Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2012.763047

51 (2013) 5821–5830
August

Degradation of methylene blue using a heterogeneous Fenton process catalyzed by ferrocene

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Received 18 October 2012; Accepted 26 December 2012

ABSTRACT

A heterogeneous Fenton process catalyzed by ferrocene (Fc) was established to investigate the degradation of methylene blue (MB). Fc was proved to be of good cyclic redox capacity and catalytic potential. Heterogeneous Fenton process catalyzed by Fc particles was predominate process in Fc/H_2O_2 system. The active radical generated in the Fc/Fenton process was hydroxyl radical ($^{\bullet}OH$) from the decomposition of H_2O_2 catalyzed by Fc. Excess H^+ and OH^- in solution resisted the decomposition of H_2O_2 and the generation of $^{\bullet}OH$. Parameters including the initial solution pH value, dosage of catalyst, and H_2O_2 influenced the efficiency of Fc/Fenton process. Maximum efficiencies of 100% MB removal and 64% chemical oxygen demand (COD) removal can be obtained with 0.372 g/L Fc and an initial $[Fc]/[H_2O_2] = 0.5077$ at pH 3, 30°C, after 120 min of reaction. With determined Fc or H_2O_2 dosage, Fc/Fenton efficiency increased as the ratio $[Fc]/[H_2O_2]$ increased. The efficiency of MB removal was much higher than COD removal indicating that the chromophore of MB were destroyed and colorless intermediates were generated, instead of CO_2 and H_2O. Fc is of high stability and the efficiency of the Fc/Fenton was still about 96.5621% after the third cycle.

Keywords: Methylene blue; Heterogeneous Fenton; Ferrocene; Hydroxyl peroxide

1. Introduction

Since it is a worldwide environmental problem, there has been significant attention to water pollutant over many decades. Dyeing wastewater usually has a high chemical oxygen demand (COD), due to a high concentration of organic chemicals, which are not only pollutants to the environment but also toxic to aquatic organisms and public health [1,2]. The treatment of water discharged from dye manufacture is particularly important because of the large quantity produced and widespread occurrence [3]. A number of technologies, including biological treatment, coagulation–flocculation, and membrane processes, are effective for such water treatment [4,5]. However, these processes are costly and the equipment is complex. The organic pollutants discharged are usually very stable, refractory, and biorefractory. In order to meet the urgent demands of development, new powerful methods for degradation of these organic materials must be established.

Advanced oxidation processes (AOPs) have been found to have widespread application for the treatment of wide range of organic pollutants in wastewater [6].

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Researchers have demonstrated that nonbiodegradable and refractory dyes can be mineralized into H_2O, CO_2 completely and other nontoxic inorganic compounds using AOPs. AOPs are based on the properties of extremely reactive and nonselective hydroxyl radicals [7] including noncatalytic and catalytic ozonation [8,9], catalytic wet peroxide oxidation [10,11], photocatalytic [12], electrochemical [13] and Fenton processes [14,15], and many other H_2O_2-assisted methods [16–19]. The Fenton process is one of the most widely used AOPs in industrial wastewater treatment [20–22] because of its low investment cost and high efficiency. However, only a small fraction of the H_2O_2 is converted into oxidants that are capable of transforming recalcitrant contaminants [23–25], leading to large H_2O_2 consumption, and Fe^{2+} used is also hard to be recycled. High consumption of chemical reagents, limited range of pH, deactivation by some ion complex agents like phosphate anions, and production of significant amounts of iron sludge [26,27] are typical disadvantages encountered in the homogeneous Fenton process [28,29]. To overcome these drawbacks, more effort was needed to develop heterogeneous Fenton processes. Solid matrixes, such as Fe clusters, Fe oxides, and Fe^{2+} or Fe^{3+} modified zeolite, meso-Al_2O_3 and SBA-15 [30–32], have been used to establish heterogeneous Fenton. Drawbacks like leaching of Fe^{2+} or Fe^{3+} in acidic surroundings and poor catalytic activity exist, and external power is needed to be introduced to improve the efficiency of heterogeneous Fenton. Thus, the cost of reaction will be improved.

Ferrocene (Fc) is a kind of organic transition metallic compound ($Fe(C_5H_5)_2$), which is highly stable and nontoxic. Fc possesses electron donor–acceptor conjugated structure [33,34] showing good redox reversible characteristics and it is of high catalytic capacity. Based on the above mentioned characteristics, Fc was proposed as catalyst in Fenton process in this study. Dyes discharged into the environment are resistant to biological treatment because of their complex structure. Methylene blue (MB) was chosen as a model pollutant in this study because of its wide use in the textile industry and strong effect on light penetration into water. In this study, the redox reversibility of Fc was investigated by cyclic voltammetry, and the catalytic capacity through comparison experiments. The distributions of adsorption, homogenerous catalytic oxidation, and heterogeneous catalytic oxidation over MB were studied and time-resolved experiments were devised to determine the optimum condition for the Fc/Fenton process. It provides a green, effective, and economic system ideal for the treatment of toxic and nonbiodegradable organic pollutants in water.

