Fe(III)-loaded collagen fiber as a heterogeneous catalyst for the photo-assisted decomposition of Malachite Green

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ABSTRACT

A heterogeneous catalyst for Fenton reaction was prepared by immobilizing Fe(III) onto collagen fiber and its catalytic activity for the photo-assisted decomposition of Malachite Green (MG) was investigated. The results indicated that this Fe(III)-immobilized collagen fiber (Fe-CF) can effectively catalyse the decoloration and decomposition/mineralization of MG in aqueous solution. Catalysed by Fe-CF, MG solution was completely decolorized in 30 min, while 55.0% of TOC was removed from the dye solution within 120 min in the presence of H_2O_2 and UVA irradiation (365 nm, 10 W). Fe-CF was recycled for seven times with certain activity loss (32.6% in decoloration, 18.5% in TOC removal), and its catalytic activity can be easily recovered by re-immobilization of Fe(III). Therefore, Fe-CF could act as an efficient and cost-effective catalyst for the photo-assisted decomposition of MG, and shows potential applications in practice.

1. Introduction

In recent years there has been an increasing concern about Fenton reaction [1–4] in the field of wastewater treatment due to its low cost and high performance in decomposing some un-biodegradable organic compounds. Iron salts are usually employed as the catalyst in a homogeneous system of Fenton reaction, however, the Fe(III) directly added into reaction solution is hard to be recovered and may cause secondary pollution [5]. This drawback can be avoided by using heterogeneous catalysts where Fe(III) are often immobilized onto some supporting matrices including inorganic and organic compounds, such as zeolite [5], clay [6–8], oxide [9], resin [2,10] and Nafion membrane [11,12]. In addition, some natural and renewable biomasses like chitosan [13], cellulose [14] and silk [15] are also used as the matrices to prepare heterogeneous catalysts. Although such catalysts showed significant performance in catalysis process, the preparation of heterogeneous catalyst with higher stability and catalytic efficiency is still a challenge.

As an abundant natural biomass, collagen fiber mainly comes from the skins of domestic animals and is traditionally used as a raw material in leather making. Collagen fiber contains plenty of functional groups in molecule, like –OH, –NH$_2$ and –COOH, and this natural biomass is capable of chemically reacting with many kinds of metal ions such as Cr(III), Fe(III) and Zr(IV) [16], according to the principles of leather processing. Fe(III) can form stable hydroxyl complex with the –COOH groups on collagen. Therefore, it can be immobilized onto collagen fiber so as to serve as a heterogeneous catalyst in Fenton reaction. As we know, the price of animal skin is very cheap as compared with other supporting matrices, usually no more than $5/kg. In addition, the immobilization of Fe onto collagen fiber follows a "tanning process" which has been developed for more than one century in leather manufacture, where no specific agents are needed. Thus, it can be deduced that the prepared catalyst, based on Fe and collagen fiber, should be cost-effective in Fenton reaction.

In our previous study [17], a novel heterogeneous catalyst was prepared by immobilizing Fe(III) onto collagen fiber. The Fe(III)-loaded collagen fiber (Fe-CF) showed strong adsorption to Orange II so that it effectively catalysed the photo-assisted decomposition of the dye. However, some dyes like Malachite Green (MG) were found unable to be adsorbed by Fe-CF, and the catalytic behaviors of Fe-CF to the photo-assisted decomposition of such type of dyes are unclear. As a typical organic dye, MG is un-biodegradable and hard to be treated by conventional wastewater-disposal methods. Some advanced oxidation processes (AOPs) were applied to degrade such organic pollutants and exhibited satisfied performance [18,19]. In

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this study, MG was used as a model compound which is unable to be adsorbed by Fe-CF, and its photo-assisted decomposition catalysed by Fe-CF was studied. The reaction conditions including pH, Fe-CF dosage and H_2O_2 concentration were optimized and the catalytic activity of recycled Fe-CF was also investigated for the purpose of practical application.

2. Experimental

2.1. Chemicals and materials

$Fe_2(SO_4)_3$, Malachite Green, hydrogen peroxide and other chemicals are all analytical reagents purchased from Kelong Chemical Reagents Co., Ltd. (Chengdu, China). Collagen fiber (CF) was prepared according to the procedures reported in our previous work [20].

