

# Synthesis of CuZnFe-LDH for Peroxymonosulfate Activation toward Reactive Blue 19 Degradation and Application in Real Textile Wastewater Treatment

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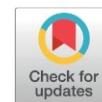
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## Abstract

In this study, CuZnFe-LDH was synthesized by a solvothermal method using analytical-grade chemicals and applied as a catalyst for PMS activation to degrade Reactive Blue 19 (RB19) in water. Material characteristics related to surface morphology, elemental composition, crystal structure, functional groups, specific surface area, and surface chemical states were analyzed using SEM/EDX, XRD, FT-IR, BET, and XPS techniques. Specifically, the specific surface area of CuZnFe-LDH, determined from N<sub>2</sub> adsorption-desorption isotherms, was 49.35 m<sup>2</sup>/g, with a pore volume of 0.093 cm<sup>3</sup>/g and an average pore diameter of 7.55 nm. The effects of PMS dosage, catalyst dosage, RB19 concentration, pH, and inorganic anions on PMS activation were investigated. The selected operating conditions were determined to be [RB19] = 50 mg/L, [CuZnFe-LDH] = 200 mg/L, pH = 7, and [PMS] = 200 mg/L, under which the degradation efficiency of RB19 reached 99.85 % within 12 min. Furthermore, the CuZnFe-LDH/PMS system exhibited the ability to effectively degrade different dyes, including MO, R3BS, and BBRF, while also showing positive results in the treatment of biologically treated real textile wastewater in terms of color and COD removal. The quenching results suggested that SO<sub>4</sub>•<sup>-</sup> made the greatest contribution to RB19 degradation, with additional contributions from O<sub>2</sub>•<sup>-</sup> and •OH. After five consecutive reuse cycles, small amounts of Cu and Zn were leached into the solution, whereas Fe was not detected; correspondingly, the RB19 degradation efficiency decreased by approximately 22.6 %, indicating the relatively good stability and reusability of CuZnFe-LDH under the investigated conditions. In future work, post-reaction catalyst characterization should be conducted to evaluate catalyst stability and clarify the specific roles of individual metals in the multi-metal LDH-based system. Additionally, mass spectrometry analyses are required to identify the degradation pathways of RB19 and assess the toxicity of the resulting intermediates. Overall, ternary LDH-based catalysts demonstrate promising potential for application in sulfate radical-based advanced oxidation processes for the removal of organic pollutants from water.

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**Keywords:** CuZnFe-LDH; Peroxymonosulfate Activation; SR-AOPs; Reactive Blue 19; Textile Wastewater Treatment

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## 1. Introduction

Textile wastewater is one of the major industrial waste streams, characterized by high discharge volumes, intense color, and complex

pollutant compositions. This type of wastewater typically contains various dye compounds with stable molecular structures and poor biodegradability. In addition, it is often accompanied by inorganic salts, surfactants, dyeing auxiliaries, and other recalcitrant organic

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compounds with high chemical stability derived from dyeing, printing, and finishing processes [1,2]. Therefore, conventional treatment processes such as coagulation, adsorption, and biological treatment are generally suitable only for specific treatment stages, while their effectiveness in color removal and mineralization of persistent organic compounds remains limited [3].

Recently, sulfate radical-based advanced oxidation processes (SR-AOPs) have attracted increasing attention due to their ability to generate highly reactive oxygen species (ROS), including sulfate radical ( $\text{SO}_4^{\bullet-}$ ), hydroxyl radical ( $\bullet\text{OH}$ ), superoxide radical ( $\text{O}_2^{\bullet-}$ ), and singlet oxygen ( $^1\text{O}_2$ ), thereby enhancing the degradation of refractory organic pollutants in water [4,5]. Numerous studies have reported the activation of PMS to utilize the generated ROS, particularly  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$ , for dye degradation [6,7]. Regarding the catalytic activation of PMS, transition metals (including Co, Cu, Fe, Mn, and Ni) and their oxides are among the promising candidates for heterogeneous catalytic systems due to their high ability to generate ROS [8,9]. Among the heterogeneous catalysts used for PMS activation, layered double hydroxides (LDHs) are considered a promising class of materials because of their layered structure, tunable metal composition, hydroxyl-rich surface, and presence of redox-active metal centers [10]. The LDH structure generally consists of positively charged divalent/trivalent metal hydroxide layers, with charge-balancing anions and water molecules located in the interlayer region; therefore, the metal composition can be adjusted to construct different active sites for catalytic oxidation reactions [11]. In particular, LDHs containing transition metals such as Co, Fe, Cu, Ni, or Mn have been demonstrated to activate PMS and generate various ROS within the same system through electron transfer and metal redox cycles [12,13]. Specifically, in the CoMn-LDH/GO/PMS system, Cobalt acts as the primary PMS activation center, promoting the generation of ROS, including  $\text{SO}_4^{\bullet-}$ ,  $\text{SO}_5^{\bullet-}$ ,  $\bullet\text{OH}$  and  $\text{O}_2^{\bullet-}$ , which subsequently contribute to the formation of  $^1\text{O}_2$ . In contrast, Mn mainly functions as a redox mediator, facilitating the regeneration of  $\text{Co}^{2+}$  and contributing to  $\text{O}_2^{\bullet-}$  generation, thereby indirectly enhancing  $^1\text{O}_2$  production. As a result, the CoMn-LDH/GO/PMS system achieved more than 98% degradation of Methylene Blue (50 mg/L) and 51.68% COD removal within 8 min. Moreover, it exhibited excellent performance toward the degradation of other organic pollutants, including dyes and antibiotics, with removal efficiencies ranging from 73.13% to 100% within only 4 - 8 min [14]. However, most current studies have focused on bimetallic LDHs. The incorporation of multiple redox-active metals into the LDH structure may promote synergistic interactions among metal

active sites, facilitate PMS activation through metal redox cycling and interfacial electron transfer, and diversify ROS generation pathways [4,15-17]. Several previous studies have demonstrated the potential of this multimetallic approach. For example, CoFeNi-LDH/PMS is capable of effectively degrading nearly 100% of Congo red (20 mg/L) and Rhodamine B (20 mg/L) within 6 and 10 minutes, respectively [18], while CuCoFe-LDH/PMS achieved 94.57% degradation of levofloxacin (10 mg/L) within 10 min and maintained high catalytic stability after five consecutive cycles [19]. In addition, in the BC@CuCoFe-LDH/PMS system, Co acts as the primary PMS activation center, while Cu and Fe mainly facilitate electron transfer and promote the regeneration of active Co species through synergistic redox cycles. These processes continuously generate  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  radicals, which are the dominant reactive species responsible for phenanthrene degradation, whereas  $\text{O}_2^{\bullet-}$  and  $^1\text{O}_2$  make relatively minor contributions. Consequently, the BC@CuCoFe-LDH/PMS system achieved 96.5% phenanthrene removal within 15 min and retained more than 80% degradation efficiency after four reuse cycles, highlighting its excellent catalytic activity and stability [20]. These findings indicate that trimetallic LDHs can exhibit higher activity than some bimetallic LDHs due to the cooperation of metal active sites within the catalytic structure. Meanwhile, cobalt, one of the most effective transition-metal catalysts, poses a risk of secondary pollution if leached into the environment.

Multi-metallic LDH systems, particularly cobalt-free trimetallic systems, such as CuZnFe-LDH for PMS activation toward dye removal, have not yet been sufficiently investigated. Nevertheless, several studies have demonstrated that the catalytic activity of ternary CuZnFe-LDH can benefit from the complementary roles of the constituent metals. Specifically, Lu *et al.* [21] demonstrated the important role of Cu species in promoting peroxide activation and proposed Cu/Fe redox processes for the complete degradation of acetaminophen in water. More recently, Kang *et al.* [22] showed that the incorporation of Zn into the CuFe system promoted LDH formation, regulated the Cu/Fe distribution, and enhanced their synergistic interaction, while selective Zn leaching during structural reconstruction exposed additional active sites. Similarly, the incorporation of Cu into ZnFe-LDH was reported to significantly enhance catalytic performance by modifying the electronic and interfacial properties of the material [23]. These findings highlight the potential advantages of integrating Cu, Zn, and Fe within a trimetallic LDH structure and provide a scientific basis for

exploring CuZnFe-LDH as a cobalt-free catalyst for PMS activation.

Based on these considerations, CuZnFe-LDH was synthesized by a simple solvothermal method and applied as a catalyst for PMS activation to degrade the Reactive Blue 19 (RB19) in water. This study explores CuZnFe-LDH as a cobalt-free trimetallic catalyst for PMS activation and systematically evaluates its performance toward RB19 degradation under different operating conditions. In addition, the application potential and catalyst stability of the system are evaluated through the degradation of different dyes and real textile wastewater, as well as five consecutive reuse cycles. These results provide further insight into the catalytic performance of CuZnFe-LDH for PMS activation and highlight the potential of cobalt-free multimetallic catalytic systems for textile wastewater treatment.

## 2. Materials and Methods

### 2.1 Preparation and Characterization of CuZnFe-LDH Catalyst

The CuZnFe-LDH was synthesized via a solvothermal method. First, a mixture containing 5 mM of each metal nitrate salt, including  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , together with 3 g of urea, was dispersed in 50 mL of ethanol. The mixture was magnetically stirred for 30 min using a magnetic stirrer. Subsequently, the suspension was transferred into an autoclave and subjected to solvothermal treatment at 120 °C for 24 h. After cooling to room temperature, the obtained material was washed with distilled water and ethanol until a neutral pH was reached. The final product was dried at 60 °C for 12 h. Several other trimetallic LDH materials, including CuNiFe-LDH and ZnNiFe-LDH, were synthesized under identical conditions, while maintaining a molar ratio of 1:1:1 among the three metal components.

