Research Article

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Photocatalytic degradation of Rhodamine B in aqueous phase by bimetallic metal-organic framework M/Fe-MOF (M = Co, Cu, and Mg)

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Abstract: Bimetallic metal-organic frameworks (MOFs) exhibit outstanding performance in a wide range of applications, including gas catalysis, adsorption, and luminescence sensor. The structure and properties of materials can be designed based on the variation of different metal ions, so this MOFs material system has unique properties. In this study, M/Fe-MOF bimetallic materials (M = Co, Cu, and Mg) were synthesized by solvothermal method and evaluated for photocatalytic activity in the degradation reaction of rhodamine B (RhB) organic pigments. The as-synthesized materials were characterized by using several physicochemical methods such as X-ray diffraction, fourier transform infrared spectroscopy (FT-IR), ultra-violet-visible spectroscopy (UV-Vis), Brunauer–Emmett–Teller (BET), scanning electron microscopy (SEM), and UV-Vis diffuse reflectance spectra. The results show that the Co/Fe-MOF, Cu/Fe-MOF, and Mg/MOF materials have

uniform grain grade, high crystallinity, with the surface area of 26.1, 25.9, and 25.9 m²/g, respectively. When modified with Co, Cu, and Mg, the crystal structure of Fe-MOF materials was unchanged, and all metal ions are inserted inside the structure of the material, as well as replacing Fe ions in the lattice crystals. At the same time, the modification also increases the light absorption in the visible light region and gives a high photocatalytic degradation of RhB organic pigments under visible light in the range of 85–92%.

Keywords: bimetallic metal-organic framework, photocatalytic degradation, rhodamine B, solvothermal

1 Introduction

Currently, the concern for the development of the community is the problem of water pollution by dyes and pigments. The removal of dyes from wastewater has become a major research direction in the field of water pollution treatment. Moreover, the molecules of many dyes are very stable, are not degraded by light, chemical, biological, and other agents, and can affect human health [1,2]. The degradation of dyes by biological methods is usually very low because biological treatment methods are not effective. Wastewater containing high concentrations of dyes is usually treated by physical or chemical methods [3,4]. Currently, heterogeneous photocatalysis, which occurs when a catalyst is irradiated with a photon of light with an energy higher than the bandgap energy (E_g) of that photocatalyst, is considered an effective green method to treat wastewater containing organic matter [5–9].

Recently, the incorporation of second metal ions into the nodes of the framework for the synthesis of bimetallic metal-organic frameworks (MOFs) has been proposed to enhance the catalytic, electronic, and luminescent properties [5,10–14]. To form bimetallic MOFs, improve structural stability, and improve performance, conventional MOFs integrate two different metal ions into the same

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lattice structure [15]. Bimetallic MOFs have wide applications compared to single-metal MOFs, especially in gas sensing, separation and storage, drug delivery, and catalysis. Therefore, different Fe-based MOFs modification techniques have been used to narrow the bandgap energy (Eg) by doping metals (Co, Cu, Ni, Mn, Sn, Pt, etc.) onto Fe-MOF to bring the activity of photocatalytic materials to the visible light region [16–18].

A recent study by the Gu group [19] investigated the influence of the $\text{Mg}^{2+}/\text{Fe}^{3+}$ ratio on the crystal formation of the MIL-88B(Fe) material structure, and its application in removing arsenic needles in wastewater. In 2018, Nguyen Huu Vinh and the research team successfully prepared a MOF-based Ni/Fe mixture with different molar ratios of $\text{Ni}^{2+}/\text{Fe}^{3+}$ through the heat capacity method. The results indicate that the Ni/Fe-MOF samples obtained based on the evaluation of the color photochemical degradation of rhodamine B (RhB) dye showed a high photocatalytic activity compared with MIL-53(Fe). The decomposition rate of Ni/Fe-MOF-0.3 can reach the highest level (91.14%) after 180 min of visible light irradiation [20]. A recent study, in 2019, by Chengdong Yang's research group has successfully synthesized and modified NH_2 -MIL-88B(Fe) into porous carbon nanomaterials. The postsynthesized material is applied in the field of catalyzing the degradation of bisphenol A, methylene blue, and tetracycline [21].