### 2.2. Preparation of heterogeneous catalyst Fe-CF

The preparation of catalyst Fe-CF was as following process. 15.0 g of collagen fiber was soaked into 400 mL distilled water at room temperature for 24 h. The pH of the distilled water was pre-adjusted to 1.7–2.0 using dilute H_2SO_4 solution. Then, 5.0 g $Fe_2(SO_4)_3$ was added into the solution, and the immobilization of Fe(III) onto collagen fiber proceeded with constant stirring at 30 °C for 4 h. Subsequently, the pH value of reaction system was gradually increased to 3.0 using $NaHCO_3$ solution (15%, w/w) within 2 h, and the immobilization reaction continued at 40 °C for another 4 h. The catalyst Fe-CF was finally obtained by filtering, washing with distilled water, and drying at 50 °C for 12 h. To determine the Fe(III) load on Fe-CF, the catalyst was completely dissolved into aqua regia, and the content of Fe(III) was analysed using Inductively Coupled Plasma Optical Emission Spectrometer (ICP-AES, PerkinElmer, USA). As a result, the Fe(III) load on catalyst Fe-CF was 91.0 mg/g.

2.3. Characterization of Fe-CF

The state of Fe(III) on Fe-CF was identified by X-ray diffraction (XRD, X′Pert Pro, Netherland), where the voltage and current of operational tube were 40 kV and 30 mA, respectively. The 2θ ranged from 10° to 50° and the scanning speed kept at 0.03 °/min. The binding site between collagen fiber and Fe(III) was investigated using X-ray photoelectron spectroscopy (XPS, Kratos XSAM-800, UK) with Mg Kα irradiation ($hv = 1253.6$ eV) at a pass energy of 31.5 eV. All the binding energy peaks of XPS spectra were calibrated by placing the principal C 1s binding energy peak at 284.7 eV.

2.4. Photoreactor and the catalytic decomposition of MG by Fe-CF

The decomposition reaction of MG was carried out in a self-designed glass reactor (Scheme 1). 1000 mL of MG solution (0.1 mM), pre-adjusted to desired pH with 0.1 mM H_2SO_4 and/or NaOH solution, was introduced into the outer glass tube of the reactor, followed by the addition of Fe-CF. Then, air was continuously pumped into the reactor to stir the mixture and make Fe-CF suspended in the solution. After 30 min of ventilation, hydrogen peroxide (30%) was added into the reactor, and the mixture was irradiated by an ultraviolet lamp (10 W, $\lambda = 365$ nm) installed inside the inner quartz tube of the reactor. To test the recyclability of Fe-CF, the catalyst was filtrated out after each run, and fully washed with distilled water and ethanol. After drying at 50 °C for 12 h, the recycled Fe-CF is ready for next run. All the photo-assisted decomposition reactions were conducted at room temperature, and 5 mL of reaction solution was sampled and diluted to 25 mL at indicated interval for UV–vis (UV-2501PC, Shimadzu, Japan), TOC (LiquiTOC, Elementar, Germany) and ICP-AES (Optima 2100DV, PerkinElmer,
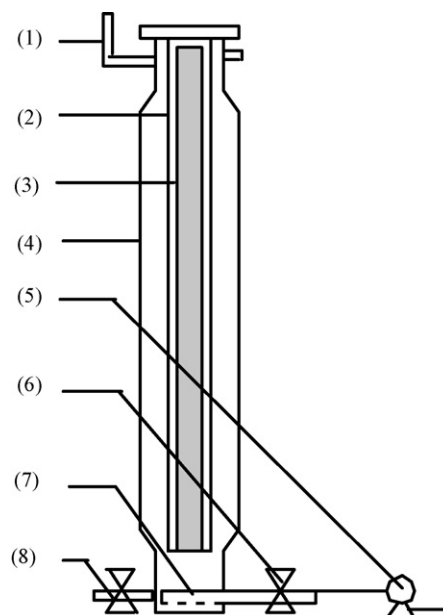
Scheme 1. Scheme of photoreactor. (1) sample inlet, (2) inner quartz tube (40 cm × 4 cm ID), (3) ultraviolet lamp, (4) outer glass tube (45 cm × 8 cm ID), (5) air pump, (6) valve, (7) bubbler, (8) sample outlet with filter.

USA) analyses. The decoloration extent of MG solution is defined as:

$$\text{Decoloration extent} (\%) = \frac{(C_0 - C)}{C_0} \times 100 \tag{1}$$

where C_0 is the initial MG concentration (mM); C is the concentration of MG remaining in solution (mM). A total organic carbon (TOC) analyser was used to measure the TOC in solution in order to characterize the mineralization degree of MG. ICP-AES was used to detect the leakage of Fe ions from catalyst Fe-CF during photo-assisted decomposition reaction. All the values reported are the means of three replications and the errors are found lower than 2.8%.

