Enhancing dye degradation using a novel cobalt metal–organic framework as a peroxymonosulfate activator

Tuotuo Li,a,b Ahmed Olalekan Omoniyi, c a,b Yuliang Wang,a,b Xiaoli Hu, a,b,* and Zhongmin Su, a,b,c

Among transition metals, cobalt ions exhibit superior catalytic activity in the peroxymonosulfate (PMS) degradation of pollutants. However, practical application is hindered by their high rate of ion leaching and the propensity for particle reunion issues. In this study, a novel cobalt metal–organic framework catalyst, denoted as CUST-565 ([Co3(BTB)2(BIPY)2]·4.5H2O·DMA), was synthesized via a one-step solvothermal method. The obtained crystal was employed as a catalyst to activate PMS for degrading two pollutants, methyl orange (MO) and rhodamine B (RhB), in wastewater. The catalyst demonstrated efficacy in PMS, achieving 97% degradation of MO and 98% degradation of RhB within 30 min at an initial concentration of 20.0 mg L⁻¹. Additionally, various factors affecting dye degradation, including PMS dosage, catalyst dosage, temperature, initial pH, and coexisting anions, were investigated. Radical quenching experiments confirmed the presence of sulfate radicals (SO₄⁻), hydroxyl radicals (HO·), superoxide radicals (O₂⁻), and singlet oxygen (¹O₂) in the system. After four cycles, CUST-565 retained its ability to catalytically degrade approximately 80% of the pollutants. These observed stability and reusability properties, corroborated by a series of characterization analyses before and after use, suggest that CUST-565 exhibits reliable performance. This work contributes to the development of cobalt-PMS catalysts for efficiently degrading dyes in wastewater.

1. Introduction

The textile industry has made significant global economic contributions, generating employment opportunities for millions of people. However, it is also considered a major contributor to the depletion of water resources. This is primarily attributed to the discharge of various dyes, including azo dyes, acid dyes, basic dyes, reactive dyes, sulphur dyes and other organic pollutants into rivers and lakes, resulting in severe damage to the environment and posing risks to human health.¹,² Contamination of surface water and groundwater is widely considered a serious global problem.³ In the past decade, many methods have been explored for water decontamination.

Advanced oxidation processes (AOPs) based on sulfate treatments have emerged as effective methods to remove pollutants from wastewater.¹,⁵ Owing to its asymmetric molecular structure and shorter O–O bond length, peroxymonosulfate (PMS, SO₄²⁻) is easier to activate than peroxodisulfate (PDS, S₂O₈²⁻) and can generate a range of highly reactive substances, such as hydroxyl radicals (HO·), sulfate radicals (SO₄⁻), superoxide radicals (O₂⁻) and singlet oxygen (¹O₂).⁶–⁸ In addition, PMS offers several advantages for pollutant degradation, including high solubility, convenient transportation, and the ability to generate active substances over a broad pH range, leading to economic benefits.⁹ During the activation process, SO₄⁻ is produced, which possesses a higher redox potential (2.5–3.1 V) than HO· (1.8–2.7 V). This enables the effective degradation of pollutants into non-toxic and environmentally harmless byproducts, namely water (H₂O) and carbon dioxide (CO₂).¹⁰,¹¹

To activate PMS, various methods have been explored, such as ultrasound,¹² ultraviolet irradiation,¹³ and thermal activation.¹⁴ However, these methods require additional energy input. On the other hand, transition metal ions (Co²⁺, Cu²⁺, Fe³⁺, Mn²⁺, etc.) and metal oxides (Co₃O₄, Fe₂O₄, CuO, etc.) can activate PMS at room temperature and atmospheric pressure without external energy input.¹⁵ Among these options, cobalt ions exhibit the most efficient catalytic effect as its standard
Metal-organic frameworks (MOFs) are a class of composite materials composed of highly porous metal ions or clusters and organic ligands. They have attracted increasing attention due to their excellent properties, including large specific surface area, adjustable pore size, excellent chemical and thermal stability, and an abundance of active centers. In recent years, MOFs have been widely used in adsorption, gas separation, energy storage, catalysis and sensing.26–30 Notably, metal–organic frameworks based on cobalt ions (Co-MOFs) are considered highly effective in activating PMS. For instance, Zhang et al. synthesized an environmentally friendly catalyst through the simple pyrolysis of zeolite imidazole frameworks (ZIFs) coated with phenolic resin. This catalyst catalyzed the degradation of 98% bisphenol A (20 ppm) within 5 min. In another study, Zhang et al. synthesized a heterogeneous catalyst composed of nitrium-doped cobalt@porous spherical structures derived from the classical cobalt-based framework ZIF-67. This catalyst demonstrated efficient PMS activation for the degradation of oxytetracycline, tetracycline and Aureomycin. Hassan Alamgholiloo et al. combined ZIF-67 with iron tetroxide nanoparticles (Fe₃O₄ NPs) using the sol–gel method, resulting in a magnetically recoverable catalyst capable of removing dexamethasone from wastewater.33

