CuO and CeO$_2$ assisted Fe$_2$O$_3$/attapulgite catalyst for heterogeneous Fenton-like oxidation of methylene blue

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In this paper, CuO and CeO$_2$ were screened as co-catalyst components for Fe$_2$O$_3$/attapulgite (ATP) catalyst, and three new catalysts (CuO–Fe$_2$O$_3$/ATP, CeO$_2$–Fe$_2$O$_3$/ATP and CuO–CeO$_2$–Fe$_2$O$_3$/ATP) were prepared for degradation of methylene blue (MB). The three catalysts’ characteristics were determined by BET, XRD, FT-IR, SEM and XPS. MB degradation in different systems and at different pH values was also studied. Under the conditions of H$_2$O$_2$ concentration of 4.9 mmol L$^{-1}$, catalyst dosage of 5 g L$^{-1}$, pH of 5, reaction temperature of 60 °C and MB initial concentration of 100 mg L$^{-1}$, the as-synthesized catalysts showed much greater reaction rate and degradation efficiency of MB than Fe$_2$O$_3$/ATP catalyst. In addition, the reusability of the as-prepared composites was evaluated. The intermediate products of MB degradation were identified by LC-MS and the possible degradation process of MB was put forward.

Introduction

With the rapid development of industry and agriculture, more and more organics, especially refractory organics, have been synthesized and used. As a result, more and more wastewater containing organics has been discharged into water in the environment and caused serious pollution. Methylene blue (MB), a common cationic dye, with a molecular weight of 373.90, is frequently used in textile, cosmetic and pharmaceutical industries. MB can cause permanent injury to humans and animals on inhalation and ingestion, and the risk of the presence of this dye in water may include a burning effect of the eye, nausea, vomiting and diarrhea. Many techniques can be applied to refractory organics removal: photocatalysis, biological treatment, adsorption, ozonation, photoysis, Fenton and Fenton-like processes. Among these techniques, heterogeneous Fenton reaction has become a research focus for its reusability, no secondary pollutants and wide pH range. UV light, electricity and ultrasonic treatment are often used as an assistant in heterogeneous Fenton reaction in degrading organics.

Attapulgite (ATP) is a kind of mixed mineral material with two-dimensional layered and rod-like structure containing water and rich magnesium aluminate. Due to its advantages of low cost, abundant reserves, high mechanical strength, good chemical stability, strong practicability, high exchange capacity and environmental friendly, it can be used in many fields like adsorbents, catalysts or doped materials for the preparation of composites, which has attracted extensive attention of researchers. In ATP applications, employing ATP as catalyst base has been made a great progress. For examples, Zhao et al. prepared silver and copper modified ATP/TiO$_2$ photocatalysts by a hydrolysis method for the degradation of methylene blue. Zhang et al. obtained ATP/SnO$_2$–TiO$_2$ via an in situ sol–gel method and investigated its photocatalytic removal ability of the methyl orange under ultraviolet radiation. Li et al. prepared ATP/Ce$_{1-x}$Zr$_x$O$_2$ nanocomposite as catalyst for the degradation of methylene blue. Attapulgite can be used as a carrier alone or in combination with other materials. Metal oxides (Fe$_2$O$_3$, ZnO, CuO, etc.) can be employed as active components, which have similar catalytic effects to Fe$^{2+}$ or Cu$^{2+}$. We have investigated the degradation of sodium dodecyl benzene sulfonate (SDBS) and methylene blue in solution with Fe$_2$O$_3$/attapulgite catalyst and the results demonstrated that Fe$_2$O$_3$/attapulgite has good abilities of catalysis and degradation of SDBS and MB. Considering the interaction between different catalytic active components can change the catalytic activity of the catalysts, two or more metal oxides are often used to prepare multi-active components catalysts.

The purpose of this work is to screen metal oxides as co-catalyst components for Fe$_2$O$_3$/ATP, and the assistant-catalytic degradation properties of screened metal oxides were studied.

Experimental

Materials

Ferric nitrate ($\text{Fe(NO}_3\text{)}_3$·9H$_2$O), copper nitrate ($\text{Cu(NO}_3\text{)}_2$·3H$_2$O), H$_2$O$_2$(30% w/w), methylene blue (MB, C$_{16}$H$_{18}$ClN$_3$·S·3H$_2$O), sodium hydroxide (NaOH), sulfuric acid (H$_2$SO$_4$),...
hydrochloric acid (HCl) were supplied by chemical reagent companies and all of them were analytical grade. Attapulgite clay (ATP) was produced from Xuji, Jiangsu, with the chemical contents of SiO$_2$ 57.006%, TiO$_2$ 0.893%, Al$_2$O$_3$ 8.583%, Fe$_2$O$_3$ 4.641%, SO$_3$ 0.007%, MnO$_2$ 0.034%, MgO 8.456%, CaO 0.216%, K$_2$O 0.994%, and Na$_2$O 0.948%, and no further purification was carried out during the experiments. Distilled water used throughout the experiments was self-made by our laboratory.