The characteristics of CuZnFe-LDH catalyst, including surface morphology, elemental composition, crystalline phase structure, surface functional groups, and specific surface area, were comprehensively characterized. Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM/EDX, JSM-IT200, JEOL, Japan) was employed to examine the surface morphology and elemental composition of CuZnFe within the analyzed region. Fourier-transform infrared spectroscopy (FTIR, Bruker ALPHA II, Germany) was used to identify the vibrational characteristics of the functional groups present in the material. The crystalline phase structure and specific surface area based on the Brunauer - Emmett - Teller (BET) method were determined by X-ray diffraction (XRD, D2 Phaser, Bruker, Germany) and a BET analyzer (BET 201A, Pore

Materials, Inc., USA), respectively. To assess catalyst stability and metal release, the leached Cu, Zn, and Fe contents in the post-reaction solutions across five cycles were measured via ICP-OES (ICPE-9820, Shimadzu, Japan). Surface chemical states and elemental compositions were analyzed by X-ray photoelectron spectroscopy (XPS, AXIS Supra, Kratos Analytical, UK) using a monochromatic Al K $\alpha$  X-ray source. The point of zero charge of the material was determined from the intersection point of the curve representing the variation in pH of the material in solutions with initial pH values ranging from 3 to 11 before and after 48 h of shaking.

### 2.2. Peroxymonosulfate Activation for the Degradation of RB19 and Textile Wastewater

The RB19 degradation experiments were conducted in 50 mL Erlenmeyer flasks with a total reaction volume of 25 mL. Specifically, 5 mL of a 250 mg/L RB19 stock solution was introduced into the reaction flask, followed by the addition of a predetermined amount of CuZnFe-LDH and 15 mL of distilled water. The mixture was then shaken thoroughly. Subsequently, the suspension was agitated for 20 min to establish adsorption-desorption equilibrium. The solution pH was adjusted using 0.01 M  $\text{H}_2\text{SO}_4$  or 0.01 M NaOH solutions. After adsorption equilibrium was attained, 5 mL of PMS solution (1000 mg/L) was added to initiate the reaction. At predetermined time intervals, the samples were withdrawn and filtered through a 0.45  $\mu\text{m}$  syringe filter (CA, Alain, China) to remove the catalyst. The filtrate was transferred into a cuvette, and the absorbance at 590 nm was measured to monitor the variation in RB19 concentration over time. Control experiments were performed following the same procedure without the addition of PMS solution. All experiments were performed in duplicate or triplicate, depending on the specific experimental series. A pseudo-first-order kinetic model, as presented in Eq. (1), was applied to estimate the apparent reaction rate constant ( $k_{\text{obs}}$ ) and compare the RB19 degradation rates under different experimental conditions. In this equation,  $C_t$  and  $C_0$  represent the RB19 concentrations at reaction time  $t$  and the initial RB19 concentration (mg/L), respectively;  $k_{\text{obs}}$  is the apparent pseudo-first-order reaction rate constant ( $\text{min}^{-1}$ ); and  $t$  denotes the reaction time (min). The removal efficiency was calculated using Eq. (2), where  $C_0$  and  $C_t$  represent the initial value and the value measured at reaction time  $t$ , respectively, for the corresponding parameter. For RB19 degradation, COD removal, and color removal,  $C$  represents the RB19 concentration (mg/L), COD (mg/L), and color value (Pt-Co), respectively.

$$\ln(C_t/C_0) = -k_{obs} \times t \quad (1)$$

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (2)$$

The applicability of the CuZnFe-LDH/PMS catalytic system was evaluated for the degradation of various reactive dyes. The concentrations of the dyes were determined using a UV-Vis spectrophotometer (DR6000, Hach, USA) based on the Beer-Lambert law at their maximum absorption wavelengths, including Reactive Blue 19 (RB19,  $\lambda_{\max} = 590$  nm), Methyl Orange (MO,  $\lambda_{\max} = 460$  nm), Reactive Red 3BS (R3BS,  $\lambda_{\max} = 525$  nm), and Brilliant Blue Reactive F (BBRF,  $\lambda_{\max} = 611$  nm). Quenching experiments were performed to identify the ROS involved in the CuZnFe-LDH/PMS catalytic system. Specifically, sodium azide (NA) was used as a scavenger for  $^1\text{O}_2$ , p-BQ was employed to quench  $\text{O}_2^{\cdot-}$ , tert-butanol (TBA) was used to inhibit  $^{\cdot}\text{OH}$ , while ethanol (EtOH) was capable of reacting with both  $\text{SO}_4^{\cdot-}$  and  $^{\cdot}\text{OH}$ . Finally, the practical application potential of the CuZnFe-LDH/PMS system was assessed using biologically treated textile wastewater collected from Gunzetal (Vietnam) Limited (VSIP II-A, Ho Chi Minh City, Vietnam). The COD, and color values after treatment were determined according to SMEWW 5220C and UV-Vis spectrophotometric analysis, respectively.

### 3. Results and Discussion

#### 3.1. Reactive Blue 19 Degradation Performance of Catalytic Systems

The PMS activation performance of different LDH-based materials toward RB19 degradation is presented in Figure 1. In the absence of PMS, the RB19 removal efficiency of CuZnFe-LDH reached only 8.21% after 12 min, indicating the negligible adsorption of RB19 by CuZnFe-LDH. Similarly, in

the absence of catalyst, PMS exhibited a low oxidation capacity toward RB19, achieving only 5.52% removal. In contrast, when both CuZnFe-LDH and PMS were present, the degradation efficiency of RB19 increased significantly and rapidly reached its maximum value. Specifically, the RB19 removal efficiencies for the CuZnFe-LDH/PMS, CuNiFe-LDH/PMS, and ZnNiFe-LDH/PMS systems all exceeded 99% after 12 min. The degradation rate constant of RB19 in the CuZnFe-LDH/PMS system ( $k = 1.0271 \text{ min}^{-1}$ ) was 168.38, 123.75, 1.79, and 1.27 times higher than those of the PMS, CuZnFe-LDH, CuNiFe-LDH/PMS, and ZnNiFe-LDH/PMS systems, respectively. Among the three LDH-based catalytic systems, the CuZnFe-LDH/PMS system exhibited the highest RB19 degradation rate and was therefore selected for subsequent characterization and catalytic experiments. This initial comparison was performed to screen the catalytic performance of the three LDH-based materials under identical experimental conditions.

#### 3.2. Characterization of CuZnFe-LDH Catalyst

The SEM results presented in Figure 2(a)-(b) revealed that the surface morphology of CuZnFe-LDH was heterogeneous, exhibiting a clear coexistence of thin plate-like structures and spherical aggregates with irregular sizes stacked upon one another without a specific arrangement. The EDX spectrum and elemental mapping analysis confirmed the presence of Cu, Zn, Fe, C, and O elements in the material, with elemental contents of 1.52%, 3.47%, 13.53%, 48.89%, and 35.74%, respectively (Figure 2(c)-(h)). Furthermore, elemental analysis revealed a uniform distribution of Cu, Zn, and Fe suggesting that these metal components are dispersed throughout the catalyst surface, which may

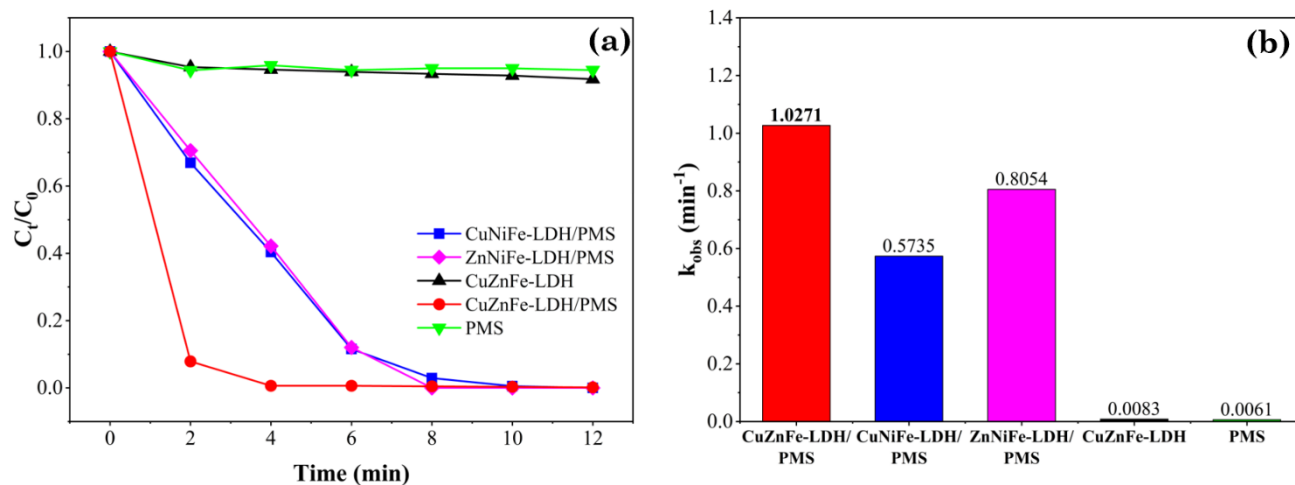


Figure 1. (a) RB19 degradation kinetics in catalytic systems and (b) the corresponding observed pseudo-first-order rate constants ( $k_{obs}$ ) (reaction conditions: [RB19] = 50 mg/L, [catalyst] = 200 mg/L, [PMS] = 200 mg/L, and pH = 7).

facilitate their participation in the catalytic process.

X-ray diffraction (XRD) analysis was employed to investigate the crystalline structure of the CuZnFe-LDH. As shown in Figure 3(a), the CuZnFe-LDH catalyst exhibited several characteristic diffraction peaks at  $2\theta$  values of 13.21, 26.23, 35.71, 60.28, and 62.31°, corresponding to the (003), (006), (012), (110), and (113) crystal planes, respectively, which are representative of layered structures [21,24,25]. The  $d(003)$  and  $d(006)$  spacings, calculated according to Bragg's law, were 0.67 nm and 0.339 nm, respectively, with  $d(003)$  approximately equal to  $2d(006)$ , confirming the well-ordered layered structure of LDHs [26]. These results confirm the successful synthesis of CuZnFe-LDH.

The Fourier-transform infrared spectrum of CuZnFe-LDH (Figure 3(b)) exhibited a broad absorption band centered at 3360  $\text{cm}^{-1}$ , which was attributed to the O–H stretching vibration of hydroxyl groups and interlayer water molecules. The absorption band observed at 2362  $\text{cm}^{-1}$  was assigned to adsorbed atmospheric  $\text{CO}_2$  on the material surface [27]. The characteristic absorption band at 1652  $\text{cm}^{-1}$  corresponded to the H–O–H bending vibration of interlayer water molecules [28]. The absorption band located at 1395  $\text{cm}^{-1}$  was mainly related to interlayer carbonate species in the LDH structure,

corresponding to the stretching vibration of carbonate O–C–O groups [29]. Furthermore, a broad absorption band centered at 837  $\text{cm}^{-1}$ , below 1000  $\text{cm}^{-1}$ , was assigned to the vibrations of metal oxygen (M–O) and metal hydroxyl bonds (M–OH) [27,30]. The presence of surface hydroxyl groups alongside M–O and M–OH bonds confirms the successful synthesis of the layered CuZnFe-LDH structure. These surface functional groups in LDH-based catalysts have been reported to facilitate PMS adsorption and its interaction with surface metal sites, thereby favoring PMS activation [31].