2. Materials and methods

2.1. Chemicals

Fc, ferrous chloride, ferric chloride, MB, $HgSO_4$, H_2O_2 (30%), and potassium titanate were obtained from Jingchun Chemical reagent Co. Ltd., Shanghai, China. $K_2Cr_2O_7$, Ag_2SO_4, HCl, NaOH, alcohol, and Li_2SO_4 were obtained from sinopharm Chemical reagent Co. Ltd., Shanghai, China. Chemicals used in this study were all analytical grades without further purification and all solutions were prepared with doubly distilled water from a water-purify system with a resistivity of 18.25 MΩ cm.

2.2. Experimental procedures

All experiments were carried out in glass vessels and the initial solution volumes were 250 mL. All solutions were freshly prepared every day, and the initial solution pH values were adjusted with 2 mol/L HCl and 1 mol/L NaOH. About 2.5, 5, and 10 mg/L MB with a serious concentrations of Fc (5, 10, 15, 20, 25, 50, 75, 120, 186, 279, 372, and 558 mg/L) and H_2O_2 (from 0.0018 to 120 mmol/L) were investigated. All solutions were thoroughly stirred to make them homogeneous before addition of the reagents. The glass vessels used as the reactors were setup in a constant temperature oscillator to attain the desired constant temperature (30–60℃) and stirred at a constant speed of 275 rpm/min. Fenton reactions were started with the addition of hydrogen peroxide (30 wt.%). Samples were taken at selected intervals and the pH value was increased to 12 with 2 mol/L NaOH to terminate the reaction. Finally, the reaction solution was filtered to separate out the catalyst particles.

2.3. Electrochemical characterization of Fc

Cyclic voltammetric (CV) measurement on Fc was performed on a LK2005A electrochemical workstation supplied by Lanlike Co., in Tianjin. It was equipped with a platinum electrode as the working electrode, a reference electrode (SCE), and an auxiliary platinum electrode between -0.2 and 0.8 V at the scan rate of 50 mV/s. Alcohol was used as the organic solvent, and 0.2 M Li_2SO_4 was used as the supporting electrolyte in CV measurement. Before the experiments, the dissolved oxygen in solution was purged with N_2, and the detections were carried out under a N_2 atmosphere.

2.4. Analysis

Samples taken out were immediately analyzed by measuring the absorbance of MB using a Shimadzu

UV–visible spectrophotometer (2450) at a wavelength of 660 nm [35], corresponding to the maximum in the absorption spectrum of MB. The COD was measured with a JiangFen HH-6 COD analyzer, and the samples were put in the bridge for 12 h to avoid the effect of H_2O_2 in solution [36]. H_2O_2 in solution was determined by the potassium (IV) oxalate method [37]. Hydroxyl radicals in solution were detected by a photometric technique [38]. Hydroxyl radicals generated in solution can only survival very short time, and the life time is less than 10^{-4} s. It is hard to be detected directly. The production of $^{\bullet}OH$ from H_2O_2/Fe^{2+} process was assayed by the oxidation of 1,10-phenanthroline-Fe^{2+} to 1,10-phenanthroline-Fe^{3+}. And the decrease of 1,10-phenanthroline-Fe^{2+} (ΔC) was the certain dosage of $^{\bullet}OH$ generated.

3. Results and discussion

3.1. Catalytic activity of Fc in Fenton process

MB was used to investigate the catalytic activity of Fc when the initial solution pH was 2. As shown in Fig. 1, color removal of MB approached 5, 8, and 97% only in the presence of H_2O_2, Fc and both H_2O_2 and Fc, respectively. With the presence of H_2O_2 or Fc alone, the color removal of MB was insignificant, while with both H_2O_2 and the catalyst, the color removal was very effective and achieved 70% in less than 30 min. Processes with presence of H_2O_2 or Fc alone, had almost negligible impact on the oxidation of MB, indicating that MB in solution was stable to H_2O_2 and Fc particles in solution adsorbed little MB on to its surface. MB in solution lost its color in presence of both Fc and H_2O_2, indicating that the Fc used in the Fenton-like system shows good catalytic activity to H_2O_2 and high concentration of strong oxidants were generated and were able to oxidize MB.

As used in Fenton process, catalyst must be of good reversible redox character [39]. So, cyclic voltammetry experiments were performed to verify the reversible redox character of Fc. Alcohol was diluted with doubly distilled water at the ratio of 1:4, and used as solvent of Fc. The experiments were performed in the presence of 0.1 mol/L Li_2SO_4, and the results are shown in Fig. 1(b). Curves *a* and *b* in Fig. 1(b) depicts the CV curves of H_2O_2 and H_2O_2 with Fc, respectively. No redox peak could be observed in the potential range for H_2O_2 showing that alcohol has no influence on the electrochemical behavior of Fc and H_2O_2 is of nonreversible redox character. As depicted in curve *b*, $i_{p,c}/i_{p,a} \approx 1$ and the anodic and cathodic peak potentials were located at 0.391 and 0.570 V, respectively. The separation of anodic and cathodic potentials was 179 mV. In actual experiments, the expected 58 mV is rarely observed because of small distortions due to solution resistance effects and electronic or mathematical "smoothing" of data [40]. The cyclic voltammetry experiments indicated good reversible redox character of Fc, and one electron gets

