

SYNTHESIS AND APPLICATION OF CuS/MnS COMPOSITE CATALYST IN SYNTHETIC DYE REMOVAL BY PERSULFATE/PERIODATE ACTIVATION

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Abstract

Water pollution from organic dyes requires efficient catalytic systems for advanced oxidation processes (AOPs). The incorporation of transition metals into composite materials offers superior catalytic synergy. In this study, CuS/MnS composite catalysts were synthesized via a simple co-precipitation method at room temperature. Physicochemical characteristics were analyzed using FTIR, XRD, zeta potential, EDS, SEM, and BET methods. Catalytic performance was evaluated by its ability to remove Congo red (CR) and methylene blue (MB) dyes under periodate or persulfate activation, combined with free radical scavenging experiments to clarify the mechanism. The results showed that the optimal CuS/MnS (3:1) possessed a mesoporous structure, a specific surface area of 11.80 m²/g, and a negative charge (-20.5 mV). The material exhibited high CR decolorization performance (over 94%) and notable MB treatment ability (up to 97%), with periodate activation showing slightly better results than persulfate. The reaction mechanism confirmed that surface metal ions are essential active sites for catalytic cleavage. The decolorization process was flexible depending on the nature of the dye and the catalyst. Free radicals were the primary oxidizing agents that broke down the CR structure, while the catalytic system simultaneously generated both free radicals and singlet oxygen in the case of MB. This confirms the material's potential in practical wastewater treatment.

Keywords: CuS/MnS composite catalyst, Dye degradation, periodate activation, persulfate activation, reactive oxygen species, synthetic dye removal.

1. Introduction

Water pollution from synthetic dyes is a serious environmental problem, stemming from the textile dyeing, printing, and chemical manufacturing industries. Wastewater containing dyes is often intensely colored, highly toxic, and difficult to treat (Kolya & Kang, 2024; Liu et al., 2024). When discharged into the environment, it reduces water transparency and affects aquatic ecosystems. Many dyes have stable structures, are difficult to biodegrade, and can produce toxic byproducts. Traditional treatment methods such as adsorption, coagulation-flocculation, membrane filtration, and biological treatment have been widely applied. However, these methods are not completely effective. Adsorption and membrane filtration only transfer pollutants to another phase, generating secondary waste. Biological treatment is often ineffective with persistent organic compounds. Coagulation processes generate more sludge and require additional chemicals. Therefore, these methods are limited in their ability to completely decompose organic pollutants, which require more efficient treatment technologies. (Nguyen & Do, 2026)

In recent years, AOPs based on persulfate or periodate activation have attracted attention as an effective solution for the complete degradation of dyes. Unlike traditional methods, these systems can mineralize pollutants into CO_2 , H_2O , and inorganic ions. The process often uses transition metal catalysts such as Fe, Co, Cu, or Mn to activate persulfate ($\text{S}_2\text{O}_8^{2-}$) or periodate (IO_4^-) (Ahn & Yun, 2019; Kang et al., 2025). Under the action of the catalyst, these oxidizers are cleaved to produce strong free radicals such as $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, or other oxidizing species. Moreover, some systems also form non-radical agents such as singlet oxygen ($^1\text{O}_2$), which increases treatment efficiency. These active species can attack and break down the stable structure of dyes, especially azo bonds or aromatic rings. As a result, complex organic compounds are broken down into smaller molecules and eventually completely mineralized. The efficiency of the process depends on the catalyst, reaction conditions, and the nature of the pollutant. Therefore, the development of efficient catalytic materials remains an important research direction. (Pattnaik et al., 2025; Zhang et al., 2024)

Transition metal catalytic systems such as Fe, Co, Mn, and Cu are highly effective in enhancing AOPs. Review studies show that iron-based catalysts are among the most investigated due to their ability to promote the $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycle and generate strong $\text{SO}_4^{\bullet-}$ radicals (Zhi et al., 2021). In addition, magnetic materials, metal oxides, and modified carbon materials are widely used to improve catalyst performance and reusability (Tian et al., 2022). Some experimental studies have demonstrated high efficiency in dye degradation using hybrid metal oxide systems, achieving yields above 90% in a short time (Anushree et al., 2021). Furthermore, advanced materials such as MXene or functionalized capillary silica also demonstrate the ability to effectively and stably activate persulfate (Li et al., 2024). Mechanistically, studies indicate that degradation can occur via both free- and non-radical pathways, including the formation of $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, and $^1\text{O}_2$ (Tian et al., 2022). For periodate, studies also show it generates similar oxidizing species under activation by transition metals (Wang et al., 2021; Xiong et al., 2024).

Although many transition metal catalysts have been studied for the activation of persulfate or periodate, dual sulfide materials have not been fully exploited. Some studies have shown that CuS is capable of efficient persulfate activation due to the flexible

$\text{Cu}^+/\text{Cu}^{2+}$ cycle, while MnS can promote electron transfer and create strong oxidizing species (Huang & Zhang, 2019; Zhu et al., 2020). However, most works have focused on individual phases, and there has been little direct comparison between the two oxidizing systems. In this study, CuS/MnS composite catalysts were synthesized with various ratios to utilize the mutually enhancing effect between the two metals. This combination is expected to improve electron transfer, increase the catalytically active sites, and promote the generation of free- and non-radical species (Tang et al., 2023). Specifically, the catalyst was used to simultaneously activate both persulfate and periodate under the same conditions, thereby allowing for direct evaluation and comparison of the performance of the two oxidation systems. This approach has been limited in previous studies. Therefore, this work provides a novel catalytic material and contributes to comparing the relative efficiency between the two enhanced oxidation processes.

