Research Article

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Efficient degradation of methyl orange and methylene blue in aqueous solution using a novel Fenton-like catalyst of CuCo-ZIFs

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Abstract: In this study, the synthesized CuCo-zeolite imidazolate framework (ZIF) catalyst was used to degrade methyl orange (MO) and methylene blue (MB) in water via a novel Fenton-like catalytic reaction. Effects of catalyst dosage, \( \text{H}_2\text{O}_2 \) concentration, initial concentration of the contaminants, and reaction time were evaluated. The results showed that MO and MB decomposition efficiencies were highly influenced by CuCo-ZIF concentration. The presence of \( \text{H}_2\text{O}_2 \) accelerated the degradation reaction of both MO and MB. Although it took 100 min to complete the removal of MB, it was 60 min for MO. At concentrations of MO and MB lower than 40 mg L\(^{-1}\), the catalyst showed an almost complete degradation. The CuCo-ZIF catalyst presented a good recyclability with more than 90% removal of MO and MB after four times and five times reuse, respectively. These results demonstrated that MO and MB were efficiently degraded by a Fenton-like catalyst of CuCo-ZIFs and its potential in industrial wastewater treatment.

Keywords: CuCo-ZIFs, heterogeneous catalyst, novel Fenton-like catalyst, methyl blue, methyl orange

1 Introduction

Dyes are currently one of the most used substances and have been applied in many industries such as textiles, leather, paint, plastics, and paper. However, the excess number of dyes that were directly discharged into the environment is one of the main reasons for water pollution and human health problems. Dyes can cause several allergic, mutagenic, and carcinogenic effects on human body organs, namely kidneys, liver, reproductive system, or neurological system [1,2]. Furthermore, these dyes are nonbiodegradable molecules with complex aromatic structures that give optical, thermal, and physico-chemical stability [3–6].

Methyl orange (MO) and methylene blue (MB) are two dyes that are detected in large quantities in textile wastewater [7]. MO is an anionic dye, contains the stable double bond \( \text{N}==\text{N} \) in structure and has been widely used in printing, textile, food, and pharmaceutical industries, whereas MB is a cationic dye with adjacent aromatic rings and used as a dying material for wool, cotton, and silk [8]. They are both toxic and cause many harmful effects, such as cyanosis, vomiting, quadriplegia, shock, jaundice, and tissue necrosis in the human body [9] (Figure 1).

Currently, there are many investigated methods to treat the dye-polluted water such as adsorption, electrochemical oxidation, reverse osmosis, and coagulation [10]. Among these methods, adsorption is the cheapest and most straightforward of all these techniques; however, some adsorbents are expensive [11], and it does not degrade the dyes but just maintains the nondegradable pollutants on the active sites; therefore, desorption process is also required, which is costly. As a result, it is critical to creating a simpler and more efficient approach for removing dyes from aqueous solutions. Another efficient method is Fenton catalysis, which is based on the advanced oxidation processes, using metals or metal oxides as a reactive center to activate the oxidant agents.
and then generate the strong oxidant radicals [12]. The Fenton-like heterogeneous catalysis has much more advantages, such as environmental friendliness, energy efficiency [13], and recyclability [14], and is widely applied in degradation of many kinds of persistent organic pollutants such as dyes [15,16], fertilizers [17], benzene and its derivatives [18], and medicines [19].