Herein, a new cobalt MOF, CUST-565, was synthesized with 2,2′-bipyridine and 1,3,5-tri[4-carboxyphenyl]benzene as ligands and cobalt nitrate hexahydrate as the metal source. The structure was characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA) and X-ray photoelectron spectroscopy (XPS). To explore the catalytic performance of CUST-565 in the removal of dyes methyl orange (MO) and rhodamine B (Rhb), we evaluated the influence of various kinds of parameters on catalytic efficiency, including catalyst dosage, the PMS amount, temperature, initial solution pH and background ionic species. Remarkably, CUST-565 achieved over 97% degradation of MO and more than 98% degradation of Rhb within 30 min. Meanwhile, quenching tests and electron paramagnetic resonance (EPR) were performed to specify the contribution of the generated reactive oxygen species (ROS). The underlying mechanisms for the degradation of MO and Rhb were proposed based on the experimental findings. These results demonstrated that the prepared CUST-565 could effectively catalyze PMS activation for degrading dyes in wastewater.

2. Materials and methods

2.1 Materials and instruments

The chemical reagents involved in this study are listed in the ESI.

The X-ray single-crystal diffraction data of the crystal were obtained at 290 K using a Bruker APEIII CCD diffractometer, with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å). The obtained data were refined by the SHELXL-97 program within the Olex2 software. Anisotropic thermal parameters for all non-hydrogen atoms were determined using the full-matrix least-squares method for F². The crystal structure was resolved using the direct method, leading to the determination of the molecular formula. The detailed data for this crystal have been deposited in the Cambridge Crystal Database under the entry number 2125812.

The crystallinity of CUST-565 was measured using powder X-ray diffraction (PXRD) with Cu Kα radiation (λ = 1.5418 Å) on a Rigaku D-Max 2550 instrument. The morphology of CUST-565 was characterized using a scanning electron microscope (SEM) (FE-SEM, S-4800, Hitachi, Japan) with 7 kV acceleration voltage.

Elemental analysis (C, H, and N) was determined using a PerkinElmer 2400CHN automatic analyzer.

Thermal stability was examined by conducting thermogravimetric analysis (TGA) on a NETZSCH STA 409 PC/PG. The analysis involved heating the sample from 20 °C to 900 °C at a heating rate of 5 °C min⁻¹ under a nitrogen atmosphere.

Surface functional groups of the crystals were analyzed using Fourier-transform infrared spectroscopy (FTIR, Nicolet 380). X-ray photoelectron spectroscopy (XPS) (ThermoFisher Scientific, K-Alpha+, UK) was employed to determine the element (O, N, C, and Co) valence states of CUST-565. The absorbance at a specific moment was measured using a UV spectrophotometer (UV–Vis, METASH, China). The UV absorption spectra corresponding to the catalytic efficiency are all presented in the ESI.

2.2 Preparation of [Co₃(BTB)₂(BIPY)₂]·4.5H₂O·DMA

In a beaker, 29.3 mg (0.100 mmol) of Co(NO₃)₂·6H₂O, 12.0 mg (0.0248 mmol) of BTB and 11.0 mg (0.0704 mmol) of BIPY were sequentially added. The mixture was dissolved in a solvent composed of 3 mL of DMA and 2 mL of deionized water. It was then subjected to ultrasound treatment for 15 min to ensure complete dissolution of the solid material. Subsequently, the resulting mixture was transferred to a stainless-steel reaction kettle with a Teflon-lined autoclave and maintained at 100 °C for 36 h. The purple block crystals obtained were subjected to three rounds of washing with a H₂O : DMA mixture in a 2 : 3 volume ratio to remove surface impurities. Finally, the crystals were dried at room temperature for use. The preparation scheme for CUST-565 is shown in Scheme 1. Elemental analysis of C₇₈H₆₄Co₃N₅O₁₇.₅: Calculated (%): C, 61.31; H, 4.22; N, 4.58. Found (%): C, 61.20; H, 4.18; N, 4.43. CCDC-2125812 contains the supplementary crystallographic data for this paper (Fig. S1 and S2†). The crystallographic parameters of CUST-565 are shown in Table S1 and bond lengths and bond angles are exhibited in Tables S2 and S3.
2.3 Degradation experiment and analysis

The catalytic performance of CUST-565 was studied using MO and RHB as model organic pollutants. Batch experiments were conducted in 50 mL conical flasks with 25 mL of either MO or RHB solution, and the mixture was agitated on a magnetic stirrer at a rotation speed of 200 rpm. A number of key parameters affecting catalyst performance were investigated, including the catalyst dosage, the PMS dosage, the reaction temperature, the presence of inorganic anions, and the initial solution pH. The pH of the initial solution was adjusted by adding 0.1 M HCl or NaOH as necessary. In a typical experiment, the CUST-565 catalyst was introduced to the MO or RHB solution, followed by the addition of PMS to initiate the degradation reaction. Absorbance measurements were taken at three-minute intervals using a UV-Vis spectrophotometer, and the pollutant degradation efficiency ($\eta$) was calculated using eqn (1):\(^{15}\)

$$\eta(\%) = \left( \frac{C_0 - C}{C_0} \times 100\% \right)$$

where $C_0$ represents the initial concentration of methyl orange or rhodamine B (mg L$^{-1}$), and $C$ denotes the concentration at a specific time $t$ when degradation occurs (mg L$^{-1}$).

