CoZnFeO₄ prepared by waste ferrous sulfate as iron source: synthesis, characterization and photocatalytic degradation of methylene blue

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ABSTRACT

In this study, a ferrate material with a narrow band gap and rapid electron hole separation ability is synthesized for degrading methylene blue from industrial wastewater. Hard ferrite (CoZnFeO₄) with octahedral structure is synthesized by solid-phase method from waste ferrous sulfate. The structure of the catalyst was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). TPR study showed that the oxidation performance of CoZnFeO₄ is improved with the addition of cobalt. The total organic carbon removal rate of methylene blue over CoZnFeO₄ catalyst is 90% within 60 min. The effects of reaction time, pollutant concentration, catalyst dosage and oxidant concentration on the removal efficiency were optimized. ESI–MS demonstrated the stability of the catalyst for leaching. X-ray diffractometry (XRD) and X-ray energy dispersive spectroscopy (XPS) showed that the catalyst could be reused. These findings provide a low cost and simple strategy for rational design and modulation of catalysts for the industrial degradation of organic pollutants. It not only realizes the use of waste to treat waste, but also accords with the current concept of green chemistry.

1 Introduction

At present, the global annual output of dyestuff exceeds 7 million tons, and the dyestuff varieties of dyestuff have more than 100,000 kinds. Nearly 15% of dyestuff is discharged into wastewater every year. Organic dyestuff wastewater has become an urgent problem to be solved in all countries [1]. Most organic dyes are in the form of aromatic groups such as benzene, naphthalene, anthracene, and quinone, which are highly mutagenic and carcinogenic and pose a growing threat to the water environment [2, 3]. Among them, methylene blue (MB) is one of the most
common dye, but it is difficult to be degraded by some conventional methods, easy to cause serious environmental pollution.

At present, the treatment of organic dye wastewater including MB dye wastewater mainly includes advanced oxidation method [4], precipitation, ion exchange, flocculation, a biological method [5], and membrane filtration [6]. In the advanced oxidation method, photocatalysis is a cheap and efficient method, which efficiently convert solar energy into chemical energy, which is one of the most ideal strategies to solve environmental pollution [7]. In 1972, the report of using TiO$_2$ electrodes to achieve photochemical decomposition of water to produce H$_2$ aroused the interest and exploration of a large number of scholars [8]. Since then, a series of systems (such as TiO$_2$, ZnO, ZnS) semiconductor photocatalysts have been reported to decolorize organic pollutants and harmful microorganisms. However, due to the large bandgap width of these semiconductor photocatalysts, they can only use the ultraviolet region (only 4% of the solar energy), which seriously hinders the full utilization of solar energy resources. So, to make more efficient use of the visible light region (> 400 nm), it’s important to use a visible-light-induced photocatalyst that improves recycling efficiency.

As a kind of important magnetic material, cubic spinel ferrites have been the subject of intense research for potential application in the recovery of photocatalysts, magnetic resonance imaging, and high-density storage, magnetic diagnosis [9] and magnetic fluid hyperthermia treatment for malignant growth [10, 11]. Among them, nanometer ZnFe$_2$O$_4$ is the most studied. Because of its nanoscale effect, ZnFe$_2$O$_4$ has remarkable super-para-magnetism, electrical properties, high stability, paramagnetism and biomedical properties [12]. Zn$^{2+}$ is located in the center of the tetrahedron gap and is covalently connected with O$^{2-}$, Fe$^{3+}$ is located in the center of the octahedron gap and is covalently connected with O$^{2-}$. Because there are a large number of covalently linked in the tetrahedron, nano ferric acid has stable physical and chemical properties. Spinel zinc ferrite has a narrow bandgap (2.11 eV), high sensitivity to visible light, photochemical stability, and low toxicity, and is expected to be a visible light catalytic catalyst. However, due to its wide bandgap and poor electron and hole separation ability, its photocatalytic activity is still a difficult problem. Therefore, to improve the ability of charge transfer, it is necessary to modify pure zinc ferrite materials. However, the catalytic activity of spinel ferrite depends entirely on octahedral position, so its catalytic activity is directly related to the cation on octahedron. Studies have shown that cobalt ions can occupy the position of ferrite octahedron. Sanadi et al. doped Co with ZnAlCrO$_4$ for photocatalytic decolorization of Rhodamine B (Rhb), and the results showed that the decolorization rate of Rhb increased from 57 to 83% after doping Co, indicating that cobalt ions can improve charge transfer, which is of great significance for photocatalysis [8].

Waste ferrous sulfate is an industrial by-product produced during the production of titanium dioxide by a sulphuric acid method. In 2018, the titanium dioxide industry produced more than 7 million tons of ferrous sulfate as a by-product [13]. With the increasing demand for titanium dioxide, the annual growth rate of by-products is more than 10%, which seriously restricts the sustainable development of the titanium dioxide industry. At present, only a small part of waste ferrous sulfate is recycled and the rest is still disposed of as industrial waste solid [14, 15]. Therefore, the accumulation of waste ferrous sulfate not only causes a huge waste of sulfur and iron resources but also causes serious environmental pollution. It has become an urgent task to explore the resource utilization of waste ferrous sulfate.

In this study, CoZnFeO$_4$ is prepared by a one-step solid-phase method with low cost, simple process, simple operation, and easy industrialization. To reduce the synthesis cost, CoZnFeO$_4$ nanoparticles are prepared with waste ferrous sulfate as an iron source and pyrite as a reducing agent, which are used as photocatalyst for decolorizing MB.

2 Experimental methods

2.1 Materials

In this study, the waste ferrous sulfate (FeSO$_4$, Panzhihua Iron & Steel Group Co. LTD, China), which is the main byproduct of titanium dioxide prepared by the sulfuric acid method. The sample composition is shown in Table 1. The sample composition of pyrite (FeS$_2$, Sichuan Hanyuan Chemical
Co. LTD, China) is shown in Table 2. Ferric oxide (Fe$_3$O$_4$), ferric oxide (Fe$_2$O$_3$), zinc oxide (ZnO), cobalt oxide (Co$_3$O$_4$), zinc sulfate (ZnSO$_4$7H$_2$O), methylene blue(C$_{16}$H$_{18}$ClN$_3$S/C$_1$$_3$H$_2$O) (Chengdu Cologne Chemicals Co. LTD, China). Cobalt sulfate (CoSO$_4$7H$_2$O), hydrogen peroxide (H$_2$O$_2$), sodium hydroxide (NaOH), muriatic acid (HCl), benzoquinone (BQ), nitrate (KNO$_3$), potassium bicarbonate (KHCO$_3$), monopotassium phosphate (KH$_2$PO$_4$), potassium chloride (KCl) (Chengdu Jinshan Chemical Reagent Co. LTD, China). All solutions are prepared using deionized water.