Metal–organic frameworks (MOFs) is a family of crystalline porous materials, which contains both metal ions and organic linkers, and possesses unique properties such as high surface areas [20] and excellent thermal and chemical stabilities [21]. Zeolitic imidazolate frameworks (ZIFs), a typical class of MOFs, are usually constructed from the tetrahedrally coordinated divalent cations (Zn$^{2+}$ or Co$^{2+}$) linked by the imidazolate ligands with sodalite-type cage-like zeolites [22]. ZIF-67 is a general-applied member of ZIFs due to its good stability, excellent pore sizes and surface areas [23], and highly applicable potential in sensing, gas separation and storage, and adsorption [23–26]. The modification of ZIF-67 is also interesting to many scientists for advanced applications such as batteries or catalysts [27–29]. The creation of bimetallic ZIFs by adding another metal into ZIFs has been studied because of the significant increase of catalysis activity and the improvement of material stability [30–32]. Copper ion (Cu$^{2+}$) is a divalent metal cation, which is currently used as a metal precursor, combining with cobalt cation (Co$^{2+}$) to generate the CuCo-ZIFs. Because the ionic radius of Cu$^{2+}$ and Co$^{2+}$ in the tetrahedral arrangement are nearly equal (0.73 Å [33] and 0.72 Å [34]), it is available for random substitution of Cu$^{2+}$ ions into Co$^{2+}$ nodes in the structure of ZIF-67, in which the 2-methylimidazole (2-MIm) ligands form a bridge with metal ions at the position of the N atom to form a porous crystal structure (Figure 2) and remain sodalite structure (SOD). The Cu-doped phase integrated both structural features and functions of ZIF-67 [35], and it showed a high gas uptake capacity and highly efficient photocatalytic for MO degradation [23], and it is used as a selective catalyst for organic reactions [36].

In this study, CuCo-ZIFs was successfully synthesized in ethanol by ultrasound method and applied as a novel Fenton-like heterogeneous catalyst for the removal of MO and MB from aqueous solutions.

2 Materials and methods

2.1 Materials

2-MIm (C$_6$H$_2$N$_2$, 99%) was purchased from Acros (Acros Organics, ThermoFisher Scientific). Cobalt(II) nitrate hexahydrate (Co(NO$_3$)$_2$.6H$_2$O, 99%), copper(II) nitrate trihydrate (Cu(NO$_3$)$_2$.3H$_2$O, 99%), and ethanol (C$_2$H$_5$OH, 99.5%) were purchased from Xilong Chemical Co., Ltd, China. All the reagents were used as received without further purification. Zeolite, activated carbon, ZIF-8, ZIF-67, and Ag/ZIF-67 were used as heterogeneous catalysts.

2.2 CuCo-ZIF catalyst preparation

Catalyst of CuCo-ZIFs was prepared by the ultrasound method at an ambient temperature in ethanol solvent.
as reported in the previous process [37]. To this end, Co(NO$_3$)$_2$·6H$_2$O (0.582 g, 2 mmol), Cu(NO$_3$)$_2$·3H$_2$O (0.483 g, 2 mmol), and 2-MIm (1.314 g, 16 mmol) were separately dissolved in ethanol (10 mL for each precursor). Subsequently, copper nitrate solution was dropped to the cobalt nitrate solution and stirred for 10 min using a magnetic stirrer to form a homogeneous mixture. Then, the homogeneous mixture was slowly dropped into the 2-MIm solution under magnetic stirring to form a purple suspension. This mixture was subjected to ultrasound for 15 min and kept at ambient temperature for 24 h. The purple precipitates were then obtained by centrifugation of 6,000 rpm within 15 min. The purple solid was immersed in 10 mL of ethanol for 4 h and then the dispersing was removed before adding the same amount of new ethanol into the sample. This step was repeated for ten times to completely remove all impurities. Finally, the sample was dried at 60°C to obtain the CuCo-ZIFs catalyst.

### 2.3 Degradation of MO and MB

The degradation experiments of MO and MB were conducted to illustrate the catalytic activity of CuCo-ZIFs. In the degradation experiment of MO, different dosages of CuCo-ZIF catalyst (0–250 mg·L$^{-1}$) were added into 10 mL MO solution at various initial concentrations (10–70 mg·L$^{-1}$) with the presence of different amount of H$_2$O$_2$ (0.025 mol·L$^{-1}$). The kinetics experiment of this reaction was conducted and sampled at different time intervals (5–90 min). The residual concentration of MO was determined by the UV-visible (UV-Vis) spectrophotometer at a wavelength of 464 nm.

The degradation experiments of MB were also run in the identical procedure but at different initial concentrations of MB (10–50 mg·L$^{-1}$) and sampling time intervals (5–140 min). The residual amount of MB in solution was analyzed by UV-Vis spectrophotometer (Shimadzu UV-1800 Spectrophotometer) at a wavelength of 664 nm.