2.4 Kinetics study

The dye degradation process was investigated using a pseudo-first-order kinetics model as expressed by eqn (2):\(^{36}\)

$$-\ln(C/C_0) = kt$$

Here, $C_0$ is the initial concentration of methyl orange or rhodamine B (mg L$^{-1}$), and $C$ is the concentration at time $t$ when degradation has occurred (mg L$^{-1}$); $k$ represents the reaction rate constant in min$^{-1}$.

3. Results and discussion

3.1 Crystal structure analysis and characterization

X-ray single-crystal diffraction studies revealed that CUST-565 crystallizes within the monoclinic $C2/c$ space group, displaying a 2D structure built on the basis of triangular carboxylate BTB ligands and Co$_2$ clusters. In the structural unit, there is a trinuclear cobalt cluster with two BTB ligands, two BIPY ligands, five H$_2$O molecules, and one DMA molecule. The asymmetric unit of CUST-565 consists of metal atoms Co1 and Co2, which are linked by the BTB and BIPY ligands (Fig. 1a). The Co1 atom exhibits a six-coordinated mode, which is coordinated by six oxygen atoms from six carboxylate BTB ligands, forming an octahedral geometry (Co1–O1$^4$, 2.206(18) Å; Co1–O1$^2$, 2.026 (18) Å; Co1–O3, 2.0498(18) Å; Co1–O3$^3$, 2.0498(18) Å; Co1–O6$^4$, 2.029(2) Å; and Co1–O6$^5$, 2.0293(19) Å). In contrast to Co1, Co2 is linked by four oxygen atoms from three BTB ligands in a bridging mode and two nitrogen atoms from one BIPY ligand, resulting in a distorted octahedral geometry (Co2–O1$^6$, 2.1696 (18) Å; Co2–O2$^7$, 2.0405(18) Å; Co2–O4$^8$, 2.248(2) Å; Co2–O5, 2.047(2) Å; Co2–N1, 2.116(2) Å; and Co2–N2, 2.160(2) Å).

As shown in Fig. 1b and c, the coordination environment of the metal cluster can be observed. The secondary building unit, $\{\text{Co}_3(\text{COO})_6\text{N}_4\}$ SUB, is formed by a trinuclear Co cluster, which binds to twelve O atoms from six BTB ligands and four N atoms from two BIPY ligands. In the sequence Co2–Co1–Co2, Co1 and Co2 are closely linked by the BTB ligand and constitute trinuclear Co clusters. These trinuclear Co clusters serve as nodes, linking with the BTB ligand in the $b$-axis direction to construct the 2D structure of CUST-565. The $\{\text{Co}_3(\text{COO})_6\text{N}_4\}$ SUB can be defined as 6-connected nodes, while the BTB ligand can be considered 3-connected nodes.

The crystal structure exhibits a (3,6)-connected topological network with the symbol $\{4^1\}^2\{4^6\cdot6^6\cdot8^3\}$. Additionally, PLATON calculations show that the effective free volume of CUST-565 occupies approximately 48.33% of the total crystal volume (Fig. 1d).

Fig. 2a illustrates the morphological features of CUST-565, exhibiting a rough, stacked surface structure. This rough structure offers the advantage of an increased contact area with pollutants, facilitating the exposure of active sites and accelerating the catalytic reactions.\(^{37}\)
The FTIR spectra reveal the functional groups of the prepared catalysts (Fig. 2b). Notable peaks in the spectra include a peak at 3440 cm$^{-1}$, corresponding to the stretching vibration of the hydroxyl groups (–OH), while the peak at 2935 cm$^{-1}$ corresponds to the stretching vibration of the C–H bond. Additionally, the peak at 2362 cm$^{-1}$ is attributed to the characteristic peak of atmospheric CO$_2$, while the peak near 1604 cm$^{-1}$ is associated with the C–O or C–C double bonds. The characteristic peaks of the C–N and C–O bonds are evident at 1400 cm$^{-1}$ and 1018 cm$^{-1}$, respectively. Furthermore, the presence of the Co–O and Co–N bonds is supported by distinctive peaks at 780 cm$^{-1}$ and 418 cm$^{-1}$, respectively.

The TGA pattern is shown as Fig. 2c. A slight mass loss (about 5%) is observed from room temperature to 100 °C, primarily attributed to the removal of water molecules anchored within the crystal structure. At 164 °C, the evaporation of DMA molecules results in a similar 5% mass loss. The curve indicates that the crystal structure maintains some degree of stability up to 445 °C, after which it gradually deteriorates and eventually decomposes with increasing temperature.