### 2.2 Preparation of CoZnFeO$_4$ and ZnFe$_2$O$_4$

CoZnFeO$_4$ is synthesized form using ferrous sulfate as the iron source and pyrite as the reducing agent, by solid-phase reduction under the condition of nitrogen. The reaction of synthetic CoZnFeO$_4$ is as follows:

$$3\text{ZnSO}_4 + 3\text{CoSO}_4 + 2\text{FeSO}_4 + \text{FeS}_2 \rightarrow 3\text{CoZnFeO}_4 + 10\text{SO}_2(g)$$

(1)

The experimental process of preparing CoZnFeO$_4$ is as follows: ferrous sulfate, pyrite, ZnSO$_4$.7H$_2$O, and CoSO$_4$.7H$_2$O are dried for 120 min at 393.15 K, respectively, and the samples are taken according to the molar ratio 4:4:3.5:1, 11.50 g ZnSO$_4$.7H$_2$O, 11.24 g CoSO$_4$.7H$_2$O, 9.73 g waste ferrous sulfate, and 1.20 g FeS$_2$ are weighed and mixed in a high-speed ball mill for 120 min. The mixture is put into a high-temperature zone of the tube furnace under nitrogen protected and heated to 823.15 K for 60 min. After natural cooling to room temperature, the impurities are wished with anhydrous ethanol and deionized water in turn. Finally, it is vacuum dried for 300 min at 372.15 K. The experimental process of preparing ZnFe$_2$O$_4$ is as follows: ferrous sulfate, pyrite, ZnSO$_4$.7H$_2$O are dried for 120 min at 393.15 K, respectively, and the samples are taken according to the molar ratio 2:3.5:1, 11.50 g ZnSO$_4$.7H$_2$O, 9.73 g waste ferrous sulfate, and 1.19 g FeS$_2$ are weighed and mixed in a high-speed ball mill for 120 min. The roasting procedure is the same as for CoZnFeO$_4$.

### 2.3 Degradation experiment of methylene blue

The decolorization rates of MB at different concentrations are studied, the effect of different nanomaterials on decolorizing Photo-Fenton reaction. A certain amount of CoZnFeO$_4$ nanoparticles are dispersed into MB solution as a catalyst, and then the given pH value of MB solution is adjusted using an automatic pH titrator (4 mol/L NaOH or 4 mol/L HCl). The dark chamber stirred for 1 h to achieve the balance of absorption and desorption. Then, the 5 mL of H$_2$O$_2$ at a certain concentration is added into the above-mixed solution and reacts under a certain wavelength for the light-ton reaction. The decolorization effect of MB under different reaction times is obtained under the parallel apparatuses. After taking out the parallel reaction solutions with different reaction times, 3.33 mL tert-butanol solution is added as the reaction inhibitor, the nanocatalyst is removed by centrifugation, and the concentration of MB in the supernatant is determined by spectrophotometer.

### 2.4 Characterization method

The crystal structure of solid powder is analyzed by X-ray diffraction (XRD, Empyrean, PANalytical). Scanning electron microscope (SEM, JSM-5900LV) and X-ray microregion analysis (EDS, JSM-5900LV) is used to analyze the sample morphology and element composition. X-ray photoelectron spectroscopy (XPS, Kratos, XSAM800) is used to analyze the surface composition of the samples. The nitrogen adsorption technique (BET, Brunner–Emmet–Teller) is used to determine the specific surface area of the sample. The surface properties of the samples are recorded by

| Compositions | Fe$_2$O$_3$ | SO$_2$ | MgO | ZnO | CaO | Al$_2$O$_3$ | NiO |
|--------------|------------|-------|-----|-----|-----|------------|-----|
| wt%          | 52.10      | 45.55 | 2.10| 0.19| 0.01| 0.012      | 0.013|

### Table 1 The chemical compositions of ferrous sulfate

### Table 2 The main chemical compositions of pyrite in the experiment

| Compositions | Fe | S  | Ca | Si | Pb | Al | Mn |
|--------------|----|----|----|----|----|----|----|
| wt%          | 48.30 | 38.05 | 3.43 | 1.08 | 0.88 | 0.32 | 0.306 |
Fourier infrared spectroscopy (FT-IR, Nicolet IS10) at wavelength range (4000–200 cm\(^{-1}\)). The optical properties of nanomaterials are analyzed by UV–Vis near-infrared spectrophotometer (Shimadzu, UV-3600) and fluorescence spectrometer (Hitachi, F-7000). Ethylene Diamine Tetraacetic Acid (EDTA), 1,4-Benzquinone (BQ), Cupric cell (Cu(NO\(_3\))\(_2\)) are used as free radical traps. The Zn, Fe, and Co ions released by the catalyst are detected by a plasma spectrometer (ICP-MS, Agilent 7700). Adjusting the pH of the solution using the automatic pH titrator (Metrohm, 916 Ti-Touch). The surface charge of nanoparticles is measured by Zetasizer Nano-ZS under different pH conditions. ESI–MS spectra are obtained on Bruker Amazon SL spectrometer (BrukerInc. Switzerland). Ion chromatography (Thermo Scientific, ICS-600) is used to measure anions.