The removal efficiency of MO and MB was defined as the following equation:

\[
\text{Removal efficiency (\%)} = \left(1 - \frac{C_e}{C_0}\right) \times 100\%
\]

where $C_0$ is the initial concentration of MO or MB (mg·L$^{-1}$), and $C_e$ is the residual concentration of MO or MB (mg·L$^{-1}$).

### 2.4 Reusability of CuCo-ZIFs

To evaluate the reusability of CuCo-ZIF catalyst in the removal of MO and MB, the catalysis experiments were conducted at the optimal conditions of degradation reaction of MO and MB. Then the catalyst material was recovered by centrifugation, washed several times with ethanol, and then dried at 60°C in 24 h and reused. This procedure was repeated, and the recovered catalyst at the last run was analyzed by powder X-ray diffraction (PXRD) and Fourier transform-infrared (FT-IR) spectroscopy to assess its structural stability.

### 3 Results and discussion

The synthesized catalyst of CuCo-ZIFs was analyzed by using several characterization techniques, namely powder X-ray diffraction (PXRD), scanning electron microscope (SEM), energy dispersive X-ray (EDX), nitrogen adsorption–desorption isotherm, fourier-transform infrared spectroscopy (FT-IR), and thermogravimetric analysis (TGA) (Figures A1–A6 in Appendix). The results showed the successful preparation of CuCo-ZIF bimetallic framework. The novel Fenton-like reaction of the prepared catalytic of CuCo-ZIFs was proved by MO and MB degradation in the presence of hydrogen peroxide.

### 3.1 Degradation of MO and MB using a novel Fenton-like CuCo-ZIF catalyst

The catalyst dosage is critical because it plays a catalytic function in the activation of H$_2$O$_2$ to produce OH free radicals – a reducing agent for the MO and MB removal process. To determine the role of CuCo-ZIFs in the removal of both contaminants, a series of experiments were conducted with different catalyst dosages from 0 to 250 mg·L$^{-1}$.

Removal yields of both MO and MB with variation of CuCo-ZIF dosage from 0 to 250 mg·L$^{-1}$ are shown in Figure 3. Generally, removal yields of both dyes significantly increased with increasing CuCo-ZIF dosage. At catalyst dosage of zero, the yields of MO and MB removal were low, at 6.8% and 17.2%, respectively. The reason could be due to the instability and self-degradation of H$_2$O$_2$ into OH that could attack the MO and MB molecules, which caused the discoloring of dyes. As the catalyst dosage increased to 50 mg·L$^{-1}$, the removal yield markedly increased to 91.8% for MO and 97.2% for MB. The highest yield could be achieved at 99.3% for MO and 97.2% for MB as catalyst dosage were at 100 mg·L$^{-1}$. The above result showed the essential role of the catalyst in the removal process of MO and MB. The active sites Cu accelerated the decomposition of H$_2$O$_2$, leading to an increase of reactive oxygen species (OH). This active
species was a strong oxidant and was attributed to crack down the structure of both contaminants. However, this radical was not selective, so it attacked itself to form H₂O (Eq. 2) and HO₂⁻ (Eq. 3), leading to reduce the OH radicals and then decrease the contaminants removal yields. This phenomenon can be observed as catalyst dosage increased from 100 to 250 mg L⁻¹ and the degradation yield slightly decreased to 97.4% for MO and 96.7% for MB. Besides the above explanation, another reason that should be accounted for is the reduction of total surface area of the catalyst. When the high amount of catalyst dosage dispersed into the solution, those microparticles and nanoparticles tended to create the aggregation of such particles that limited the total active sites on the catalyst surface. Hence, to maintain a high removal efficiency in the following experiments, CuCo-ZIF dosage was chosen at 100 mg L⁻¹ for MO and 50 mg L⁻¹ for MB.

$$OH + OH \rightarrow H_2$$

(2)

$$H_2O_2 + OH \rightarrow HO_2 + H_2O$$

(3)

H₂O₂ is the main factor that directly attacks contaminants by producing the OH radicals; hence, it is necessary to determine the effect of H₂O₂ concentration on the degradation performance. To study the effect of H₂O₂ concentration on the MO and MB removal efficiency, the variation of H₂O₂ concentration was conducted from 0 to 0.25 mol L⁻¹, and the results are shown in Figure 4.