2. Materials and methods

2.1. Materials

Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\geq 99\%$), manganese (II) sulfate monohydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 98%), polyethylene glycol (PEG-400, $M_n = 400$ g/mol, industrial product), sodium sulfide nonahydrate ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, $\geq 98\%$), methylene blue trihydrate (indicator, 98.5%), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\geq 98\%$), potassium periodate (KIO_4 , $\geq 99\%$), isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$, 99.7%), and ethylenediaminetetraacetic acid ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, $>99.5\%$) were provided by Xilong Scientific. Congo red dye (indicator) was bought from Himedia Labs. Sodium azide (NaN_3 , $\geq 99\%$) was from Thermo Fisher Scientific.

2.2. Methods

2.2.1. Catalyst preparation

Certain masses of two salts, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, with molar ratios of Cu:Mn of 1:0, 3:1, 1:1, 1:3, and 0:1, respectively, were added to a 500 mL beaker containing 450 mL of distilled water. Next, 1.0 mL of PEG-400 was added to the beaker, and the mixture was stirred vigorously at 400 rpm for 30 min to dissolve the substances. Then, 50 mL of a solution containing an excess of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ was slowly added to the mixture while it was still stirred vigorously. A black precipitate is present in the solution as sulfide ions are added. After adding the 50 mL of the solution, the mixture in the beaker was stirred vigorously for another 1 h. The solid product was then vacuum-filtered, washed with distilled water and alcohol, and then dried at 70 °C for 24 h. Products at different initial ratios are denoted as 1:0, 3:1, 1:1, 1:3, and 0:1, respectively.

2.2.2. Adsorption experiment

In this experiment, two dyes were used: CR and MB. CR dye was prepared at concentrations of 20 mg/L and 40 mg/L, while MB dye was prepared at a concentration of 10 mg/L. 0.04 g of the catalyst at different ratios was added to a 250 mL beaker containing 150 mL of dye solution under unmodified pH and room temperature. The mixture in the beaker was then stirred at 250 rpm for 120 min. Next, 5.0 mL of the mixture was transferred to a 15 mL test tube and centrifuged at 6000 rpm for 6 min to allow the solid catalyst to settle. The supernatant was measured for absorbance at wavelengths of 497 nm (CR) and 664 nm (MB). Each adsorption experiment was conducted in triplicate. The concentration of the remaining dye in the solution after adsorption was determined using the calibration curve of the CR or MB solution. The adsorption efficiency was calculated using the following formula:

$$R\% = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \quad (1)$$

Where $R\%$ is the dye removal rate (%), C_t is the dye concentration at time t (mg/L), and C_0 is the initial dye concentration (mg/L).

2.2.3. Dye decolorization experiment

In this experiment, the dyes used were still CR and MB. CR dye was prepared at concentrations of 40 mg/L, 80 mg/L, and 120 mg/L, while MB dye was prepared at a concentration of 20 mg/L. Similarly, 150 mL of dye solution was placed in a 250 mL beaker and stirred at 250 rpm. Next, 0.04 g of catalyst and 0.02 g of ammonium persulfate or potassium periodate were added to the beaker, and the mixture was stirred for 30 min under unmodified pH and room temperature. Then, 5.0 mL of the mixture in the beaker was transferred to a 15 mL test tube and centrifuged at 6000 rpm for 6 min. The absorbance of the supernatant was measured at the wavelength above. Each decolorization experiment were conducted in triplicate. The concentration of the remaining dye solution was also calculated from the calibration curve, and the dye decolorization efficiency was calculated from equation 1.

2.2.4. Trapping test

In this experiment, the dyes used were CR 120 mg/L and MB 20 mg/L. The procedure was similar to the dye decolorization experiment, but scavengers (1.5 mmol) were added to the reaction mixture simultaneously with the catalyst. The scavengers used were isopropyl alcohol (IPA), sodium azide (NaN_3), and ethylenediaminetetraacetic acid (EDTA). These scavengers are substances that capture the active agents, namely free radicals, singlet oxygen, and copper ions on the material surface, respectively. If the dye decolorization efficiency with scavengers is lower than without them, then the corresponding reactive species plays the main role in dye decolorization.

2.2.5. Materials characterization

FTIR spectra were measured on a Frontier FT-IR/NIR instrument with 20 scans, a wavenumber range of 4000–400 cm^{-1} , a resolution of 4 cm^{-1} , and 3601 points. XRD patterns were measured on an Empyrean instrument with $\text{Cu-K}\alpha_1$ of 1.540598 Å and $\text{K}\alpha_2$ of 1.544426 Å, a 2θ range of 5.0–80°, a scan step size of 0.0262606, and 2857 points. Zeta potential was measured on a Horiba SZ-100 instrument at a temperature of 24.8 °C, a water medium viscosity of 0.899 mPa·s, and an electrode voltage of 3.3 V under unmodified pH or ionic strength. EDS spectra were measured under conditions where the material was coated with a thin layer of Pt, an electron beam potential of 15.0 kV, and 2048 points. The materials' surface area and pore size were identified by nitrogen gas adsorption-desorption analysis using a Quantachrome analyzer, with a sample mass of 0.0403 g, an analysis gas of N_2 , a bath temperature of 77.3 K, and an outgas temperature of 150.0 °C.

3. Results and Discussion

3.1. Materials characterization

The FTIR spectrum of the 3:1CuS/MnS catalyst shows characteristic absorption peaks of the material. Specifically, the broad band at $\sim 3400 \text{ cm}^{-1}$ and the peak at $\sim 1600 \text{ cm}^{-1}$ are the stretching and bending vibrations of the O-H bonds of adsorbed water molecules on the surface, respectively. The clear signal at $\sim 1100 \text{ cm}^{-1}$ originates from the stretching

vibration of the S-O bonds, reflecting the presence of residual sulfate (SO_4^{2-}) from precursor salts or due to mild oxidation. Notably, the strong absorption band in the $\sim 600 \text{ cm}^{-1}$ region confirms the formation of metal-sulfur bonds (Cu-S and Mn-S). This analysis is in agreement with the results in (Nachimuthu et al., 2022), which synthesized the NiS/CuS, in which the stretching of the M-S bonds was also clearly defined at a wavenumber of $\sim 600 \text{ cm}^{-1}$.