3 Results and discussion

3.1 Characterization of nanomaterials

Figure 1a shows the XRD pattern of the synthesized CoZnFeO\(_4\) nanoparticles. The XRD located at \(2\theta = 18.04^\circ, 29.81^\circ, 35.14^\circ, 36.99^\circ, 42.74^\circ, 53.12^\circ, 56.60^\circ, 62.19^\circ, 70.46^\circ, 73.60^\circ, 74.58^\circ, \) and \(78.57^\circ\) diffraction angles, which corresponds to the crystal surface of \([\text{Fe}^{3+}]_A[\text{M}^{2+}\text{Fe}^{3+}]\text{BO}_4\) (111), (220), (311), (222), (400), (422), (511), (440), (620), (533), (622), (444) \((\text{ZnFe}_2\text{O}_4); \text{JCPDS Card No.79-1150 and CoFe}_2\text{O}_4; \text{JCPDS Card No.22-1086})\), indicating that the formation of the CoZnFeO\(_4\) nanoparticles are composed of single phase. It indicates that CoZnFeO\(_4\) may be formed. According to the famous Debye–Scherer equation [16], the average grain size of the synthesized CMFNPs is estimated to be 27 nm. The infrared spectrum of the nanoparticle is shown in Fig. 1b broadband at 3445 cm\(^{-1}\) and, 1632 cm\(^{-1}\) can be considered as the stretching vibration of –OH. Besides, the absorption peak of 1376 cm\(^{-1}\) also indicates the presence of a large amount of –OH. Moreover, the absorption peaks of 1074 cm\(^{-1}\) indicate the existence H\(_2\)O deformation vibration. The strong characteristic bands observed at 572 cm\(^{-1}\) can be attributed to the stretching vibration of M\(^{3+}\).O\(^{2-}\) octahedron of typical spinel ferrite, it also indicates that CoZnFeO\(_4\) may be produced. The surface composition and chemical state of the molded sample are determined by X-ray photoelectric spectrometry, as shown in Fig. 2. The peaks of Fe, Co, Zn, and O are observed in Fig. 2a. In Fig. 2b, the two main peaks of the combined energy 780.3 eV and 795.2 eV belong to the core energy levels of Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\) [7, 17], this indicates the existence of Co\(^{3+}\) in nanomaterials. In Fig. 2c, the peaks of the binding energies of 711.2 eV and 724.63 eV belong to the core energy levels of Fe 2p\(_{3/2}\) and Fe 2p\(_{1/2}\) [18, 19], this is typical of Fe(III) in inverse spinel ferrite. The synthesis of CoZnFeO\(_4\) is demonstrated by XRD and FTIR. In Fig. 2d, O1s spectrum is divided into absorption peaks of 530.15 eV, 531.69 eV, and 532.64 eV, corresponding to lattice oxygen (O\(^{2-}\)) in metal oxides, the hydroxyl group (–OH) is hydroxylated on the surface and physically adsorbed the water on the sample surface [20].

To understand the morphological characteristics of nanomaterials, FE-SEM, and EDS analysis are performed on the prepared materials (as shown in Fig. 3). In Fig. 3a, most of the CoZnFeO\(_4\)
nanoparticles are uniform with a narrow particle size distribution, and the average particle size is a spherical particle of 30 nm. In addition, there is a certain agglomeration of particles from the figure, which may be due to electrostatic attraction and van der Waals force, some primary particles tend to aggregate in local areas. In Fig. 3b–f, the presence of Fe, Co, O, and Zn by EDS testing indicates that the synthesized substances are made of Fe, Co, O, and Zn. The elemental atlas confirmed that the distribution of Zn, Co, Fe, and O is relatively uniform, which is beneficial to enhance the catalytic activity.

The adsorption–desorption isotherms of the samples are tested under liquid nitrogen conditions. BET equation is used to calculate specific surface area and the BJH method is used to calculate the aperture from the desorption branch of isotherm. Figure 4a shows the N₂ adsorption–desorption isotherms of the prepared CoZnFeO₄ and ZnFe₂O₄ nanomaterials. According to the classification of IUPAC, both the CoZnFeO₄ spinel oxide and the N₂ adsorption–desorption isotherms of ZnFe₂O₄ studied are type IV, indicating the mesoporous structure of the prepared materials [21]. Also, accompanied by the H1 hysteretic loop, such a strong hysteresis phenomenon is generally believed to be related to capillary condensation of large pore channels [22]. As shown in Fig. 4b, the pore diameter of CoZnFeO₄ nanomaterials is mainly mesoporous, the pore diameter distribution curve is a single peak,
Fig. 3  a The SEM image, b–f EDS patterns of copper magnesium ferrite nanoparticles, g Energy dispersive X-ray spectroscopy (EDS) patterns of CoZnFeO₄
and the pore diameter is mainly centered at 25 nm. The pore diameter distribution of ZnFe₂O₄ nanoparticles is mainly concentrated around 8 nm. In addition, as shown in Table 3, the total specific surface area and pore volume of CoZnFeO₄ are 38.416 m²/g and 0.283 cm³/g, respectively, and the total specific surface area and pore volume of ZnFe₂O₄ are 19.651 m²/g and 0.066 cm³/g, respectively. The surface area of the doped zinc ferrite depends on the properties of the dopant. The particle size and specific surface area of the nano-zinc ferrite particles change significantly with the substitution of cobalt. The total specific surface area ratio of CoZnFeO₄ is twice that of ZnFe₂O₄, which may be caused by the interaction between Co³⁺ and other metal ions (electrostatic effect, ion motion radius). Another reason is that the cobalt atom radius is smaller than the iron atom radius. As the iron atom is replaced, the crystal size decreases, increasing its surface area [8]. Through comparison, it is found that the surface and pore diameter of ZnFe₂O₄ doped with Co³⁺ are significantly larger, which can greatly increase the light-receiving area of the catalyst, reduce the diffusion distance of photogenic carriers, and improve the absorption efficiency of the material to light [23].

To compare the redox activity of CoZnFeO₄ and ZnFe₂O₄, the redox activity is analyzed by the H₂-TPR test. As shown in Fig. 5, there is only one peak of ZnFe₂O₄ within the range of 500–700 °C, which is the peak of Fe³⁺ reduced to Fe²⁺. In contrast, there are three peaks in CoZnFeO₄ which are Co³⁺ reduced to Co²⁺ at 350–450 °C, Fe³⁺ reduced to Fe³⁺/²⁺ intermediate state at 450–600 °C, and Fe³⁺/²⁺ converted to Fe²⁺ at 600–800 °C [19]. Multiple reduction peaks appeared in CoZnFeO₄ and the initial peak of the reduction peak shifted to a lower temperature. This may be due to the addition of cobalt, so that when Co³⁺/Co²⁺ is reduced in the same range, Fe³⁺/Fe²⁺ is also changed, leading to the interference of the reduction curve. As is known to all, reduction reactions first occur on the surface of materials, and the reduction peak moves to the low-temperature zone, which not only proves the surface occupancy of cobalt ions but also indicates that CoZnFeO₄ has a strong reduction performance.

