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Decolorization of Methylene Blue and Congo Red by attapulgite-based heterogeneous Fenton catalyst

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ABSTRACT

A kind of heterogeneous Fenton catalyst, attapulgite (ATP)-based catalyst (Fe_2O_3/ATP) was prepared. Its heterogeneous Fenton-like reactions were investigated for the decolorization of non-biodegradable dyes Methylene Blue (MB) and Congo Red (CR). Through a number of batch decolorization experiments under various conditions, it was found that the Fe_2O_3/ATP catalyst could serve as a Fenton catalyst and was effective in MB and CR decolorization. MB undergoes different decolorization performance when compared to CR because CR is a kind of azo dye otherwise MB is not. And this catalyst shows good stability during MB and CR decolorization in water in a wide range of pH (2.0–12.0).

Keywords: Attapulgite-based catalyst; Fe_2O_3; Heterogeneous reaction; Methylene blue; Congo red; Decolorization

1. Introduction

Advanced oxidation processes (AOPs) may be more appropriate for degrading hard-to-degradation organics than other chemical and biological oxidation methods. It has attracted considerable attention in the past decade such as Fenton's reagent [Fe(II)+H_2O_2], the generation of highly reactive and non-selective hydroxyl radicals ($^{\cdot}OH$) can oxidize and mineralize most of the organic compounds. The reaction process involving the generation of highly reactive $^{\cdot}OH$ means that a very strong and non-specific oxidant can oxidize almost all organic compounds [1]. In order to enhance the efficiency of degradation, many methods such as microwave [2], photo and UV [3,4], electric [5,6], ultrasound [7], etc. were combined with Fenton method. Although these homogeneous catalysts are generally very efficient for degradation of organic compounds, the catalysts of iron ions are dissolved in water, and their separation and reuse are rather difficult at the end of the treatment. And a kind of secondary pollutants, the ferric ions are generated. The removal of iron ions from the treated water needs a large amount of chemicals and manpower, which will increase the cost of treatment. Another drawback is the tight range of pH in homogeneous Fenton systems. The pH of solution should be adjusted between 2 and 4 beforehand to carry out the Fenton pretreatment, and the acidification is more costly than the energy and oxidant used in Fenton degradation [8].

To overcome these disadvantages, several studies have been conducted to explore heterogeneous catalysts for substitution of deliquescent Fe(II) reagent. Heterogeneous Fenton-like reactions on solid catalysts

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can effectively catalyze the oxidation of organic pollutants at wide pH conditions, which is beneficial for *in situ* remediation of polluted groundwater and soil [9], and can be reused for further runs [10–16].

Some catalysts used in the Fenton-like system were natural iron-bearing earth materials, such as ferrihydrite, hematite, goethite, lepidocrocite, magnetite, pyrite, and schorl [1,9]. They are wide spread in the natural environment and can be easily applied to *in situ* remediation processes.

The other kind of heterogeneous catalysts are porous materials such as zeolite, activated carbon, and activated aluminum oxide loaded with irons. Hassan and Hameed [17] carried out a study of the decolorization of azo dye, Acid Red 1 (AR1), in an aqueous solution using Fe–zeolite Y type (Fe–ZYT) catalyst. Zhong et al. [18] prepared iron-containing mesostructured silica (Fe_2O_3/SBA-15) and used it as heterogeneous catalyst in the integrated sono–photo-Fenton process. Muthukumari et al. [11] studied photo-assisted Fenton mineralization of two azo dyes Direct Red23 (DR23) and Reactive Orange 4 (RO4) in detail using a Fe(II)-loaded Al_2O_3 as a heterogeneous catalyst in presence of H_2O_2 and UV-A light.

Clays, such as montomorillonite, kaoline, are often in use of heterogeneous catalysts, in order to lower the treatment cost of wastewater. For example, Feng et al. [19] studied the discoloration and mineralization of an azo dye Orange II by using a bentonite clay-based Fe nanocomposite (Fe–B) film as a heterogeneous photo-Fenton catalyst in the presence of UV-C light and H_2O_2. Under optimal conditions (pH 3.0, 10 mM H_2O_2, and 1 × 8 W UVC), 100% discoloration and 50–60% TOC removal of 0.2 mM Orange II can be achieved in 90 and 120 min, respectively. Chen and Zhu [14,15] successfully prepared OH^--Fe-pillared bentonite (H–Fe–P–B) through cation exchange reaction and used it as a solid catalyst for UV–Fenton to degrade non-biodegradable azo-dye Orange II. Compared with raw bentonite, the content of iron, interlamellar distance, and external surface area of H–Fe–P–B increased remarkably.