In 2020, the Hong-Tham T. Nguyen research group used microwave-assisted method to successfully synthesize MIL-88B(Fe) and the Al/Fe bimetallic framework (Al/Fe-MOF). The Fenton photodegradation of RhB under visible light irradiation was carried out in the presence of the synthesized samples as an efficient catalyst. Al/Fe-MOF catalyst degrades more than 96% RhB in up to 120 min [22]. Most of the synthesis of MOFs is carried out by hydrothermal or solvent-thermal methods, based on the change of the polar solvent combined with the appropriate temperature. Specifically, a mixture of ligands and metal salts dissolved in a solvent (or mixture of solvents) is heated less than 300°C for 8–48 h to grow crystals [23]. By solvent and hydrothermal methods, it is possible to synthesize MOFs with high crystalline strength to determine the structure. However, these methods also have limitations such as long reaction times, limited large-scale synthesis, and high error; other alternative synthesis processes have been investigated, such as support microwave, electrochemical, sonication, and mechanical ball milling [24]. But these methods cannot yield crystals of sufficient quality for structure determination compared with solvent and hydrothermal methods. In addition, the synthesis of materials by solvent and hydrothermal methods is simple, the morphology

of crystals can be controlled by changing the synthesis conditions, and is less expensive. However, based on the characterization of the modified material with crystal structure and controlled crystal size, it exhibits superior photochemical and adsorption activity.

In addition, earlier domestic studies have not focused on the synthesis of structural modifications of Fe-MOF with Co^{2+} , Cu^{2+} , and Mg^{2+} ions and their application in photochemical reactions for the degradation of harmful substances under the influence of sunlight or visible light. However, metal ion doping increases its luminescence to the visible light region of the catalyst surface and reduces the bandgap energy, increasing the photocatalytic activity.

Therefore, the main objective of this study is to synthesize and determine the characteristic properties of Fe-MOF-based bimetallic materials with Co^{2+} , Cu^{2+} , and Mg^{2+} by using solvothermal method. At the same time, studying the structural, morphological, and physicochemical properties of the composites determined by physicochemical methods such as X-ray diffraction (XRD), FT-IR, UV-Vis, SEM, BET, and UV-Vis diffuse reflectance spectra (DRS). Specifically, the efficiency of the material is applied in a photocatalytic reaction that decomposes RhB dye under visible light.

2 Material and methods

2.1 Materials

Metal salts include iron(III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98.5%, China); copper(II) nitrate trihydrate, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%, China); cobalt nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (China 99%); and magnesium chloride, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (China 99%). The solvents used were acetonitrile, CH_3CN (Merck, Germany 99.5 %); terephthalic acid, H_2BDC (Sigma Aldrich 98%); methanol, CH_3OH (China); *N,N*-dimethylformamide, DMF (China 99.5%); and RhB, $\text{C}_{28}\text{H}_{31}\text{ClN}_2\text{O}_3$ (Sigma Aldrich).

2.2 Preparation of M/Fe-MOF (M = Co, Cu, and Mg)

The bimetallic organic framework, M/Fe-MOF (M = Co, Cu, and Mg), was prepared by the solvothermal method, based on the synthesis process published in the earlier literature [25]. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.1455 mmol), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0145 mmol) and 1,4 benzene dicarboxylic acid (0.18 mmol) and 40 mL

DMF. Next, 40 mL of CH_3CN was added with stirring at room temperature to form a transparent solution. The mixture was then placed in a 100 mL Teflon flask and transferred to a reactor heated at 150°C for 12 h. After cooling, the precipitate was collected by centrifugation. To remove impurities, the material was washed three more times with DMF and three times with methanol. Finally, the product was dried at 150°C under a vacuum. The synthesis processes of Cu/Fe-MOF and Mg/Fe-MOF materials are similar to that of Co/Fe-MOF.