### 3.2 Effects of several parameters on MB decolorization

#### 3.2.1 Study on the decolorizing methylene blue activity of CoZnFeO₄ nanomaterials

Figure 6 shows the effect of magnetic CoZnFeO₄ nanomaterials synthesized by the solid-phase

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**Table 3** Data of particle size and surface properties of CoZnFeO₄ nanocomposites and ZnFe₂O₄

| Catalyst   | Crystallite size D (nm) | Surface area (SBET) (m²/g) | Pore size (cm³/g) |
|------------|-------------------------|-----------------------------|-------------------|
| CoZnFeO₄   | 23.66                   | 38.416                      | 0.283             |
| ZnFe₂O₄    | 26.10                   | 19.651                      | 0.066             |
As shown in Fig. 6, under the condition of $\text{H}_2\text{O}_2 + \text{Light}$, the decolorization of MB is only 2.15%, which may be due to the decolorization of MB by hydroxyl radicals generated by the photolysis of $\text{H}_2\text{O}_2$ under the Light condition ($\text{H}_2\text{O}_2 + \text{Light} \rightarrow \text{OH} + \cdot\text{OH}^-$) [24]. In the case of $\text{ZnFe}_2\text{O}_4 + \text{Dark}$, the decolorization rate of 30 min MB is only about 2.99%, which may be due to the adsorption effect of $\text{ZnFe}_2\text{O}_4$ nanomaterials (To exclude adsorption, subsequent experiments are stirred in dark for 1 h in advance). However, under the $\text{ZnFe}_2\text{O}_4 + \text{Light}$ condition, the decolorization rate is 7.89% within 30 min, higher than that under the no Light condition. This indicates that the catalyst not only has adsorption, but also generates photogenerated electrons and holes ($e^-/h^+$) excited by $\text{CoZnFeO}_4$ under light conditions, and photogenerated holes can directly oxidize MB [25]. Under the condition of $\text{CoZnFeO}_4 + \text{H}_2\text{O}_2 + \text{Dark}$, decolorization is completed within 15 min, which may be due to the decomposition of transition metal on $\text{H}_2\text{O}_2$ into $\cdot\text{OH}$, thus promoting the decolorization of MB [26]. Among all the samples, the decolorization rate of $\text{CoZnFeO}_4 + \text{H}_2\text{O}_2 + \text{Light}$ is the fastest, which is 46.7% higher than that in the Light condition. This indicates that $\text{H}_2\text{O}_2$, as an electron capture agent in the photocatalytic process, can capture photogenerated electrons and separate electron holes, thus improving the efficiency of photocatalysis.

### 3.2.2 Influence of different catalysts on MB decolorization rate

To comprehensively evaluate the decolorization of MB by $\text{CoZnFeO}_4$ nanocatalyst, as shown in Fig. 7a, we conducted comparative experiments on the decolorization of MB using $\text{CoZnFeO}_4$, $\text{Co}_3\text{O}_4$, $\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, and $\text{ZnO}$ as catalysts. Within 30 min, the decolorization rate of MB is $\text{CoZnFeO}_4 > \text{Co}_3\text{O}_4 > \text{Fe}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{ZnO}$, and the decolorization rate is 100%, 50%, 40%, 24% and 18%, respectively. $\text{CoZnFeO}_4$ decolorized MB at the fastest rate, and the decolorization of MB is completed at the 8th min. This indicates that the coexistence of several metals improves the catalytic activity of catalysts. As shown in Fig. 7b, compared with $\text{ZnO}$, $\text{Co}_3\text{O}_4$ and $\text{Fe}_2\text{O}_3$ have a faster decolorization rate for MB, which indicates that Fe and Co may have a synergistic effect in the reaction system, which improves the utilization efficiency of photogenerated electrons and the surface-active site of $\text{CoZnFeO}_4$ catalyst, thus improving the catalytic efficiency.
3.2.3 Influence of pH

pH is an important factor in catalytic decolorization because it determines the surface charge properties of the catalyst and the size of the aggregates it forms, which affects the formation and reaction mechanism of free radicals [27]. Figure 8a analyzes the influence of pH value on the photocatalytic decolorization rate. As shown in Fig. 8a, the decolorization rate of MB gradually decreases when pH is from 2 to 10, indicating that pH has a great influence on the degradation of MB.

If catalysis is considered to follow a first-order kinetic equation, the decomposition rate of MB can be calculated using the following equation:

$$\ln\left(\frac{C_0}{C}\right) = kt$$

(2)

where, $C_0$ is the initial concentration of MB, and $C$ is the concentration of MB at any time. As shown in Fig. 8b, slope constant $k$ of the ratio of $\ln(C_0/C)$ to time under different pH (2, 4, 6, 8, 10) and light illumination conditions. With the increase of pH, the catalytic activity of CoZnFeO$_4$ nanomaterials decreased gradually, leading to a gradual decrease in
rate constant $k$. As shown in Table 4, the rate constant $k$ at pH 2 is 1.7078 min$^{-1}$, which is about ten times faster than the rate constant $k$ at pH 10, which is 0.17147 min$^{-1}$. This indicates that the catalytic rate of CoZnFeO$_4$ is fast under acidic conditions and that the catalyst can still maintain high catalytic activity in a wide pH range, which is of great value for industrial applications.

pH value affects the efficiency of the decolorization process and is related to the generation of positive pore, surface coverage, adsorption behavior, and ion leaching rate [28]. To explain the cause of MB decolorization, 0.1 g CoZnFeO$_4$ catalyst is dissolved in 50 mL MB solution, and pH is adjusted. Finally, the surface electromotive force (EMF) of the suspension is measured by ultrasonic under illumination for 20 min. As shown in Fig. 9a, under acidic conditions, the surface of the catalyst is positively charged. According to the infrared analysis of Fig. 1b and XPS analysis of Fig. 2d, it can be seen that the nano-materials synthesized by the solid-phase reduction method contain a large number of hydroxyl functional groups, indicating that the variable valence metals mainly exist in Fe–OH and Co–OH. The high concentration of H$^+$ protonates the surface of nanomaterials, forming functional groups with a positive charge (Eqs. 3, 4). However, when pH is above 8.42, a high concentration of OH$^-$ deprotonates nanomaterials and forms negative charge functional groups on the surface (Eqs. 5, 6) [29, 30]. The reaction is as follows:

\begin{equation}
\text{FeOH} + \text{H}^+ \rightleftharpoons \text{FeOH}^+ \quad (3)
\end{equation}

\begin{equation}
\text{CoOH} + \text{H}^+ \rightleftharpoons \text{CoOH}_2^+ \quad (4)
\end{equation}

\begin{equation}
\text{FeOH} + \text{OH}^- \rightleftharpoons \text{FeO}^- + \text{H}_2\text{O} \quad (5)
\end{equation}

\begin{equation}
\text{CoOH} + \text{OH}^- \rightleftharpoons \text{CoO}^- + \text{H}_2\text{O} \quad (6)
\end{equation}

The relative charge on the surface of nanoparticles is a determining parameter that reflects whether the interaction between particles and the degraded material is repulsive or attractive. According to the DLVO theory, the surface charge properties of nanoparticles are sensitively dependent on their heteroelectron points. When pH is higher or lower than isoelectron (IEP), the surface charge of the particle is positive or negative, respectively. Electrostatic interactions between semiconductor surfaces lead to higher surface coverage, the farther the pH is from IEP, the greater the charge between the particles, the better the particle dispersion [31]. As shown in Fig. 9b, when pH is 2–8.43, the surface charge of nanoparticles changes from 25.93 to $-0.36$ mV, and IEP is predicted to be 8.3, that is, when pH < IEP, the surface charge of nanoparticles is positive. And positively charged particles will generate positively charged holes (oxidation holes) [32], which can react with hydroxide radicals to generate hydroxyl radicals, thus oxidizing organic compounds. When