Among the perspective clays, attapulgite clay is a promising choice. Attapulgite is a crystalline hydrated magnesium aluminum silicate with unique three-dimensional structure and has a fibrous morphology. Due to its structural properties, attapulgite has received considerable attention with regard to the adsorption of organics on the clay surface and to their use as support for catalysts [20–22]. Fe_2O_3/attapulgite is a new catalyst we prepared for degradation SDBS [23,24]. It has some advantages over other catalysts: (1) It utilizes attapulgite as its supporter and possesses high specific area and mesoporosity, (2) in Fe_2O_3/attapulgite/H_2O_2 systems, Fe_2O_3/attapulgite can be easily separated from the solution and can be reused for several times, and (3) Fe_2O_3/attapulgite/H_2O_2 systems have high efficiency of degradation with almost no Fe ion leaching in the solution. These characteristics make it feasible to use Fe_2O_3/attapulgite as an economic and ecological catalyst for water treatment, meeting the trend of "low carbon economy".

Previous studies have showed Fe_2O_3/attapulgite is an efficient catalyst for organics. Our researches have investigated the degradation of SDBS in solution with Fe_2O_3/attapulgite particles and the results demonstrated that Fe_2O_3/attapulgite has good abilities of catalysis and degradation of SDBS [23,24]. However, SDBS is a kind of organics with relatively simple structure. The novel features of our studies are: (1) We use Fe_2O_3/attapulgite as the catalyst for the heterogeneous Fenton-like system to remove the dyes from water at a relatively high concentration, (2) we compare two dyes decolorization processes, one is an azo dye, and another is not.

2. Experimental

2.1. Materials

Attapulgite clay was obtained from Xuyi, Jiangsu, China (specific surface area 146–210 m^2/g), with ATP content of 60–70%, hydromica and montmorillonite content of 15–28%, dolomite and quartz content of 10–20%, dolomite and montmorillonite content of trace. Its chemical components (%) are as follows: SiO_2, 57.006; TiO_2, 0.893; Al_2O_3, 8.583; Fe_2O_3, 4.641; SO_3, 0.007; MnO, 0.034; MgO, 8.456; CaO, 0.216; K_2O, 0.094; Na_2O, 0.948.

Methylene Blue (MB, $C_{16}H_{18}ClN_3S$, analysis purity) and Congo Red (CR, $C_{32}H_{22}N_6Na_2O_6S_2$, analysis purity) were purchased as aiming pollutants. $Fe(NO_3)_3$, H_2O_2 (30%), NaOH, H_2SO_4 supplied by their manufacturers were all analytical grade.

2.2. Preparation method of Fe_2O_3/ATP

Fe_2O_3/ATP samples were prepared by incipient wetness technique. ATP and some water were mixed and well-distributed. After a day, the mixture was shaped to spheroidal particles (2–3 mm), and dried in the oven at the temperature of 105℃. After that, the samples were roasted in the high temperature oven at 600℃ for 2 h, then cooled in the ambient. $Fe(NO_3)_3$ was used as precursor salt to prepare Fe_2O_3/ATP. 5 g $Fe(NO_3)_3$ were dissolved in 95 mL distilled water. Then, $Fe(NO_3)_3$ (5 wt.%) mixed solution were obtained. 20 g ATP particles prepared before were immersed in the mixed solution for 4 h and dried and roasted at 600℃ for 2 h, then cooled in the ambient. The Fe_2O_3/ATP catalyst samples were obtained. The physicochemical characteristics of the synthesized samples were evaluated by various techniques such as XRD, SEM, and FTIR [23].

After the introduction of iron species into ATP, the surface area, total pore volume, and average pore size of Fe_2O_3/ATP all decreased (Table 1). This might be caused by the embedding and coating of nanosized Fe_2O_3 particles onto the surface of ATP.