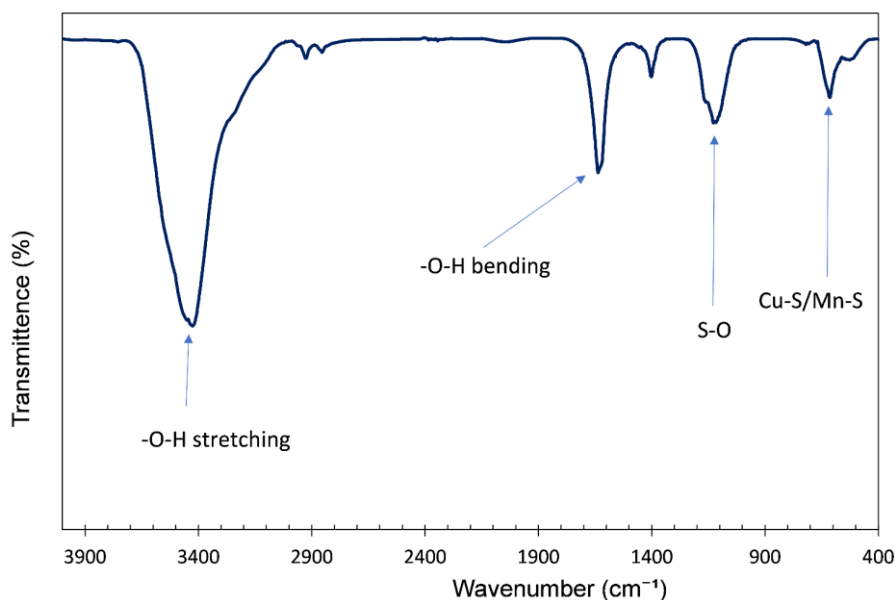


Figure 1. FTIR spectrum of 3:1CuS/MnS catalyst

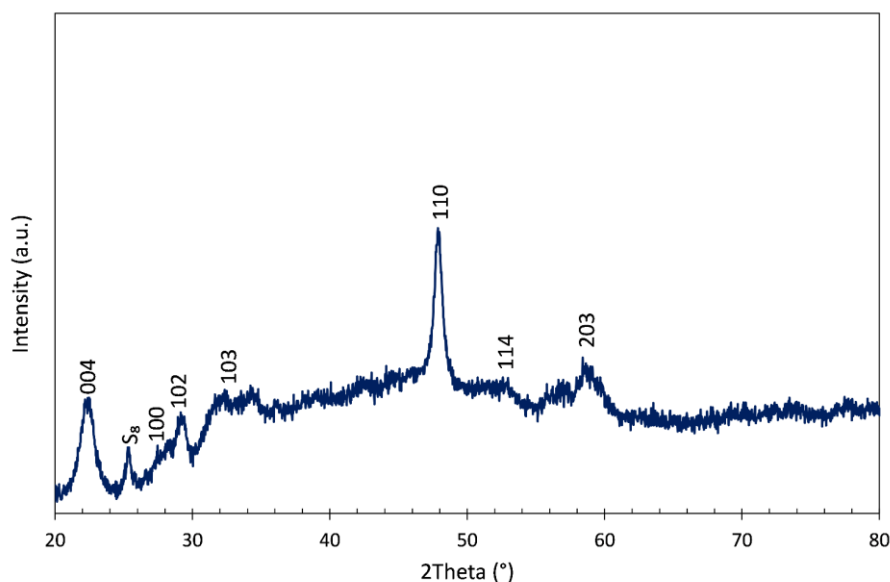


Figure 2. XRD pattern of 3:1CuS/MnS catalyst

The XRD pattern of 3:1CuS/MnS shows diffraction characteristics belonging to the covellite CuS crystalline phase. The 2θ positions at 22° , 28° , 29° , 32° , 48° , and 59° correspond precisely to the (004), (100), (102), (103), (110), and (203) lattice planes of this phase, respectively. The high and extended background from 20° to 40° confirms the presence of the amorphous MnS phase, interbedded with a small amount of elemental

sulfur (S₈) at 25°. The interwoven structure of the CuS nanocrystalline and the amorphous MnS background is quite similar to that of (Riyaz et al., 2016). Furthermore, the broad peaks of CuS are directly demonstrated for small particle sizes and the fast precipitation at room temperature.

The zeta potential results in neutral water showed that the surfaces of both CuS (1:0) and CuS/MnS (3:1) catalysts were negatively charged, with values of -22.6 mV and -20.5 mV, respectively. Under the same conditions, MB molecules exhibited a large negative potential (-48.9 mV), resulting in strong electrostatic repulsion between MB and the catalyst surface. In contrast, Congo Red (CR) had a zeta potential of only -0.9 mV (almost neutral), significantly reducing this electrostatic repulsion barrier. As a result, instead of being repelled like MB, CR molecules more easily approach the material surface and are effectively adsorbed through other interactions (such as hydrogen bonding or π - π interactions). The adsorption mechanism is less efficient with MB and preferentially surface-selective with CR due to this electrostatic repulsion difference, which is consistent with the adsorption of ionic dyes from aqueous solutions (Lu et al., 2023).