**Table 4** Kinetic parameters of MB with different pH drop solutions

| pH  | $k$ (min$^{-1}$) | $R^2$  |
|-----|-----------------|--------|
| 2   | 1.7288          | 0.9958 |
| 4   | 0.8366          | 0.9953 |
| 6   | 0.4747          | 0.9880 |
| 8   | 0.3286          | 0.9840 |
| 10  | 0.1750          | 0.9977 |

**Fig. 9**

a Under different pH conditions, the potential of CoZnFeO$_4$ nanoparticles is measured by Marvin instrument; b Zeta potential of CoZnFeO$_4$ nanoparticles as a function of pH
pH < IEP, the surface positive charge of particles gradually decreases with the increase of pH, that is, the attraction of positive charge holes to hydroxyl radicals decreases, and the rate of producing hydroxyl radicals slows down. Therefore, the decolorization rate of MB decreases as pH increases. Although MB has a positive charge, the negative charge on the surface of the particle at pH \( \text{IEP} \) will hinder the generation of oxidized holes, and the decolorization rate depends on the adsorption capacity of MB and the competitive effect of hydroxide on holes. It can be seen from Fig. 8a that the decolorization rate of MB gradually decreases with the increase of pH, indicating that the competition of hydroxide to hole is lower than that of MB, leading to a decrease in the decolorization rate of target substances. When the pH is close to IEP, the particles are severely agglomerated due to the lack of repulsive force, under which case they settle at the fastest rate. In this case, there are fewer particles in the suspension and the oxidation hole is low, so MB has the lowest decoloration rate. However, as shown in Fig. 8a, the decolorization rate is higher than that at pH 10 when pH 8, indicating that the reaction may occur not only on the particle surface but also in the solution. To verify this hypothesis, the concentration of metal ions in the suspension is tested.

The content of metal ions in the solution is tested by ICP-MS, as shown in Table 5. Under different pH values (2, 4, 6, 8, 10), with the rise of pH, the leaching rate of metal ions gradually decreased, and the decolorization rate of MB gradually decreased, indicating that metal ions in the solution may have a certain role in the decolorization process of MB [33]. In photocatalysis, transition metal ions in solution capture electrons, which are easily transferred to H\(_2\)O\(_2\) to form hydroxyl radicals (Eqs. 7, 8). The hydroxyl radicals produced are very reactive substances that react with most organic matter. At the same time, H\(_2\)O\(_2\) as an electron capture agent can also capture photogenerated electrons (e\(^-\)) (Eq. 9), thus enabling the separation of photogenerated electrons from photogenerated holes and improving the efficiency of photocatalysis [32]. The specific reaction is as follows:

\[
M^{3+} + e^- \rightarrow OH^- + OH \quad (7)
\]

\[
M^{2+} + H_2O_2 \rightarrow M^{3+} + OH^- + OH \quad (8)
\]

\[
H_2O_2 + e^- \rightarrow OH^- + OH \quad (9)
\]

However, although pH 2 has the fastest decolorization rate of MB, it will cause excessive dissolution of metal elements, which may lead to excessive heavy metals in the water. Therefore, in the subsequent experiments, we will try to choose a more appropriate pH for the experiment.

3.2.4 Influence of light wavelength on methylene blue decolorization

Through UV–Visible diffuse reflection absorption spectrum, the optical absorption properties of synthetic materials within the range of UV–Visible spectrum can be explored, and the bandwidth of the material can be calculated, and then the photocatalytic ability of the material can be inferred indirectly. Fig. S1 shows the bandgap width of the catalyst is 2.02 eV, which is consistent with literature reports [34], and the lower the energy required for the electron transition reaction, the easier the photocatalysts, and Lan [35] reported bandgap of ZnFe\(_2\)O\(_4\) is 2.11 eV. This indicates that the doping of Co, which replaces the position of Fe, forms impurity levels in the bandgap and reduces the energy required for electron transition, which is beneficial to the light absorption capacity.

In this work, the optimal wavelength of MB decolorization is studied. As shown in Fig. 10, the decolorization efficiency gradually decreases with the increase of wavelength, which is consistent with the UV-Vis test results. The light wavelength reflects the energy intensity of incident light and is directly related to electron transition, which determines the concentration of hydroxyl radical produced. However, due to the presence of an appropriate concentration of H\(_2\)O\(_2\), it also has a better decolorization effect under dark conditions.
3.2.5 Influence of hydrogen peroxide concentration on MB decolorization rate

The H$_2$O$_2$ concentration is an important factor affecting MB decolorization in photocatalytic reactions. As shown in Fig. 11, the decolorization rate of MB increases, and decolorization time shorten with the increase of H$_2$O$_2$ concentration. When the concentration of H$_2$O$_2$ increases from 20 to 25 mM, the overdosing of H$_2$O$_2$ will decrease the decolorization rate of MB. At a low H$_2$O$_2$ concentration, the improvement of the decolorization rate may be due to the following reasons. Firstly, The H$_2$O$_2$ can produce hydroxyl radical under light conditions due to the main rate improvement mechanism for this process (Eq. 10). Ollis [36] and Ilisz [37] suggest the possible mechanisms in the H$_2$O$_2$ is considered to be a better electron acceptor than oxygen which will reduce the chances of electron–hole pair recombination, which may result in a hydroxyl radical (Eq. 11) rather than a weak radical (Eq. 12) [38]. This shows that the more HO$^•$ can be used for MB oxidation at the appropriate range of the H$_2$O$_2$ adding. However, at the high H$_2$O$_2$ doses, the excess H$_2$O$_2$ molecules clear HO$^•$ (Eq. 13) generated by direct photolysis of H$_2$O$_2$ [39, 40], or the oxidation of h$^+$ with OH$^-$ (Eq. 14) to a less oxidizing (Eq. 15) [41]. Therefore, accession H$_2$O$_2$ becomes an inhibitor of MB removal. In the rest of the study, the use concentration of H$_2$O$_2$ is determined as 20 mM.

$$\text{H}_2\text{O}_2 + \text{HO}^• \rightarrow \text{H}_2\text{O} + \text{HO}_2$$ \hspace{1cm} (10)
$$\text{H}_2\text{O}_2 + e^- \rightarrow \text{HO}^- + \text{OH}^-$$ \hspace{1cm} (11)
$$\text{O}_2 + e^- \rightarrow \text{O}_2^-$$ \hspace{1cm} (12)
$$\text{OH}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$$ \hspace{1cm} (13)
$$\text{h}^+ + \text{OH}^- \rightarrow \text{HO}^-$$ \hspace{1cm} (14)
$$\text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{H}_2\text{O} + \text{HO}_2$$ \hspace{1cm} (15)