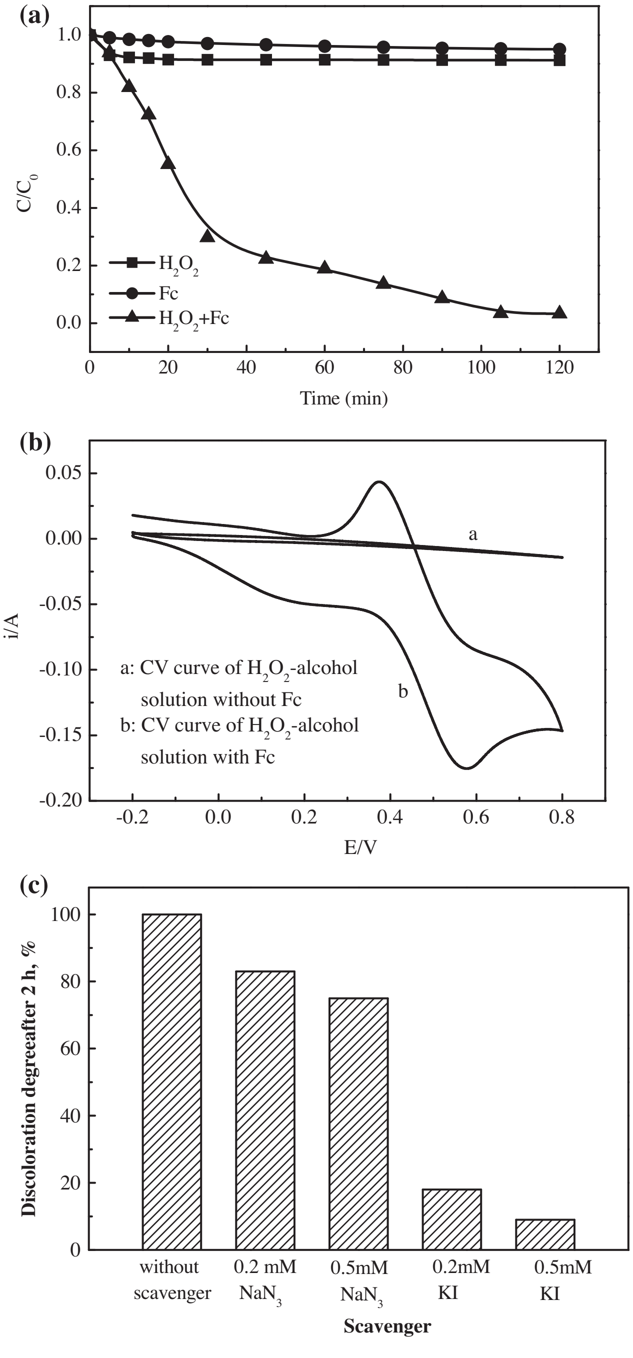

Fig. 1. Catalytic activity (a) and cyclic voltammetry character (b) of Fc and determination of $^{\bullet}OH$ in the heterogeneous Fenton system (c).

transferred in the reaction [41], so that Fc dissolved in solution may be oxidized to Fc^+ and Fc can be regenerated with an electron transfer. Accordingly, Fc/Fc^+ has good reversible redox properties.

Comparative experiments using scavenger-loaded conditions were undertaken to determine the main active species responsible for the degradation of MB. The formation of several possible oxidative intermediate species, such as oxygen and hydroxyl radical, were investigated using appropriate quenchers of these species [42]. KI was used as the quencher of the $^\bullet OH$ radical on the catalyst surface and NaN_3 as a quencher of oxygen and $^\bullet OH$. It can be seen from Fig. 1(c) that the percentage of discoloration decreases from 100 to 83% when using 0.2 mM NaN_3, and falls to 75% when the concentration of NaN_3 is increased to 0.5 mM. The percentage of discoloration was 18% when using 0.2 mM KI, and falls to 9% when the concentration of KI is increased to 0.5 mM. These results show that both oxygen and $^\bullet OH$ are involved in the discoloration of MB, but $^\bullet OH$ on the catalyst surface played the main role. pH variation during the process was also detected at initial pH of 4. After 120 min, the pH was measured to be 3.43. Based on the experimental results mentioned above, a possible reaction mechanism was proposed:

$$Fc + H_2O_2 \longrightarrow Fc^+ + {}^\bullet OH + OH^- \tag{1}$$

$$Fc^+ + H_2O \longrightarrow Fc + {}^\bullet OH + H^+ \tag{2}$$

$$2Fc^+ + H_2O_2 \longrightarrow 2Fc + O_2 + 2H^+ \tag{3}$$

3.2. Determination of the predominate process in Fc/H_2O_2 system

As a heterogeneous catalyst, dyestuffs may be removed by adsorption of Fc (A) and oxidation by Fenton catalyzed by Fc (C). Experiments were established to determine the main process in the disappearance of MB, and the results are shown in Fig. 2. As shown in Fig. 2, in the process of adsorption of MB followed by catalytic degradation (A + C), the removal of MB after 2 h adsorption in the dark was about 12%. After filtering out Fc from the solution, and adding H_2O_2, the solution began a rapid oxidation process. After another 2 h reaction, the removal efficiency was about 23.2%. Fc in the solution can adsorb some dyestuff on to its surface, but the removal efficiency by this process was not significant, and the result is the same as shown in Fig. 1(a). In the subsequent catalytic oxidation process, 23.2% MB could still be removed after filtering out Fc, for even a little Fc in solution catalyzed the generation of $^\bullet OH$. In the simultaneous adsorption and catalytic degradation (A/C) process, 100% color removal was achieved in a reaction time of 75 min. The penetration of light decreased a little as the reaction proceeded due to the dissolution of Fc in the solution. From the results presented in Fig. 2, it might be inferred that color removal of MB in solution was due to the combined adsorption of Fc particles, generous Fenton process, and heterogeneous Fenton processes. Heterogeneous Fenton reaction catalyzed by Fc suspended in solution played the main role, as a 12% reduction of MB was reached after adsorption in the dark, and 23% removal was achieved due to the vigorous Fenton reaction. All the efficiencies in the following experiments refer to the complete removal of MB in the A/P process.

The dissolution of Fc was also investigated in this study, and the results are depicted in Fig. 2(b). Fc

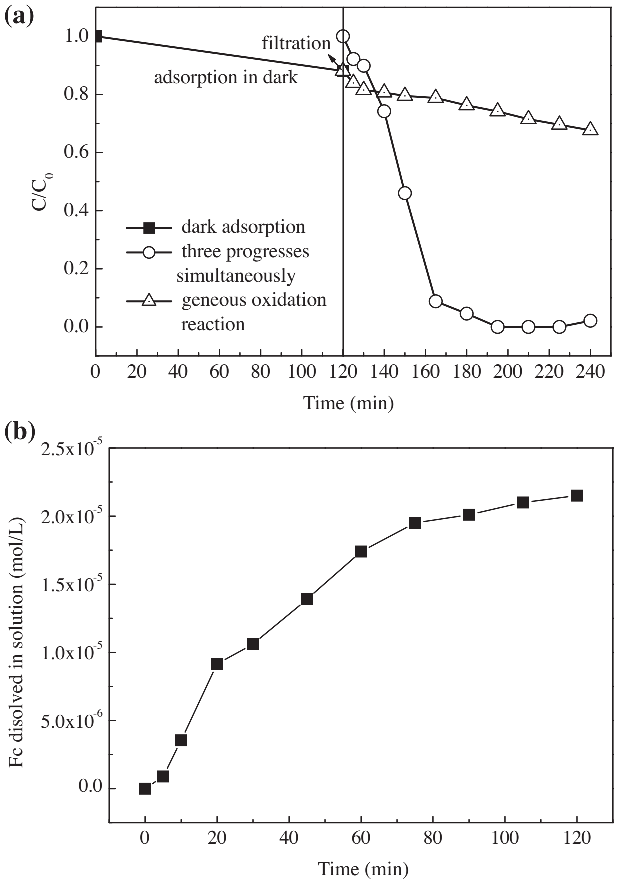

Fig. 2. (a) Constitutions in Fc/H_2O_2 system including adsorption, homogeneous Fenton catalyzed by dissolved Fc and heterogeneous Fenton catalyzed by solid Fc particles, under conditions: pH 3, 30°C, 0.372 g/L Fc, 10 mg/L MB, and $[H_2O_2]/[MB] = 3.17$; (b) dissolution of Fc in A/C process.

dissolved as reaction progressed, and the concentration of dissolved Fc in solution after 120 was detected to be 2.15×10^{-5} mol/L. Initial concentration of Fc added was 0.372 g/L (1.9946×10^{-3} mol/L), and Fc insoluble was calculated to be 1.9729×10^{-3} mol/L. In A + C process, MB removed in Fenton process catalyzed by dissolved Fc was 23.2%. MB removal catalyzed by solid Fc was 64.8%. Thus, the catalytic efficiency of Fc dissolved was calculated to be 32.85 times of the efficiency of insoluble Fc suspended in solution.

3.3. Effect of catalyst dosage

Fc acted as catalyst in the heterogeneous Fenton process. Variation of catalyst concentration could influence the oxidation rate. In traditional Fenton process consisting ferrous and hydrogen peroxide, ferrous ion in solution can activate hydrogen peroxide to form hydroxyl radicals, however, Fe^{2+} can also be the scavengers of hydroxyl radicals. The excess amounts of ferrous ion react with hydroxyl radicals and then the hydroxyl radicals in system will decrease and the percentage of organics degraded in solution will also be reduced. To evaluate the effect of Fc concentration on efficiency of Fc/Fenton system, experiments were conducted to investigate the effect of the dose of Fc on the degradation of MB. The proportion of Fc added varied from 5 to 558 mg/L, the experiment was carried out at pH 3, H_2O_2 = 23.58 mmol/L, and 30℃ and the results are presented in Fig. 3. It can be seen from Fig. 3 that increasing the Fc concentration from 5 to 25 mg/L enhanced the MB removal efficiency obviously. The removal of MB increased from 34.46, 69.13, 84.37, 94.89 to 98.81% when Fc applied from 5, 10, 15, 20 to 25 mg/L, respectively. The removal of MB gets the range around 99.4–100% with the increase of Fc concentration from 50, 75, 120, 186, 279, 372 to 558 mg/L. The highest removal efficiency of MB was achieved when 120 mg/L Fc was applied.