The surface area and porous characteristics of the material were determined by  $\text{N}_2$  adsorption-desorption analysis using the Brunauer-Emmett-Teller (BET) method. As shown in Figure 3(c), the  $\text{N}_2$  adsorption-desorption isotherm of CuZnFe-LDH exhibited a typical type IV isotherm, which is characteristic of mesoporous materials with pore sizes ranging from 2 to 50 nm. In addition, a H3-type hysteresis loop was observed within the relative pressure range ( $P/P_0$ ) of approximately 0.2 - 0.8. These features are commonly associated with layered structures. The BET specific surface area, pore volume, and average pore diameter of CuZnFe-LDH were determined to be 49.53  $\text{m}^2/\text{g}$ , 0.093  $\text{cm}^3/\text{g}$ , and 7.55 nm, respectively. The pore size distribution was mainly concentrated within the range of 0 - 10 nm (Figure 3(d)). Compared

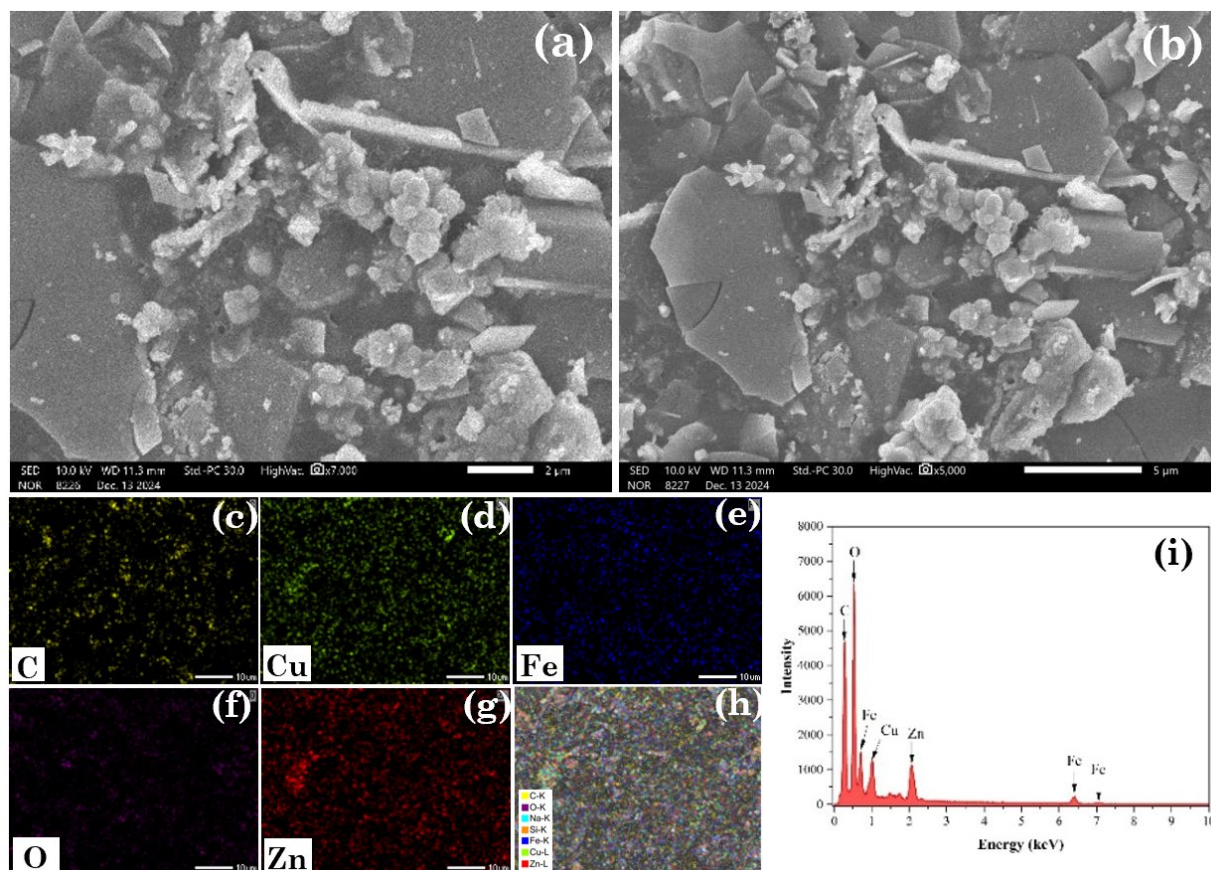


Figure 2. (a)-(b) SEM images, (c)-(h) EDX elemental mappings, and (i) EDX spectrum of CuZnFe-LDH.

with the study reported by Lu *et al.* [21], the CuZnFe-LDH synthesized in this work exhibited a larger specific surface area, while possessing considerably lower pore volume and average pore diameter. These features may provide more accessible contact sites and facilitate the diffusion and interaction among RB19, PMS, and the catalyst. This can improve the utilization of surface active sites and consequently favor PMS activation [32].

XPS analysis was performed to determine the surface elemental composition and chemical states of CuZnFe-LDH. As shown in Figure 4(a), the survey spectrum confirmed the presence of Cu, Zn, Fe, O, and C. In the high-resolution Cu 2p spectrum (Figure 4(b)), the peaks at 934.1 and 953.9 eV were assigned to Cu<sup>+</sup> 2p<sub>3/2</sub> and Cu<sup>+</sup> 2p<sub>1/2</sub>, respectively, while the peaks at 935.3 and 955.1 eV were attributed to Cu<sup>2+</sup> 2p<sub>3/2</sub> and Cu<sup>2+</sup> 2p<sub>1/2</sub>. The coexistence of Cu<sup>+</sup> and Cu<sup>2+</sup> has also been reported for Cu-containing multimetallic LDHs [33,34]. The satellite peaks observed at 941.9 and 962.6 eV were characteristic of Cu<sup>2+</sup> species. The Zn 2p spectrum (Figure 4(c)) exhibited two characteristic peaks at 1021.8 and 1044.9 eV, corresponding to Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub>,

respectively, indicating that Zn predominantly existed as Zn<sup>2+</sup> in the LDH structure [35]. As shown in Figure 4(d), the Fe 2p spectrum was deconvoluted into Fe<sup>2+</sup> and Fe<sup>3+</sup> components. The peaks at 710.5 and 724.2 eV were assigned to Fe<sup>2+</sup> 2p<sub>3/2</sub> and Fe<sup>2+</sup> 2p<sub>1/2</sub>, respectively, while the peaks at 712.9 and 727.3 eV were attributed to Fe<sup>3+</sup> 2p<sub>3/2</sub> and Fe<sup>3+</sup> 2p<sub>1/2</sub>. Satellite peaks were also observed in the higher binding energy region. Fe<sup>2+</sup> and Fe<sup>3+</sup> states with similar binding energies have been reported in Fe-containing LDH materials [22,33]. The coexistence of Cu<sup>+</sup>/Cu<sup>2+</sup> and Fe<sup>2+</sup>/Fe<sup>3+</sup> species suggests the presence of redox-active metal sites on the CuZnFe-LDH surface, which may facilitate electron transfer during PMS activation.

The C 1s spectrum (Figure 4(e)) was deconvoluted into three components at 284.8, 285.8, and 289.0 eV, assigned to C–C/C–H, C–O, and O–C=O, respectively. The O–C=O component at higher binding energy was associated with carbonate species in the LDH structure [16]. Combined with the characteristic absorption band of carbonate in the FTIR spectrum, this result supports the presence of CO<sub>3</sub><sup>2-</sup> in the interlayer region of CuZnFe-LDH. For the O 1s