3.2.6 Influence of CoZnFeO$_4$ dosage on MB decolorization rate

From the economic point of view, the amount of catalyst is one of the important parameters in decolorization MB. To choose the adding of catalysts, it is necessary to determine the optimal amount of load for the effective removal of MB dyes. The effect of the catalyst load on dye removal rate is investigated, and the results are shown in Fig. 12. As can be seen, the decolorization rate of MB gradually increases with the increase of catalyst dosage from 0.5 to 1.0 g/L. This is due to an increase in the number of active sites, and the more active sites there are, the more opportunities there are to receive light. However, when the amount of catalyst increased from 1.0 to 3.0 g/L, the decolorization rate decreased, which may be because the high concentration of catalyst led to the aggregation of catalyst particles, which led to the reduction of the number of surface-active sites and reduced the catalytic
efficiency. Besides, the high concentration of catalyst will increase the opacity of suspension and the scattering of light, thus reducing the number of times that the irradiated light passes through the catalyst. In this study, economic and environmental factors are taken into account to determine the optimal catalyst usage of 1.0 g/L.

3.2.7 Influence of methylene blue concentration on decolorization rate

The effect of MB concentration from 200 to 500 mg/L on decolorization rate is investigated under the optimal conditions of the dosage CoZnFeO$_4$ under the given wavelength. As shown in Fig. 13, the time for decoloration of MB is extended from 6 to 12 min with the initial concentration of MB increasing from 200 to 500 mg/L. Photocatalytic decolorization is completely dependent on the generation of hydroxyl radicals and positively charged holes. However, with the increase of MB concentration, the hydroxyl radical yield is decreased, resulting in the decolorization rate decreased. Moreover, with the continuous increase of MB concentration, MB molecules per unit volume increase and occupy more active sites [42, 43]. Besides, lots of dye molecules hinder the utilization efficiency of light [44]. Therefore, in photocatalytic decolorization, the decolorization rate decreases with the increase of MB concentration.

3.2.8 CoZnFeO$_4$ the oxidation of different pollutants

The cyclic degradation performance of CoZnFeO$_4$ on different pollutants such as ciprofloxacin(CIP), methyl orange(MO) and RhB is shown in figure. Figure 6 showed that the degradation rates of MB, CIP, MO and RhB within 30 min were 100%, 95%, 74% and 62%, respectively, $K$ are 0.1106, 0.0825, 0.04218 and 0.0309 min$^{-1}$, Compared with the other three pollutants, the degradation rate of MB is the highest (Fig. 14).

In addition, compared with the recently reported catalysts, the performance of zinc ferrite is obviously better than that of other catalysts [45, 46].

3.2.9 Effect of temperature on decolorization MB

Temperature is one of the important factors of photocatalysis. The effect of temperature (15 °C, 25 °C, 35 °C, 45 °C) on the decolorizing MB reaction rate constant of CoZnFeO$_4$ is studied. As can be seen from Fig. 15a, the reaction rate constant gradually increases with the rise of temperature, indicating that the leaching of CoZnFeO$_4$ metal ions may be an endothermic process [47].

The higher temperature is favorable for CoZnFeO$_4$ decolorization MB reaction because the higher temperature can provide energy for reactant molecules to overcome the activation energy barrier [48]. Therefore, the kinetic constants of the generation of free radicals and the regeneration of Fe$^{3+}$/Fe$^{2+}$ and

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**Fig. 12** Effect of catalyst dosage on the decolorization of MB. Conditions: wavelength = 395 nm, H$_2$O$_2$ = 20 mM/L, $T$ = 298 K, pH 5.78

**Fig. 13** Effect of MB concentration on decolorization rate. Conditions: wavelength = 395 nm, solid-to-liquid ratio = 1:1000, $T$ = 298 K, pH 5.78
Co$^{3+}$/Co$^{2+}$ increase with the rise of temperature [49, 50]. Miller and Sotolongo established the relationship between the reaction temperature and the decomposition rate constant of H$_2$O$_2$. The results show that at a certain temperature, the decomposition rate of H$_2$O$_2$ is accelerated with the increase of temperature, thus promoting the generation of HO$^·$ [51].

Through experiments at different temperatures, the Arrhenius equation (Eq. 16) is used to calculate the activation energy of the reaction [52]:

\[
K = A \exp \left( -\frac{E}{RT} \right)
\]  

(16)

where $A$ is the front factor, $E$ is the apparent activation energy (J/mol), $R$ is the ideal gas constant (8.314 J/mol/K), and $T$ is the reaction temperature (K).

The Arrhenius diagram of lnK and 1/T is shown in Fig. 15b, there is a good linear relationship between the natural lnK and 1/T. Activation energy $E$ obtained from Arrhenius in Fig. 15b is 31.102 kJ/mol, and $A$ value is $1.157 \times 10^5$ M$^{-1}$ min$^{-1}$. In general,
reaction activation energies for general thermal reactions are between 60 and 250 kJ/mol [53].

3.2.10 Comparison of decolorization MB with other catalysts

As shown in Table 6, the decolorization performance of the synthesized CoZnFeO₄ catalyst for MB is compared with other catalysts reported in the literature [53–58]. It can be observed that CoZnFeO₄ decolorizes MB within 8 min under normal pH. This indicates that the nanocatalysts prepared from waste materials have better catalytic activity than other catalysts. It also proves that the method of site control has the prospect of large-scale industrialization.

3.3 Structure and stability of the catalyst

The application of catalyst in wastewater treatment requires it to be stable for metal ion leaching in the liquid phase under operating conditions. Continuous and progressive leaching not only leads to deactivation of the catalyst but also pollute water further.