X-ray photoelectron spectroscopy (XPS) analysis of CUST-565 revealed significant variations in elemental composition, mainly comprising the Co, O, N and C elements (Fig. 3a). The O 1s XPS spectrum (Fig. 3b) was deconvoluted into three distinct peaks. The peak at 531.5 eV is attributed to the C–O bond or surface adsorbed oxygen species, while peaks at 532.7 eV and 533.8 eV correspond to the Co–O bond and C–O bonds, respectively.

High-resolution N 1s spectrum analysis also yielded three peaks at 399.5 eV, 400.2 eV and 401.5 eV, representing the Co–N, C–N–C and N–H bonds, respectively (Fig. 3c). In the C 1s spectrum (Fig. 3d), peaks at binding energies of 284.7 eV, 286.1 eV, 288.2 eV and 290.8 eV were assigned to the C–C bonds, C–O/C–N bonds, C=O bonds and the –COOH groups, respectively.

Analysis of the Co 2p spectrum (Fig. 3e) revealed the presence of two Co 2p$_{3/2}$ and Co 2p$_{1/2}$ peaks, corresponding to Co$^{3+}$ at low binding energy and Co$^{2+}$ at high binding energy. To better understand the catalytic mechanism, the XPS spectra of CUST-565 before and after use were compared (Fig. 3f and Fig. S3†). Remarkably, Co$^{2+}$ was identified as the active species for PMS activation. The intensity ratio of Co$^{2+}$ (798.0 eV) to Co$^{3+}$ (796.3 eV) at Co 2p$_{1/2}$ remained relatively unchanged after use. Meanwhile, the Co 2p$_{3/2}$ peak at 780.8 eV was considered to be Co$^{2+}$, with relative intensity ratios before and after use of 57.0% and 48.0%, respectively.

### 3.2 Evaluation of catalytic performance

#### 3.2.1 Comparison of catalytic performances of different systems

Fig. 4 presents a comparison of the catalytic performances of the different systems in the degradation of MO and RhB. As shown in Fig. 4a and c, the adsorption of the two dyes on CUST-565 within the initial 30 min was negligible (Fig. S4†), resulting in minimal dye removal. Conversely, inactivated PMS alone demonstrated effective dye removal, with approximately 86% of MO and 53% of RhB degraded within the same time frame. When CUST-565 was used to activate the PMS catalyst (CUST-565/PMS), it exhibited a superior MO and RhB degradation rate, achieving approximately 97% degradation of MO and 98% degradation of RhB within 30 min. A control experiment using Co(NO$_3$)$_2$·6H$_2$O as the catalyst efficiently activated PMS and achieved 99% and 100% degradation of MO and RhB, respectively within 6 min (Fig. S5 and
Table S4†, demonstrating the high catalytic activity of cobalt metal. However, Co(NO$_3$)$_2$·6H$_2$O has some drawbacks, such as causing secondary pollution due to leaching of cobalt ions, easy agglomeration and the catalyst cannot be recovered after one cycle. Therefore, CUST-565 was superior to Co(NO$_3$)$_2$·6H$_2$O as a catalyst for PMS oxidation of dyes, as it was more stable and reusable. The corresponding UV spectra of the different systems are shown in Fig. S6.†

The degradation of MO and RhB aligns with the analysis of a pseudo-first-order kinetics model. Notably, although the addition of CUST-565 only increased the MO degradation rate by 11%, the degradation rate constant ($k$) for the MO degradation by CUST-565 was 0.122 min$^{-1}$. This value was 1.82 times higher than the rate when PMS was used alone (0.067 min$^{-1}$) in the system (Fig. 4b). For the RhB degradation, the corresponding $k$ value increased to 0.131 min$^{-1}$, which was 5.23 times higher than the degradation rate when PMS was used alone (Fig. 4d).

### 3.2.2 Effects of catalyst dose

As shown in Fig. 5 and Fig. S7,† the effects of four different loadings of CUST-565 on the degradation of MO and RhB are depicted, and the experimental data fit well with the pseudo-first-order model. The removal of the two dyes was increased when the catalyst dosage was increased from 0.08 g L$^{-1}$ to 0.16 g L$^{-1}$. The degradation efficiency of MO rose from 90% to 98% within 30 min (Fig. 5a), with the corresponding $k$ value increasing from 0.076 min$^{-1}$ to 0.125 min$^{-1}$ (Fig. 5b). Similarly, the degradation efficiency of RhB increased from 58% to 98% (Fig. 5c), with its $k$ value substantially rising from 0.025 min$^{-1}$ to 0.211 min$^{-1}$ (Fig. 5d).

However, when the catalyst dose reached 0.20 g L$^{-1}$, the degradation efficiency decreased. This decline can be attributed to two reasons: first, excess catalyst led to aggregation, causing a loss of available active sites; second, the presence of excess catalyst affected free radical scavenging (eqn (3)). Therefore, considering both degradation efficiency and cost, the catalyst dose of 0.16 g L$^{-1}$ was selected for subsequent degradation experiments, as it achieved over 97% degradation of MO and over 98% degradation of RhB within 30 min.

$$\text{SO}_4^{2-} + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_8^{2-}$$ (3)

Fig. 4 (a) Degradation efficiency of MO; (b) kinetic fitting curves of MO; (c) degradation efficiency of RhB; (d) kinetic fitting curves of RhB in the different systems. [MO] = [RhB] = 20 mg L$^{-1}$, MO’s initial pH = 5.5, RhB’s initial pH = 5.8, $T = 295$ K.

