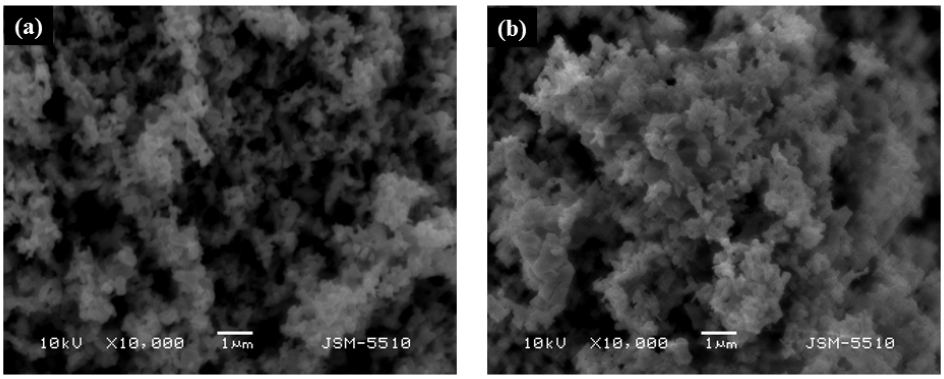


Figure 2 | SEM micrographs of (a) pristine ZnO and (b) ZnO modified with 2 mol% La_2O_3.

The measured La content (6.68 wt.%) is in good agreement with the nominal value of approximately 6.44 wt.% for the 2 mol% La_2O_3 composition. However, the relatively high oxygen atomic concentrations (61.81–64.90 at.%) should be interpreted with caution due to the semiquantitative nature of EDS analysis, particularly for light elements, and cannot be considered direct evidence of oxygen nonstoichiometry.

The detection of lanthanum confirms the presence of La-containing species in the modified material. Nevertheless, EDS analysis alone cannot establish the incorporation of La^{3+} ions into the ZnO crystal lattice, their chemical state, or their spatial distribution. Overall, the combined SEM–EDS observations indicate changes in particle aggregation following modification and confirm the presence of lanthanum in the modified ZnO sample.

Figure 3a illustrates the temporal evolution of the normalized concentration (C/C_0) of RB5 during tribocatalytic treatment with pristine ZnO and ZnO modified with different La_2O_3 contents. All investigated samples exhibited a progressive decrease in RB5 concentration over the 6 h reaction period, although the extent of decolorization varied considerably depending on the modifier concentration. Compared with pristine ZnO, the La_2O_3-modified samples generally demonstrated enhanced tribocatalytic activity, with the most pronounced decrease in RB5 concentration observed for the sample containing 2 mol% La_2O_3. Increasing the modifier content beyond this concentration resulted in a gradual reduction in decolorization efficiency, indicating a non-linear dependence of tribocatalytic performance on La_2O_3 loading.

The corresponding apparent reaction rate constants, calculated according to the pseudo-first-order kinetic model, are presented in **Figure 3b**. Pristine ZnO exhibited a rate constant of 0.1222 h^{-1}, whereas the incorporation of La_2O_3 led to a progressive increase in the reaction rate, reaching a maximum value of 0.2814 h^{-1} at 2 mol% La_2O_3. This represents an approximately 2.3-fold increase compared with unmodified ZnO. At higher modifier concentrations of 2.5 and 3 mol%, the apparent rate constants decreased, following the same trend observed in the concentration–time profiles. The agreement between the kinetic parameters and the experimental concentration profiles confirms that the highest tribocatalytic activity within the investigated series was achieved at a La_2O_3 content of 2 mol%. The apparent pseudo-first-order rate constants and the corresponding coefficients of determination (R^2) for all seven investigated samples are summarized in **Table 1**. The highest rate constant was obtained for ZnO modified with 2 mol% La_2O_3 (0.2814 h^{-1}), which is approximately 2.3 times higher than that of pristine ZnO (0.1222 h^{-1}). The effect of different scavengers on RB5 tribocatalytic decolorization was investigated using pristine ZnO and ZnO modified with 2 mol% La_2O_3. The experimental results are summarized in **Table 2**. In the absence of scavengers, RB5 decolorization efficiencies of 52.60% and 79.87% were obtained for pristine and La_2O_3-modified ZnO, respectively. The addition of AA decreased the corresponding efficiencies to 37.31% and 64.32%.