**Preparation of ATP-based catalysts**

20 g ATP clay was mixed with 1 mol L$^{-1}$ HCl with magnetic stirring for 1 hour, then ATP was separated by filtration and dry at 105 °C for 2 hours. The dried ATP was ground, sieved and calcined at 600 °C for 2 hours to obtain purified ATP clay powder as catalyst carrier. Weigh a certain Fe(NO$_3$)$_3$ $\cdot$ 9H$_2$O and other metal salts (such as Cu(NO$_3$)$_2$ $\cdot$ 3H$_2$O, Ce(NO$_3$)$_3$ $\cdot$ 6H$_2$O, Ni(NO$_3$)$_2$, Co(NO$_3$)$_2$ $\cdot$ 6H$_2$O, etc.), and mix them at a certain ratio. The mixture of the metal salts were dissolved in 195 mL of water, and the purified ATP clay was put into the metal salts solution, sonicated for 30 min and separated by filtration. Then the samples were dried at 110 °C for 2 hours, and calcined at 300 °C for 2 hours to obtain metal oxides assisted Fe$_2$O$_3$/ATP catalysts. The diameter of the catalysts is about 70 μm.

**Characterization**

The N$_2$ adsorption isotherm of the sample was measured at −196 °C using an ASAP 2010 type specific surface area measuring instrument manufactured by Micromiritics (USA), and the specific surface area, pore volume and pore diameter were calculated by the BET equation. The apparent morphology of the catalyst was observed by JSM-5500 scanning electron microscopy (SEM). The acceleration voltage was 20 kV, and the surface area, pore volume and pore diameter of the catalyst was observed by JSM-5500 scanning electron microscopy (SEM). The acceleration voltage was 20 kV, and the surface area, pore volume and pore diameter of the catalyst was observed by JSM-5500 scanning electron microscopy (SEM). The acceleration voltage was 20 kV, and the surface area, pore volume and pore diameter of the catalyst was observed by JSM-5500 scanning electron microscopy (SEM).

**Table 1** Mass ratios of different metal salts on the catalysts$^a$

| Samples | Assistant components | Mass ratio of metal salts |
|---------|---------------------|--------------------------|
| SA1-1   | CuO                 | Cu(s) : Fe(s) 0.3 : 4.7 |
| SA1-2   | CuO                 | 0.5 : 4.5                |
| SA1-3   | CuO                 | 0.7 : 4.3                |
| SA1-4   | CuO                 | 1.0 : 4.0                |
| SA1-5   | CuO                 | 1.5 : 3.5                |
| SA2-1   | CeO$_2$             | Ce(s) : Fe(s) 0.3 : 4.7  |
| SA2-2   | CeO$_2$             | 0.5 : 4.5                |
| SA2-3   | CeO$_2$             | 0.7 : 4.3                |
| SA2-4   | CeO$_2$             | 1.0 : 4.0                |
| SA2-5   | CeO$_2$             | 1.5 : 3.5                |
| SA3-1   | CuO–CeO$_2$         | Cu(s) : Ce(s) : Fe(s) 0.5 : 0.5 : 4.0 |
| SA3-2   | CuO–CeO$_2$         | 0.7 : 0.3 : 4.0          |
| SA3-3   | CuO–CeO$_2$         | 0.3 : 0.7 : 4.0          |
| SA3-4   | CuO–CeO$_2$         | 0.5 : 1.0 : 3.5          |
| SA3-5   | CuO–CeO$_2$         | 1.0 : 0.5 : 3.5          |

$^a$ Cu(s) means Cu(NO$_3$)$_2$ $\cdot$ 3H$_2$O, Fe(s) means Fe(NO$_3$)$_3$ $\cdot$ 9H$_2$O and Ce(s) means Ce(NO$_3$)$_3$ $\cdot$ 6H$_2$O.

infrared spectrometer with a scan range of 4500 cm$^{-1}$ to 400 cm$^{-1}$. The crystal form was identified using a Panalytical X'Pert PRO XRD instrument with operating voltages and currents of 40 kV and 150 mA, diffraction angles of 5° to 80°, and scanning steps of 0.02° s$^{-1}$.