Fig. 5 Effects of the catalyst dose on MO: (a) degradation efficiency and (b) kinetic fitting curves; effects of the catalyst dose on RhB: (c) degradation efficiency and (d) kinetic fitting curves. [MO] = [RhB] = 20 mg L$^{-1}$, [PMS] = 0.12 g L$^{-1}$, MO’s initial pH = 5.5, RhB’s initial pH = 5.8, $T = 295$ K.

Fig. 6 Effects of the PMS dose on MO: (a) degradation efficiency and (b) kinetic fitting curves; effects of the PMS dose on RhB: (c) degradation efficiency and (d) kinetic fitting curves. [MO] = [RhB] = 20 mg L$^{-1}$, [catalyst] = 0.16 g L$^{-1}$, MO’s initial pH = 5.5, RhB’s initial pH = 5.8, $T = 295$ K.
3.2.3 Effects of PMS dose. PMS is widely recognized as a source of reactive oxygen species (ROS), and its concentration is directly proportional to ROS availability. As shown in Fig. 6 and Fig. S8, the impact of different PMS dosages on the degradation of two dyes is illustrated. When the PMS concentration increased from 0.08 g L$^{-1}$ to 0.16 g L$^{-1}$, the removal efficiency of MO increased from 83% to 97% (Fig. 6a), with a corresponding increase in $k$ value by a factor of 1.94 (Fig. 6b). Similarly, the degradation efficiency of RhB increased from 89% to over 99% (Fig. 6c), and the reaction kinetics accelerated by a factor of 2.88 (Fig. 6d). However, a further increase in the PMS concentration from 0.16 g L$^{-1}$ to 0.20 g L$^{-1}$ resulted in a decline in pollutant degradation. This decline can be attributed to the self-scavenging effect of free radicals caused by the presence of excess PMS.44 To maintain a balance between catalyst performance and operational costs, a PMS dosage of 0.12 g L$^{-1}$ was selected for subsequent experiments. The influence of the catalyst and PMS dosage on degradation is more explicitly illustrated in Tables S5 and S6.†

3.2.4 Effects of the reaction temperature. In exploring the influence of temperature, all experimental conditions remained unchanged, varying only the temperature to 20, 40, and 50 °C. The thermally assisted approach enhances the activation of PMS, leading to the self-decomposition of the PMS as described by eqn (4).45 This leads to an increase in the rate of free radical production. As presented in Fig. 7 and Fig. S9, the degradation rate of dyes increased with the rise in temperature. When the temperatures were 20, 40, and 50 °C, the degradation efficiency of MO exceeded 92% within 30 min (Fig. 7a), and the corresponding $k$ values were 0.087 min$^{-1}$, 0.1537 min$^{-1}$, and 0.2292 min$^{-1}$, respectively (Fig. 7b). Furthermore, Fig. 7d demonstrates that higher temperatures consistently enhanced RhB decolorization and improved the reaction kinetics for the CUST-565/Rhb systems. Under the three experimental temperatures, the degradation efficiency of RhB reached over 98% within 30 min, and even approached 100% at 50 °C. The reaction rate constants at 20 °C, 40 °C, and 50 °C were 0.132 min$^{-1}$, 0.245 min$^{-1}$, and 0.554 min$^{-1}$, respectively (Fig. 7e). To further analyze the impact of temperature, the activation energy of dye degradation was calculated using the Arrhenius equation (eqn (5)):46

$$\text{HSO}_5^- \xrightarrow{\text{heat}} \text{SO}_4^{2-} + \text{HO}^+$$

(4)

$$\ln k = -\frac{E_a}{RT} + \ln A$$

(5)

Here, $k$ is the reaction rate constant at temperature $T; A$ is the pre-factor, also known as the Arrhenius constant; $E_a$ is the experimental activation energy [kJ mol$^{-1}$], which is a constant independent of temperature; $T$ is the absolute temperature (K); and $R$ is the molar gas constant (8.314 J (mol K)$^{-1}$). The calculated activation energies of MO and RhB degradation in the system were 25.89 kJ mol$^{-1}$ and 35.43 kJ mol$^{-1}$, respectively. The lower activation energy facilitated easier decolorization of dye molecules under heated conditions.49 In addition, the calculated $E_a$ values were much higher than those of the diffusion-controlled reaction (10–13 kJ mol$^{-1}$). This suggested that in the process of degradation, the reaction rate was not controlled by the mass transfer rate, but rather by the chemical reaction rate on the catalyst’s surface.48 These results demonstrated that the degradation efficiency of RhB was significantly higher than that of MO, even in the absence of the catalyst (Fig. S16 and S17†).