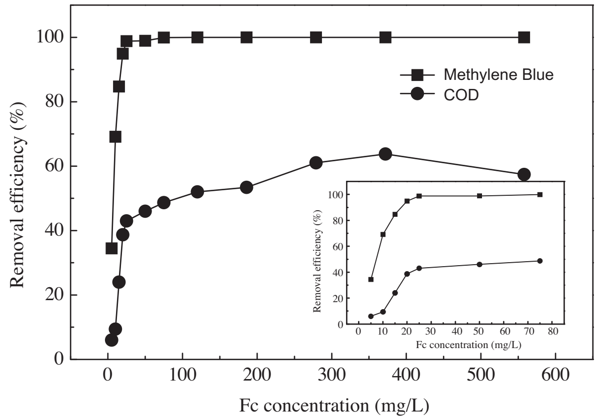

Fig. 3. Effect of catalyst dosage on the decoloration and mineralization of MB under the following conditions: initial MB solution pH = 3, $[H_2O_2]/[MB] = 3.17$, 30℃.

Discoloration of dyes maybe attributed to the destruction of the chromophore or the decomposition of the entire dye molecular. These two possibilities can be distinguished by detecting the COD value in the reaction solution. If the discoloration is achieved by destruction of the chromophore, the COD value will not change very much. In contrast, oxidizing the dye molecule into H_2O and CO_2 may lead to 100% COD reduction. In fact, using the above conditions, COD reduction was detected with the results shown in Fig. 3. COD removal increased as the Fc concentration increased from 5 to 372 mg/L as shown in Fig. 3. The highest COD removal efficiency (63.75%) was reached at Fc concentration of 372 mg/L. The COD removal efficiency started going down at Fc concentrations higher than 372 mg/L. As a typical heterogeneous catalyst, three reasons are there for the phenomenon depicted in Fig. 3. First, more Fc in solution could adsorb more MB molecules, leading to higher efficiency. Second, more Fc in the reaction solution can promote the decomposition of H_2O_2 to generate more $^{\bullet}OH$, which can react with most organic pollutants. Third, Fc in organic solution may dissolve, resulting in reduced light penetration and an increase in COD.

Efficiencies of Fc/Fenton system at pH 3 with 3.9294 mmol/L H_2O_2 are summarized in Table 1. The results showed that initial degradation efficiency increased from 34.4546 to 100% when $[Fc]/[H_2O_2]$ increased from 0.0068 to 0.1638. Further increase the ratio of $[Fc]/[H_2O_2]$ to 0.7614, the removal efficiencies of MB kept 100%. The optimum ratio of $[Fc]/[H_2O_2]$ was found to be 0.1638 with 3.9294 mmol/L H_2O_2 presented.

3.4. Effect of H_2O_2 dosage

Many studies have been carried out on the effect of H_2O_2 dosage on the decoloration [43,44]. Theoretically, a higher dosage of H_2O_2 leads to more efficient color removal. In Fenton process, H_2O_2 is the source of hydroxyl radicals, as well as precursor of hydroxyl radicals. With excess H_2O_2 presented, O_2 and $^{\bullet}HO_2$ were generated instead of $^{\bullet}OH$, thus, oxidation reaction is limited. In this study, experiments were also performed to study the effects of H_2O_2 concentration on Fc/Fenton reaction for the treatment of MB. In this section, about 10 mg/L MB, 0.372 g/L Fc, pH 3, and 30℃ were fixed as the initial conditions, while H_2O_2 concentrations varied from 1.96 to 49.12 mmol/L, and the results are shown in Fig. 4. The results indicated

Table 1
Effects of Fc concentration on MB removal efficiency by Fc/Fenton process (MB = 10 mg/L, pH = 3, $[H_2O_2]$ = 3.9249 mmol/L)

Fc (mg/L)	Fc (mmol/L)	H_2O_2 (mmol/L)	Fc/H_2O_2	Removal efficiency (%)
5	0.0268	3.9294	0.0068	34.4565
10	0.0536	3.9294	0.0137	69.1304
15	0.0804	3.9294	0.0205	84.7283
20	0.1072	3.9294	0.0273	94.891
25	0.1341	3.9294	0.0342	98.8044
50	0.2681	3.9294	0.0683	98.9130
75	0.4022	3.9294	0.1024	99.9457
120	0.6435	3.9294	0.1638	100
186	0.9973	3.9294	0.2539	100
279	1.4960	3.9294	0.3808	100
372	1.9946	3.9294	0.5077	100
558	2.9920	3.9294	0.7614	100

that the increase of H_2O_2 concentration from 1.96 to 23.58 mmol/L can enhance MB removal. About 97.14% degradation of MB was achieved when an initial concentration of 1.96 mmol/L H_2O_2 was added. The removal efficiency increased to 100% with the initial concentration of H_2O_2 increased to 23.58 mmol/L. The presence of more H_2O_2 in solution can improve the generation of $^{\bullet}OH$, and more MB was degraded. Removal of MB was limited to some extent at initial concentrations higher than 23.58 mmol/L.