The intermediate products of aromatic ring were determined by HPLC-MS, which is performed by an Agilent 1200 high performance liquid chromatography and a 6130 quadrupole mass spectrometer. The column used for separation is a ZORBAX Eclipse XDB-C18 column (5 μm, 4.6 × 150 mm). The mobile phase is a mixture of methanol and formic acid (40/60, V/V), with a flow rate of 0.5 mL min$^{-1}$, an injection volume of 20 μL and a chamber temperature of 30 °C. The mass spectrometer detector operates with selective ion monitoring (SIM) at the negative electrode. The operating conditions are: debris guidance of 90, dry gas flow rate of 12 L min$^{-1}$, sprayer pressure 45 of lb sq$^{-1}$, dry gas temperature of 300 °C, steam temperature of 150 °C, capillary voltage of 2500 V, corona current of 4 μA and voltage of 2000 V.

**Experimental methods**

1 g L$^{-1}$ MB stock solution was prepared using distilled water for dilution to the concentration required for subsequent experiments. 180 mL of distilled water and 20 mL of MB stock solution (1 g L$^{-1}$) were placed in an Erlenmeyer flask to obtain 200 mL of a 100 mg L$^{-1}$ MB solution. The pH was adjusted with sulfuric acid (1 : 9) and the Erlenmeyer flask was placed in a water bath thermostat. Add a certain amount of catalysts and hydrogen peroxide to the Erlenmeyer flask, turn on the shaker at 120 rpm for 100 min, and start timing. The supernatant was taken every 10 min to measure the absorbance, and the absorbance of the MB solution was measured by UV-1900 ultraviolet-visible spectrophotometer at λ = 664 nm. The degradation ratio of the MB solution can be calculated by the following formula:

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

where $C_0$ is the initial concentration of MB dye wastewater, and $C_t$ is the concentration of MB dye wastewater when the reaction time is $t$.

**Measurement of \cdot OH concentration**

\cdot OH will react with salicylic acid to produce a chemical substance called 2,3-dihydroxybenzoic acid with maximum absorption peak at the wavelength of 510 nm. So \cdot OH can be measured by following method: 100 mL salicylic acid standard solution was placed in a 250 mL conical flask, after adding 1 g L$^{-1}$ as-synthesized catalysts and 0.1 mL 30% (w/w) H$_2$O$_2$, the conical bottle was placed in water bath under 60 °C. Every 10 minutes the \cdot OH concentration of the solution was measured by UV-1900 ultraviolet-visible spectrophotometer at λ of 510 nm.

**Results and discussion**

**Screening of co-catalyst components**

In order to make sure which metal oxide has the synergistic effect with Fe$_2$O$_3$/ATP, four metal oxide precursors were chosen
to corporate with Fe$_2$O$_3$/ATP and their co-catalysis properties were studied. The experimental conditions are: catalyst dosage of 5 g L$^{-1}$, H$_2$O$_2$ concentration of 4.9 mmol L$^{-1}$, pH value of 5, reaction temperature of 60 °C and MB initial concentration of 100 mg L$^{-1}$. The results can be seen in Fig. 1. Except Co$_3$O$_4$, the other tested metal oxides all had assist-catalytic effect to Fe$_2$O$_3$/ATP catalyst according to the higher decolorization ratios of MB by co-catalysts than that by only Fe$_2$O$_3$/ATP. CuO and CeO$_2$ presented excellent assist-catalytic performances and the MB decolorization ratios can reach over 95% within 10 min reaction when catalyzing by CuO–Fe$_2$O$_3$/ATP or CeO$_2$–Fe$_2$O$_3$/ATP. All catalysts had close and almost same decolorization ratios of MB within 70 min and 100 min reaction, which were over 97% and over 99% respectively. The decolorization ratios of MB by CuO–Fe$_2$O$_3$/ATP and CeO$_2$–Fe$_2$O$_3$/ATP can reach 99.72% and 99.75% respectively within 100 min reaction. Compared with Fe$_2$O$_3$/ATP catalyst, CuO–Fe$_2$O$_3$/ATP and CeO$_2$–Fe$_2$O$_3$/ATP expressed excellent catalytic performances during the early stage of the reaction (0–30 min), indicating that the co-catalytic effect of CuO and CeO$_2$ is to drastically enhance the catalytic reacting rate.