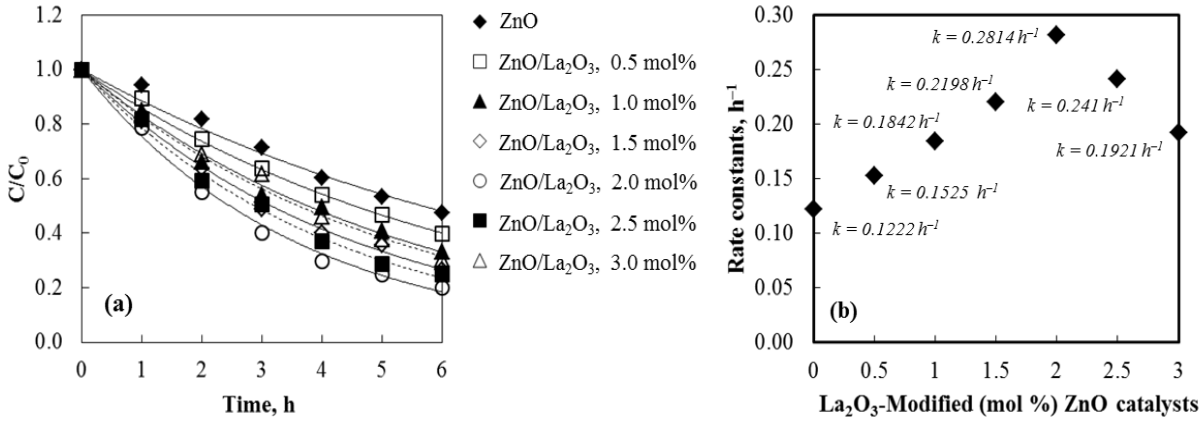


Figure 3 | Effect of La_2O_3 content on the tribocatalytic decolorization of Reactive Black 5 using pristine and La_2O_3-modified ZnO powders: (a) temporal evolution of the normalized dye concentration (C/C_0) and (b) corresponding apparent pseudo-first-order rate constants.

Table 1 | Apparent pseudo-first-order rate constants (k) and coefficients of determination (R^2) for RB5 tribocatalytic decolorization using pristine and La_2O_3-modified ZnO powders.

Catalysts	k , h^{-1}	R^2
ZnO	0.1222	0.9847
ZnO/ 0.5 mol% La_2O_3	0.1525	0.9968
ZnO/ 1.0 mol% La_2O_3	0.1842	0.991
ZnO/ 1.5 mol% La_2O_3	0.2198	0.9927
ZnO/ 2.0 mol% La_2O_3	0.2814	0.9902
ZnO/ 2.5 mol% La_2O_3	0.241	0.9935
ZnO/ 3.0 mol% La_2O_3	0.1921	0.9907

Table 2 | Effect of different scavengers on RB5 tribocatalytic decolorization using pristine ZnO and ZnO modified with 2 mol% La_2O_3.