2.3 Characterization of catalyst

The determination of the presence of functional groups present in the material is based on analytical method FT-IR infrared spectroscopy recorded in the range of $500\text{--}4,000/\text{cm}$ was measured on Nicolet 6700 – Thermo Fisher Scientific (USA). The crystalline phase composition of the material was determined based on the XRD method and measured on a D8 Advanced – Hitachi (Germany) instrument using Cu K α radiation ($\lambda = 1.54188 \text{ \AA}$). The UV-Vis DRS diffuse reflectance spectroscopy method was measured on a Shimadzu UV-2450 instrument with wavelengths from 200 to 800 nm. The surface morphology and particle size of the samples were investigated through SEM images by the device S4800 – JEOL (Japan). Specific surface and capillary characteristics of porous materials were determined by nitrogen adsorption–desorption isotherms on Micromeritics 2020 – Micromeritics, USA. The UV-Vis visible and ultra-violet absorption spectroscopy methods were used to determine the concentration of the pigment solution during the photocatalytic activity test of the materials recorded on a UV-Vis visible spectrometer (Aligent Cary 60, Malaysia).

2.4 Catalytic activity test

The process of evaluating the photocatalytic activity of the synthesized materials was carried out based on the ability to decompose RhB pigments with a light source of 40 W LED, with a distance of 15 cm between the light source and the RhB solution. The reaction solution mixture consisted of 5 mg of catalyst material dispersed in 100 mL of RhB solution at a concentration of $3 \cdot 10^{-5} \text{ M}$, 1 mL of a 1 mM H_2O_2 solution in a 250 mL (Jacket Glass Beaker-NANSHIN-China) heat-resistant reaction beaker under visible light. Each spout at the top and bottom of the beaker is used to connect flexible hoses that allow water to pass through to cool the reaction system. The mixture was stirred in the dark for 1 h so that the adsorption–desorption process reached equilibrium. During

illumination, 4 mL was removed from the reaction system at intervals of 120 min. After taking out, the samples were centrifuged at 6,000 rpm for 10 min to completely remove the solids.

3 Results and discussion

The XRD patterns of these materials are shown in Figure 1. All samples show similar XRD patterns, which is consistent with the topology of Fe-MOF. Notably, compared with Fe-MOFs, the XRD patterns of M/Fe-MOF shift toward higher angles at 11.42° , whereas at 19.38° , they shift toward lower angles. This observation is generally consistent with earlier reports, based on the breathing effect and flexibility of the Fe-based MOF structure, where simultaneous displacements occur from lower and higher angles in both directions [26]. Partial replacement of Fe^{3+} ions with other divalent metal ions (M^{2+}) will lead to a slight decrease in the Fe–O bond length and a slight increase in the Fe–O–Fe angle, which is explained. Correspondingly, the parameters and unit cell volume of the formed MOFs are influenced by the change of the diffraction peaks.

FT-IR spectra were used to determine the bonds in CoFe-MOF, CuFe-MOF, and MgFe-MOF materials in the wavenumber region from 500 to $4,000 \text{ cm}^{-1}$ and obtained the results as shown in Figure 2. FTIR spectra appear that

Figure 1: XRD patterns of M/Fe-MOF (M = Co, Cu, and Mg).