**Optimization of catalysts preparation**

According to Fig. 1, CuO and CeO$_2$ were chosen as assistant components of Fe$_2$O$_3$/ATP. That means, Cu(NO$_3$)$_2$·3H$_2$O and Ce(NO$_3$)$_3$·6H$_2$O were used as precursors to prepare the co-catalysts. In order to make sure preparing catalysts at which proportion of the precursors can get the high catalytic efficiency, different mass ratios of metal salts were employed to prepare the catalysts, as can be seen in Table 1.

The co-effects of CuO or CeO$_2$ with Fe$_2$O$_3$/ATP on their catalytic performances are studied and the results were shown in Fig. 2. The MB decolorization experiments were carried out at different mass ratios of metal salts on the ATP support. As can be seen from Fig. 2, the proportion of precursors did not heavily affect the catalytic performances of the catalysts, and the decolorization ratios are almost the same at different mass ratios of metal salts on the ATP support. The results show that the catalysts of CuO–Fe$_2$O$_3$/ATP and CeO$_2$–Fe$_2$O$_3$/ATP had better catalytic performance when the proportion of the assistant precursor component to the total-active components of catalyst is 1 : 5, while the different proportions in CuO–CeO$_2$–Fe$_2$O$_3$/ATP made almost no difference in MB decolorization. Under optimum preparation conditions, the degradation ratios of MB by CuO–Fe$_2$O$_3$/ATP and CeO$_2$–Fe$_2$O$_3$/ATP and CuO–CeO$_2$–Fe$_2$O$_3$/ATP were 99.71%, 99.73% and 99.11%, separately.

**Characterization**

Table 2 is the BET measurement results of catalysts samples. As can be seen that the BET surface areas of CuO–Fe$_2$O$_3$/ATP, CeO$_2$–Fe$_2$O$_3$/ATP and CuO–CeO$_2$–Fe$_2$O$_3$/ATP are all higher than ATP, which means that introducing metal oxides to ATP can enhance the surface area of ATP and the metal oxides can act as the upholders between ATP rod-shaped particles. The BET surface areas of CuO–Fe$_2$O$_3$/ATP and CeO$_2$–Fe$_2$O$_3$/ATP are almost the same, while CuO–CeO$_2$–Fe$_2$O$_3$/ATP has higher surface area than the two catalysts above.

Nitrogen adsorption–desorption isotherms were measured to determine the specific surface area and pore structure of these four samples, as shown in Fig. 3. The adsorption–desorption curves of the four samples show type II isotherms according to IUPAC classification, representing their microporous structure, which is in accordance with the characteristic result of SEM images. Both of samples clearly show H3 hysteresis loops indicating material with flaky granules or slotted pores, and there is no adsorption limit in the region of high relative pressure. After coated by metal oxides, the samples have higher adsorption capacity than ATP, and their pore sizes become smaller (1.0–170 nm of CuO–Fe$_2$O$_3$/ATP, 1.9–190 nm of CeO$_2$–Fe$_2$O$_3$/ATP, 2.0–140 nm of CuO–CeO$_2$–Fe$_2$O$_3$/ATP) compared with those of ATP (1.9–232 nm), which also is in accordance with the characteristic results of SEM images.

SEM micrographs were collected to illustrate the morphologies of ATP and as-prepared catalysts samples, as depicted in Fig. 4. Rod-shaped particles with lengths of 500–700 nm and widths of 100–150 nm are visible in Fig. 4a. After the introduction of iron and copper or cerium species into ATP, nano-Fe$_2$O$_3$ and CuO or CeO$_2$ particles with diameters ranging from 10–50 nm were stuck to the surface of ATP according to the Fig. 4b–d. The Fe$_2$O$_3$ and CuO or CeO$_2$ particles were not very

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**Fig. 1** Screening of assistant components of the catalysts.

**Fig. 2** Co-effect of CuO or CeO$_2$ with Fe$_2$O$_3$/ATP on their catalytic performances.
clearly distinguished from the SEM images; however, metal oxide nanoparticles were well dispersed on ATP particles as circled in TEM images. The elemental composition of the as-synthesized CuO–Fe2O3/ATP, CeO2–Fe2O3/ATP and CuO–CeO2–Fe2O3/ATP composites from energy dispersive spectrometry (EDS) [Fig. 4e–g] stated that the composites contained Cu, Fe and Ce.