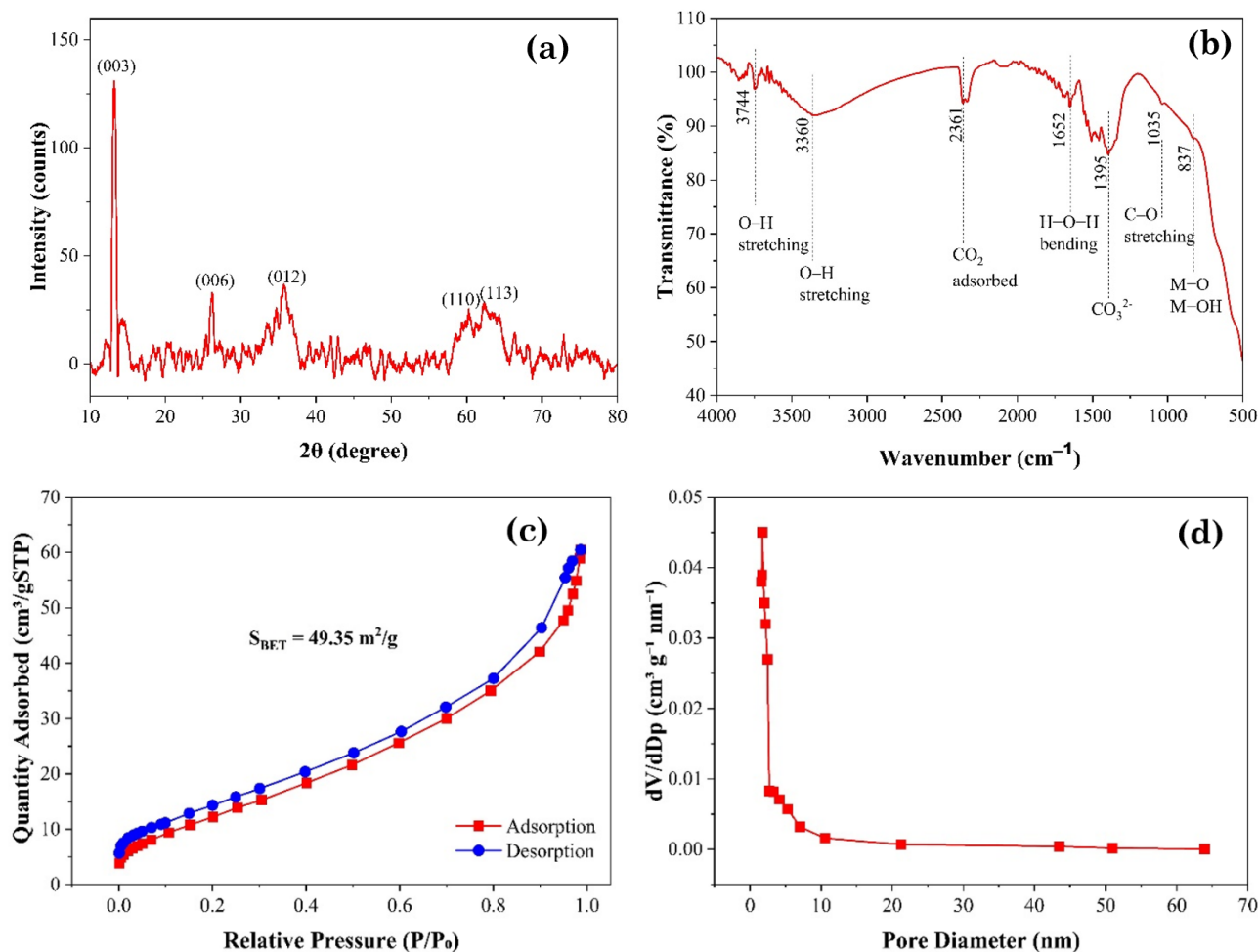


Figure 3. (a) XRD pattern, (b) FTIR spectrum, (c) N<sub>2</sub> adsorption-desorption isotherm, and (d) pore size distribution of CuZnFe-LDH.

spectrum (Figure 4(f)), three components at 529.6, 531.4, and 532.8 eV were assigned to lattice oxygen ( $O_{lac}$ ), defect-related oxygen ( $O_{def}$ ), and adsorbed oxygen species ( $O_{ads}$ ), respectively. Similar binding energy regions have been reported for different surface oxygen species in LDH-based materials [23,33]. Overall, the XPS results revealed the coexistence of multiple oxidation states of Cu and Fe, along with  $Zn^{2+}$  and various surface oxygen species in CuZnFe-LDH, confirming its successful synthesis and providing a basis for further discussion on the mechanism of PMS activation.

### 3.3. Effects of Operational Factors

The PMS concentration directly affects the generation of ROS in the CuZnFe-LDH/PMS system. Therefore, the effect of PMS concentration (0 - 500 mg/L) was investigated. As shown in Figure 5(a), both the RB19 removal efficiency and reaction rate increased rapidly with increasing PMS concentration from 0 to 300 mg/L, and then slightly decreased when the PMS concentration was further increased to 500 mg/L. The high concentration of  $HSO_5^-$  in solution promoted competitive side reactions that

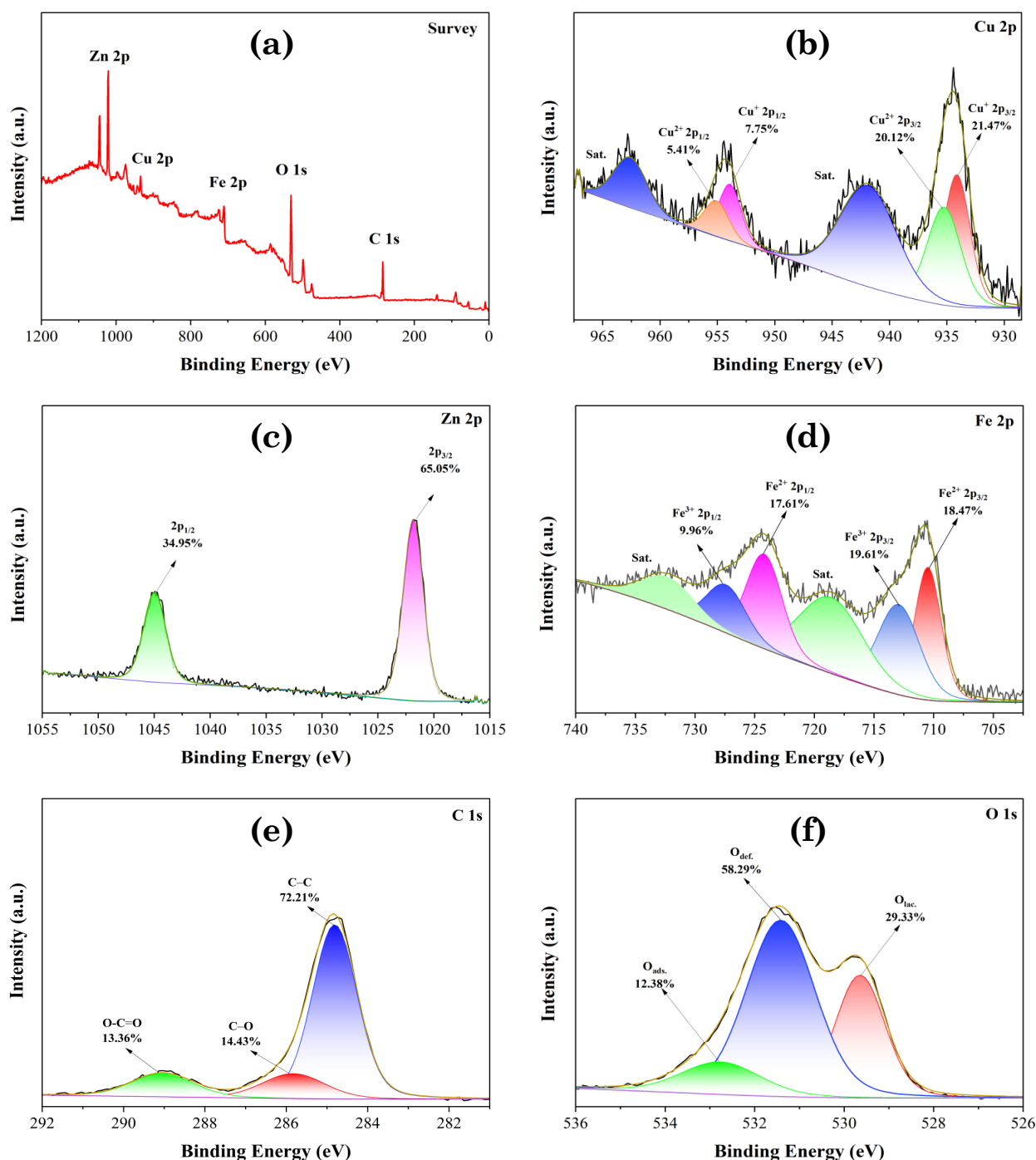
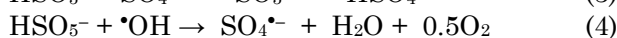
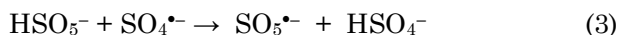


Figure 4. XPS spectra of the synthesized CuZnFe-LDH catalyst: (a) survey spectrum, and high-resolution spectra of (b) Cu 2p, (c) Zn 2p, (d) Fe 2p, (e) C 1s, and (f) O 1s.

consumed ROS through Eqs. (3) - (6), resulting in a slight decrease in RB19 degradation efficiency. Therefore, a PMS concentration of 200 mg/L was selected as the operating PMS concentration in this study.



The catalyst dosage provides active sites for PMS activation and the generation of ROS. The effect of CuZnFe-LDH dosage on RB19 degradation is shown in Figure 5(b). As the catalyst dosage increased from 50 to 200 mg/L, the RB19 removal efficiency increased from 14.01% to 99.85%, while the corresponding degradation rate constant increased rapidly from 0.01204 to 1.0271 min<sup>-1</sup>. The enhanced RB19 removal can be attributed to the increase in the number of active sites available for PMS activation at higher catalyst dosages, thereby promoting the generation of ROS and accelerating RB19 degradation. However, a further increase in catalyst dosage to 500 mg/L resulted in only a

negligible improvement in RB19 removal efficiency. Considering economic feasibility and environmental safety associated with the use of a catalyst containing multiple metal components, the optimum catalyst dosage was determined to be 200 mg/L.

LDH/PMS systems can degrade dyes effectively under a broad pH range, with pH-dependent radical generation and catalytic activity [7]. In this study, the initial solution pH was varied from 3 to 11 to evaluate its effect on RB19 removal efficiency. As shown in Figure 5(c), acidic conditions significantly affected the performance of the CuZnFe-LDH/PMS system. The  $\text{pH}_{\text{pzc}}$  of CuZnFe-LDH was determined to be 8.06, as shown in the inset of Figure 5(c). At  $\text{pH} < 8.06$ , the catalyst surface is predominantly positively charged, whereas at  $\text{pH} > 8.06$ , the surface becomes negatively charged. Therefore, at pH values below the  $\text{pH}_{\text{pzc}}$ , the positively charged catalyst surface may promote electrostatic interactions with anionic RB19, whereas at  $\text{pH} > 8.06$ , electrostatic repulsion may occur between the negatively charged catalyst surface and anionic species. However, the enhanced RB19 degradation observed under