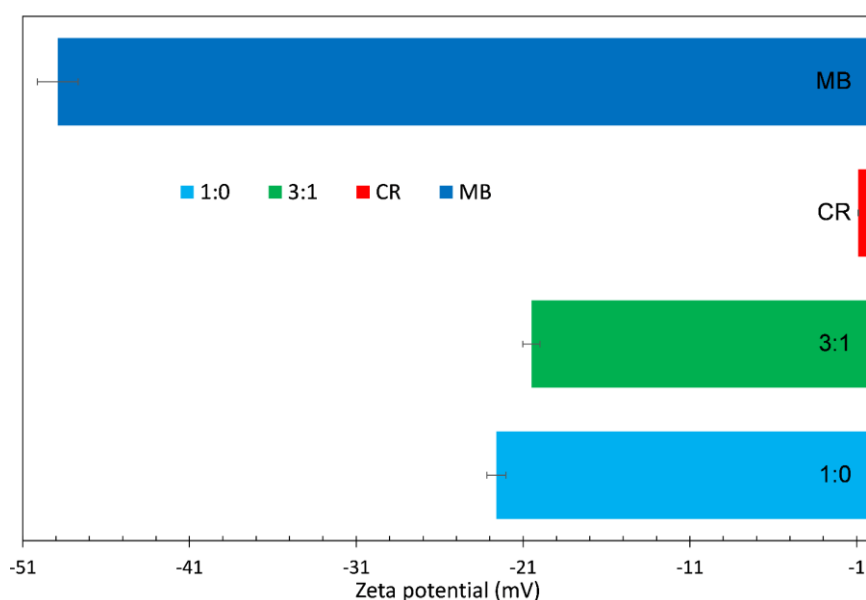


Figure 3. Zeta potential of catalyst 1:0, 3:1 and the dye CR, MB

Table 1. Elemental composition of 3:1CuS/MnS catalyst

Element	Line type	Weight (%)	Atomic (%)
O	K series	9.46	24.45
S	K series	23.58	30.42
Mn	K series	14.11	11.37
Cu	L series	51.86	33.76
Total		100	100

Energy dispersive X-ray spectroscopy (EDS) analysis confirmed the presence of four key elements constituting the catalyst sample: Cu, Mn, S, and O. Specifically, based on atomic percentages, the ratio between copper (33.76%) and manganese (11.37%) was approximately 2.97:1. This value perfectly matched the initial pre-mixing ratio (Cu:Mn

= 3:1), demonstrating that the co-precipitation process to create the CuS/MnS composite was uniform and well-controlled. The abundant sulfur (30.42%) confirmed the successful sulfidation process. Furthermore, the oxygen (24.45%) was mainly due to the material's surface adsorption of moisture and atmospheric oxygen, which is consistent with the previous FTIR analysis results.

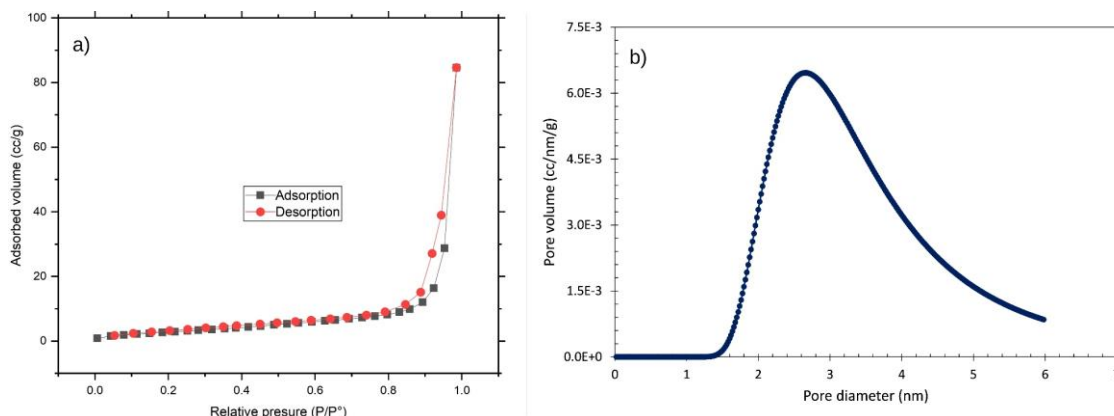


Figure 4. N_2 adsorption-desorption isotherm (a) and DA pore size distribution (b) of 3:1CuS/MnS catalyst