Table 6 Comparison of performance of CoZnFeO₄ catalyst with some previously reported catalyst for MB decolorization

| Catalyst         | Decolorization process | Initial pH | MB (mg/L) | Catalyst amount | Oxidant/Reductant | Decolorization time | Removal efficiency (%) | References |
|------------------|------------------------|------------|-----------|-----------------|-------------------|---------------------|------------------------|------------|
| CoZnFeO₄         | Photo-catalytic         | 5.78       | 200       | 1 g/L           | H₂O₂ 20 mM/L      | 8 min               | 100.0                  | This study |
| α-Bi₂O₃ NPS      | Photo-catalytic         | 2.00       | 10        | 1 g/L           | HNO₃:H₂O 1:5      | 90 min              | 90.0                   | [53]       |
| CoMnFeO₄         | Photo-catalytic         | 2.00       | 15        | 20 mg/L         | H₂O₂:MB 1:50      | 20 min              | 99.3                   | [54]       |
| ZnO/CaFe₂O₄      | UV                      | 2.00       | 32        | 2 g/L           | H₂O₂ 30% 2 mL     | 20 min              | 57.0                   | [55]       |
| Ag₃VO₄/CaFe₂O₄   | Photo-catalytic         | No data    | 32        | 2 g/L           | H₂O₂ 50%         | No data             | 59.3                   | [56]       |
| ZnFe₂O₄          | λ > 420 nm              | 13.00      | 10        | 1 g/L           | None              | 360 min             | 8.0                    | [57]       |
| Fe₃O₄            | None                    | No data    | 100       | 30 g/L          | H₂O₂ 2.5 M/L      | 50 min              | 10.0                   | [58]       |
Stability is one of the key factors affecting the catalyst application [59]. In this study, CoZnFeO₄ samples are continuously used five times under the same conditions to evaluate the maintenance of their photocatalytic activity. Among them, MB is photocatalysts decolorization, CoZnFeO₄ particles are recovered (such as centrifugation and magnetic adsorption), organic pollutants are removed with deionized water and ethanol, and finally, freeze-drying is carried out. As can be seen from Fig. 16a, within 5 cycles, the decolorization rate of MB does not change significantly, and the complete decolorization of MB is completed within 12 min. This indicates that the CoZnFeO₄ catalyst can maintain high catalytic activity after repeated use many times. However, after 5 cycles, the decolorization rate is slightly slowed down, which may be because of the continuous operation. In addition to, the slight inactivation caused by metal leaching, it may also be due to the deposition of carbon compounds in the active part of the catalyst, resulting in the decrease of activity [60]. As shown in Fig. 16b, by comparing the XRD patterns of CoZnFeO₄ before and after the reaction, there is no obvious change. At the same time, it can be seen from Fig. 17a that the FTIR of CoZnFeO₄ catalyst did not change significantly before and after the reaction, which also indicated that the CoZnFeO₄ nanometer material maintained a good reuse performance and a long service life. Besides, as shown in Fig. 16b, compared with other reported results [59], the leaching amount of metal ions in the reaction mixture (g/L) is quite low. Among them, the leaching amount of Co³⁺ ions is higher than that of Fe³⁺, indicating that the interaction between Co³⁺ ions and reactants is greater than that of Fe³⁺, that is, the surface occupancy rate of Co³⁺ is higher. As shown in Fig. 18, the EDS of CoZnFeO₄ after reaction shows that the metal elements still maintain a relatively uniform distribution, which indicates the stability of the octahedral structure in spinel ferrite. Meanwhile, by comparing the mass fraction of metal ions in Fig. 18f, the leaching rate of Co³⁺ and Zn²⁺ after the reaction is higher than that of Fe³⁺, which is consistent with the test structure in Fig. 18b, that is, the surface occupancy rate of Co³⁺ is higher.

### 3.4 Decolorization mechanism

To study the active components in the photocatalytic bleaching MB reaction of CoZnFeO₄, tert-butanol (TBA), ethylene diamine tetraacetic acid (EDTA), 1, 4-benzoquinone (BQ), and copper nitrate (CN) are selected as the capture agents to scavenging hydroxyl radical (HO·), hole (h⁺), superoxide radical (O₂⁻) and electron (e⁻) [43]. Figure 19 shows the effects of different scavengers on the photocatalytic activity of CoZnFeO₄.

It is found that in the presence of BQ, the decolorization effect of MB is not significant, indicating that O₂⁻ is not the main factor determining the photocatalytic decolorization of MB by CoZnFeO₄. After
the addition of TBA, CN and EDTA, the decolorization rate of MB decreased from 100 to 49%, 67% and 81% within 5 min. These results indicated that HO- and hole (h+) are the main active substances in the process of CoZnFeO₄ decolorization of MB. In the presence of electron-trapping CN, reactive oxygen...
species (O$_2^-$, HO$^-$) cannot be generated because conductive electrons (e$^-$) cannot be reduced to oxygen [61]. Therefore, the decolorization of dyes is not significantly inhibited under visible light irradiation, that is, e$^-$ play a secondary role in this process [62, 63]. At the same time, it can be seen in the figure that compared to the ideal state, the presence of N$_2$ has been decolorized by about 97% MB. This verifies that the whole reaction is not formed, that N$_2$ is not inhibited in the reaction [64]. Therefore, we conclude that the presence of O$_2$ in the reaction has less effect on the process.

To further analyze the reaction mechanism of the system, it is realized by photoluminescence characterization. The intensity of PL emission reflects the recombination rate of photogenic electron–hole pairs [65]. In general, lower intensity indicates rapid transfer or annihilation of excited electrons, while higher intensity indicates a high rate of recombination of excited electrons [66]. Figure 20 shows the CoZnFeO$_4$ and ZnFeO$_4$ systems excited by 350 nm. It can be seen that the emission intensity of CoZnFeO$_4$ samples is significantly lower than that of ZnFeO$_4$, which indicates that the charge transfer and separation capability of CoZnFeO$_4$ are relatively strong. Among them, the peaks at 415.09 nm and 435.26 nm correspond to characteristic near-band-Edge (NBE) blue emission, which is mainly attributed to the characteristic NBE blue emission, namely intermittent zinc deficiency, which is caused by the recombination of electrons in oxygen vacancies and photogenic holes generated at tetrahedral and octahedral positions [66–68]. The peaks at 627.13 nm and 569.40 nm are due to the transition of Fe$^{3+}$ from 3d$^5$ to 3d$^4$ 4s. The conduction band electrons from the 3d$^5$ state balance the 4S orbital of Fe 3p [69]. Compared with CoZnFeO$_4$, the lower PL emission intensity is because doping Co ions can produce a large number of defects, reduce the luminescence intensity of zinc ferrite, and lead to the reduction of photoelectron–hole pair recombination rate. In the process of MB photocatalysis, when the visible light energy larger than the energy gap irradiates the catalyst, the electrons move to the conduction band, and the valence band thus produces photogenic holes. Valence band electrons (e$^-$) are excited to the conduction band of the CoZnFeO$_4$ catalyst. Then the valence band generates photogenic holes (h$^+$), oxidizes H$_2$O into HO$_2^-$, and forms (–OH) hydroxyl group on the surface of the CoZnFeO$_4$ nanometer sheet after adsorption. The photogenerated electron has high electron mobility, which can decompose O$_2$ into -OH. The separation of holes and photogenerated electrons leads to a decrease in the recombination rate between them and leads to the migration of more charge carriers to the surface of the CoZnFeO$_4$ nanosheet [37–39]. The unpaired photogenerated electrons in the conduction band can generate hydroxyl radicals with H$_2$O$_2$, while the holes in the valence band can also react.
with H2O to generate hydroxyl radicals, and then decolorize MB dyes [70].