Figure 2: FTIR spectra of M/Fe-MOF (M = Co, Cu, and Mg).

the peak oscillation peak at about 3108.7 cm^{-1} is the oscillation of the O–H bond of the water molecules absorbed on the surface of the material. In addition, the peak at

750.1 cm^{-1} , due to fluctuations in the C–H bonds of the BDC ligands. The presence of valence vibrations (Fe–O) at 552.5 cm^{-1} indicates the formation of a metal–oxo bond between the carboxylic group of terephthalic acid and Fe(III). For Fe-MOF, the oscillation of the central oxygen in the Fe_3O cluster combines with the D_{3h} symmetry to produce adsorption that peaks around 613 cm^{-1} . However, the symmetry is reduced from D_{3h} to C_{2v} when the iron present in the trinuclear metal cluster is displaced and replaced by another metal ion [27]. The change of metal ions in the lattice will lead to a change of the peak position, indicating successful coordination between different metal ions and binders. The above results demonstrated the formation of Fe-MOF structure in all materials and confirmed the successful synthesis of Fe_2MO clusters in $\text{Fe}_2\text{M-MOF}$.

The crystal shape, grain size, and grain distribution of the materials were observed through SEM images (Figure 3). When doping with other metal ions, in general, the morphology of the material is changed compared to the original Fe-MOF, the material has an octahedral crystal structure, and the crystal strength is quite high. The results show that Co/Fe-MOF and Cu/Fe-MOF, and Mg/Fe-MOF samples have uneven surface morphology, large particle size, unclear grain boundaries, and agglomeration of particles. These results also demonstrate the

Figure 3: SEM images of M/Fe-MOF (M = Co, Cu, and Mg).

formation of Co/Fe-MOF, Cu/Fe-MOF, and Mg/Fe-MOF. The results are consistent with some previously published studies. Tang and Wang FE-SEM analysis, showed significant morphological changes in three $\text{Fe}_x\text{Cu}_{1-x}$ (BDC) samples [28]. Compared with the Fe (BDC) and Cu (BDC) samples with the presence of octahedral microcrystals, Cu (BDC) samples have a cubic layered structure. The introduction of Cu into the Fe framework (BDC) causes the decomposition of the original octahedron into small irregular particles. With the change with increasing copper ratio in $\text{Fe}_x\text{Cu}_{1-x}$ (BDC), the granular structure formed a scaly irregular structure and grew in a two-dimensional direction [28]. In which, the incorporation of the second metal element can affect the final morphology of Fe-MOF, which is completely consistent with previous reports [19].

The average capillary structure of the M/Fe-MOF bimetallic material was confirmed through the nitrogen adsorption–desorption isotherm (BET) study as shown in Figure 4. Nitrogen adsorption–desorption curves of type II (according to IUPAC classification) are typical for the presence of micro and medium capillary types.

The specific surface area of BET has a difference between metal ions in Fe-MOF bimetallic materials, specifically Co/Fe-MOF ($26.1 \text{ m}^2/\text{g}$), Cu/Fe-MOF ($25.9 \text{ m}^2/\text{g}$), and Mg/Fe-MOF ($28.6 \text{ m}^2/\text{g}$). The corresponding specific surface area is increased by the incorporation of more light metals (Mg) in the Fe/Mg-Mil-88B bimetal. The results of research group Yue Gu (2018) showed that the specific surface area (BET) of Fe/Mg-MIL-88B at the ratios of 0.5, 1, and 2 was synthesized to be 360, 282, and $218 \text{ m}^2/\text{g}$, respectively. It is noteworthy that the Fe-MIL-88B ($57 \text{ m}^2/\text{g}$) crystals have a markedly lower BET surface area than the Fe/Mg-MIL-88B(n) bimetallic structures [19].

The inclusion of the secondary metal in the Fe-MOF framework is beneficial to promote full contact of the active sites of the resulting bimetallic M/Fe-MOF. Furthermore, the pore volume and specific surface area tend to increase with the M/Fe molar ratio. The results of this study are similar to the study reported by Jiao *et al.* on Mg/Ni-MOF-74, in which the BET surface area decreased when replacing heavier transition metal [29].

Figure 4: N_2 adsorption–desorption isotherms of M/Fe-MOF (M = Co, Cu, and Mg): (a) Fe-MOF, (b) Co/Fe-MOF, (c) Cu/Fe-MOF, and (d) Mg/Fe-MOF.