Scavenger	ZnO	ZnO/2.0 mol % La2O3
No scavenger	52.60	79.87
AA ($\bullet O_2^-$)	37.31	64.32
IPA ($\bullet$OH)	45.26	72.16
EDTA-Na (h^+)	48.74	75.54

In the presence of IPA, the decolorization efficiencies were 45.26% and 72.16%, while the addition of EDTA-Na resulted in values of 48.74% and 75.54%, respectively. For both catalysts, the inhibitory effect followed the same order: AA > IPA > EDTA-Na. The largest decrease in decolorization efficiency was observed with AA (15.29 and 15.55 percentage points for pristine and modified ZnO, respectively), whereas EDTA-Na produced the smallest effect. **Figure 4** presents the time-dependent UV–Vis absorption spectra of RB5 during tribocatalytic treatment with pristine ZnO (a) and ZnO modified with 2 mol% La_2O_3 (b). The initial RB5 solution exhibited a characteristic absorption maximum at approximately 595 nm, associated with the chromophoric azo structure of the dye. A progressive decrease in the intensity of this absorption band was observed for both catalysts, indicating gradual dye decolorization during mechanical stirring in the dark. As shown in **Figure 4a**, pristine ZnO exhibited a gradual reduction in absorbance at 595 nm from an initial value of 0.154 to 0.145, 0.126, and 0.110 after 1h, 2, and 3 h, respectively, corresponding to decolorization efficiencies of 5.84%, 18.18%, and 28.57%. With increasing treatment time, the efficiency reached 39.61% after 4 h, 46.75% after 5 h, and 52.60% after 6 h. A substantially faster decrease in absorption intensity was observed for ZnO modified with 2 mol% La_2O_3 (**Figure 4b**). The absorbance at 595 nm decreased from 0.154 to 0.121 after 1 h, corresponding to 21.43% decolorization. The efficiency subsequently increased to 44.81%, 59.74%, and 70.13% after 2, 3, and 4 h, respectively. After 5 h, the decolorization efficiency reached 75.32%, increasing further to 79.87% after 6 h, with a final absorbance of 0.031. The comparison of the two spectral series demonstrates a pronounced enhancement in RB5 decolorization following La_2O_3 modification. After 6 h, the modified catalyst achieved a decolorization efficiency approximately 27.3 percentage points higher than that of pristine ZnO. The progressive decrease in the characteristic absorption band at 595 nm is consistent with the disruption or transformation of the dye chromophore, although UV-Vis spectroscopy alone does not establish complete decolorization or mineralization.

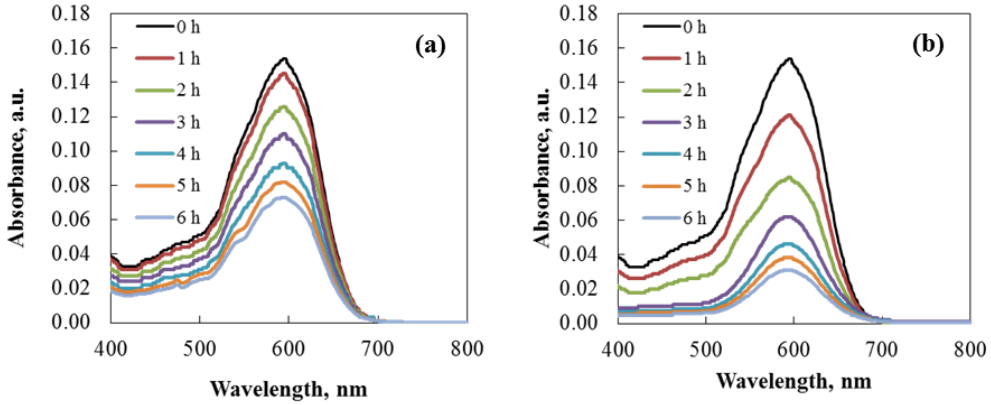


Figure 4 | UV–Vis absorption spectra of Reactive Black 5 (RB5) recorded at different reaction times during tribocatalytic decolorization using pristine ZnO and ZnO modified with 2 mol% La_2O_3. Initial RB5 concentration: 5 mg/L.