To determine the chemical state changes and reaction mechanism of CoZnFeO4 before and after decolorizing MB, XPS is used to analyze the samples. As shown in Fig. 21a, the peak position before and after the reaction did not deviate significantly, indicating that the CoZnFeO4 octahedral structure is stable and no lattice distortion occurred. At the same time, there is an extra N spectrum after the reaction, which may be caused by the residue of small molecules broken in MB on CoZnFeO4. Figure 21b, c shows the high-resolution XPS spectrum of Fe 2p3/2 between 705 and 720 eV before and after the catalytic reaction. Peaks of Fe(III) and Fe(II) ions correspond to 712.6 eV and 710.5 eV, respectively [71, 72]. After the reaction, the proportion of Fe(II) increased to 32.93% compared with Co(III), indicating that part of Fe(III) is converted into Fe(II) and the proportion of Fe(III) decreased to 62.07%, showing that part of Fe(III)/Fe(II) (0.77 V) [78], so Co 3+ potential of Co(III)/Co(II) (1.81 V) is higher than that of the catalyst (2.02 eV). The decolorization of MB is mainly carried out through the decomposition of H2O2 into hydroxyl radicals, and then completes the recycling process [81]. The specific reaction steps are shown below:

Co3+ + H2O2 → Co2+ + OOH + H+ (17)
Fe3+ + H2O2 → Fe2+ + OOH + H+ (18)
Co2+ + H2O2 → Co3+ + HO + OH− (19)
Fe2+ + Co3+ → Fe3+ + Co2+(E0 = 1.04V) (20)
Co2+ + H2O2 → Co3+ + HO + OH− (21)
MB + HO → CO2 + H2O (22)

Pathway 2: When visible light irradiates the semiconductor, the band gap (< 3.147 eV) is larger than that of the catalyst (2.02 eV). Some of the electrons in the valence band will be excited and jump from the valence band over the forbidden band to the conduction band, thus generating photogenenic electrons and h+ (h+), respectively, in the conduction band and the valence band [82]. The conduction band gap (0.3975 eV) of CoZnFeO4 is not lower than that of CoZnFeO4 (~ 0.33 eV); therefore, electrons in the conduction band cannot react with oxygen molecules to form superoxide radicals [59]. On the contrary, the photogenerated electrons in the CoZnFeO4 conduction band react with H2O2 to produce more, which leads to the oxidation reaction. Moreover, the hole (h+) has a high oxidation potential, which can lead to direct oxidation of MB. At the same time, the valence band of CoZnFeO4 (2.41 eV) has a higher potential than that of (1.99 eV), so that the hole can directly participate in the oxidation of MB, and can also react with hydroxide ions to generate hydroxyl radical. So under the action of hydroxyl radicals and holes, it leads to the decolorization of MB. The decolorization mechanism is shown as follows:

CoZnFeO4 + hv → e−(CB) + h+(VB) (23)
e− + H2O2 → HO − + OH− (24)
MB + (OH−, h+(VB)) → CO2 + H2O (25)
Fig. 21 The XPS spectra of a wide-scan, b Co 2p c Fe 2p d O 1s of copper magnesium ferrite nanoparticles.
3.5 MB intermediate and degradation pathway

At present, the research on photocatalytic degradation of dyes mainly focuses on the preparation of photocatalysts, the optimization of photocatalytic conditions, and reaction kinetics. While less attention is paid to the photocatalytic degradation mechanism of dye molecules [82]. Spadaro et al. [7] proposed that the photocatalytic degradation of dyes is mainly carried out by adding HO· to the carbon–nitrogen bond, and a series of unstable intermediates are formed and decomposed during the structural decomposition of dye chromophore [83]. Some intermediates may be more toxic than the parent molecule. Therefore, it is of great significance to determine the intermediates and whether there are intermediates that are difficult to be degraded.

MB is a kind of dye with a complex molecular structure. Its color is usually determined by the chromophobe group. This means that the decolorization of MB is caused by the destruction of chromogenic groups, but often the dye has not been completely degraded, there are still a large number of toxic intermediates. To determine the degradation pathways and intermediates of MB, ion chromatography and ESI–MS are used for analysis (Fig. S3). We performed TOC tests on methylene blue at 200 mg/L and methylene blue degraded for 25 min. The TOC of the original methylene blue is 413.34 mg/L, after degradation for 25 min, TOC is 40.26 mg/L. The TOC removal rate is 90.25%. As shown in Fig. 23, the anions in the solution are determined by ion chromatography, and the MB produced Cl−, NO3− and SO42− during the degradation process. The results showed that C–N, S–Cl, and C–S bonds are broken during the degradation of MB, thus Cl−, NO3− and SO42− are generated in the solution. To further determine the degradation pathway of MB, the degradation of products at different reaction times are identified by ESI–MS. As shown in Fig. 23, MB first deionized, S–Cl bond broke and Cl− (m/z = 284) is lost, and then HO· attacked C–S=C to generate sulfoxide (C–S(=O)–C) and –NH2 fracture (m/z = 303). The rest of the structure degrades in two ways, with the –CH3 bond having the lowest energy and breaking first (m/z = 270, 256, 281), Or –CH3 is oxidized to HCHO on the surface of nucleophilic oxygen by chemical adsorption (m/z = 332). Sulfoxide then breaks under the hydroxyl radical attack. The involvement of the two pathways in MB degradation depends on the competition between surface chemisorption and direct hydroxylation of MB [84]. Finally, under the action of hydrogen peroxide, MB is broken down into small molecules such as carbon dioxide and water (Fig. 24).

4 Conclusions

In this study, a CoZnFeO4 magnetic material with narrow band gap and rapid electron hole separation is designed and used for photocatalytic degradation of methylene blue in wastewater. CoZnFeO4 with octahedral structure is synthesized from waste
Fig. 24  Methylene blue degradation pathway
ferrous sulfate by solid-phase method in one-step. Under the optimal photocatalytic degradation conditions, green and efficient degradation of methylene blue is achieved. Meanwhile, the synthesis mechanism of CoZnFeO$_4$ nanomaterial and its photocatalytic degradation of methylene blue are explored. This study provided an effective solution for degrading dye wastewater by CoZnFeO$_4$ and exhibits great potential for the industrial application of ferrous sulfate waste.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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