Dang et al. evaluated the specific surface area of Fe/Co-MOF materials. The N_2 adsorption-desorption isotherms of Co-MOFs, Fe-MOFs, and MFC-MOFs (1:3) showed type IV isotherms [17]. Compared to the BET surface of 47.8 and 7.8 m^2/g for Fe-MOF and Co-MOF alone, MFC-MOF (1:3) actually possesses a significantly larger BET surface area of 215.6 m^2/g [17]. Tang and Wang also showed that with the increasing proportion of copper in the bimetal due to the collapsing of nanoholes due to Cu incorporation, a change in pore size distribution can be observed from microparticles (<2 nm) to medium particles (2–50 nm) in Fe_xCu_{1-x} (BDC) [28]. The measured BET surface area of Fe (BDC) was 715.8 m^2/g , decreasing to 264.9 m^2/g for $Fe_{0.80}Cu_{0.20}$ (BDC), 219.4 m^2/g for $Fe_{0.75}Cu_{0.25}$ (BDC), and 52.6 m^2/g for $Fe_{0.67}Cu_{0.33}$ (BDC), respectively [28].

The light absorption ability in the long-wavelength region (visible light region) of the catalyst samples was studied through solid UV-Vis spectroscopy. Figure 5 shows that the solid UV-Vis spectrum measured in the wavelength range of 200–1,400 nm shows that the bimetallic samples have a strong absorption range in the wavelength region from 200 to 400 nm.

The bandgap energy (E_g) of M/Fe-MOF materials synthesized by the solvothermal method is 2.42 eV (Mg/Fe-MOF), 2.3 eV (Cu/Fe-MOF), and 2.32 eV (Co/Fe-MOF). Moreover, the presence of the second metal helps to disperse the Fe-MOF crystals evenly, creating small-sized particles, and the second metal has a very important role in receiving electrons from the conduction band of the metal. MOFs photocatalysts, reducing and limiting the recombination between electrons and holes h^+ , effectively increase the catalytic activity as well as the catalytic stability.

The photocatalytic activity of three bimetallic samples M/Fe-MOF (M = Co, Cu, and Mg) was investigated through the photochemical degradation of RhB in the presence of H_2O_2 . The photocatalytic results of the modified materials are presented in Figure 6. The decomposition efficiency is in the range of 85–92% after 120 min of light. The transformation of MOFs depends on the influence of the central metal and the substitution metal, leading to a different photocatalytic performance. The relation of characterization results includes surface area, bandgap energy, and catalytic activity. The metal ion doping reduces the energy of the semiconductor region of the material, prevents the recombination of the e^- and h^+ pairs, and thereby increases the impact performance of the material. In addition, the M/Fe metal frame consists of Fe_2MO metal clusters (M = Co, Cu, Mg) with a higher pore diameter and specific surface area than the Fe monocentric metal framework. Therefore, M/Fe-MOF exhibits high photocatalytic activity in RhB degradation. Ding et al. showed that the degradation of tetrabromobisphenol A by $CuFe_2O_4$ magnetic nanoparticles exhibits high catalytic efficiency for peroxymonosulfate (PMS) [30]. In a recent publication, Chen et al. conducted the synthesis of Co/Fe bimetal oxide to degrade norfloxacin by PMS activation, with a 100% degradation rate under optical conditions [31]. In addition, Ren et al. showed that other bimetallic oxides MFe_2O_4 (M $\frac{1}{4}$ Cu, Co, Zn, and Mn) are also good heterogeneous catalysts of PMS [32]. In general, the expression of novel properties through mutual enhancement or modification is due to the synergistic advantage of the individual components of multicomponent catalysts. Therefore, the potential discovery of new bimetallic organic frameworks has become a new research direction with many

Figure 5: (a) UV-Vis diffuse reflectance spectra (UV-Vis DRS) and (b) bandgap energies (E_g) of M/Fe-MOF (M = Co, Cu, and Mg).