2.3. Degradation methods

Methylene Blue (MB), a common cationic dye, molecular weight of 373.90, Congo Red (CR), a common azo and anionic dye, molecular weight of 696.68, were selected as model pollutants. Their structures are show in Fig. 1. A stock solution containing MB (1,000 mg/L) and another containing CR (1,000 mg/L) were prepared using distilled water, subsequently diluted to the required concentrations for the experimental work. 90 mL distilled water and 10 mL dye solution (MB or CR, 1,000 mg/L) were added in a conical flask, and 100 mg/L dye solution (MB or CR) was obtained. The pH was adjusted by addition of sodium hydroxide or sulfur acid to the dye solutions. Then, ATP-base catalyst samples were added into 100 mL, 100 mg/L MB or CR solution in the conical flask, and required dosage of hydrogen peroxide (30% w/w) was added in. After being sealed, the conical flasks were placed in a constant-temperature water-bath. For H_2O_2 solution and solid catalyst, metric units of concentration used in this study were mol/L and g/L, respectively. The MB and CR concentrations were measured using a INESA 752N type ultraviolet-visible spectrophotometer by Methylene Blue spectrophotometry at λ of 664 nm and Congo Red spectrophotometry at λ of 510 nm, respectively. The degradation ratio, i.e. the removal degree of MB can be calculated using Eq. (1),

$$\eta = (C_0 - C_t)/C_0 \times 100\% \tag{1}$$

where C_0 is the initial concentration of MB or CR wastewater and C_t is the concentration at contact time t. In order to check the reproducibility of the results, random tests were done under different experimental conditions.

Table 1
Characteristics of catalyst

	ATP	Fe_2O_3/ATP
Surface area ($m^2\,g^{-1}$)	144.6	132.8
Pore volume ($mL\,g^{-1}$)	0.3911	0.3585
Pore size (nm)	7.9	7.1
Particle size (mm)	2–3	2–3

3. Results and discussion

3.1. Catalytic activity of Fenton catalyst

Successive runs demonstrate that the reactivity of the systems vary by, respectively, time (Fig. 2), H_2O_2 concentration (Fig. 3), Fe_2O_3/ATP catalyst dosage (Fig. 4), temperature (Fig. 5), and pH (Fig. 6).

In order to gain an insight into the process of the MB and CR decolorization by Fe_2O_3/ATP/H_2O_2 system, comparative experiments were undertaken in the presence of (a) H_2O_2 only and (b) both Fe_2O_3/ATP and H_2O_2. The results are shown in Fig. 2. It can be observed from Fig. 2(a) that in presence of H_2O_2 only, decolorization ratio of CR reaches 50% within 4 h and obtains 60% within 36 h, but that of MB only achieves 20% after 36 h. It means chromophores N=N of CR is easy to break, even H_2O_2 can partially oxidize CR and make it faded. While chromophores –S– of MB is harder to be oxidized by H_2O_2. Fig. 2(b) shows that catalytic activities of Fe_2O_3/ATP in presence of H_2O_2 do not show significant MB and CR decolorization, achieving above 23 and 44% decolorization ratio, respectively, in 1 h of reaction at room temperature. And they all achieved 99% decolorization ratios over 36 h. At earlier stage (before 20 h) CR decolorization ratio is higher than that of MB, while at later stage (after 20 h) the contrary is the case. It can be seen that MB can be mineralized by OH radicals produced from Fe_2O_3/ATP/H_2O_2 system rather than H_2O_2. Because of low reaction temperature, the rate of OH radicals producing is very low, and the decolorization ratio of MB is very low at earlier stage (before 20 h). While CR is mainly oxidized by H_2O_2 at that stage, and it obtained a higher decolorization ratio than MB. With OH radicals generating, the decolorization ratio of MB increases greatly, while only a part of H_2O_2 in CR solution can generate OH radicals and oxidize CR (another part oxidizes CR directly). And OH radicals have much stronger oxidation ability than H_2O_2, so the decolorization ratio of MB is higher than that of CR at later stage (after 20 h). These results evidenced the catalytic activity of Fe_2O_3/ATP as Fenton catalyst for decolorizing MB and CR, but the reactions need longer hours (36 h or more) at room temperature.