The reusability of pristine ZnO and ZnO modified with 2 mol% La_2O_3 was investigated over three consecutive RB5 tribocatalytic decolorization cycles. After each cycle, the catalyst was recovered by centrifugation, dried, and reused in a fresh dye solution. Both catalysts retained most of their initial decolorization activity after repeated use. Compared with the corresponding fresh catalysts, the decolorization efficiency decreased by approximately 6% for pristine ZnO and 5% for ZnO modified with 2 mol% La_2O_3 after three consecutive cycles. The slightly smaller decrease observed for the modified sample suggests comparable or marginally better retention of catalytic performance under the investigated conditions. These results indicate that both ZnO-based materials can be reused over three consecutive cycles with a relatively limited loss of decolorization efficiency. Nevertheless, additional cycling experiments and post-reaction structural characterization would be necessary to assess their long-term operational stability.

4. Discussion

The enhanced tribocatalytic performance of La_2O_3-modified ZnO compared with pristine ZnO can be interpreted in terms of structural characteristics, surface modification, and mechanically induced interfacial processes. XRD analysis confirmed that both materials retained the characteristic hexagonal wurtzite structure, indicating that modification with La_2O_3 did not produce a detectable transformation of the principal ZnO crystalline phase. Slight variations in lattice parameters and diffraction peak broadening were nevertheless observed. The apparent average crystallite size increased from 29.22 nm for pristine ZnO to 32.12 nm for ZnO modified with 2 mol% La_2O_3, while the estimated microstrain increased from 5.93×10^{-4} to 9.05×10^{-4}. These differences suggest changes in crystallite characteristics and structural heterogeneity following modification. However, because instrumental broadening was not independently corrected, the calculated values should be regarded as approximate estimates rather than definitive evidence of structural changes. SEM observations revealed differences in particle aggregation, with the La_2O_3-modified sample exhibiting a more compact and coarser granular morphology. EDS analysis confirmed the presence of lanthanum at a concentration of 1.74 at.%, supporting the introduction of La-containing species into the investigated material. From a chemical perspective, lanthanum-containing surface regions may influence the coordination environment of ZnO and its interactions with water molecules, hydroxyl groups, and dissolved oxygen. Such interactions are potentially relevant to heterogeneous oxidative processes because their efficiency depends on both the generation of electrical charges and the availability of adsorbed reactants. Nevertheless, the present characterization does not establish the precise chemical state or spatial distribution of lanthanum, and these possible surface effects remain mechanistic interpretations. Although La_2O_3 was introduced directly as the modifying oxide, partial interaction with atmospheric moisture and CO_2 during preparation and handling cannot be excluded. The thermal treatment at 100 °C was intended primarily to remove residual ethanol and adsorbed moisture and does not ensure complete decomposition of possible lanthanum hydroxide or carbonate species. Therefore, the presence of hydroxylated or carbonated lanthanum-containing surface species remains possible. Since XRD and EDS do not provide sufficient evidence to determine the chemical state of lanthanum unambiguously, the modifier content is expressed as the nominal La_2O_3 loading. The improved tribocatalytic activity may also involve the piezoelectric properties of ZnO. Owing to its non-centrosymmetric wurtzite structure, ZnO can develop electrical polarization under mechanical deformation [19]. During magnetic stirring, collisions between catalyst particles and their interactions with the PTFE-coated stirring bar and reactor walls may produce localized mechanical stresses and interfacial electrical effects. These processes could facilitate charge separation and transfer to adsorbed species. Electrons transferred to dissolved oxygen may contribute to the formation of superoxide radicals ($\bullet O_2^-$), while sufficiently oxidizing positive charges may participate in reactions involving water or surface hydroxyl groups, potentially generating hydroxyl radicals ($\bullet OH$) [20]. These reactive species could contribute to transformations of the RB5 chromophore, resulting in a progressive decrease in its characteristic absorption band at approximately 595 nm. The scavenger experiments provide indirect information about the possible involvement of reactive species in RB5 decolorization. The strongest inhibition was observed in the presence of AA, consistent with a possible contribution from superoxide radicals ($\bullet O_2^-$). The smaller inhibitory effects of IPA and EDTA-Na suggest that hydroxyl radicals ($\bullet OH$) and positive charge carriers (h^+) may also participate in the process [21]. The inhibition sequence AA > IPA > EDTA-Na was observed for both pristine and La_2O_3-modified ZnO, indicating a similar response to the investigated scavengers. Nevertheless, these reagents are not entirely selective, and their effects may involve changes in surface reactions or solution chemistry. Consequently, the scavenger results cannot independently establish the identity or relative contributions of the reactive species or determine the dominant charge-generation mechanism [22]. Direct identification of reactive intermediates would be necessary to confirm the proposed reaction pathways. The presence of La-containing species may modify the local electrostatic environment and interfacial charge-transfer characteristics of ZnO. Interfaces between ZnO and lanthanum-containing surface regions could influence charge accumulation and the accessibility of adsorbed reactants. Changes in particle aggregation and structural heterogeneity may also affect the distribution of local mechanical stresses. However, enhanced charge separation and the generation of specific reactive oxygen species were not directly demonstrated. Therefore, these effects should be considered plausible contributions to the observed catalytic behavior rather than experimentally established mechanisms. The dependence of tribocatalytic activity on modifier concentration provides further insight into the role of La_2O_3. The apparent pseudo-first-order rate constant increased from 0.1222 h^{-1} for pristine ZnO to 0.2814 h^{-1} for ZnO modified with 2 mol% La_2O_3, corresponding to an approximately 2.3-fold enhancement. The maximum activity at this composition suggests a favorable balance between surface modification and the preservation of accessible, mechanically responsive ZnO regions. At lower modifier concentrations, the amount of La-containing species may be insufficient to establish the