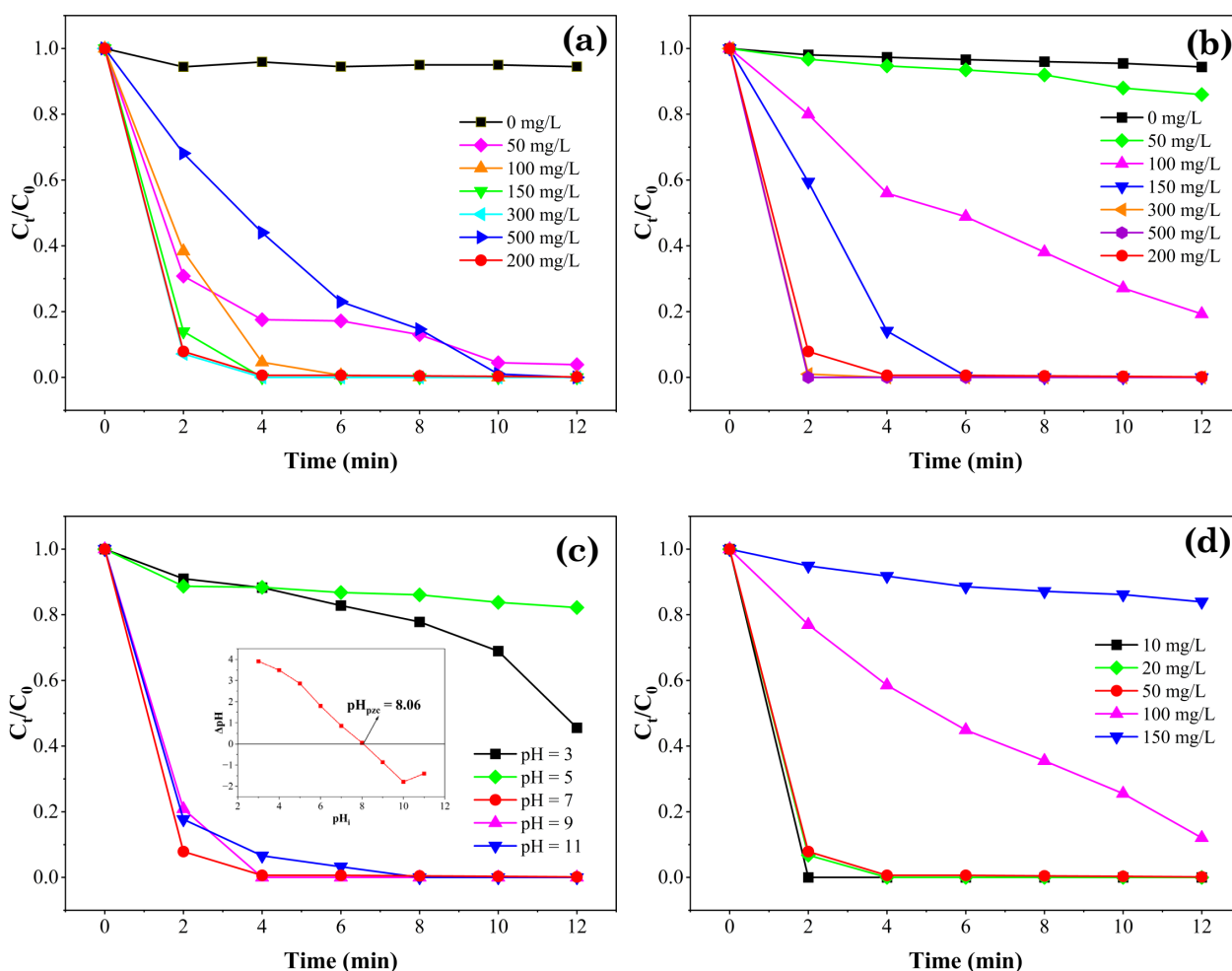
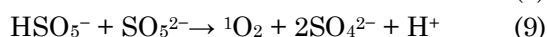


Figure 5. Effects of (a) PMS concentration, (b) catalyst dosage, (c) pH, and (d) initial RB19 concentration on RB19 degradation kinetics (inset of panel (c):  $\text{pH}_{\text{pzc}}$  of CuZnFe-LDH).

neutral-to-alkaline conditions indicates that electrostatic interactions are not the dominant factor controlling the catalytic performance, and the pH-dependent activation of PMS and generation of reactive species likely play more important roles.

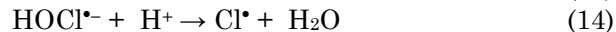
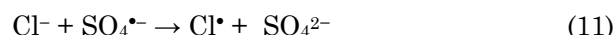
At pH 3 and 5, PMS predominantly existed in the form of  $\text{HSO}_5^-$ . The active sites on the catalyst surface activated  $\text{HSO}_5^-$  to generate both  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  radicals [14]. However, under strongly acidic conditions, excess  $\text{H}^+$  may suppress the generation and effective utilization of these reactive radicals (Eqs. (7) and (8)), thereby reducing the oxidation capacity of the system [17,36]. Furthermore, under strongly acidic conditions, the LDH structure can be significantly affected, and partial self-degradation may reduce catalytic activity while metal leaching may occur, resulting in a considerable decrease in RB19 degradation efficiency. Under neutral and alkaline conditions, PMS mainly existed as  $\text{HSO}_5^-$ , while partial deprotonation to  $\text{SO}_5^{2-}$  could occur as the pH increased ( $\sim 10$ ). The coexistence of  $\text{HSO}_5^-$  and  $\text{SO}_5^{2-}$  may promote PMS self-decomposition to generate  $^1\text{O}_2$  according to Eq. (9). Singlet oxygen is recognized as a strong oxidizing species with selective reactivity toward organic compounds containing aromatic structures. In addition, the self-decomposition of  $\text{SO}_4^{\bullet-}$  could lead to the formation of  $\bullet\text{OH}$ , which are highly reactive and capable of non-selective oxidation of organic pollutants (Eq. (10)) [16]. Consequently, the coexistence of  $\text{SO}_4^{\bullet-}$ ,  $^1\text{O}_2$ , and  $\bullet\text{OH}$  enhanced the degradation of RB19. As a result, both the reaction rate constant and RB19 removal efficiency reached their highest values within this pH range.

Under strongly alkaline conditions (pH = 11), PMS predominantly existed in the form of  $\text{SO}_5^{2-}$ , and the conversion of sulfate radicals into hydroxyl radicals became more favorable [37]. Hydroxyl radicals possess a relatively short lifetime, and their oxidation ability is less effective under alkaline conditions. Therefore, a decrease in RB19 degradation efficiency would generally be expected. Nevertheless, in the present study, the removal efficiency of RB19 was not significantly inhibited at pH of 11. Under practical conditions, neutral pH is always the preferred option for safe, sustainable, and cost-effective applications. Therefore, the natural pH of approximately 7, without pH adjustment, was selected as the operating condition for all subsequent experiments.



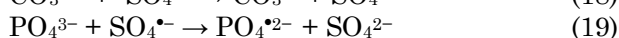
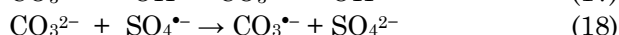
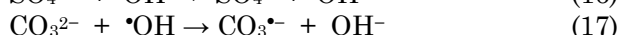
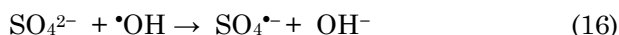
The initial concentration of RB19 reflects the maximum operating capacity of the system under different pollutant loading conditions. In this study, the initial RB19 concentration was varied from 10 to 150 mg/L to evaluate the performance of the CuZnFe-LDH/PMS system. As shown in Figure 5(d), the RB19 removal efficiency gradually decreased with increasing initial RB19 concentration. The degradation rate of RB19 is closely related to the generation of ROS ( $\text{SO}_4^{\bullet-}$ ,  $^1\text{O}_2$ , and  $\bullet\text{OH}$ ) on the catalyst surface and their subsequent reactions with RB19 molecules. As the initial RB19 concentration increased, a greater amount of ROS was required for effective degradation. However, only a limited amount of ROS could be generated under a fixed dosage of catalyst and PMS. Therefore, when the initial RB19 concentration was excessively high, the degradation efficiency decreased. These results suggest that, under practical conditions, the overloading of the treatment system should be carefully evaluated to ensure treatment efficiency as well as environmental safety before discharge into receiving water bodies.

The composition of textile wastewater is highly complex and contains various inorganic ions. At certain concentrations, the presence of inorganic anions can significantly affect the activity of ROS [38]. In this study, inorganic anions including  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  were added into the reaction system at concentrations of 5 and 20 mM to evaluate their effects on RB19 degradation (Figure 6(a)-(b)). The results showed that  $\text{Cl}^-$  slightly increased the degradation efficiency of RB19 at high concentration. In contrast,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  clearly inhibited RB19 degradation. As the concentration of these ions increased, their inhibitory effects became more pronounced.



$\text{Cl}^-$  reacted with  $\text{SO}_4^{\bullet-}$  and  $\bullet\text{OH}$  radicals to generate other chlorine-containing radicals through Eqs. (11) - (15) [37]. These radicals also possess strong oxidation ability, thereby slightly enhancing the degradation efficiency of RB19.  $\text{SO}_4^{2-}$  can react with  $\bullet\text{OH}$  radicals to form  $\text{SO}_4^{\bullet-}$  according to Eq. (16). Sulfate radicals exhibit oxidation potentials similar to or even higher than those of  $\bullet\text{OH}$ . However, for some organic pollutants,  $\bullet\text{OH}$  show higher reaction rates than  $\text{SO}_4^{\bullet-}$  [39]. Therefore, the conversion of  $\bullet\text{OH}$  into  $\text{SO}_4^{\bullet-}$  in the presence of  $\text{SO}_4^{2-}$  may partially contribute to the slight inhibition observed. In addition, high concentrations of  $\text{SO}_4^{2-}$  may affect

PMS activation and the reaction environment, resulting in a decrease in RB19 degradation efficiency.



At high concentrations,  $\text{CO}_3^{2-}$  can react with  $\cdot\text{OH}$  and  $\text{SO}_4^{\cdot-}$  radicals to generate  $\text{CO}_3^{\cdot-}$  according to Eqs. (17) and (18). Since  $\text{CO}_3^{\cdot-}$  possesses weaker oxidation ability, the amount of effective ROS decreases [19], resulting in lower RB19 degradation efficiency. The presence of  $\text{PO}_4^{3-}$  strongly inhibited RB19 degradation even at low concentrations. This inhibition is due to the reaction between  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{\cdot-}$  radicals, generating  $\text{PO}_4^{\cdot2-}$  radicals with weaker oxidation ability according to Eq. (19) [37]. In addition, phosphate species can coordinate with Fe(III) and may also occupy metal active sites on the catalyst surface, thereby limiting the interaction between PMS and the active sites, and reducing the efficiency of the process [40]. Overall, these results indicate that the effects of inorganic anions on the

CuZnFe-LDH/PMS system are associated not only with ROS scavenging or transformation but also with their interactions with catalyst active sites and PMS activation pathways. These combined effects may account for the different influences of  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  on RB19 degradation.