The FT-IR results of ATP, CuO–Fe2O3/ATP, CeO2–Fe2O3/ATP and CuO–CeO2–Fe2O3/ATP can be seen in Fig. 5a. The strong wide absorption bands appeared at 3420 cm−1 associated with the surface hydroxyl groups. The weak sharp absorption bands at 1630 cm−1 is flexural vibrations of water H−O−H. The strong wide absorption bands at 1040 cm−1 is dissymmetry stretching vibrations of Si−O−Si, and the absorption bands at 777 cm−1 and 476 cm−1 are symmetry stretching and flexural vibrations of Si−O. Some peaks were observed at lower wave numbers (480 cm−1 and 565 cm−1) corresponding to vibration modes of Fe−O bonds of Fe2O3 nanoparticles on the surface of ATP. Absorption bands of Cu−O and Ce−O bonds cannot be seen in Fig. 5a due to the low loading deposition level.

Fig. 5b shows the wide-angle XRD diffractions of as-synthesized CuO–Fe2O3/ATP, CeO2–Fe2O3/ATP and CuO–CeO2–Fe2O3/ATP composites. The diffraction peak at 2θ = 8.2° was assigned to attapulgite. The diffraction peak at 26.5° was assigned to quartz and the peaks at 19−22° belonged to kaolinite and quartz, which are all the impurities of attapulgite clay. The diffraction peaks at 2θ = 24.1, 33.1, 40.8, 49.4, 54, and 62.4° were assigned to α−Fe2O3 (JCPDS data: 89-596), the diffraction peaks at 2θ = 35.6, 38.7, 53.5, 58.3 and 65.9° were assigned to CuO(PDF#80-1268), and the diffraction peaks at 2θ = 28.3, 32.5, 47.2, 56.1 and 59.0° were assigned to CeO2 (PDF #34-0394). XRD diffractions of SA1 showed crystallization of Fe2O3 and CuO, XRD diffractions of SA2 showed crystallization of Fe2O3 and CeO2, and XRD diffractions of SA3 showed crystallization of Fe2O3, CuO and CeO2. The intensity peaks of Fe2O3, CuO and CeO2 were all very low resulting from low loading deposition level, well dispersion, and poor crystalline with a small size of metal oxide particles in the composites.

The chemical states of metal elements in the three catalysts were studied by XPS analysis and their responding XPS characteristic spectra are shown in Fig. 6. In comparison, the binding energies of C 1s and O 1s of the samples were almost no change, which reveals that the loading metal oxides did not affect the valent states of C and O (Fig. 6a). The survey spectra of the samples confirm that besides C and O, Fe were also present in these three samples, while Cu and Ce cannot be seen due to the low loading deposition level, which agree well with the explanation of XRD results. The peaks at 531 eV (Fig. 6b) in three samples were due to O 1s bonded to Fe (Cu, Ce) and Si, whereas the peaks at higher binding energy of 532.4 eV were ascribed to the presence of OH− groups, indicating surface hydroxyl groups of ATP. The peaks at 285.7 eV, 286.2 eV and 286.8 eV [Fig. 6c] in three samples were due to C 1s bonded to H, N and O, which might be formed during the roasting of the samples. High resolution XPS spectrum of Fe 2p in Fig. 3d located at the binding energies of 713.6 eV and 726.8 eV were indicative of Fe 2p3/2 and Fe 2p1/2 of the oxidation state Fe3+ in three samples, respectively.

### Degradation of methylene blue

In order to determine the catalytic degradation performance of these three heterogeneous catalysts, comparison experiments were carried out to treat MB dye wastewater in the presence of (i) only H2O2 with the reaction conditions of H2O2 concentration 4.9 mmol L−1, pH 5, reaction temperature 60 °C and MB initial concentration 100 mg L−1, (ii) catalyst only (CuO–Fe2O3/ATP, CeO2–Fe2O3/ATP or CuO–CeO2–Fe2O3/ATP) with the reaction conditions of catalyst dosage 5 g L−1, pH 5, reaction temperature 60 °C and MB initial concentration 100 mg L−1, and (iii) both catalyst and H2O2 with the reaction conditions of H2O2 concentration 4.9 mmol L−1, catalyst dosage 5 g L−1, pH 5, reaction temperature 60 °C and MB initial concentration 100 mg L−1. The results were shown in Fig. 7a. It can be seen that when only H2O2 is present in the system, the degradation ratio of MB is relatively low, which showed that MB can be oxidized and degraded by H2O2 but the efficiency is not very high. When the system only contains one of the catalysts, the decolorization ratio of MB can reach around 60% due to the adsorptive ability or the catalytic reaction occurring on catalysts with light and oxygen. And it also can be seen that CuO–Fe2O3/ATP has higher adsorption performance than CeO2–Fe2O3/ATP or CuO–CeO2–Fe2O3/ATP, which can be explained by the fact that Ce has larger atom size and more positive charge than Cu and Fe, so it has larger repulsive interaction than Cu and Fe when ATP adsorbing the cationic dye methylene blue. When both catalysts and H2O2 were all present in MB containing solution, over 90% decolorization ratios of MB can be obtained within 10 min reaction. Especially in CuO–Fe2O3/ATP/H2O2 and CuO–CeO2–Fe2O3/ATP/H2O2 systems, the decolorization ratio of MB reached 95% within 10 min reaction, which means CuO has