COD removal efficiency also followed the same trend as MB removal efficiency. More H_2O_2 in solution led to higher concentration $^{\bullet}OH$ in solution, thus, more $^{\bullet}OH$ in solution are available for MB degradation. The removal efficiency of MB increased as the initial H_2O_2 concentration increased, until 0.01995 mmol/L. Further increase the initial H_2O_2 concentration to 0.12 mmol/L, MB removal efficiency and COD removal efficiency decreased to 96.59 and 45.23%, respectively. The same results were also found in the other research [43]. This was probably due to the competition of intermediates with MB on $^{\bullet}OH$, and $^{\bullet}OH$ in solution was scavenged by extra H_2O_2 to generate H_2O, and $^{\bullet}HO_2$, or H_2O_2 was regenerated or $^{\bullet}HO_2$ was generated instead of $^{\bullet}OH$ (Eqs. (4)–(8)), so the COD was not reduced for higher initial concentrations of H_2O_2.

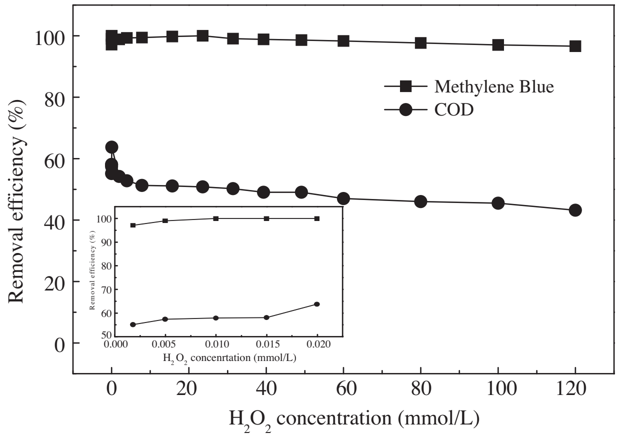

Fig. 4. Effect of initial $[H_2O_2]/[MB]$ on the decoloration and mineralization of 10 mg/L MB under the following conditions: initial solution pH = 3, 0.372 g/L Fc, 30°C.

$$O_2 + e^- \longrightarrow {}^{\bullet}O_2^- \quad (4)$$

$$^{\bullet}O_2^- + H^+ \longrightarrow {}^{\bullet}HO_2 \quad (5)$$

$$^{\bullet}HO_2 + {}^{\bullet}HO_2 \longrightarrow H_2O_2 + O_2 \quad (6)$$

$$^{\bullet}OH + H_2O_2 \longrightarrow H_2O + {}^{\bullet}OOH \quad (7)$$

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \quad (8)$$

Removal efficiencies of MB at pH 3 with 1.9946 mmol/L Fc and varying $[Fc]/[H_2O_2]$ were summarized in Table 2. The removal of 97.136% was observed at 0.0018 mmol/L H_2O_2 and the ratio of $[Fc]/[H_2O_2]$ 1180.132. About 100% removal of MB was obtained at $[Fc]/[H_2O_2]$ ranges from 133.1534 to 401.3356. However, the removal efficiency at the ratio 133.1543, the results showed that the removal efficiency decreased as the ratio $[Fc]/[H_2O_2]$ decreased.

3.5. Effect of initial MB concentration

As can be seen in Fig. 5, the removal efficiency of dye at the end of the process with 10 mg/L MB is

Table 2
Effects of H_2O_2 concentration on MB removal efficiency by Fc/Fenton process (MB = 10 mg/L, pH = 3, [Fc] = 1.9946 mmol/L)

Fc (mmol/L)	H_2O_2 (mmol/L)	Fc/H_2O_2	Removal efficiency (%)
1.9946	0.0018	1108.1320	97.1360
1.9946	0.0050	401.3356	100
1.9946	0.0100	200.0640	100
1.9946	0.0150	133.1534	100
1.9946	0.0200	99.9819	98.8587
1.9946	1.9647	1.0152	99.2935
1.9946	7.8588	0.2538	99.4022
1.9946	15.7176	0.1269	99.7826
1.9946	23.5764	0.0846	99.3200
1.9946	31.4352	0.0635	99.0761
1.9946	39.2940	0.0508	98.8044
1.9946	49.1175	0.0406	98.5870
1.9946	60.0000	0.0332	98.3210
1.9946	80.0000	0.0249	97.6720
1.9946	100.0000	0.0199	97.0130
1.9946	120.0000	0.0166	96.5870

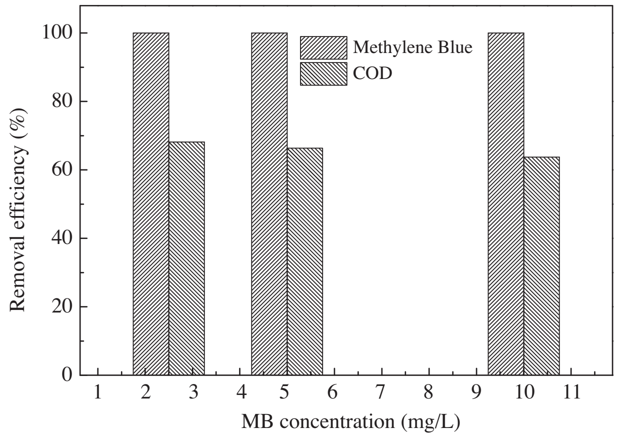

Fig. 5. Effect of initial solution concentration on the decoloration and mineralization of MB under the following conditions: pH = 3, 0.372 g/L Fc, $[H_2O_2]/[MB] = 3.17$, 30˚C.