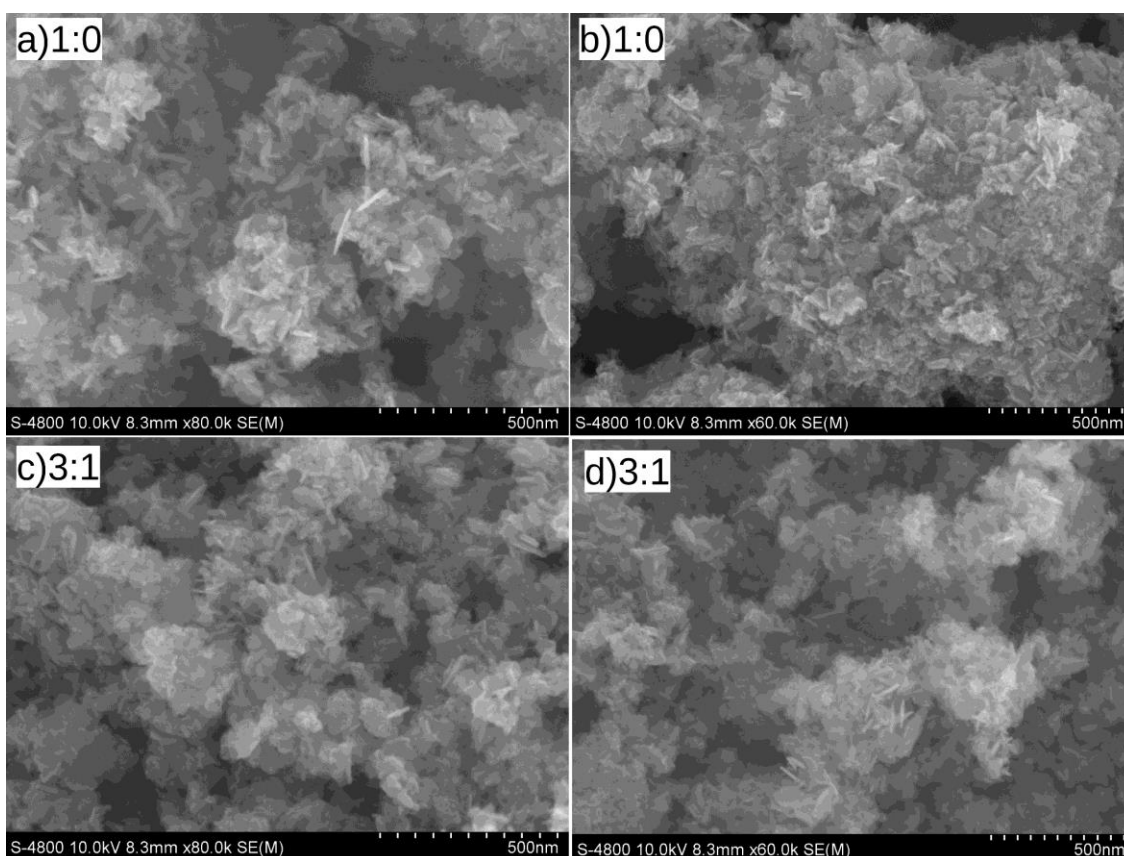


Figure 5. SEM images of 1:0 sample (a, b) and 3:1 sample (c, d)

The N_2 adsorption-desorption isotherm (Figure 4a) shows a Type IV curve with a narrow hysteresis loop. This indicates the material has a mesoporous structure with a BET specific surface area of $11.80 \text{ m}^2/\text{g}$. This hysteresis loop is characteristic of a slit-like pore system, formed from the natural aggregation of catalytic nanocrystals. The pore size

distribution graph using the DA method (Figure 4b) confirms this characteristic with a distinct pore peak at 2.66 nm. This mesoporous structure, combined with the favorable specific surface area, creates favorable diffusion channels. This allows dye molecules to penetrate deep inside to contact the active sites. These isotherm and pore classification assessments are consistent with the IUPAC standard system (Thommes et al., 2015).

SEM images of sample 1:0 clearly reveal the highly aggregated nanoparticle morphology. The small crystals interlock and adhere tightly to each other, forming rough, large masses. This aggregation stems from the rapid precipitation kinetics at room temperature. For the 3:1 sample, the overall matrix structure remained virtually unchanged. The amorphous MnS phase was dispersed and adhered evenly to the CuS particle network. This visual observation is consistent with the amorphous matrix on the XRD pattern. Furthermore, the interlocked aggregation of the particle masses generated numerous microcracks. This theoretical basis directly explains the formation of the grooved mesoporous system. The specific surface area of 11.80 m²/g measured by BET also originates from this structural roughness. The porous, rough surface combined with a negative charge creates an ideal spatial network for trapping the CR dye. This aggregated morphological characteristic of the composite system is also consistent with the observations of (Heiba et al., 2021).

3.2. Persulfate/periodate activation-induced dye decolorization

As shown in Figure 6a, CR concentration of 20 mg/L, the adsorption efficiency reached its maximum at the 1:1 composite (61.1%), significantly outperforming the pure phases 1:0 (57.5%) and 0:1 (36.1%). For CR concentration of 40 mg/L (Figure 6b), the removal rates gradually decreased due to the saturation of the surface-active sites. However, at this high concentration, the 3:1 sample showed the advantage, exhibiting the best adsorption capacity at 42.0%. This result confirms that the combination of CuS and MnS possesses a combined effect, optimizing the porous structure and enhancing adsorption capacity.

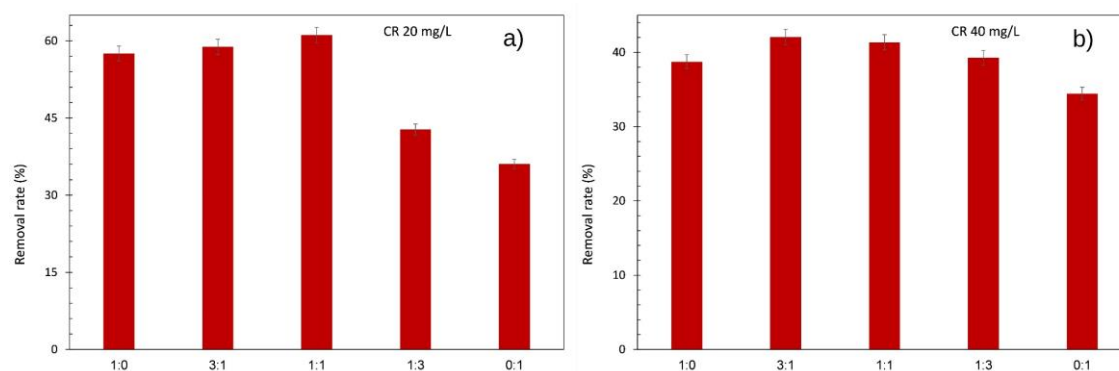
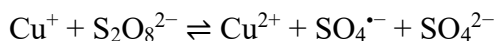


Figure 6. CR adsorptions on the catalysts at initial CR concentration of 20 mg/L (a) and 40 mg/L (b)

Figure 7a–c illustrates the CR decolorization efficiency through periodate activation, where the 3:1 composite sample consistently achieved the highest efficiency (96.2–97.1%) at all dye concentrations. This result outperformed the pure phases of 1:0 and especially 0:1, demonstrating a catalytic complementary effect between the two metal components. Notably, when the CR concentration increased to very high levels (120 mg/L), the efficiency of the 3:1 sample remained stable (97.1%). Meanwhile, the samples containing more Mn (1:3 and 0:1) showed a significant decrease in activation capacity. This good decolorization is directly related to the rough aggregate structure and

mesoporous system, as confirmed by SEM and BET analysis. This porous structure and favorable surface area not only help to trap dyes effectively but also provide numerous surface-active sites for contact and cleavage of periodate molecules into oxidizing species. The redox cycles of $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Mn}^{2+}/\text{Mn}^{3+}$ combined with periodate/persulfate caused generation of reactive oxygen species (ROS):