3.2.5 Effects of pH. In comparison with the traditional Fenton process, the peroxymonosulfate catalytic technique usually has good effect in a wider pH range.49 To assess the catalyst’s applicability across varying acidity levels, its catalytic effects in acidic, neutral and alkaline aqueous solutions at nine distinct pH values were investigated. As shown in Fig. 8, Fig. S10 and S11,† the removal rate of MO exceeded 84% within the pH range from 4 to 11, while the degradation of RhB surpassed 87% in the pH range from 4 to 10. This observation underscores the catalyst’s effectiveness in degrading these two dyes over a wide pH range, rendering it suitable for various aqueous environments with different acidity and alkalinity levels.

In highly acidic conditions (pH = 3) and highly alkaline conditions (pH = 11), the degradation efficiency of the two dyes was noticeably reduced. There were two reasons contributing to this effect: on the one hand, SO$_4^{2-}$ was easily neutral-

![Fig. 7](image1.png)

**Fig. 7** Effects of temperature on MO: (a) degradation efficiency curves, (b) kinetic fitting curves, and (c) correlation between the rate constant and temperature; effects of temperature on RhB: (d) degradation efficiency curves, (e) kinetic fitting curves, and (f) correlation between the rate constant and temperature of the kinetic fitting curve. [MO] = [RhB] = 20 mg L$^{-1}$, [PMS] = 0.12 g L$^{-1}$, [catalyst] = 0.16 g L$^{-1}$, MO’s initial pH = 5.5, RhB’s initial pH = 5.8.

![Fig. 8](image2.png)

**Fig. 8** Effects of pH on the degradation efficiency of (a) MO and (b) RhB. [MO] = [RhB] = 20 mg L$^{-1}$, [PMS] = 0.12 g L$^{-1}$, [catalyst] = 0.16 g L$^{-1}$, $T = 295$ K.
ized in both highly acidic and alkaline environments (eqn (6) and (7)); on the other hand, PMS has a pH1 of 9.4, the primary form being HSO5− at pH ≤ 8.5. This form acts as a source of O3 responsible for the pollutant removal via non-free radical reactions (eqn (8)).

When the pH = 10, PMS existed in a less oxidized SO2−3 form, leading to a gradual reduction in the degradation efficiency of the two dyes. Given that the typical pH range of wastewater falls between 5 and 9, the CUST-565/PMS system demonstrates the ability to effectively remove pollutants across a wide pH range. This characteristic makes the CUST-565/PMS system a promising solution for various environmental conditions:

\[
\begin{align*}
    
    H^+ + SO_4^{2−} + e^- &\rightarrow HSO_4^- \\
    SO_4^{2−} + OH^- &\rightarrow SO_4^{2−} + HO' \\
    HSO_4^- + SO_2^{2−} &\rightarrow HSO_4^- + SO_4^{2−} + O_2 
\end{align*}
\]

3.2.6 The influence of inorganic anions. In actual wastewater, various substances are present alongside dyes and pollutants, including inorganic salts such as sodium chloride and sodium sulfate. These inorganic salts are often added to the dyeing process as inorganic auxiliaries. Therefore, it is very necessary to explore the effects of inorganic anions on the removal of dyes such as MO and RhB. In this study, the effects of NaCl, NaH2PO4, NaHCO3, Na2SO4, and Na2CO3 on the degradation using the CUST-565/PMS system were investigated. As depicted in Fig. 9, the addition of NaCl, NaH2PO4, and Na2CO3 had an inhibitory effect on the degradation efficiency of MO and RhB to some extent. Notably, the inhibitory effect decreased in the order: Na2CO3 > NaCl > NaH2PO4, NaHCO3 and Na2SO4 had little effect on the degradation rate of the two dyes.

The inhibition by NaCl can be attributed to the fact that Cl− can consume free radicals and further generate Cl2− according to eqn (9)–(11). However, the reactivity of this chlorine-based byproduct is relatively weak. This is due to the fact that the oxidation–reduction potential of sulfate radicals (E0(SO4^{2−}/SO_4^{2−}) = 2.5–3.1 V), chloride radicals (E0(Cl'/Cl') = 2.4 V), and Cl2− (E0(Cl2^−/2Cl') = 2.1 V) varies, affecting their effectiveness.

As for SO2−3, it is a well-known radical quenching agent that hinders catalytic reactions, as indicated in eqn (12). The inhibition by H2PO4− is a result of its relatively strong affinity for the active site of the catalyst and its potential reaction with SO4^{2−} (eqn (13)). These interactions alter the active species, leading to reaction inhibition. The corresponding UV spectra are shown in Fig. S12 and S13.