### Table 2 BET measurement results of samples

| Samples             | BET surface area (m² g⁻¹) | Total pore volume (cm³ g⁻¹) | Average pore diameter (nm) |
|---------------------|---------------------------|-----------------------------|---------------------------|
| CuO–Fe2O3/ATP      | 127.65                    | 9.13                        | 0.34                      |
| CeO2–Fe2O3/ATP     | 121.57                    | 9.58                        | 0.29                      |
| CuO–CeO2–Fe2O3/ATP | 150.83                    | 9.38                        | 0.35                      |
| ATP                 | 114.50                    | 8.29                        | 0.24                      |
the better co-catalysis performance than CeO₂, and CuO and CeO₂ have a synergy in assistant-catalysis of the CuO–CeO₂–Fe₂O₃/ATP catalyst.

Compared with other conditions, pH value plays an important role in catalytic degradation of MB. The decolorization of MB in aqueous solution in the presence of three
different catalysts was studied in the pH range between 2 and 12. Fig. 7b shows the decolorization efficiencies of MB after 60 min at different pH values with an initial solution containing 100 mg L$^{-1}$ MB, 5 g L$^{-1}$ catalyst and 4.9 mmol L$^{-1}$ H$_2$O$_2$. Almost complete decolorization ratios were achieved at pH 5 (99.76%, 99.73% and 99.83% of CuO–Fe$_2$O$_3$/ATP, CeO$_2$–Fe$_2$O$_3$/ATP and CuO–CeO$_2$–Fe$_2$O$_3$/ATP respectively). The stability of H$_2$O$_2$ was dependent on pH value. H$_2$O$_2$ seldom decomposed at acidic pH, and most of the H$_2$O$_2$ was transformed to OH radicals when catalyzed by the catalysts. At alkaline pH conditions, a lot of H$_2$O$_2$ decomposed to H$_2$O and O$_2$ and only a small part of H$_2$O$_2$ was catalysed and produced OH radicals. And the oxidation potential of OH radicals was shown to be lower in alkaline than in acidic conditions.

Three times repeated decolorization experiments were performed to test the stability of these three catalysts (Fig. 7c). After each decolorization experiment, the catalyst will be filtered and washed by distilled water to ensure recycling. After the first run, the decolorization efficiencies of MB were all over 99% in three heterogeneous Fenton systems. In subsequent runs, the decolorization efficiencies just decreased a little. At the end of the third runs, the efficiencies were still as high as 98%. The experiments showed that catalyst Fe$_2$O$_3$/ATP did not lose its catalytic function (active Fe$_2$O$_3$ or CuO or CeO$_2$) from the catalyst surface after several runs, which is suitable for practical application.
Mechanism of the degradation of MB

In literatures, the processes of degrading organic matters by heterogeneous Fenton systems often were interpreted by conforming to the theory of free radicals, that is to say, the organics degradation process is mainly based on the oxidation of $\cdot$OH. In order to prove the degradation of MB processes by these catalysts belonging to heterogeneous Fenton reactions, the $\cdot$OH trapping experiments were also carried out to prove that MB degradation reaction is a heterogeneous Fenton process. The $\cdot$OH trapping experiments were conducted under the optimized condition of pH 5, reaction temperature 60 °C, catalysts dosage 5 g L$^{-1}$, and H$_2$O$_2$ concentration 4.9 mmol L$^{-1}$. The $\cdot$OH concentration produced in the reaction at different times were measured, shown in Fig. 8. As can be seen that with the reaction time increased, the $\cdot$OH concentration increased accordingly, and the $\cdot$OH concentrations of CuO–Fe$_2$O$_3$/ATP/H$_2$O$_2$, CeO$_2$–Fe$_2$O$_3$/ATP/H$_2$O$_2$ and CuO–CeO$_2$–Fe$_2$O$_3$/ATP/H$_2$O$_2$ systems were much higher than that of Fe$_2$O$_3$/ATP/H$_2$O$_2$ system, which were according with the results of Fig. 7a and explained the excellent MB decolorization performances of the former three systems.