comparable with the results at lower dye concentrations, and the same result was shown by Idel-aouad [45]. COD reduction of MB with different initial concentrations was also determined. The COD reduction was about 68.2% for an initial MB concentration of 2.5 mg/L after 120 min reaction, but decreased to 66.4 and 62.1% for initial concentrations of 5 and 10 mg/L, respectively. This may be attributed to: (i) higher initial concentrations of MB, with predetermined dosages of H_2O_2 and Fc results in a low $[H_2O_2]/[MB]$ value, so a fixed number of $^{\bullet}OH$ species generated in solution acts on more MB molecules; (ii) at higher concentrations of MB, the concentration of intermediates increases which may also be important scavengers of $^{\bullet}OH$ [39,46].

3.6. Effect of initial solution pH

pH is an important parameter that influences the removal efficiency of organics. According to some researchers, the initial solution pH significantly affects the efficiency of the Fenton process [25,47]. To determine the effect of pH, the degradation of MB was investigated at pH values ranging from 2 to 5, and the results obtained are shown in Fig. 6(a). The degradation kinetics was greatly influenced by the initial solution pH. The maximum degradation, of 100%, was obtained at an initial solution pH of 3, and the degradation efficiency was lower at pH values 2, 4, and 5. The variation of COD as a function of time at pH values ranging from 2 to 5 was also investigated, showing that pH = 3 was the optimal condition for COD removal, which is the same as for decoloration. The COD reductions were calculated to be 60.2, 62.5, 61.0, and 58.4% for pH values 2, 3, 4, and 5, respectively. This optimal pH was the same with traditional Fenton.

Parameters including concentrations of H_2O_2 and $^{\bullet}OH$ and Fc dissolved in solution can influence the efficiency of Fc/Fenton. The initial pH value of the aqueous solution, since it determines the decomposition of H_2O_2 and the generation of $^{\bullet}OH$, is an important parameter that influence the overall catalytic oxidation process. Experiments were conducted to investigate these parameters and the results are depicted in Fig. 6(b)–(d).

As the pH value increased from 2 to 5, the dissolution of Fc, decomposition of H_2O_2, and generation of $^{\bullet}OH$ progressed as the reactions moved on, and the promotion was a maximum at pH 3. Fc dissolved in solution after 120 min were 1.68×10^{-5}, 2.15×10^{-5}, 1.80×10^{-5}, and 9.74×10^{-6} mol/L, respectively, according to the result calculated from Fig. 2. The catalytic efficiency of Fc in homogeneous Fenton was 33.8528 times of that in heterogeneous Fenton. Dissolution of Fc can active H_2O_2 in solution to form $^{\bullet}OH$ more efficiently. Residual H_2O_2 and $^{\bullet}OH$ generated in solution reached 51.43% and 1.49×10^{-5} g/L at pH 3. This result is consistent with the decoloration and mineralization of MB, as discussed above. At pH 2, 4, and 5, the decomposition of H_2O_2 and generation of $^{\bullet}OH$ were lower. This could explain the removal of MB, as shown in Fig. 6(a). On the other hand, excess of H^+ and OH^- in solution could resist the decompo-