most favorable interfacial conditions. Conversely, the decrease in activity above 2 mol% La_2O_3 may be associated with excessive surface coverage, changes in particle aggregation, or less effective mechanical stress transfer to ZnO. These explanations remain tentative because the individual contributions of these factors were not experimentally isolated. The importance of mechanical activation was further demonstrated by the control experiments conducted under dark conditions. No measurable RB5 decolorization was observed in the absence of both catalyst and stirring. Similarly, mechanical stirring at 500 rpm without catalyst resulted in 0% decolorization, indicating that agitation alone did not produce detectable dye decolorization. In contrast, the experiment performed with ZnO modified with 2 mol% La_2O_3 without stirring showed an 8% decrease in RB5 concentration, attributable primarily to adsorption. These findings demonstrate that neither passive adsorption nor mechanical agitation alone can explain the substantially higher decolorization efficiencies obtained when the catalyst was subjected to mechanical stirring. The simultaneous presence of the catalyst and mechanical excitation is therefore essential for the pronounced decolorization observed under the investigated conditions. However, these controls do not independently distinguish between piezoelectric, triboelectric, and other possible interfacial contributions [23,24]. The influence of catalyst composition and mechanical excitation conditions has also been demonstrated in independent tribocatalytic investigations. Kumar et al. [26] studied the tribocatalytic removal of organic dyes using $BiVO_4$, demonstrating the applicability of mechanically driven catalytic processes to semiconductor oxides other than ZnO. Similarly, Mao et al. [27] examined the tribocatalytic performance of different commercial metal oxide powders, including ZnO and TiO_2, and reported particularly high activity for DXN-RT30 TiO_2 toward Methyl Orange and Methylene Blue under mechanical stirring. These studies emphasize that tribocatalytic performance depends on both the physicochemical characteristics of the catalyst and the experimental conditions. The enhanced RB5 decolorization observed for ZnO modified with 2 mol% La_2O_3 in the present study is consistent with the importance of catalyst composition. Nevertheless, direct quantitative comparisons are limited by differences in dye structure, catalyst properties, mechanical excitation conditions, and reaction duration. An important comparison can be made with the previously reported photocatalytic decolorization of RB5 using pristine and La-modified ZnO powders [2]. In that investigation, the highest photocatalytic activity was observed for a composition designated as 2 mol% La, with RB5 decolorization efficiencies of 92.04% under UV irradiation and 61.86% under visible light irradiation after 30 min. The corresponding apparent rate constants were 0.0811 and 0.0334 min^{-1}, respectively. Although the earlier study used the designation "2 mol% La", the optimal samples in both investigations were prepared using identical weighed amounts of ZnO and La_2O_3, corresponding to the same nominal modifier loading. This agreement suggests that lanthanum-containing modification may favorably influence the catalytic behavior of ZnO under both photocatalytic and tribocatalytic activation. The faster RB5 decolorization observed under UV irradiation can be associated with direct photoexcitation of ZnO. When the incident photon energy is sufficient