Fig. 9b and d illustrate the reaction kinetics. Interestingly, the addition of NaHCO3 and Na2SO4 promoted the catalytic process. HCO3−, for instance, can react with PMS to produce free radicals (eqn (14)), while SO2−3 can react with hydroxyl radicals to form sulfate radicals (eqn (15)). Here, the cationic dye RhB was more significantly affected by inorganic anions than the anionic dye MO (Fig. 9a and c). These findings provide valuable insights into the complex interactions between inorganic ions and the degradation of dyes in wastewater:

\[
\begin{align*}
    SO_4^{2−} + Cl^- &\rightarrow SO_4^{2−} + Cl' \\
    HO' + Cl^- &\rightarrow OH^- + Cl' \\
    Cl^- + Cl' &\rightarrow Cl_2^- \\
    CO_2^{2−} + SO_4^{2−} &\rightarrow SO_4^{2−} + CO_3^{2−} \\
    H_2PO_4^- + SO_4^{2−} &\rightarrow SO_4^{2−} + H_2PO_4^- \\
    HCO_3^- + HSO_4^- &\rightarrow SO_4^{2−} + 2OH^- + CO_2 \\
    HO' + SO_4^{2−} &\rightarrow SO_4^{2−} + OH^- 
\end{align*}
\]

3.3 Active oxygen species and possible degradation mechanism

Generally, the activation of PMS for pollutant degradation can occur through two mechanisms: free radical degradation and non-free radical degradation. To elucidate the mechanisms behind PMS activation by the prepared CUST-565, experiments with different concentrations of free radical quenchers were carried out to generate ROS. Fig. 10 and Fig. S14 show the adverse effect of scavenger interference on dye removal. Methanol (MeOH) was found to quench SO4^{2−} and HO' (k_MeOH = 9.7 × 10^8 M^−1 s^−1, k_H2O = 1.6 × 10^7 M^−1 s^−1), tert-butyl alcohol (TBA) principally captured HO' (k_TBA = 3.8–7.6 × 10^8 M^−1 s^−1), p-benzoquinone (p-BQ) acted as a quencher for O2− (k_BQ = 0.9–1.0 × 10^8 M^−1 s^−1), and l-histidine (l-his) effectively quenched O2− (k = 3.2 × 10^7 M^−1 s^−1). For the anionic dye MO, the degradation efficiency rates (94.9% and 93.2%) were slightly inhibited at a molar concentration ratio of MeOH and TBA to PMS of 100:1, with negligible quenching effects at lower concentrations of MeOH and TBA.
This suggests that during the process of RhB degradation, obviously. As the concentration of L-histidine was increased from 1 to 5, the degradation efficiency of MO decreased from approximately 98% to 6.0%.

The degradation efficiency of MO decreased from 86.4% to 80.6% when the concentration of p-benzoquinone increased from 5 to 10. This indicates a more significant inhibitory effect compared to the other quenchers. With L-His : PMS = 5 : 1 and 10 : 1, L-histidine had a more significant inhibitory effect compared to the other quenchers. With L-His : PMS = 5 : 1 and 10 : 1, L-histidine had a more significant inhibitory effect compared to the other quenchers.

Scheme 2 Schematic diagram of MO and RhB degradation.

The presence of ROS was determined through free radical quenching experiments, providing insights into the mechanisms of pollutant degradation. PMS exhibited self-decomposition to produce small amounts of SO$_4^{2-}$ and HO$^-$ (eqn (3)). Upon the addition of CUST-565 to the reaction system, cobalt metal species contained in the catalyst react with PMS to enhance the decomposition of the PMS. Analysis of the cobalt element's valence state before and after the reaction, using XPS, revealed the participation of Co$^{2+}$ and Co$^{3+}$ in the catalytic activation of PMS. Meanwhile, the redox cycle between Co$^{2+}$ and Co$^{3+}$ played an important role in maintaining the catalytic activity of CUST-565 (Fig. S3†).

The proposed mechanisms for dye removal by CUST-565 can be summarized as follows: first, Co$^{2+}$ ions initiate the activation of PMS to produce active species (eqn (16) and (17)). The generated SO$_4^{2-}$ species readily combine with OH$^-$ and H$_2$O to form HO$^-$ (eqn (18) and (19)). Additionally, Co$^{3+}$ ions can react with PMS to form Co$^{2+}$ ions and active intermediates, thereby promoting the conversion of Co$^{3+}$ to Co$^{2+}$ and facilitating the redox cycle between Co$^{2+}$ and Co$^{3+}$ (eqn (20)).

The primary ROS responsible for RhB degradation is identified as $^1$O$_2$, based on the quenching experiments. Three sources of $^1$O$_2$ are identified in the system: (1) self-decomposition of PMS (eqn (8)), (2) formation of the SO$_4^{2-}$ species during the redox cycle between Co$^{2+}$ and Co$^{3+}$, which subsequently decompose or react with H$_2$O (eqn (21) and (22)), and (3) interaction of HO$^-$ with active intermediate O$_2$$^{.-}$ (eqn (23)–(27)). Eventually, MO and RhB molecules are degraded into intermediates (Scheme 2) through the action of the active species generated during the catalytic process. This culminates in mineralization into CO$_2$ and H$_2$O (eqn (28)).