### 3.4. Applicability of the CuZnFe-LDH/PMS System for the Degradation of Different Textile Dyes

To evaluate the treatment ability of the CuZnFe-LDH/PMS system, degradation experiments were conducted using different dyes, including MO, RB19, R3BS, and BBRF. The concentrations of these dyes were determined by spectrophotometric analysis based on their maximum absorption wavelengths. Specifically, the  $\lambda_{\text{max}}$  values of MO, R3BS, RB19, and BBRF were 460, 525, 590, and 611 nm, respectively. The results are presented in Figure 6(c)-(d). The heterogeneous CuZnFe-LDH/PMS catalytic system was capable of treating various reactive dyes within a short reaction time. The degradation efficiency of the reactive dyes

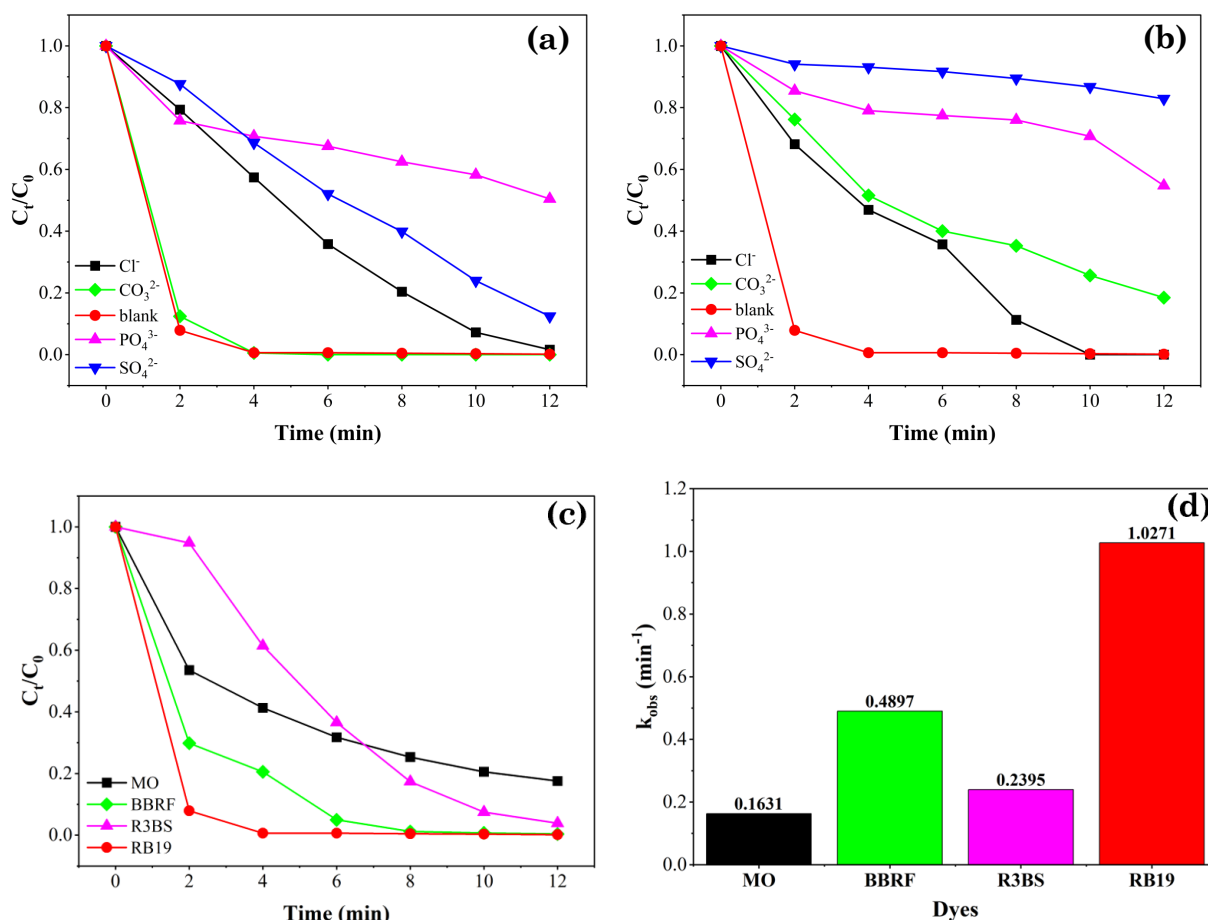


Figure 6. Effects of inorganic anions at concentrations of (a) 5 mM and (b) 20 mM on RB19 degradation kinetics, and the degradation performance of different dyes by the CuZnFe-LDH/PMS system: (c) degradation kinetics and (d) the corresponding  $k_{\text{obs}}$  values (reaction conditions: [dye] = 50 mg/L, [CuZnFe-LDH] = 200 mg/L, [PMS] = 200 mg/L, and pH = 7).

followed the order: RB19 > BBRF > R3BS > MO. The azo dye showed a slightly lower degradation efficiency, reaching 82.21% for MO. The difference in degradation efficiency among these dyes was due to differences in their molecular structures. The structure of azo dyes contains at least one azo bond ( $-N=N-$ ) linking two aromatic rings or organic substituent groups, resulting in lower degradation efficiency than reactive dyes. In addition, the difference is also related to the selectivity of the ROS generated in the CuZnFe-LDH/PMS system. This leads to significant differences in the dye removal performance of the CuZnFe-LDH/PMS system. Nevertheless, the CuZnFe-LDH/PMS catalytic system exhibited versatility in the treatment of different dyes.

As shown in Figure 7(a), the color and COD removal efficiencies for the RB19 solution were relatively low, reaching only 42% and 19.23%, respectively, after 12 min, although the RB19 degradation efficiency exceeded 99% under the same reaction conditions. ROS generated in the CuZnFe-LDH/PMS system effectively degraded the original RB19 molecules; however, the degradation process may also generate

intermediate products that are more resistant to further oxidation and therefore require a longer reaction time for complete mineralization. The residual color after treatment may also be associated with these intermediate products. Therefore, considering the complex composition of wastewater, the performance of the treatment system should not be evaluated solely based on the degradation of a target pollutant, but should also consider additional water quality parameters for a more comprehensive assessment.

To further evaluate the practical applicability of the CuZnFe-LDH/PMS system, real textile wastewater collected from the effluent of the settling tank after biological treatment at the wastewater treatment plant of Gunzetal Co., Ltd. (VSIP II-A Industrial Park, Ho Chi Minh City, Vietnam) was used. As shown in Figure 7(b), COD decreased from 96 mg/L to 51 mg/L, corresponding to a removal efficiency of 46.87%, while color decreased from 75 Pt-Co to 13.33 Pt-Co, achieving a removal efficiency of 82.22%. Interestingly, the COD value dropped rapidly from 96 mg/L to approximately 27 mg/L within 6

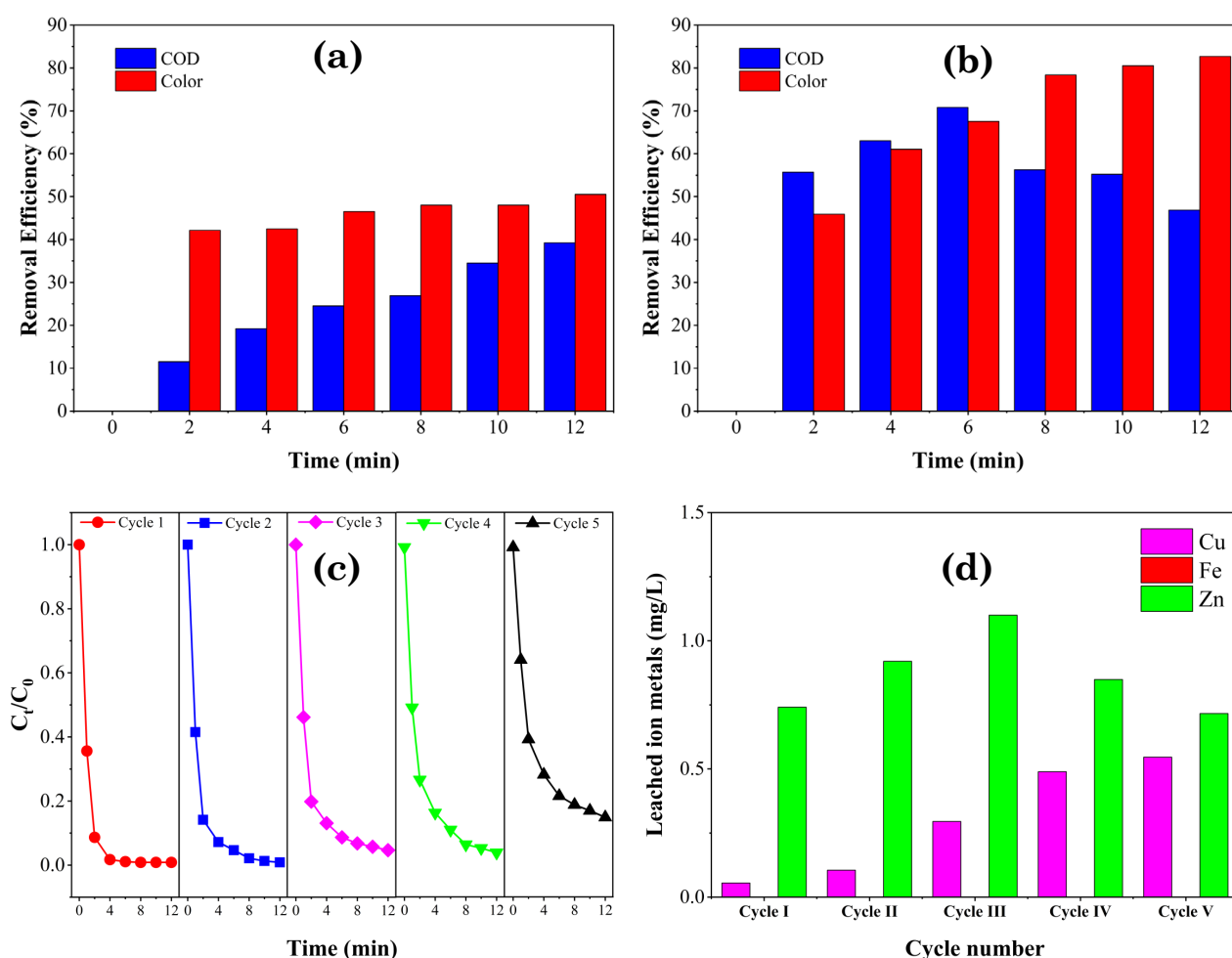


Figure 7. COD and color removal efficiencies of (a) RB19 solution and (b) real textile wastewater by the CuZnFe-LDH/PMS system; (c) RB19 degradation efficiency and (d) leached Fe, Cu, and Zn concentrations after five cycles.

min but subsequently increased to 51 mg/L at 12 min. This COD rebound may be attributed to the complex matrix of the biologically treated textile wastewater, in which oxidative transformation and solubilization of organic matter can alter the measured COD during treatment [41]. Furthermore, although residual PMS was quenched with  $\text{Na}_2\text{SO}_3$  prior to COD analysis, matrix interference affecting the dichromate-based COD determination cannot be completely excluded [42]. Therefore, further investigation, including TOC analysis, is warranted. Notably, the final COD and color values were lower than the corresponding discharge limits specified in Vietnamese National Technical Regulation on Industrial Effluent (QCVN 40:2025/BTNMT, Column A), which are 60 mg/L and 50 Pt-Co, respectively. These results suggest the potential of the CuZnFe-LDH/PMS system for further investigation toward practical applications in textile wastewater treatment. However, to fully evaluate the practical application of the CuZnFe-LDH/PMS system for real textile wastewater, future studies will necessitate a comprehensive characterization of the wastewater matrix, rather than relying exclusively on COD and color indicators.