For persulfate activation:



For periodate activation:



Interactive redox cycle regenerating the active sites:

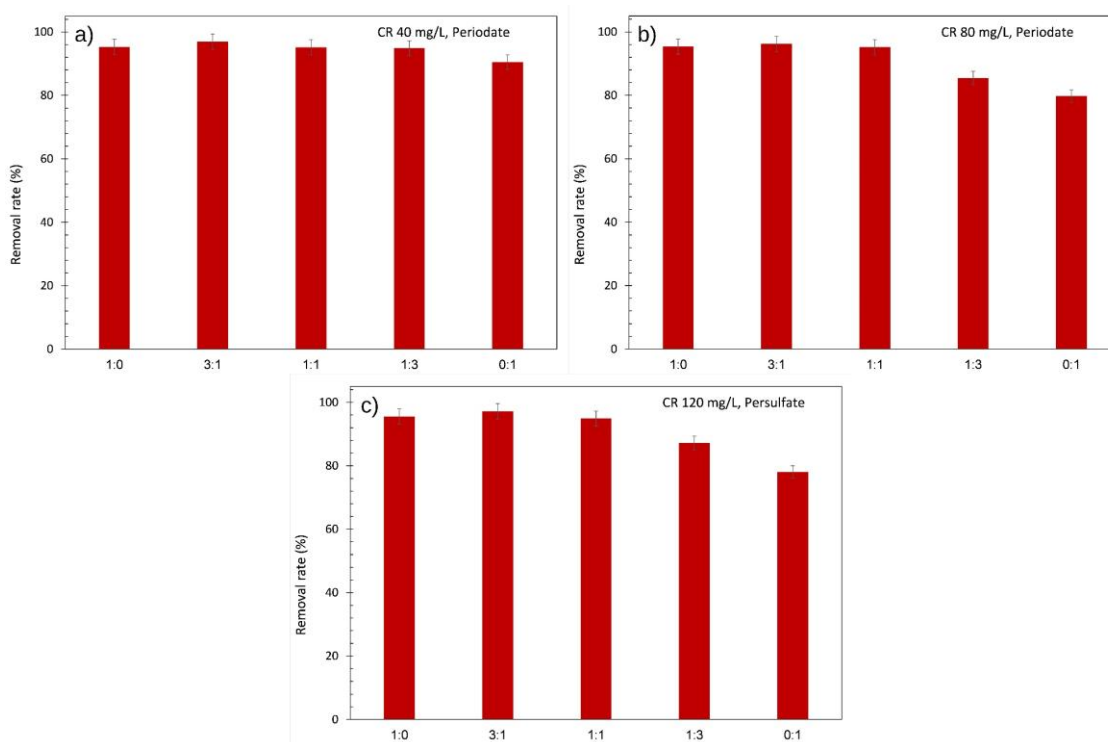
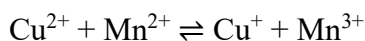


Figure 7. Periodate activation-induced CR decolorizations by the catalysts at initial CR concentration of 40 mg/L (a), 80 mg/L (b), and 120 mg/L (c)

Figure 8a-c shows that the CR decolorization via persulfate activation tends to be similar to the periodate system, where copper-rich samples (1:0 and 3:1) continue to outperform manganese-rich samples. In particular, the 3:1 maintained superior stability as CR concentrations increased (reaching 97.7% at 80 mg/L and 94.6% at 120 mg/L). The catalytic activity in this work outperforms the similar catalyst (1:1 molar ratio) in the work (Zhou et al., 2021); under their experimental conditions of 15 mg catalyst, 50 mL Orange II at a concentration of 70 mg/L, and 0.1 g persulfate, the degradation efficiency was 98.2% in 120 min. When comparing the two systems, the CR decolorization by

persulfate was generally slightly lower than that of periodate under the same experimental conditions (especially Mn-rich samples). This difference indicates that the active sites on the porous surface react more readily, thereby breaking down periodate molecules into strong oxidizing species more easily and efficiently than persulfate.