Fig. 3 shows MB and CR decolorization ratios vs. different H_2O_2 concentration conditions (from 0.049 to 0.245 mol/L). The data indicate that decolorization

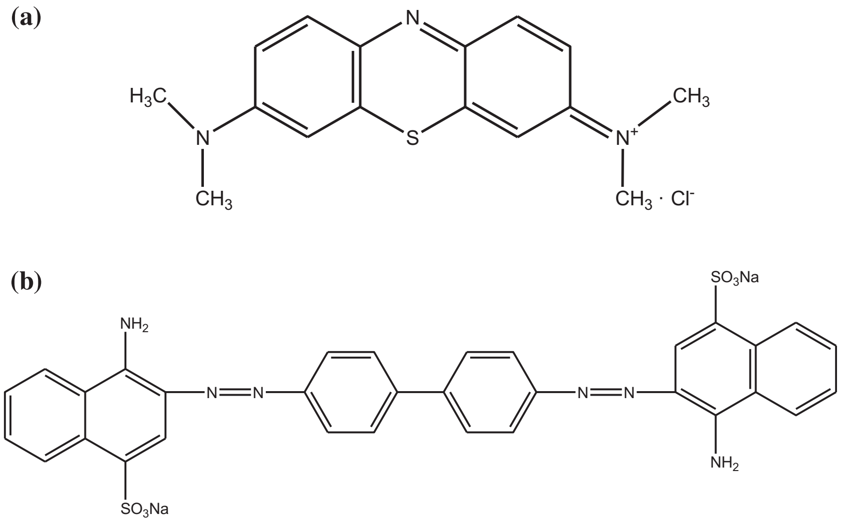

Fig. 1. Structures of Methylene Blue (a) and Congo Red (b).

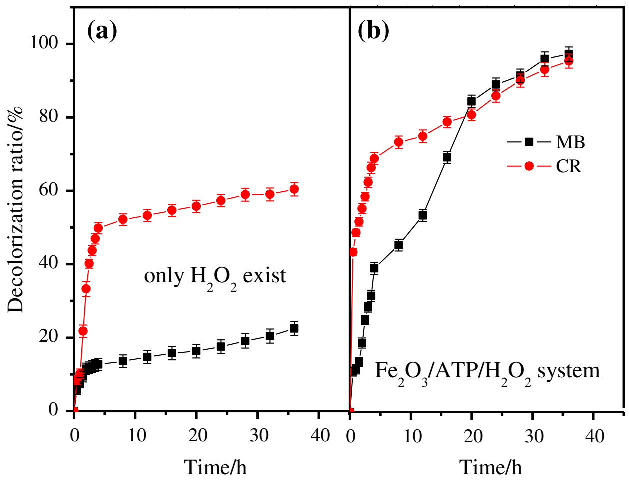

Fig. 2. Effect of time on the MB or CR decolorization in different systems ($T = 20$℃, pH 5, $[MB]_0 = 100$ mg/L, $[CR]_0 = 100$ mg/L, $[H_2O_2]_0 = 0.098$ mol/L, and Fe_2O_3/ATP dosage = 1 g/100 mL).

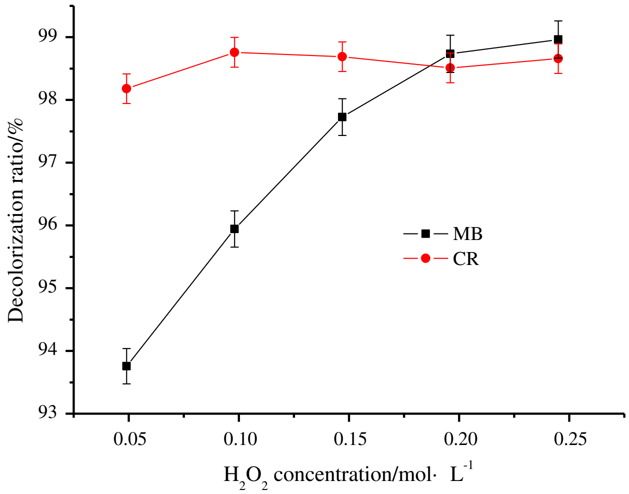

Fig. 3. Effect of H_2O_2 concentration on the MB or CR decolorization ($T = 20$℃, pH 5, reacting time = 24 h, $[MB]_0 = 100$ mg/L, $[CR]_0 = 100$ mg/L, and Fe_2O_3/ATP dosage = 1 g/100 mL).

ratio of MB increases with increasing initial H_2O_2 concentration, while that of CR does not. That is because CR is easier to be oxidized and the OH radicals decomposed from a small amount of H_2O_2 can decolorize CR mostly when a certain amount of catalysts exist, whereas it needs more OH radicals, or to say, more H_2O_2 to obtain higher MB decolorization ratio. Moreover, decolorization ratios of MB and CR change a little at different initial H_2O_2 concentration. When initial H_2O_2 concentration increases, decolorization ratios of MB and CR change from 93.7 to 99% and from 98.2 to 98.7%, respectively. For saving H_2O_2 and taking good advantage of Fe_2O_3/ATP catalyst, the H_2O_2 concentration should be 0.098 mol/L at later experiments.