The application of LDH-based catalytic systems to textile wastewater treatment remains relatively limited. Most previous studies have primarily evaluated the catalytic performance of LDH-based materials for PMS activation using synthetic dye solutions under controlled conditions [12,43,44]. Specifically, CuFe-LDH-based catalysts have also shown promising catalytic performance for the degradation of various dyes [16,45,46]. However, direct reports on the application of CuZnFe-LDH for PMS activation and dye degradation remain scarce, particularly for RB19. Therefore, the present study provides additional evidence for the applicability of the Co-free CuZnFe-LDH/PMS system for the treatment of both synthetic dye solutions and more complex real textile wastewater.

As summarized in Table 1, only a limited number of heterogeneous catalysts have been reported for PMS activation toward RB19 degradation. Notably, the present CuZnFe-LDH/PMS system achieved 99.85% RB19 degradation within 12 min at a relatively high initial RB19 concentration of 50 mg/L, demonstrating its rapid catalytic performance under the investigated conditions. However, further evaluation of residual PMS, sulfate formation, toxicity, and treatment cost, together with direct ROS identification by EPR/ESR and post-reaction catalyst characterization, is required to further clarify the reaction mechanism and assess the practical applicability of the CuZnFe-LDH/PMS system.

### 3.5. Reusability and Stability of CuZnFe-LDH

To evaluate practical application potential, the CuZnFe-LDH catalyst was recovered and reused over five consecutive cycles. As shown in Figure 7(c), the RB19 removal efficiency dropped from 99.85% to 77.22% after five cycles. ICP-OES analysis revealed that Cu and Zn leached into the solution post-reaction, with Cu leaching increasing gradually from 0.055 mg/L to 0.55 mg/L, whereas Zn leaching exhibited an unclear trend. Specifically, Zn leaching spiked at the third cycle and progressively decreased upon further reusability in the fifth cycle. Meanwhile, Fe remained undetected (Figure 7(d)). The decrease in RB19 removal performance can be attributed to: (i) the loss of a portion of active surface sites due to the partial leaching of Cu and Zn, which reduces the catalytic centers responsible for PMS activation, and (ii) site blockage or coverage caused by the accumulation of degradation intermediates or sulfate species [47]. Notably, the absence of detectable Fe leaching suggests that Fe species were relatively stable within the LDH matrix. The Fe(III)/Fe(II) redox cycle has been widely reported to play an important role in PMS activation and the continuous generation of reactive species in Fe-based sulfate radical systems [32,48,49], which may contribute to maintaining the catalytic activity during reuse. Meanwhile, despite the minor leaching of Cu and Zn, these metals may play a synergistic role in PMS activation; thus, their slight loss accounts for the overall 22.63% reduction in RB19 removal efficiency. Overall, CuZnFe-LDH exhibits acceptable stability for relatively good stability and reusability over five consecutive cycles. However, post-reaction characterization using XRD, FTIR, and XPS should be performed to further evaluate possible changes in the crystal structure, surface functional groups, and chemical states of the catalyst, thereby providing a more comprehensive assessment of its structural and chemical stability after repeated use.

### 3.6. Degradation mechanism of RB19 by the CuZnFe-LDH/PMS system

PMS-based catalytic activation processes can generate various ROS, including  $\text{SO}_4^{\bullet-}$ ,  $\bullet\text{OH}$ ,  $\text{O}_2^{\bullet-}$ , and  $^1\text{O}_2$ . In this study, several scavengers at a concentration of 2 mM were used to identify the formation and roles of ROS in the CuZnFe-LDH/PMS system. Specifically, EtOH exhibits high reactivity toward both  $\bullet\text{OH}$  ( $k_{\bullet\text{OH}} = 3.2 \times 10^6 \text{ M}^{-1}\cdot\text{s}^{-1}$ ) and  $\text{SO}_4^{\bullet-}$  ( $k_{\text{SO}_4^{\bullet-}} = 9.7 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$ ). TBA was used to quench  $\bullet\text{OH}$  and  $\text{SO}_4^{\bullet-}$  radicals ( $k_{\bullet\text{OH}} = 3.8 - 7.6 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1}$ ;  $k_{\text{SO}_4^{\bullet-}} = 4.0 - 9.1 \times 10^5 \text{ M}^{-1}\cdot\text{s}^{-1}$ ). p-BQ was used as a scavenger for  $\text{O}_2^{\bullet-}$  ( $k_{\text{O}_2^{\bullet-}} = 0.9 - 1.0 \times 10^9 \text{ M}^{-1}\cdot\text{s}^{-1}$ ), while NA was

employed as a scavenger for  $^1\text{O}_2$  and can also react with  $\bullet\text{OH}$  [37,50]. Among them,  $\text{SO}_4^{\bullet-}$  and  $\text{O}_2^{\bullet-}$  can be generated through PMS activation and subsequent ROS transformation pathways. Singlet oxygen can be generated through the reaction between  $\text{O}_2^{\bullet-}$  and  $\bullet\text{OH}$  or through the recombination of  $\text{O}_2^{\bullet-}$ . The effects of different scavengers on RB19 degradation are shown in Figure 8. The presence of scavengers caused a clear inhibition of catalytic activity. Specifically, after the addition of scavengers, the degradation efficiencies of RB19 followed the order: NA (99.54%) > TBA (96.37%) > p-BQ (79.57%) > EtOH

(75.24%). These results indicate that TBA, p-BQ, and EtOH affected the degradation of RB19 in the CuZnFe-LDH/PMS system. The scavenging experiments preliminarily suggested that  $\text{SO}_4^{\bullet-}$  was the dominant reactive species, while  $\text{O}_2^{\bullet-}$  and  $\bullet\text{OH}$  also contributed to the degradation process. The negligible inhibition observed in the presence of NA suggests that  $^1\text{O}_2$  was not the dominant reactive species under the investigated conditions. Therefore, the quenching results suggested the following apparent order of ROS contributions:  $\text{SO}_4^{\bullet-} > \text{O}_2^{\bullet-} > \bullet\text{OH} \gg ^1\text{O}_2$ .

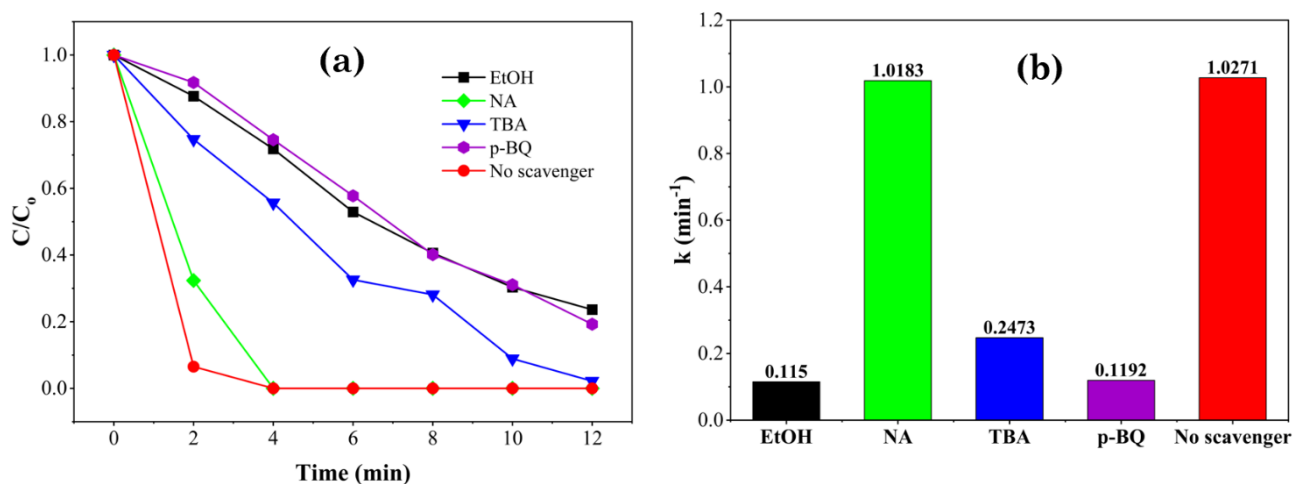


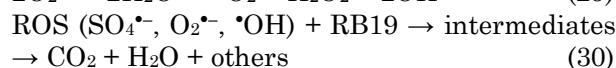
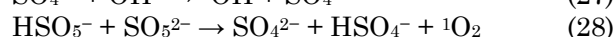
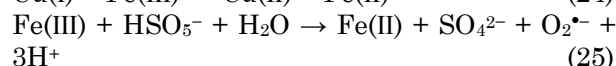
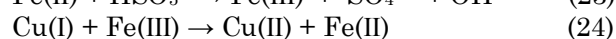
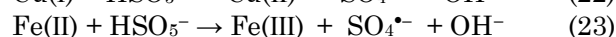
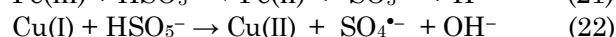
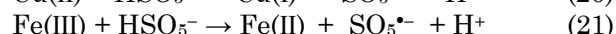
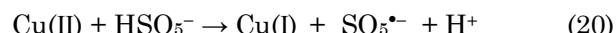
Figure 8. Effect of scavengers on (a) RB19 degradation kinetics and (b) the corresponding  $k_{\text{obs}}$  values in the CuZnFe-LDH/PMS system (reaction conditions: [RB19] = 50 mg/L, [CuZnFe-LDH] = 200 mg/L, [PMS] = 200 mg/L, and pH = 7).