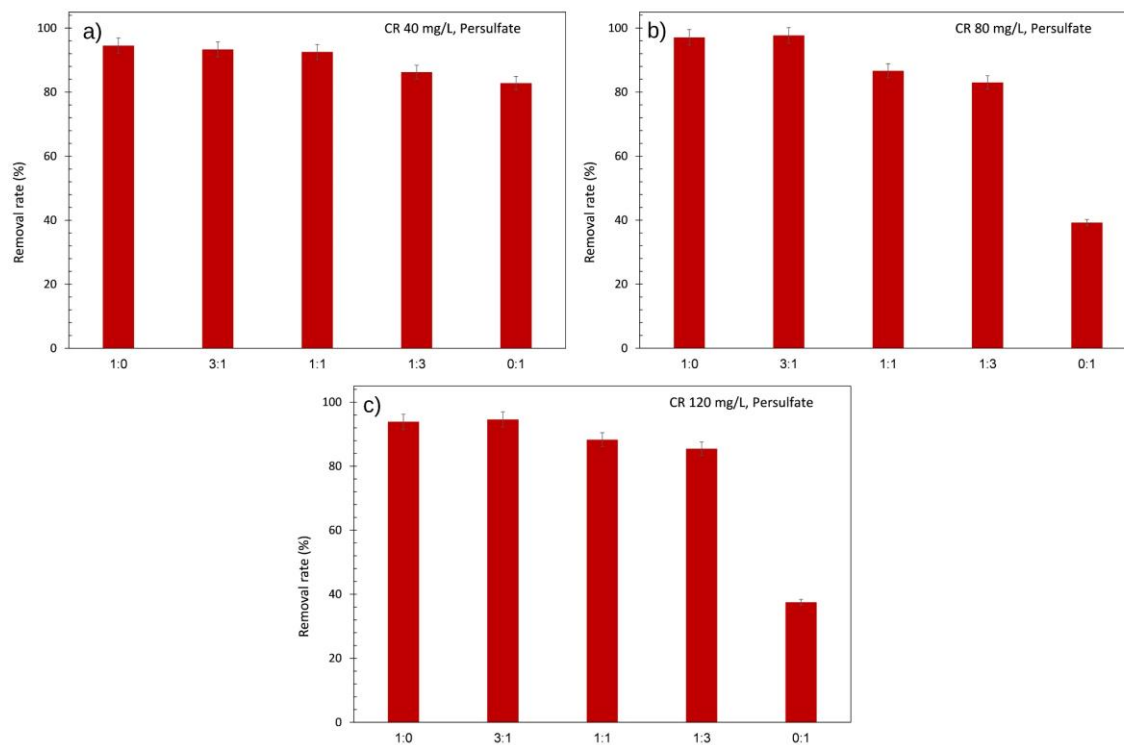


Figure 8. Persulfate activation-induced CR decolorizations by the catalysts at initial CR concentration of 40 mg/L (a), 80 mg/L (b), and 120 mg/L (c)

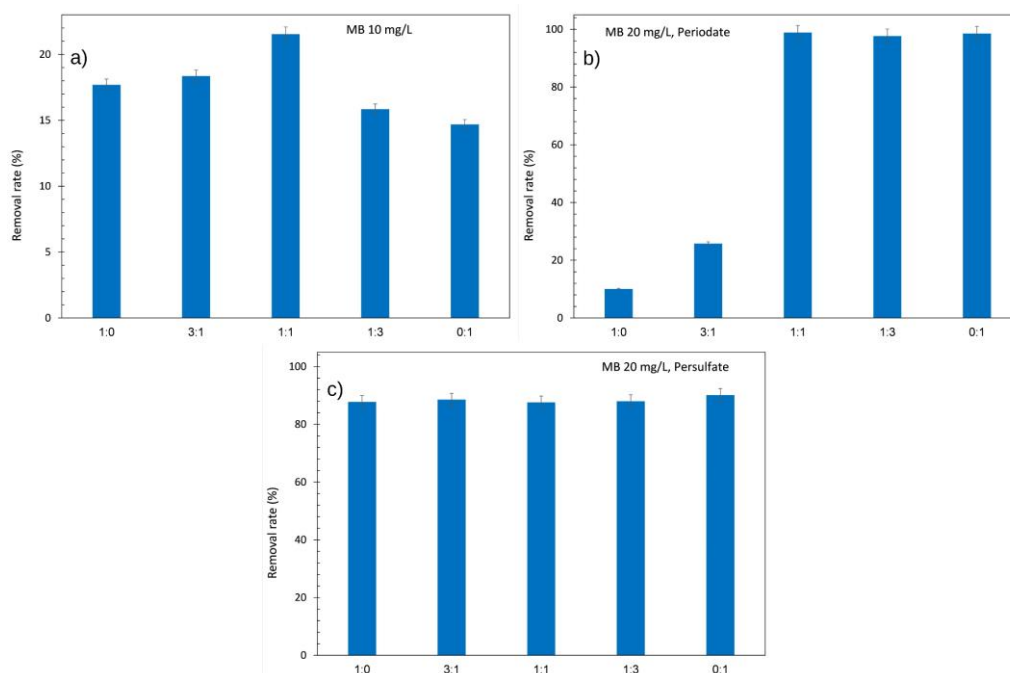


Figure 9. MB adsorptions (a) and periodate activation-(b) and persulfate activation-(c) induced MB decolorizations by the catalysts

As shown in Figure 9a, the MB adsorption efficiency of all catalyst samples was very low (ranging from only 14.7% to 21.5%), significantly lower than that of CR adsorption. This result clearly demonstrates the electrostatic repulsion barrier between MB molecules and the negatively charged catalyst surface, as analyzed in the zeta potential section. However, for the periodate activation process (Figure 9b), a completely reversed catalytic trend compared to the CR system emerged. This time, manganese-rich samples (1:1, 1:3, and 0:1) exhibited superior MB decolorization rates (over 97%), while copper-rich samples performed poorly. For the persulfate activation system (Figure 9c), MB treatment efficiency was more uniform and stable across all material ratios, maintaining at 87–90%. The strong contrast between the two dyes demonstrates that the MnS-based catalytic sites generate highly reactive species under periodate activation, making them suitable for breaking down the specific structure of MB.