The intermediate products of MB degradation were identified by LC-MS after 100 min catalytic reaction by CuO–CeO$_2$–Fe$_2$O$_3$/ATP/H$_2$O$_2$ system. The main identified products were benzoquinone ([M – H]$^{-}$m/z 107, RT 3.161 min), hydroquinone ([M – H]$^{-}$m/z 109, RT 3.098 min), catechol ([M – H]$^{-}$m/z 109, RT 3.308 min), resorcinol ([M – H]$^{-}$m/z 109, RT 5.098 min).

According to the identified main aromatic intermediate products, the possible degradation process of MB in CuO–CeO$_2$–Fe$_2$O$_3$/ATP/H$_2$O$_2$ catalytic system, for example, was shown in Fig. 9. Firstly, H$_2$O$_2$ was adsorbed by the catalyst and decomposed on the surface of it and generated $\cdot$OH radicals, then $\cdot$OH radicals attacked the –S= bond and –N= bond of MB, splitting the macromolecular MB into two parts. The second step was that $\cdot$OH radicals oxidized the products into phenol, diphenol and other products. Because of the presence of electron donor –OH on the benzene ring, phenol and diphenol are particularly conducive to the electrophilic attack of $\cdot$OH, especially in the presence of –OH on the ortho and para positions. Phenol can be oxidized to hydroquinone, catechol, resorcinol and so on. Diphenol can be oxidized to benzoquinone quickly. In the third step, the intermediate products of aromatic ring were further oxidized by $\cdot$OH to short chain carboxylic acids such as fumaric acid, oxalic acid, formic acid, etc., which can be quickly degraded to CO$_2$ and H$_2$O.
### Table 3: Comparison of different heterogeneous catalysts in degrading MB

| Catalysts       | pH  | C(H₂O₂)/mM | C (cat)/g L⁻¹ | C (MB)/mg L⁻¹ | T° C | Time/min | V/mL | η%    |
|-----------------|-----|------------|---------------|--------------|------|----------|------|-------|
| Fe₃O₄/TiO₂ core/shell nanotubes⁴⁹ | 3   | 8900       | 50            | 1870         | 25   | 5        | 1    | 99    |
| Fe₃O₄/Fe(µ)-LDHs³⁰ | 3   | 0.01       | 1.0           | 10           | 25   | 60       | 100  | 100   |
| Fe₃O₄/MWCNTs carbon nanotubes⁵¹ | 3.5 | 10         | 0.5           | 74.78        | 25   | 30       | —    | 99    |
| C-Fe,O₃ [ref. 52] | —   | 245        | 0.5           | 50           | 40   | 420      | 200  | 96    |
| NC-CuFe [ref. 53] | —   | 245        | 0.5           | 50           | 40   | 180      | 200  | 97.4  |
| MgFeO₄ [ref. 54]  | 4   | 20         | 0.5           | 50           | 20   | 30       | 50   | 98    |
| CuO–CeO₂–Fe₂O₃/ATP | 5   | 4.9        | 5             | 100          | 60   | 60       | 200  | 99.8  |

The degradation of MB by as-synthesis catalyst compared with other catalysts

The catalytic performances of as-synthesized catalysts were compared with different catalysts from recent literatures.⁴⁹–⁵⁴ The reaction condition and degradation efficiency of these catalysts are listed in Table 3. Since each study evaluated the removal capacity under different conditions, direct comparison among catalysts is challenging, but the relative performance of these as-synthesized catalysts can be evaluated indirectly.

Table 3 shows the comparison of different heterogeneous Fenton catalysts for MB degradation. It can be seen that the Fe₃O₄/TiO₂ core–shell nanotube catalyst⁴⁹ can decolorize high MB pollutant concentration in a short time and reach a high decolorization ratio, but the concentration of H₂O₂ and catalyst used in the reaction is relatively high, and the volume of pollutant solution is very small. In Fe(µ) Fe(µ)-LDHs nanotubes/H₂O₂ system,⁵⁰ it also can achieve a high decolorization ratio with relatively low concentration of H₂O₂ and catalyst due to its low MB concentration. Fe₃O₄/MWCNTs⁵¹ showed its good catalytic performance with small amount of catalyst and short reaction time. C-Fe₂O₃ [ref. 52] and NC-CuFe⁵³ also have high MB degradation ratio at almost same condition, but the reaction time is very long (420 min and 180 min respectively). While the degradation efficiency of MB on CuO–CeO₂–Fe₂O₃/ATP composite within 60 min was higher than that of Fe₃O₄/TiO₂ core/shell nanotubes, and even Fe₂O₃/MWCNTs carbon nanotubes, C-Fe₂O₃, NC-CuFe and MgFeO₄ [ref. 54] under visible light. The degradation efficiency was lower than that of Fe₃O₄/Fe(µ)-LDHs, but the reaction pH of CuO–CeO₂–Fe₂O₃/ATP/H₂O₂ was not so harsh. Therefore, CuO–CeO₂–Fe₂O₃/ATP composite prepared by the facile method is expected to reduce the cost of catalyst for large scale application.