The carboxyl group (–COOH) and nitrogen elements (N) in the ligand are all coordinated with cobalt metal. This complete coordination with the metal likely contributes to the low adsorption and high catalytic effect on the dyes. The trinuclear cobalt metal clusters of the catalyst activate PMS to promote the generation of reactive oxygen species. In addition,
CUST-565 has a two-dimensional structure, open metal sites, and good chemical and thermal stability. These features enable the catalyst to contact PMS fully and improve catalytic efficiency. The catalyst is also eco-friendly, as it can be recycled and reused:

\[
\begin{align*}
\text{Co}^{2+} + \text{HSO}_5^- & \rightarrow \text{Co}^{3+} + \text{SO}_4^{2-} + \text{OH}^- \\
\text{Co}^{2+} + \text{HSO}_5^- & \rightarrow \text{Co}^{3+} + \text{HO}^- + \text{SO}_4^{2-} \\
\text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow \text{SO}_4^{2-} + \text{HO}^- + \text{H}^+ \\
\text{SO}_4^{2-} + \text{OH}^- & \rightarrow \text{SO}_4^{2-} + \text{HO}^- \\
\text{Co}^{3+} + \text{HSO}_5^- + \text{OH}^- & \rightarrow \text{SO}_4^{2-} + \text{Co}^{2+} + \text{H}_2\text{O} \\
2\text{SO}_4^{2-} & \rightarrow 2\text{SO}_4^{2-} + \text{O}_2 \\
2\text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow 2\text{HSO}_4^{2-} + 1.5\text{O}_2 \\
\text{HSO}_4^- + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{O}_2 + \text{HSO}_4^- \\
\text{H}_2\text{O}_2 + \text{Co}^{3+} & \rightarrow \text{Co}^{2+} + \text{HO}_2^- + \text{H}^+ \\
\text{HO}_2^- & \rightarrow \text{O}_2^- + \text{H}^+ \\
\text{O}_2^- + \text{HO}^- & \rightarrow \text{OH}^- \\
2\text{O}_2^- + 2\text{H}^+ & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \\
\text{HO}^-/\text{SO}_4^{2-}/\text{O}_2^-/\text{O}_2 & \rightarrow \text{MO}/\text{RhB} \\
& \rightarrow \text{intermediates} \rightarrow \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

3.4 Stability and reusability of CUST-565

The stability and reusability of a catalyst are important factors for evaluating its performance, especially in practical application. CUST-565 underwent four consecutive cycles of usage, and the catalytic performance in each cycle is shown in Fig. 11 and Fig. S15.† The CUST-565 crystals were immersed in water with different pH values for 45 min. As seen from Fig. S18,† CUST-565 had a wide range of stabilities in acidic, neutral, and basic conditions, indicating that CUST-565 was resistant to water-induced degradation. The recycled and soaked crystals were then characterized by infrared spectroscopy and XRD. As shown in Fig. S19 and S22,† the corresponding characteristic peaks were unchanged. The used CUST-565 was tested using SEM and XRD, and the results are shown in Fig. S20 and S21.† With their increasing frequency of use, the crystals became smaller due to the magnon agitation, but did not dissolve or collapse. The XRD pattern also showed that the crystalline phase structure of the catalyst had not changed. The results indicate a gradual decrease in catalytic degradation efficiency with an increase in the number of times the catalyst is used. After four cycles of experiments, CUST-565 maintained approximately 80% of its efficiency in removing MO and 79% in removing RhB (Fig. 11a and b). Similarly, the PXRD pattern of the catalyst was simulated using Mercury software and compared with that of the used catalyst. The simulated PXRD pattern agrees well with the bulk sample of CUST-565 after usage, as shown in Fig. S21.† This reduction in catalytic activity can be attributed to two primary factors: a decrease in active sites during repeated use and the accumulation of intermediate products on the catalyst’s surface.

In summary, after four consecutive usage cycles, CUST-565 maintained an efficiency of around 80% in catalytically degrading both MO and RhB. Analysis using infrared, XRD and SEM characterization techniques before and after catalyst use showed that the catalyst maintains good crystallinity, indicating its stability and reusability.

4. Conclusion

In this work, a novel cobalt-based catalyst, CUST-565, was successfully synthesized using a hydrothermal method. CUST-565 demonstrated remarkable efficiency in activating PMS to degrade pollutants such as MO and RhB in aqueous solution. It effectively degraded 97% of MO and 98% of RhB within 30 min. The cobalt species in CUST-565 endowed the catalyst with a satisfactory catalytic performance across a wide pH range (pH 4–10). While the introduction of most inorganic anions had little impact on RhB degradation, the addition of CO$_3^{2-}$ significantly reduced the degradation efficiency. The free radical quenching experiment revealed that the ROS involved in the MO degradation included SO$_4^{2-}$, HO$, \text{O}_2^-$ and $^1\text{O}_2$. However, in the case of RhB degradation, $^1\text{O}_2$ played a predominant role, suggesting that the degradation process of RhB primarily occurred through a non-free radical pathway. CUST-565 maintained approximately 80% degradation efficiency after four cycles, indicating its potential for long-term use in wastewater treatment applications. This study pro-
vides a feasible approach for developing an efficient PMS catalyst for sustainable wastewater treatment.

Author contributions

Conflicts of interest
There are no conflicts to declare.

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