3. Results and discussions

3.1. Characterization of Fe-CF

As shown in Fig. 1, the intensity of diffraction peak of Fe-CF was greatly reduced due to the cross-linking between Fe(III) and collagen fiber [21]. Moreover, no new diffraction peak was found for Fe-CF, even after it catalysed the photo-assisted decomposition of MG, which suggests that the Fe(III)-loaded on Fe-CF is stable and in complex state, and no crystal structure was generated. XPS analysis indicates that the C 1s spectra of Fe-CF are almost the same to those of collagen fiber (Fig. 2); however, the binding energy at maximum peak in the N 1s and O 1s spectra of Fe-CF shows an increase of 0.4 and 0.7 eV, respectively. These observations suggest that the immobilization of Fe(III) on collagen fiber may take place at the N and O sites in collagen molecule, which is accordant with the result of reported study [22].

3.2. General results of the catalytic decomposition of MG by Fe-CF

As shown in Fig. 3A, Fe-CF led to the decoloration and mineralization of MG in solution in the presence of H_2O_2 and UVA (365 nm), which the dye solution was nearly totally decolorized within 30 min, and the mineralization extent was 55.0% at 120 min. However, the decoloration extent is lower than 30% when any of
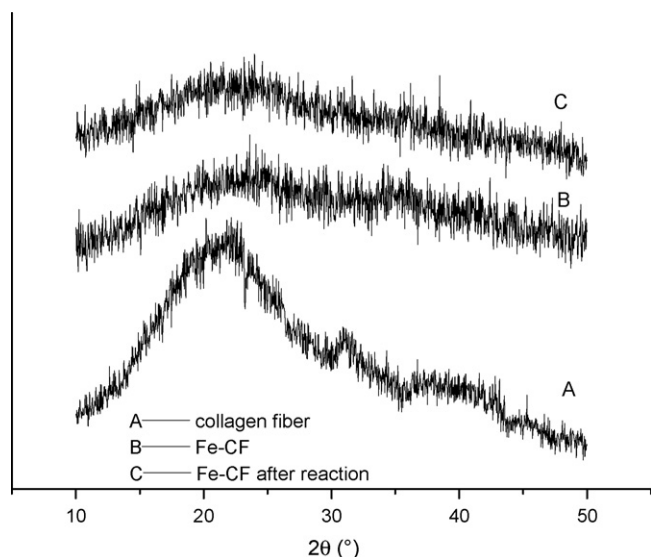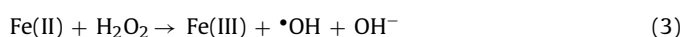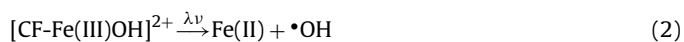
Fig. 1. XRD patterns of collagen fiber and Fe-CF before and after being used to catalyse the photo-assisted decomposition of MG.

the three factors, H_2O_2, Fe-CF and UVA, is absent in reaction system (Fig. 3(a), B–E), indicating that the three factors are all necessary for MG solution to be decolorized effectively. It is known that H_2O_2 may be decomposed to release O_2 at irradiation of light, and MG is sensitive to UVA. So, both factors, H_2O_2 and UVA, can affect the decoloration of MG. As shown in Fig. 3(a), the decoloration of MG occurred to some extent in the presence of H_2O_2 or UVA (B and D). However, only the simultaneous presence of Fe-CF, H_2O_2 and UVA can allow a drastic mineralization of MG, as shown in Fig. 3(b).

In a previous study [17], Fe-CF was found following an adsorption–degradation mechanism when it catalysed the photo-assisted decomposition of Orange II, where the adsorption of Fe-CF to the dye accelerated the decoloration and decomposition process. However, Fe-CF did not show any adsorption to MG, as illustrated in Fig. 3E where the decoloration and mineralization extent of MG solution kept at zero in 120 min. Therefore, all the observations above indicate that, without adsorption effect, Fe-CF is capable of effectively catalyzing the photo-assisted decomposition of MG. It can be deduced that Fe-CF might also exhibit catalytic activity in the photo-Fenton reaction of similar dyes.