From Fig. 4, it can be seen that decolorization ratios of MB and CR all increase with catalyst dosage. They suggest that more catalysts, the more active Fe_2O_3 sites on catalyst surface for accelerating decomposition of H_2O_2, lead to an increase in the number of OH radicals. It also can be seen that decolorization of CR changes more due to the variation of catalyst dosage than that of MB. Catalyst dosage increasing from 2.5 to 20 g/L, decolorization ratio of MB and CR

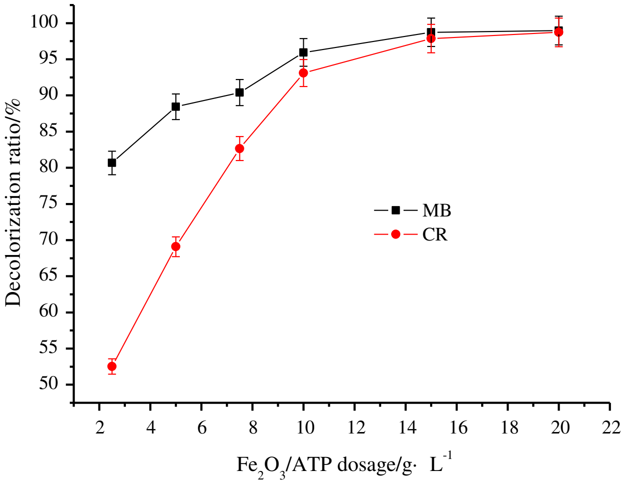

Fig. 4. Effect of Fe_2O_3/ATP dosage on the MB or CR decolorization with H_2O_2 (T = 20℃, pH 5, reacting time = 24 h, $[MB]_0 = 100$ mg/L, $[CR]_0 = 100$ mg/L, and $[H_2O_2]_0 = 0.098$ mol/L).

increase from 80 to 99%, and from 52.5 to 98.7%, respectively. It indicates that OH radicals generating from even low catalyst dosage with certain amount of H_2O_2 can oxidize MB immediately; on the other hand, at low catalyst dosage, CR is oxidized by H_2O_2 prior to OH radicals, while when catalyst dosage increases, H_2O_2 reacts with Fe_2O_3/ATP and generates OH radicals to oxidize CR rather than oxidizing CR directly. In order to maintain high decolorization ratio and because of reusable performance of the catalyst, we adopt catalyst dosage of 10 g/L in later experiments.

The effect of reaction temperature on decolorization of MB and CR were also studied, and the results are presented in Fig. 5. It can be seen that the reactivity of the system is enhanced with increasing the reaction temperature. It is because at higher temperature faster catalysis to decompose H_2O_2 results in increase in the number of OH radicals. Another possible reason put forward to interpret this phenomenon is that higher temperature can provide more energy for reactant molecules to overcome reaction activation energy. We also can see that decolorization of MB increases much greatly than that of CR when temperature increases. It is probably because that part of H_2O_2 oxidize CR directly and cannot generate enough OH radicals at 40℃. While at 60℃, reaction rate increases rapidly, and more OH radicals are released to oxidize CR and a high decolorization ratio is obtained. According to the experiment, the reaction temperature should be 60℃ for obtaining a rapid (within one hour) decolorization.