In the absence of H₂O₂, the removal efficiency of MO and MB were at 20.28% and 26.68%, respectively. The reason could be the adsorption capacity of CuCo-ZIFs due to its porous crystal structure and high surface area (1,555 m² g⁻¹). However, the low yields of adsorption mechanisms are not the main purpose of this research, and thus H₂O₂ was added before the adsorption occurred. When the H₂O₂ concentration increased from 0 to 0.25 mol L⁻¹, the MO and MB removal tended to increase, except for the MO removal at 0.25 mol L⁻¹ of H₂O₂. When the concentration of H₂O₂ varied from 0.05 to 0.2 mol L⁻¹, the removal efficiency increased from 64.57% to 98.53% for MO and from 62.90% to 96.89% for MB. At 0.25 mol L⁻¹ of H₂O₂, the removal efficiency of MO dropped down to 90.08%, whereas the MB removal efficiency maintained at 96.89%. This result can be attributed to the nonselectivity of OH. When a great amount of free radicals is generated but there is not enough time for MO degradation, these radicals not only attack H₂O₂ but also themselves, thus reducing the removal process. For MB removal, the efficiency kept constant at 96.89% when increasing the H₂O₂ concentration from 0.2 to 0.25 mol L⁻¹. These results showed that the addition of a higher concentration of H₂O₂ did not improve the removal efficiency. Therefore, the optimum H₂O₂ concentration for MO and MB removal were, respectively, found at 0.2 and 0.1 mol L⁻¹ for further experiments.

Determination of the initial organic dye concentration is required because in the wastewater, this concentration also varied. The initial measured pH values of MO and MB at different initial concentrations were 7.0 and 3.0, respectively. The initial dye concentration range varied as highest as possible to measure the exceptional catalytic activity of CuCo-ZIFs. The results were depicted in Figure 5 with an initial concentration in a range of 10–70 mg L⁻¹ of MO (Figure 5a) and in a range of 10–50 mg L⁻¹ of MB (Figure 5b). In Figure 5a, while the removal of MO remained unchanged at about 97–98% in a range of 10–50 mg L⁻¹ and dropped down to 85% and 71.84% at 60 and 70 mg MO L⁻¹, respectively. Similarly, in
Figure 5b, the removal of MB presented a high efficiency at 97–98% as initial concentration of MB varied from 10 to 40 mg MB·L⁻¹ and significantly reduced to 88.1% at 50 mg MB·L⁻¹. Basically, at the high concentration of dyes, more reaction between dye molecules and active centers was required to maintain the high removal efficiency. However, when there are more dye molecules dispersed into solution, they dominate the whole space of solution and are covered and adsorbed on the surface of catalyst particles. Therefore, the active sites were limited to interact with H₂O₂ leading to reduced reactive oxygen species. This could cause a decrease in degradation efficiency of both MO and MB at a very high concentration. One more reason is that 60 min is not enough for the catalyst to generate a large amount of free radicals for the degradation reaction. The different structures between MO and MB also led to the different behaviors of two dyes at high concentration, when MO structure contains only two aromatic rings whereas MB has three adjacent rings, which made MB structure more stable and then lower degrading yield compared to MO at the same concentration. Then, initial concentrations of 50 mg MO·L⁻¹ and 40 mg MB·L⁻¹ were chosen as optimum dye concentration for further experiments.

The reaction time is one of the important parameters of the degradation reaction because it affects the productivity of the removal process. If the time is short and not enough, it will lead to an incomplete reaction, reducing the contaminants decomposition efficiency; in contrast, if it is too long, it will cause unnecessary waste. A series of experiments were conducted at different time periods, from 5 to 90 min for MO and from 5 to 140 min for MB. The MB degradation required longer time because of the MB complex structure. The MO removal efficiency presented an increasing tendency within the first 60 min, thereafter the yield did not markedly change. More detailed, the efficiency of MO degradation achieved 35% in the first 5 min and increased to 87.9%, 91.8%, 96.7%, and 98.3% after 15, 30, 45, and 60 min, respectively. After that, when the reaction time continuously went to 75 and 90 min, the efficiency changed at very small levels to 98.8% and 99.4%, respectively. For MB, the degradation efficiency trend seemed like the MO removal, for which the efficiency showed a positive correlation with the reaction.
time. Figure 6b shows that the removal of MB achieved high efficiency in the first 20 min, dramatically increased from 36% to 88%, and reached 98% at 100 min. After that, it tended to reach an equilibrium of efficiency despite the longer time.