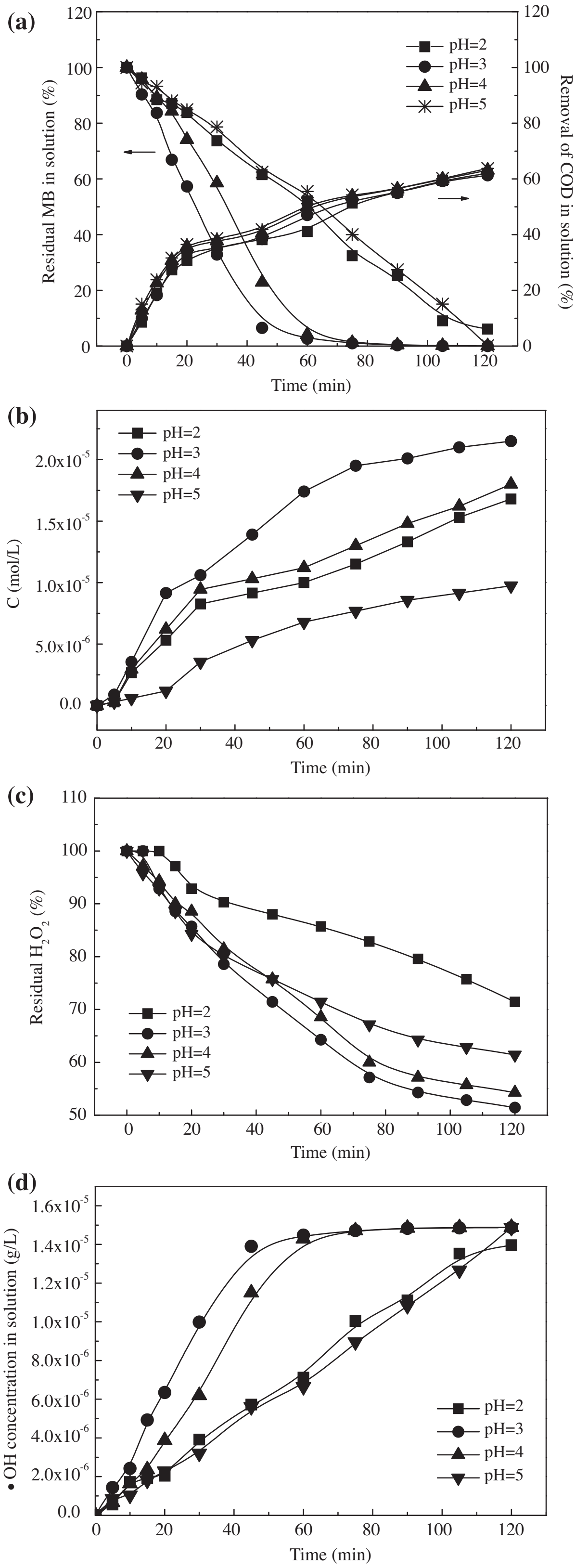

Fig. 6. Effect of initial solution pH on the efficiency of the Fc/Fenton system under the following conditions: 0.372 g/L Fc, $[H_2O_2]/[MB] = 3.17$, 30˚C.

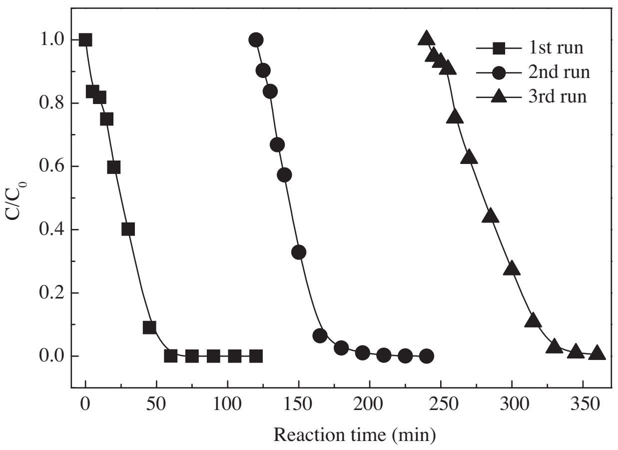

Fig. 7. Stability of Fc during 10 mg/L MB treatment process. The conditions were pH = 3, 30˚C, 0.6435 mmol/L Fc, $[Fc]/[H_2O_2] = 0.1638$.

sition of H_2O_2 and the generation of $^{\bullet}OH$ [48] (Eqs. (1) and (2)). The scavenging effect of hydroxyl radicals was significant under acid condition, resulting in less decoloration and mineralization. The oxidation potential of $^{\bullet}OH$ also decreases at higher pH, in that the oxidation potential is 2.8 V at pH 3, and decreases to 1.9 V at pH 7 [46,49].

3.6. Stability of the catalyst

The durability of Fc was examined by recovering the material and re-using is under the same conditions of pH 3, 30˚C, 10 mg/L MB, 0.6435 mmol/L Fc, 3.9294 mmol/L H_2O_2. Under conditions mentioned above, the ratio $[Fc]/[H_2O_2]$ is 0.1638. The Fc was recovered by simple filtration and drying at room temperature and the results are shown in Fig. 7. As depicted in Fig. 7, residual MB in solution is 0, 0.9904, and 3.4376% according to the first, second, and third cycle use of Fc. The catalytic activity of Fc was still very good and no obvious deactivation of the catalyst was observed after three cycles, compared to the first cycle. This result indicates that Fc has remarkably high chemical stability.

4. Conclusions

The treatment of MB using the heterogeneous Fenton process catalyzed by Fc directly has been studied in detail. The catalyst was verified to be of reasonable good catalytic activity and possessed good reversible redox properties through CV experiments. Dissolved oxygen and hydroxyl radicals were generated from the activation of H_2O_2 by Fc, but the active radical playing the main role in MB degradation was

$^{\bullet}$OH, which generated from the decomposition of H_2O_2 catalyzed by Fc. The dosages of catalyst and added H_2O_2, the initial concentration of MB, and the initial solution pH all influenced the degradation efficiency, especially the initial solution pH value. The optimum conditions found were 0.372 g/L Fc with an initial $[Fc]/[H_2O_2] = 0.5077$at pH 3, 30℃, after 120 min of reaction. Fc/Fenton efficiency increased as the ratio $[Fc]/[H_2O_2]$ increased, with fixed Fc or H_2O_2 dosage. Fc was proved to be of high stability, and residual MB in solution was 3.4397% after the third cycle use of Fc.

Acknowledgments

This work was financially supported by National Science Foundation of China (20607008; 21077048), Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, China and the Analysis and Testing Foundation of Kunming University of Science and Technology (2010150).

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