Fig. 6 shows that at the adopted experimental conditions there is a dependence of the system reactivity upon the pH of the solution. The behaviors of MB and CR decolorization are different at acidic, neutral, and alkaline pH. At acidic pH, the CR decolorization ratios are higher than those at alkaline pH whenever at high temperature or at low temperature. However, the MB decolorization ratios varied a little by changing the pH value. Fe_2O_3/ATP will adsorb dye molecules; and the more the alkaline is, the stronger the adsorption will be. When Fe_2O_3/ATP is saturated adsorption, the surface of catalyst is coated by dye molecules and the

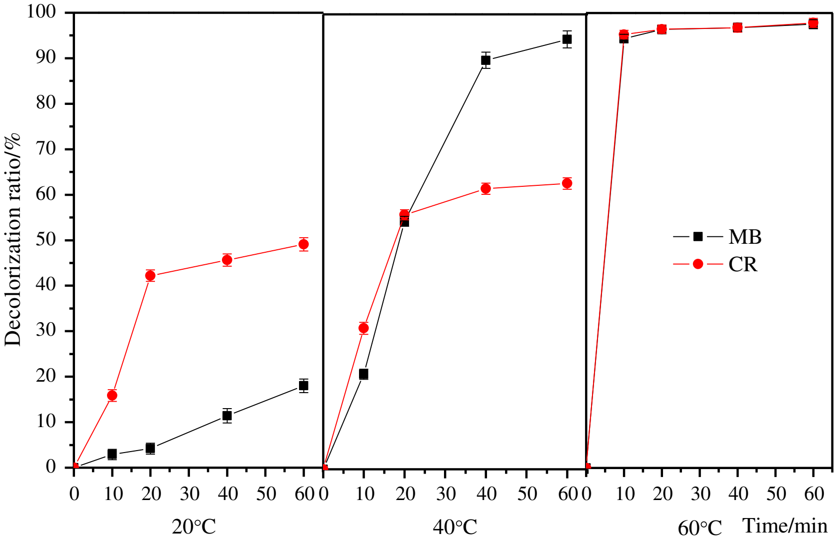

Fig. 5. Effect of reaction temperature and time on the MB or CR decolorization (pH 5, $[MB]_0 = 100$ mg/L, $[CR]_0 = 100$ mg/L, $[H_2O_2]_0 = 0.098$ mol/L, and Fe_2O_3/ATP dosage = 1 g/100 mL).

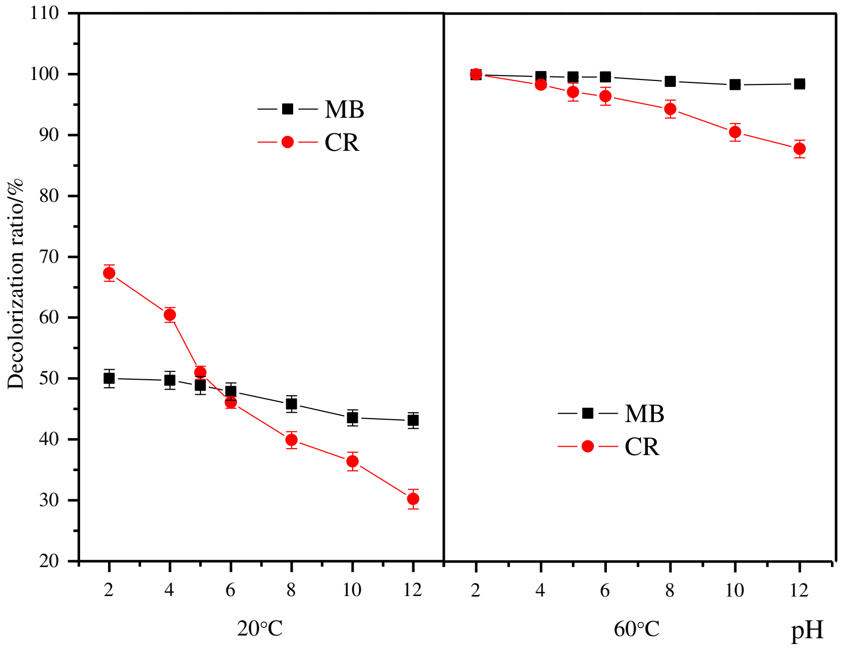

Fig. 6. Effect of pH on the MB or CR decolorization (reacting time = 1 h, $[MB]_0$ = 100 mg/L, $[CR]_0$ = 100 mg/L and $[H_2O_2]_0$ = 0.098 mol/L, and Fe_2O_3/ATP dosage = 1 g/100 mL).

degradation ratio goes down, while at higher temperature, the influence of adsorption will decrease. And because molecular of CR is bigger than that of MB, at same amount of catalyst, the adsorption quantity of CR by Fe_2O_3/ATP is less than that of MB, and the decolorization ratio of CR is lower than that of MB at alkaline pH condition.