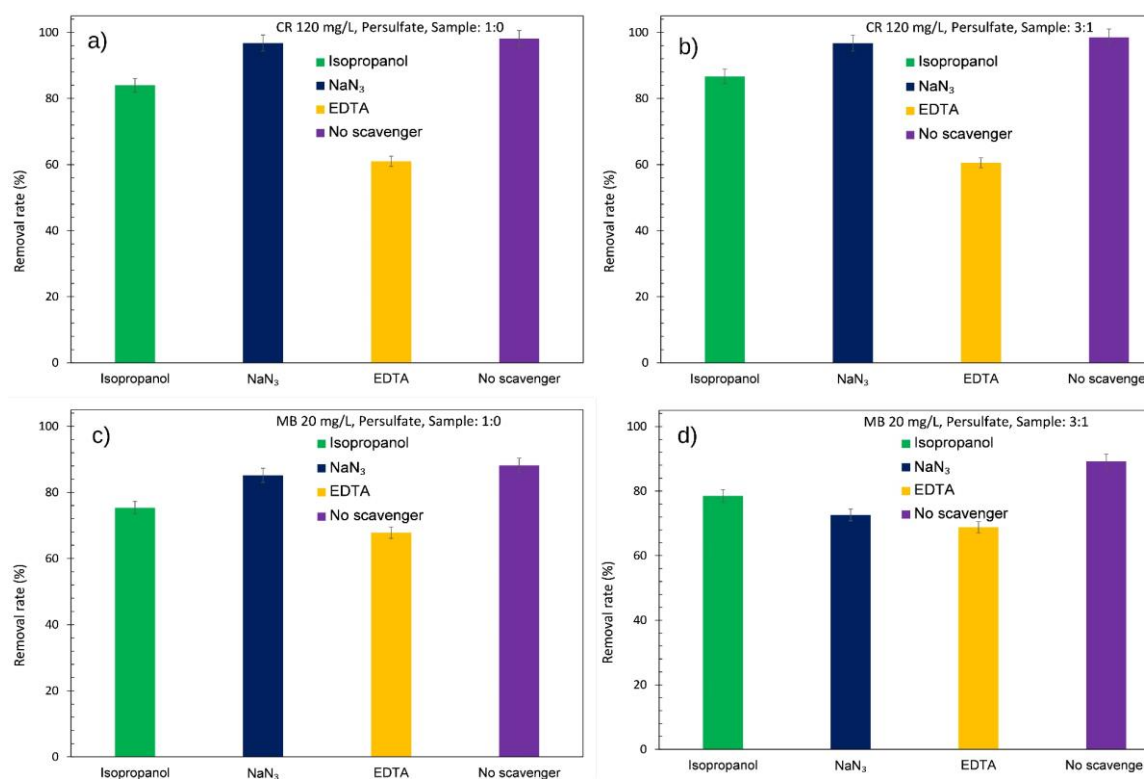


Figure 10. Trapping test for CR decolorization using 1:0 (a) and 3:1 (b) catalysts and for MB decolorization using 1:0 (c) and 3:1 (d) catalysts

Experimental results (Figure 10a-d) show that the EDTA scavenger consistently caused the largest decrease in decolorization efficiency under all reaction conditions. This confirms that the metal ions (Cu, Mn) on the catalyst surface played a major role as active centers for persulfate cleavage. For the CR treatment with the 3:1 sample (Figure 10b), IPA reduced the decolorization efficiency to 86.7%, while that was 98.5% without a scavenger. This result demonstrates that free radicals are the main oxidizing agents for CR decolorization. Conversely, for MB dye with the same 3:1 sample (Figure 10d), the decolorization efficiencies with IPA (78.5%) and by NaN₃ (72.6%) were nearly equivalent and significantly lower than without a scavenger (89.2%). Therefore, the catalyst preferentially activates via the pathway that generates both free radicals and singlet oxygen as the main attacking agents. For 1:0 catalyst (Figures 10a and 10c), the main

agents causing dye decolorization are only free radicals (IPA scavenger), while NaN_3 hardly reduces the decolorization efficiency significantly. This flexible switching demonstrates that the reaction mechanism depends on the specific interactions between the catalytic system and the dye molecule. Figure 11 shows that the CR decolorization efficiency at a concentration of 40 mg/L remained stable over 3 consecutive cycles with minimal and acceptable performance degradation.

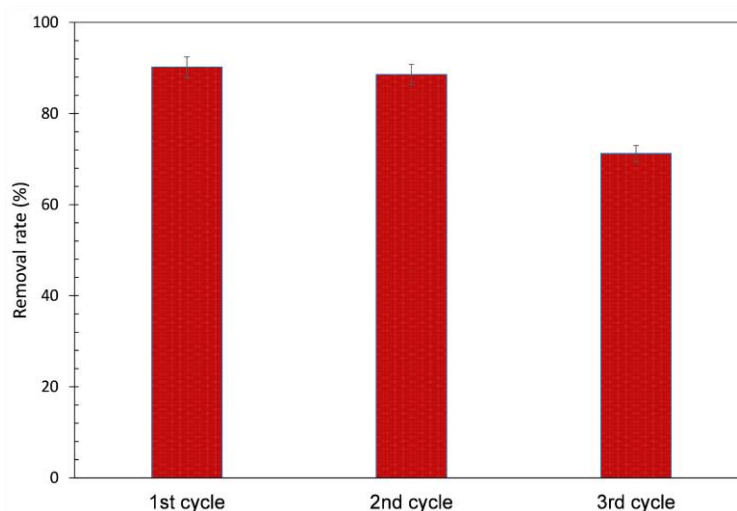


Figure 11. Performance cycle test of CR decolorization by 3:1 sample

4. Conclusion

This study successfully synthesized CuS/MnS composite catalysts using a simple co-precipitation method at room temperature. The materials' structural and physicochemical characteristics were confirmed through FTIR, XRD, zeta potential, EDS, SEM, and BET analysis. The material exhibited a uniform interwoven structure between the CuS nanocrystalline phase (covellite) and the amorphous MnS matrix. Notably, the optimized CuS/MnS (3:1) possessed a negatively charged surface (-20.5 mV), a mesoporous system with a pore peak of 2.66 nm, and a specific surface area of 11.80 m²/g. In terms of treatment performance, the composite synergistically demonstrated efficient adsorption and decolorization of CR dye (achieving over 94-97%) even at high concentrations (120 mg/L). For MB dyes, although the adsorption efficiency is limited, the catalytic decolorization performance remains remarkable (ranging from 87% to over 97%). When comparing the two oxidation systems, the periodate activation process shows slightly better decolorization efficiency than persulfate. The reaction mechanism indicates that the surface metal ions (Cu, Mn) act as the main active sites for catalyzing the oxidizer. The reactive species depend on the dye and the catalyst. The CuS/MnS composite material shows potential for application in practical textile wastewater treatment.

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