to overcome the semiconductor band gap, electrons are promoted from the valence band to the conduction band, generating electron–hole pairs that can participate in surface redox reactions. In contrast, tribocatalytic activation depends on mechanical interactions, including particle collisions, friction, and localized deformation. The resulting charge generation and interfacial transfer processes are likely to depend on the frequency and intensity of mechanical contacts. Consequently, the different activation mechanisms may contribute to the observed differences in decolorization rates. However, the photocatalytic and tribocatalytic experiments were performed under different conditions, including different initial dye concentrations, treatment durations, and energy inputs. Therefore, their apparent rate constants and decolorization efficiencies should not be interpreted as direct measures of intrinsic catalytic performance. A rigorous comparison would require standardized experimental conditions and quantitative evaluation of the corresponding energy consumption. Despite the longer treatment time, tribocatalysis offers the possibility of activating ZnO-based materials through mechanical energy without external light irradiation. This feature may be relevant to highly colored or optically dense wastewater, where light absorption and scattering can limit photon penetration. Mechanically activated catalytic systems could potentially utilize energy available from mixing, agitation, or flowing water. Nevertheless, the practical energy efficiency and economic advantages of tribocatalysis remain to be demonstrated through direct measurements of mechanical power consumption and treatment performance. The present findings can also be compared with independent studies on friction-driven catalytic removal of organic dyes. Chong et al. [13] investigated ZnO materials with different morphologies and specific surface areas, reporting approximately 95% dye removal after 12 h for ZnO nanostars under mechanical stirring. Their results highlighted the importance of surface area and particle morphology in tribocatalytic performance. Sun et al. [28] demonstrated 97% Rhodamine B removal within 2 h using $Ba_4Nd_2Fe_2Nb_8O_{30}$ powders under PTFE-assisted stirring, emphasizing the possible contribution of triboelectric interactions. In addition, Gaur et al. [29] reported the tribocatalytic activity of $CaCu_3Ti_4O_{12}$ nanoparticles toward organic dyes, illustrating the applicability of friction-driven catalytic processes to other metal oxide systems. In comparison, ZnO modified with 2 mol% La_2O_3 achieved 79.87% RB5 decolorization within 6 h under dark conditions in the present study. Although the reported efficiencies demonstrate the potential of different tribocatalytic materials, their direct comparison is limited by differences in dye composition, catalyst characteristics, mechanical excitation conditions, and reaction duration. Nevertheless, these independent investigations highlight the importance of material properties and interfacial interactions in determining tribocatalytic performance. A further consideration concerns the extent of pollutant removal achieved during tribocatalytic treatment. The time-dependent UV–Vis spectra showed a progressive decrease in the characteristic absorption band of RB5, but complete decolorization was not achieved within the investigated 6 h reaction period. The highest decolorization efficiency was 79.87% for ZnO modified with 2 mol% La_2O_3, compared with 52.60% for pristine ZnO. Importantly,