As we know, homogeneous Fenton systems have the tight range of pH. The pH value of solution should be adjusted between 2 and 4 beforehand to carry out the Fenton pretreatment [8], while Fe_2O_3/ATP catalyst can extend the range of pH for Fenton oxidant from 2 to 12, according to the experiment.

3.2. Stability and reusability of catalysts

The experiments on repeating the usage of the catalyst were conducted in our present study. After decolorization of MB and CR, the catalysts used in the experiment were just washed with distilled water. The experiments were carried out in ten consecutive runs under the same conditions of $T = 60℃$, pH 5, reacting time = 1 h, $[MB]_0$ = 100 mg/L, $[CR]_0$ = 100 mg/L, $[H_2O_2]_0$ = 0.098 mol/L, and Fe_2O_3/ATP dosage = 1.0 g/100 mL. It was found that after ten times of recycle reaction, MB and CR decolorization retain a high efficiency (Fig. 7). Because there is no iron ion leaching and active sites maintain high activities.

The absorption characteristics of MB and CR are shown in Figs. 8 and 9, which also presented the absorption spectra of an aqueous solution of MB and CR in heterogeneous Fenton process before and after degradation. It can be seen that the absorption peak at 664 nm of MB and the absorption peak at 510 nm of CR disappear, without the appearance of new

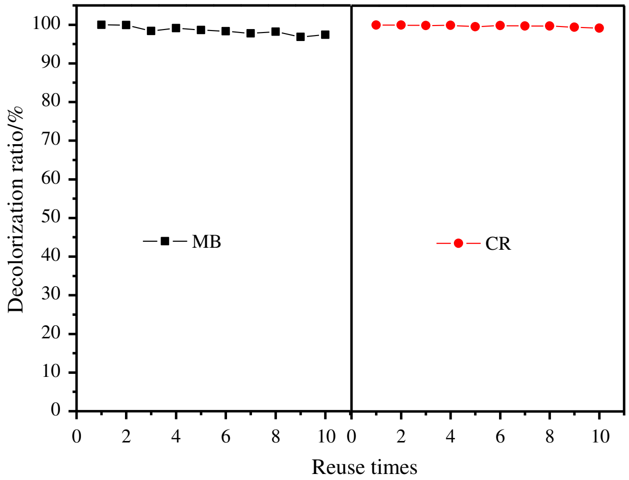

Fig. 7. Ten consecutive runs under the conditions of $T = 60℃$, pH 5, reacting time = 1 h, $[MB]_0$ = 100 mg/L, $[CR]_0$ = 100 mg/L, $[H_2O_2]_0$ = 0.098 mol/L, and Fe_2O_3/ATP dosage = 1.0 g/100 mL.

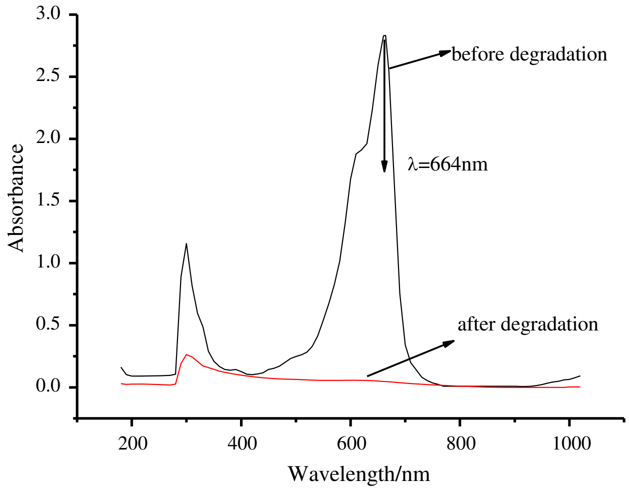

Fig. 8. UV–vis spectral changes before and after degradation of MB in heterogeneous Fenton process.