Figure 6: (a) Photodegradation of RhB, (b) UV-Vis spectral of RhB of Co/Fe-MOF, (c) Cu/Fe-MOF, and (d) và Mg/Fe-MOF.

potential applications. For example, El-sharkawy *et al.* prepared bimetallic organic frameworks and used them to catalyze the oxidation color degradation of Acid-Blue 92 in the presence of H_2O_2 [33]. In a recent publication, Li *et al.* showed that the catalytic activity of Fe/Co-MOF in 15 min removes almost 100% of methyl blue (MB) by the unsaturated metal active site of Fe(II), and Co(II) contributes to the generation of sulfate ($\text{SO}_4^{\cdot-}$) and hydroxyl ($\text{OH}^{\cdot}$) radicals, improving the ability to degrade MB [18].

Under the influence of visible light, photocatalysis took place in the presence of bimetallic materials M/Fe-MOF (M = Co, Cu, and Mg) in the RhB colorant solution, the electrons (e^-) jump from highest occupied molecular orbital to lowest unoccupied molecular orbital creating electrons (e^-) and holes (h^+). The second metal ion doping has a very important role to accept electrons from the conduction band of MOF photocatalysts, reducing and limiting the recombination ability between electrons (e^-) and holes (h^+), and the efficiency is to increase the catalytic activity and catalytic stability. Hole (h^+) reacts with H_2O to generate free radicals $\text{OH}^{\cdot}$ and e^- reacts with O_2 to produce free radicals $\text{O}_2^{\cdot-}$. These free radicals have a high

reducing potential, which is capable of oxidizing RhB, which thoroughly processes pollutants into CO_2 and H_2O . Due to the synergistic effect of $\text{O}_2^{\cdot-}$, $\text{OH}^{\cdot}$ radicals, RhB is broken into many pieces. The final products will be completely decomposed to produce CO_2 , H_2O , and other small organic acids. Besides, the presence of H_2O_2 is evaluated as a better electron acceptor than O_2 , preventing the recombination of the e^- and h^+ pairs. Besides, H_2O_2 is a hydrophilic substance, in contact with the hydroxylated M/Fe-MOF particles, while retaining the e^- photochemical process, accelerating the oxidation of organic compounds [34].

In addition, the photocatalytic degradation of RhB shown in Figure 7 shows the corresponding pseudo-first-order kinetics by the following equation:

$$-\ln(C/C_0) = kt, \quad (1)$$

where C_0 and C are the concentrations of RhB in solution at the initial concentrations of RhB and the concentrations of RhB at time t , respectively, the value of k is the apparent first-order rate constant. According to the equation, the RhB degradation rate is calculated as 0.01508/min (Fe-MOF), 0.01786/min (Cu/Fe-MOF), 0.01831/min

Figure 7: Kinetics study of photocatalytic RhB degradation using of M/Fe-MOF (M = Co, Cu, and Mg) catalyst.

(Mg/Fe-MOF), and 0.02257/min (Co/Fe-MOF). The results show that when doping the second metal ion into the lattice framework, the pseudo-first-order rate constant is higher than that of the single-metal MOF sample.

4 Conclusion

In this study, M/Fe-MOF materials modified with Co, Cu, and Mg were synthesized by solvothermal method. When Fe-MOF is modified with Co, Cu, and Mg, the resulting material has a specific surface area and pore volume as follows: Co/Fe-MOF (26.1 m²/g and 8.2 nm), Cu/Fe-MOF (25.9 m²/g and 9.26 nm), and Mg/Fe-MOF (28.6 m²/g and 1.52 nm). Moreover, the M/Fe-MOF material has a low band gap of 2.3–2.42 eV, which is favorable for sunlight absorption and might confer improved catalytic activity. In photocatalytic experiment against RhB dyes in aqueous media, M/Fe-MOF materials exhibited high photocatalytic ability, which achieved about 85–92% conversion after 120 min of reaction. The present results open up the potential and application of Fe-MOF bimetallic materials in the field of heterogeneous photocatalysis for environmental treatment.

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