Table 1. Comparison of different catalysts for PMS activation toward RB19 degradation.

| No. | Catalyst                                             | Synthesis method       | Reaction conditions                                                                                               | Removal | Dominant ROS                                                              | Ref.       |
|-----|------------------------------------------------------|------------------------|-------------------------------------------------------------------------------------------------------------------|---------|---------------------------------------------------------------------------|------------|
| 1   | Co-OMS-2                                             | Pre-incorporation      | RB19 = $3.75 \times 10^{-4}$ mmol; PMS = $3.75 \times 10^{-3}$ mmol; catalyst = 5 mg; pH = NR; $t$ = 167 s; 25 °C | 99%     | $\text{SO}_4^{\bullet-}$                                                  | [53]       |
| 2   | CuO–CeO <sub>2</sub>                                 | Hydrothermal           | RB19 = 0.05; mM; PMS = 1.6 mM; catalyst = 0.4 g/L; pH = 7; $t$ = 60 min                                           | 72.84%  | $^1\text{O}_2$                                                            | [54]       |
| 3   | CuO/eggshell                                         | Impregnation           | RB19 = 20 mg/L; PMS = 0.36 mM; catalyst = 0.2 g/L; pH = 7.12; $t$ = 20 min                                        | ~100%   | $^1\text{O}_2$                                                            | [55]       |
| 4   | CuFe <sub>2</sub> O <sub>4</sub> /kaolin-CTS-Laccase | One-step solvothermal  | RB19 = 20 mg/L; PMS = 0.1 g/L; catalyst = 0.4 g/L; pH = 5; $t$ = 90 min; 35 °C                                    | 98.40%  | $\text{O}_2^{\bullet-}$ (major) and $^1\text{O}_2$                        | [56]       |
| 5   | PCBs-CuO                                             | Leaching–precipitation | RB19 = 20 mg/L; PMS = 0.5 mM; catalyst = 0.2 g/L; pH = 6.82; $t$ = 15 min; 25 °C                                  | 100%    | $^1\text{O}_2$ and $\bullet\text{OH}$                                     | [57]       |
| 6   | CuZnFe-LDH                                           | Solvothermal           | RB19 = 50 mg/L; PMS = 200 mg/L; catalyst = 200 mg/L; pH = 7; $t$ = 12 min;                                        | 99.85%  | $\text{SO}_4^{\bullet-}$ , $\text{O}_2^{\bullet-}$ and $\bullet\text{OH}$ | This study |

The quenching experiments in this study provide indirect evidence for ROS involvement, as scavengers may have limited selectivity and can also interact with other components in the reaction system. However, based on the remarkable decrease in RB19 degradation in the presence of scavengers, the reaction mechanism for PMS activation by the CuZnFe-LDH catalyst to degrade RB19 is proposed as shown in Figure 9. At pH of 7, PMS mainly exists as  $\text{HSO}_5^-$ , while partial deprotonation to  $\text{SO}_5^{2-}$  may occur under alkaline conditions.  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  can react with  $\text{HSO}_5^-$  to form  $\text{SO}_5^{\bullet-}$  and the corresponding reduced metal species (Eqs. (20) and (21)), whereas  $\text{Cu}^+$  and  $\text{Fe}^{2+}$  can activate  $\text{HSO}_5^-$  to generate  $\text{SO}_4^{\bullet-}$  and regenerate  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  (Eqs. (22) and (23)). In addition,  $\text{Cu}^+$  may reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (Eq. (24)), facilitating electron transfer between Cu and Fe sites and the regeneration of  $\text{Fe}^{2+}$  during PMS activation [16]. The  $\text{Fe}^{3+}/\text{Fe}^{2+}$  cycle may also contribute to the formation of  $\text{O}_2^{\bullet-}$  through the reaction of  $\text{Fe}^{3+}$  with  $\text{HSO}_5^-$  and  $\text{H}_2\text{O}$  (Eq. (25)) [51]. The generated  $\text{SO}_4^{\bullet-}$  can further react with  $\text{H}_2\text{O}$  or  $\text{OH}^-$  to form  $\bullet\text{OH}$  (Eqs. (26) and (27)). Thus, the redox cycling of Cu and Fe may contribute to the simultaneous generation of  $\text{SO}_4^{\bullet-}$ ,  $\text{O}_2^{\bullet-}$ , and  $\bullet\text{OH}$  in the CuZnFe-LDH/PMS system. Besides,  $\text{Zn}^{2+}$  may mainly contribute to maintaining the LDH framework and modifying the local chemical environment surrounding the Cu and Fe active sites. A similar role of Zn-containing hydroxide moieties in regulating the local reaction environment has been reported for ZnFe-LDH/PMS systems [52].

In addition to these radical pathways, the interaction between  $\text{HSO}_5^-$  and  $\text{SO}_5^{2-}$  may contribute to the formation of  $^1\text{O}_2$  (Eq. (28)).  $\text{O}_2^{\bullet-}$  may also participate in subsequent reactions leading to  $^1\text{O}_2$  formation (Eq. (29)). Based on the quenching results,  $\text{SO}_4^{\bullet-}$  appeared to make the greatest contribution to RB19 degradation, while  $\text{O}_2^{\bullet-}$  and  $\bullet\text{OH}$  participated in the reaction. These ROS participated in the oxidation of RB19, leading to dye decomposition and partial mineralization, as represented in Eq. (30), thereby significantly reducing the RB19 concentration and color in water.



In summary, the  $\text{Cu}^{2+}/\text{Cu}^+$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couples may cooperatively facilitate electron transfer and PMS activation, leading to the formation of  $\text{SO}_4^{\bullet-}$ ,  $\text{O}_2^{\bullet-}$ ,  $\bullet\text{OH}$ , while  $\text{Zn}^{2+}$  mainly contributes to the LDH framework and local surface environment. Nevertheless, the proposed mechanism is mainly based on the quenching experiments and XPS characterization of the fresh catalyst. Further EPR/ESR analysis and post-reaction XPS characterization are therefore required to directly identify the reactive species and verify the proposed changes in the oxidation states of Cu and Fe during PMS activation.

#### 4. Conclusions

CuZnFe-LDH was successfully synthesized by the solvothermal method and exhibited several characteristic properties consistent with the LDH structure. The CuZnFe-LDH/PMS system showed high efficiency in RB19 degradation. Under the selected operating conditions of  $[\text{RB19}] = 50 \text{ mg/L}$ ,  $[\text{catalyst}] = 200 \text{ mg/L}$ ,  $\text{pH} = 7$ , and  $[\text{PMS}] = 200 \text{ mg/L}$ , a degradation efficiency of 99.85% was achieved within 12 min. The presence of anions such as  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  at a concentration of 20 mM negatively affected the RB19 degradation efficiency of the system. Notably, the catalytic system was capable of treating different types of dyes and showed potential for the degradation of color and organic matter in real textile

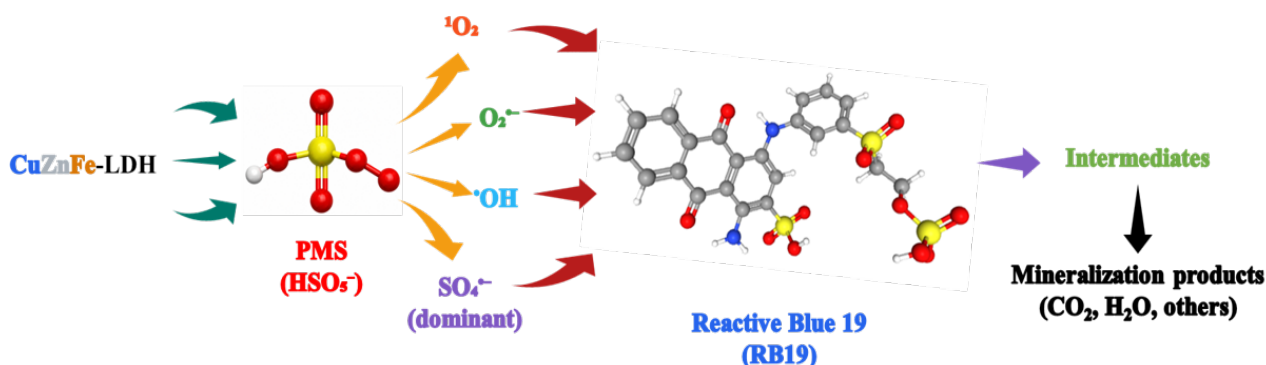


Figure 9. Proposed mechanism for RB19 degradation by the CuZnFe-LDH/PMS system.

wastewater, yielding positive results in color and COD removal. The quenching results suggested that  $\text{SO}_4^{\bullet-}$  was the dominant reactive species, while  $\text{O}_2^{\bullet-}$  and  $\cdot\text{OH}$  also contributed to RB19 degradation. However, the lack of EPR/ESR analysis and post-reaction catalyst characterization limits the direct identification of reactive species and further assessment of catalyst stability, while detailed mineralization and transformation pathways remain to be elucidated. Future studies should address these limitations through advanced mass spectrometric analyses, together with further evaluation of the economic feasibility and applicability to other emerging organic pollutants. Overall, these findings demonstrate the potential of Co-free trimetallic LDH materials as effective catalysts for PMS activation and dye degradation in aqueous systems.

### Acknowledgment

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Author Contributions: Tran Minh Bao: Funding Acquisition, Methodology, Writing – Original Draft Preparation; Nguyen Hoang Hung: Investigation, Formal Analysis; Pham Xuan Truong: Investigation; Nguyen Thi Cam Tien: Writing – Original Draft Preparation, Data Curation, Formal Analysis; Nguyen Huynh Nghia: Investigation; Le Ngan Phuc Tam: Investigation; Tran Vu Anh Khoa: Investigation; Nguyen Thanh Minh: Investigation, Data Curation; Nguyen Nhat Huy: Conceptualization, Methodology, Supervision, Writing – Review and Editing. All authors have read and agreed to the published version of the manuscript.

### Use of Generative AI and AI-assisted Technologies

The authors confirm that AI-assisted technologies were used only to improve the readability and English language of the manuscript

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