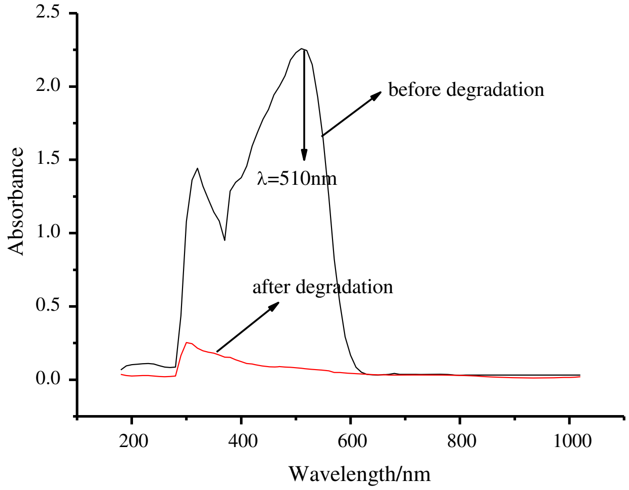

Fig. 9. UV–vis spectral changes before and after degradation of CR in heterogeneous Fenton process under acidic condition.

adsorption peaks. The absorbance peaks at around 300 nm that represent the aromatic content of dye also have decayed.

3.3. Comparative experiments

Fe_2O_3/ATP-catalyzed Fenton-like reaction was compared with homogeneous Fenton reaction (Fe^{2+}/H_2O_2), and the result is shown in Fig. 10. It can be seen that Fe_2O_3/ATP-catalyzed Fenton-like reaction almost has the same efficiency as homogeneous Fenton reaction, while the former has a wide pH range, has no secondary pollutants and Fe_2O_3/ATP catalyst can be reused.

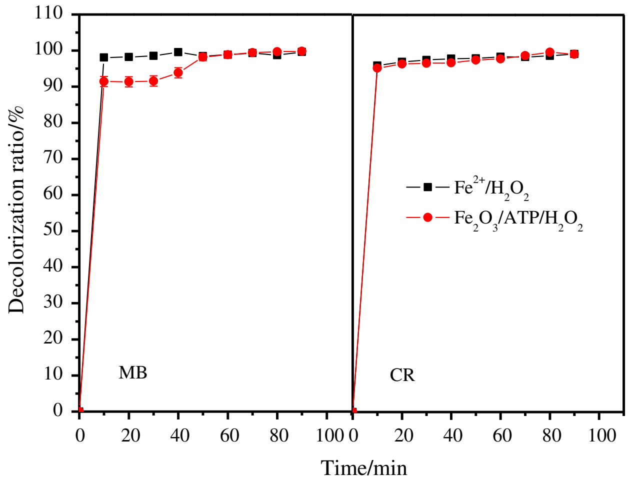

Fig. 10. Comparative analyses for the MB and CR decolorization ratios under different contact time in presence of (1) both H_2O_2 and Fe_2O_3/ATP (T = 60℃, pH 5, $[MB]_0$ = 100 mg/L, $[CR]_0$ = 100 mg/L, $[H_2O_2]_0$ = 0.098 mol/L, Fe_2O_3/ATP dosage = 1.0 g/100 mL) and (2) both H_2O_2 and Fe^{2+} (T = 60℃, pH 3, $[MB]_0$ = 100 mg/L, $[CR]_0$ = 100 mg/L, Fe^{2+}/H_2O_2 = 1/5).

4. Conclusions

Fe_2O_3/ATP was successfully prepared and its decolorization reactions of MB and CR were compared. The experimental results demonstrated that Fe_2O_3/ATP had good catalyst reactivity in decolorization MB and CR. But the results also showed some differences between MB and CR when they are decolorized by Fe_2O_3/ATP/H_2O_2 system. That is probably because CR is an azo dye but MB is not. CR is easier to be oxidized; even H_2O_2 can partially oxidize CR and make it faded. While MB is harder to be oxidized by H_2O_2, only OH radicals decomposed from H_2O_2 can decolorize MB. This makes the decolorization of MB and CR to have different performances when H_2O_2 concentration and catalyst dosage changes. Furthermore, catalytic reactions almost did not vary in different pH values from 2 to 12 in MB decolorization, but decreased little in CR decolorization. Fe_2O_3/ATP catalysts can be reused at least ten times in both MB and CR decolorization, still with high catalytic activity. Compared with homogeneous Fenton reagent, Fe_2O_3/ATP catalyzed Fenton-like system has unique advantages of easy separation of heterogeneous catalysts from the treated wastewater, high catalytic reactivity at wider pH range, repeated usage, and absence of secondary pollutants.

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