the decrease in absorbance reflects the reduction in the characteristic visible absorption of the dye but does not independently establish complete chemical degradation or mineralization. The formation and persistence of transformation products cannot be excluded based on UV-Vis measurements alone. Therefore, additional investigations, including total organic carbon analysis and identification of possible transformation products, are required to determine the extent of pollutant removal and evaluate the environmental applicability of the process. Overall, the results indicate that controlled La_2O_3 modification can improve the tribocatalytic decolorization performance of ZnO under mechanical stirring. The observed enhancement, together with the control experiments and preliminary reusability results, supports further investigation of La_2O_3-modified ZnO as a mechanically activated catalytic material. However, clarification of the charge-generation mechanisms, identification of transformation products, and quantitative evaluation of energy efficiency remain necessary before the practical applicability of the system to wastewater treatment can be established.

5. Concluding Remarks

This study investigated the influence of La_2O_3 modification on the structural, morphological, and tribocatalytic properties of ZnO powders for the degradation of RB5 under dark conditions. XRD analysis confirmed that the hexagonal wurtzite structure of ZnO was preserved following modification, while changes in crystallite characteristics and particle aggregation were observed. SEM–EDS analysis further confirmed the presence of lanthanum in the modified material. The tribocatalytic activity was strongly dependent on La_2O_3 content, with the highest performance achieved at 2 mol% La_2O_3. The apparent pseudo-first-order rate constant increased from 0.1222 h^{-1} for pristine ZnO to 0.2814 h^{-1} for the optimally modified sample, corresponding to an approximately 2.3-fold enhancement. Further increases in La_2O_3 concentration resulted in reduced catalytic activity, indicating the importance of controlling the modifier content. Control experiments demonstrated that mechanical stirring alone did not induce measurable dye removal, whereas adsorption in the absence of stirring accounted for only 8%, supporting the essential role of mechanically activated catalyst-assisted processes. The optimal nominal La_2O_3 modifier loading identified in the present study corresponds to that used for the most active sample in the previously reported photocatalytic investigation [2], despite the different compositional notation adopted in the earlier publication. This observation suggests that controlled lanthanum-containing modification can favorably influence the catalytic properties of ZnO under different excitation conditions. Although photocatalysis exhibited faster RB5 decolorization under the previously investigated irradiation conditions, tribocatalysis enabled substantial dye decolorization without external light irradiation. Scavenger experiments provided additional insight into the possible involvement of reactive species in the tribocatalytic process. The strongest inhibition was observed in the presence of ascorbic acid, followed by isopropyl alcohol and EDTA-Na, suggesting possible contributions from superoxide radicals ($\bullet O_2^-$), hydroxyl radicals ($\bullet OH$), and positive charge carriers (h^+). These observations are consistent with mechanically induced charge generation and subsequent interfacial redox reactions. However, the individual contributions of these species cannot be conclusively established from scavenger experiments alone. Contact electrification involving the PTFE-coated stirring bar may also contribute to charge generation, although its relative importance remains to be determined. Reusability experiments conducted over three consecutive cycles showed that both catalysts retained most of their initial decolorization activity, with reported decreases of approximately 6% for pristine ZnO and 5% for ZnO modified with 2 mol% La_2O_3. These results provide preliminary evidence of catalyst reusability under the investigated conditions. Nevertheless, further investigations involving direct identification of reactive species, surface-sensitive characterization, and extended cycling experiments are required to clarify the reaction pathways and establish long-term operational stability. The solution pH was not monitored during the present experiments. Therefore, possible pH variations associated with La_2O_3 modification and their influence on RB5 adsorption and tribocatalytic decolorization cannot be excluded. A systematic investigation of these effects will be included in future work. Overall, the findings demonstrate the potential of La_2O_3-modified ZnO for mechanically driven decolorization of dye-containing aqueous solutions without external light irradiation. However, the observed decrease in RB5 absorbance does not establish complete chemical degradation or mineralization, and possible transformation products were not identified in the present study. Further investigations, including total organic carbon analysis and identification of transformation products, are therefore necessary to evaluate the extent of pollutant removal and the environmental applicability of the process.

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