Generally, the removal of both MO and MB went fast and reached more than 90% in 30 min for MO and 40 min for MB. The optimum reaction time was chosen as 60 min for MO removal and 100 min for MB removal, with efficiency for both dyes above 98%.

The possible mechanism of MO and MB removal by CuCo-ZIFs is illustrated by the novel Fenton process and summarized in Figure 7.

The degradation of mixture of dyes was also studied at optimal parameters by using a solution of MO 50 ppm and MB 40 ppm. CuCo-ZIFs presented a good ability to accelerate H₂O₂ for dye mixture degradation. The results showed a high degrading performance on a two dye mixture within 60 min, demonstrating the promising potential of CuCo-ZIF material for the dye-polluted wastewater treatment (Figure 8).

3.2 Comparison catalytic activity of CuCo-ZIFs with other catalysts

For both the MO and MB removal processes, the catalytic activity of CuCo-ZIFs was compared to that of various homogeneous and heterogeneous catalysts. Homogeneous catalysts included 2-MIm, cobalt nitrate salt, and copper nitrate salt, which were the reactants for CuCo-ZIF synthesis.
Five types of heterogeneous catalysts, including zeolite, activated carbon, ZIF-8, ZIF-67, and Ag/ZIF-67, were also used to compare with CuCo-ZIFs under the identical conditions for each dye (Figure 10). The optimum conditions for MO and MB removal included catalyst dosage, $\text{H}_2\text{O}_2$ concentration, initial dye concentration, and reaction time from previous experiments were used. For MO, they were 100 mg·L$^{-1}$ catalyst, 0.2 mol·L$^{-1}$ $\text{H}_2\text{O}_2$, 50 mg·MO·L$^{-1}$, 60 min, and a pH value of 7.0 at ambient temperature, respectively. The optimal conditions of MB removal were 50 mg·L$^{-1}$ catalyst, 0.1 mol·L$^{-1}$ $\text{H}_2\text{O}_2$, 40 mg·MB·L$^{-1}$, reaction in 100 min and at a pH value of 3.0, and ambient temperature, respectively.

As shown in Figure 9, the MO removal efficiency of homogeneous catalysts was low. The efficiencies of using cobalt salt, 2-MIm, and copper salt achieved, respectively, 9.7%, 10.5%, and 18.3% after 60 min reaction. Obviously, they were much lower than the efficiency of using CuCo-ZIFs (98%). For MB, the catalytic activities of cobalt salt and 2-MIm were lower than 20%, whereas that of the copper salt performed a high efficiency at 80%; however, this value was still lower than that of CuCo-ZIFs (98%). Generally, the degradation of MO and MB using cobalt salt and 2-MIm was attributed to the presence of $\text{H}_2\text{O}_2$ only. In the meantime, the removal of MO and MB using copper salt in the presence of $\text{H}_2\text{O}_2$ was known as a Fenton reaction [40]. Nevertheless, the degradation of MO was lower than that of MB because the Fenton reaction was strong at low pH. That is the main reason for the higher removal performance of copper salt at pH 3.0 for MB. In terms of CuCo-ZIFs, the degradation of both MO and MB was a novel Fenton-like reaction, which is a synergistic catalyst between CuCo and ZIFs [41]. Chen et al. showed that reactive oxygen species, namely $^1\text{OH}$ and $^1\text{O}_2$, were the dominant reactive centers accelerating the degradation of two dyes [41]. The novel Fenton-like catalysis of this catalyst was also presented by its high performance at neutral pH (pH 7.0) instead of acidic pH.