**Conflicts of interest**

There are no conflicts to declare.

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**The degradation of MB by as-synthesis catalyst compared with other catalysts**

The catalytic performances of as-synthesized catalysts were compared with different catalysts from recent literatures.⁴⁹–⁵⁴ The reaction condition and degradation efficiency of these catalysts are listed in Table 3. Since each study evaluated the removal capacity under different conditions, direct comparison among catalysts is challenging, but the relative performance of these as-synthesized catalysts can be evaluated indirectly.

Table 3 shows the comparison of different heterogeneous catalysts in degrading MB. The degradation of MB by as-synthesis catalyst compared with other catalysts is shown in Table 3. The catalytic performances of as-synthesized catalysts were compared with different catalysts from recent literatures.⁴⁹–⁵⁴ The reaction condition and degradation efficiency of these catalysts are listed in Table 3. Since each study evaluated the removal capacity under different conditions, direct comparison among catalysts is challenging, but the relative performance of these as-synthesized catalysts can be evaluated indirectly.

Table 3 compares the catalytic performance of different heterogeneous catalysts in degrading MB. The catalytic performance of CuO and CeO₂ is good co-catalysis components for Fe₂O₃/ATP catalyst; still they have synergy effect in CuO–CeO₂–Fe₂O₃/ATP catalyst to degrade MB. MB degradation ratios at acid conditions were higher than that at alkaline conditions due to decomposing capacity of H₂O₂ at different pH value, and at pH 5, MB decolorization by the heterogeneous Fenton systems had the highest ratios. Under the optimum conditions, MB degradation ratios of the three systems (CuO–Fe₂O₃/ATP, CeO₂–Fe₂O₃/ATP and CuO–CeO₂–Fe₂O₃/ATP) can reach 99.76%, 99.73% and 99.83%, respectively. The repeatable tests showed that the as-synthesized catalysts can be reused for many times, which meets the trend of low carbon lifestyle. The intermediate products of MB degradation were identified by LC-MS. According to the main identified products, the possible degradation process of MB in CuO–CeO₂–Fe₂O₃/ATP catalytic system was put forward.

**Conclusions**

In this study, two metal oxides, CuO and CeO₂, were screened as co-catalyst components for Fe₂O₃/ATP, and three catalysts (CuO–Fe₂O₃/ATP, CeO₂–Fe₂O₃/ATP and CuO–CeO₂–Fe₂O₃/ATP) were prepared for degradation of a phenothiazine dye MB. The three catalysts samples were determined by BET, XRD, FT-IR, SEM and XPS. The characterization results showed that the doping two or three metal oxides on ATP did not change the surface morphology and some characteristics of ATP, for example the adsorption capacity, but dramatically promote their catalytic performances. CuO and CeO₂ can be good co-catalysis components for Fe₂O₃/ATP catalyst; still they have synergy effect in CuO–CeO₂–Fe₂O₃/ATP catalyst to degrade MB. MB degradation ratios at acid conditions were higher than that at alkaline conditions due to decomposing capacity of H₂O₂ at different pH value, and at pH 5, MB decolorization by the heterogeneous Fenton systems had the highest ratios. Under the optimum conditions, MB degradation ratios of the three systems (CuO–Fe₂O₃/ATP, CeO₂–Fe₂O₃/ATP and CuO–CeO₂–Fe₂O₃/ATP) can reach 99.76%, 99.73% and 99.83%, respectively. The repeatable tests showed that the as-synthesized catalysts can be reused for many times, which meets the trend of low carbon lifestyle. The intermediate products of MB degradation were identified by LC-MS. According to the main identified products, the possible degradation process of MB in CuO–CeO₂–Fe₂O₃/ATP catalytic system was put forward.

**Conflicts of interest**

There are no conflicts to declare.

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