In Figure 10, the catalytic activity of CuCo-ZIFs in comparison to that of heterogeneous materials is demonstrated. The results showed that the MO and MB removal efficiency of using other heterogeneous catalysts were
still lower than CuCo-ZIFs. For MO, the efficiency of using zeolite, activated carbon, ZIF-8, ZIF-67, and Ag/ZIF-67 increased in this order after 60 min. However, the catalytic efficiency of CuCo-ZIFs was still the highest one. For MB, the efficiency of using ZIF-8 was the lowest, and the efficiency orderly increased with activated carbon, zeolite, ZIF-67, Ag/ZIF-67, and CuCo-ZIFs. Zeolite showed very low and not remarkable efficiency due to the adsorption, whereas activated carbon and other ZIFs presented higher removal yields because of their interaction with H₂O₂ under stirring condition, which activated carbon and metal ions in ZIFs, accelerated the producing of hydroxyl radicals as presented in the following equations, and resulted in the breaking down of the structure of dyes [42–44].

\[
\begin{align*}
\text{AC} + \text{H}_2\text{O}_2 & \rightarrow \text{AC}^+ + \text{HO}^- + \text{HO} \\
\text{Co}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Co}^{3+} + \text{OH}^- + \text{OH}^- \\
\text{Cu}^+ + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{OH}^+ + \text{OH}^-
\end{align*}
\]

Moreover, Zn(II) in ZIF-8 is weaker than Co(II) in ZIF-67, so ZIF-8 presented a lower catalytic ability compared to ZIF-67. Both Ag/ZIF-67 and ZIF-67 showed a similar catalytic ability, and this might be because Ag(II) does not involve or play any important role in this reaction when it is doped on the ZIF structure. Consequently, those compared heterogeneous catalysts possessed Fenton-like catalytic activity, but the heterogeneous catalyst (CuCo-ZIFs) in this study presented a novel Fenton-like catalytic activity via the synergistic catalysis between CuCo and ZIFs.

### 3.3 Reusability of CuCo-ZIF catalyst

Reusability is a crucial parameter to consider in a heterogeneous catalysis. CuCo-ZIFs used in the experiment at optimal conditions for MO and MB removal were washed with ethanol and dried after using. Figure 11 depicted the results. The high efficiency is still retained after many times of recycling processes. For MO, the removal efficiency decreased from 98% at the first use to 89% at the fourth use of the catalyst, and for MB, this value fell from 99% to 87% after five times of recycling.

The determination of the material structure after many times of usage was also conducted by using PXRD and FT-IR analysis (Figure 12).

Infrared spectrum of the reused CuCo-ZIFs, in comparison with the fresh one, still maintained the peaks at the featured positions, although there was a little change, this change was relatively small and can be considered as

![Figure 11: The removal efficiency of MO after four times (a) and MB after five times (b) reusing of CuCo-ZIFs. MO: pH 7.0, catalyst dosage = 100 mg·L⁻¹, [H₂O₂] = 0.2 mol·L⁻¹, initial [MO] = 35 mg·L⁻¹, time = 60 min, and ambient temperature. MB: pH 3.0, catalyst dosage = 50 mg·L⁻¹, [H₂O₂] = 0.1 mol·L⁻¹, initial [MB] = 40 mg·L⁻¹, time = 100 min, and ambient temperature.](image)

![Figure 12: FT-IR spectrum of reused-CuCo-ZIFs, in comparison to fresh material.](image)
The efficient degradation of both dyes (almost 98%) was obtained at a low catalyst dosage (50–100 mg L\(^{-1}\)), \(\text{H}_2\text{O}_2\) concentration of 0.1–0.2 mol L\(^{-1}\), reaction time of 60–100 min, ambient temperature, and a pH of 3.0–7.0. The as-synthesized solid catalyst also maintained its high catalytic activity at least up to four times with MO and five times with MB degradation without significant reduction in catalytic structure. In conclusion, the CuCo-ZIFs catalyst showed a novel Fenton-like synthesis for the effective removal of both anionic and cationic dyes from aqueous solutions.

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**References**


Appendix

Figure A1: PXRD of CuCo-ZIFs.

Figure A2: SEM images of CuCo-ZIFs at different magnification ratios: (a) 20,000×, (b) 80,000×, and (c) 100,000×.

Figure A3: EDX spectra of CuCo-ZIFs.
Figure A4: Nitrogen adsorption–desorption isotherm of CuCo-ZIFs.

Figure A5: FT-IR spectra of CuCo-ZIFs and 2-MIm.

Figure A6: TGA analysis of CuCo-ZIFs.