3.3. Effect of pH on the catalytic decomposition of MG by Fe-CF

The mechanism of Fe-CF-involved Fenton reaction can be illustrated using Eqs. (2) and (3). The Fe(III) on catalyst is reduced to Fe(II) due to the electron transfer from OH^- group under UVA irradiation, and then the Fe(II) is oxidized back to Fe(III) by H_2O_2 in solution. The hydroxyl radical generating ability of Fe-CF can be preserved providing that the Fe(III) present in solution was re-immobilized onto collagen fiber, otherwise Fe ions may leak from Fe-CF, resulting in activity loss of the catalyst. Based on the recognitions above, it can be deduced that pH plays an important role in the catalytic decomposition of MG, since both the catalytic activity of Fe-CF and the generation of hydroxyl radical are pH-dependent.

$$[CF\text{-}Fe(III)OH]^{2+} \xrightarrow{\lambda\upsilon} Fe(II) + {}^{\bullet}OH \tag{2}$$

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^- \tag{3}$$

Fenton reaction is commonly carried out at low pH to allow the continuous production of hydroxyl radical being capable of decomposing substrates [23], however, a strong acid condition is

unsuitable for Fe-CF to serve as a heterogeneous catalyst in consideration of its stability. As shown in Fig. 4a, MG solution was decolorized quickly in the presence of Fe-CF at pH 2.0, but this decoloration was accompanied by a lower TOC removal than that occurred in the case of pH 3.0 (Fig. 4b). This fact indicates that Fe-CF quickly resulted in a breakdown of the chromophoric groups on MG at pH 2.0, but meanwhile it could not lead to a drastic mineralization of the dye, which may be attributed to its rapid inactivation due to Fe leakage. No substantial Fe leakage (<2.5 mg/L) was observed during the catalytic decomposition process of MG at pH 3, 4 and 5 (Fig. 4c). However, the Fe leakage increased to 30.0 mg/L in 120 min when pH was adjusted to 2.0, meaning that more than one third of the Fe on Fe-CF (Fe load 91 mg/g) was leaked into solution. So, it can be concluded that a strong acid condition should be avoided when Fe-CF is employed as a heterogeneous catalyst in Fenton reactions.

In the case of pH 4.0 and 5.0, the color of MG solution almost disappeared in 60 min (Fig. 4a); meanwhile the dye solution showed low TOC removal which was 24.8% and 7.1%, respectively, and further prolongation of reaction duration did not lead to effective mineralization of the dye (Fig. 4b). This result might be due to that an environmental pH higher than 3.0 does not benefit the generation of hydroxyl radical during Fenton reaction. Namely, at pH 4.0 and 5.0, hydroxyl radical cannot be produced enough to allow an effective mineralization of MG, though few Fe ions were leaked from Fe-CF under such a pH condition (Fig. 4c) [24]. In a recent report, the generation of hydroxyl radical was found to be suppressed due to the precipitation of Fe(III) at pH higher than 3.4 [25]. It was also reported that, in comparison with un-absorbable substrates, the degradation of absorbable ones can take place in a relatively wider pH range in Fenton reaction [26]. In a previous study [17], Fe-CF showed adsorption to Orange II and this adsorption process is accompanied by the release of protons. So the decrease of pH can facilitate the degradation of the dye even at higher initial pH. While in the case of MG which is unable to be adsorbed by Fe-CF (Fig. 3), the decrease of pH was limited. Therefore, a proper acidic pH is required for the degradation of MG catalysed by Fe-CF, and the catalyst can lead to an optimal decomposition/mineralization of MG at pH 3.0.

3.4. Effect of Fe-CF dosage on the photo-assisted decomposition of MG

Without the presence of Fe-CF, H_2O_2 may be induced to produce few OH radicals under UVA irradiation at 365 nm (Eq. (4)) [27], which cannot effectively decompose substrates in Fenton reaction. So, MG solution shows very limited decoloration and TOC removal in the absence of Fe-CF (Fig. 5), indicating an ignorable decomposition of the dye.

$$H_2O_2 + h\upsilon \rightarrow 2{}^{\bullet}OH \tag{4}$$

With the offer of Fe-CF in the range of 0.50–1.25 g/L, MG solution shows varying decoloration efficiency, and TOC analyses demonstrate that the dye was mineralized during the decoloration process. In general, a higher decolorization/mineralization efficiency was observed when more Fe-CF was used during the first 30 min of decomposition reaction, but all the catalyst usages resulted in total decoloration of MG solution with different TOC removals within 60 min.

Fe-CF, as a heterogeneous catalyst, can work with two different effects during the photo-assisted decomposition of MG. A high offer of Fe-CF can promote catalytic decomposition reaction, allowing a fast decoloration of MG solution. On the other hand, a Fe-CF dosage exceeding saturation can also prevent UV from penetrating solution and weaken the mineralization of the dye [28]. So, the increase of Fe-CF from 1.0 g to 1.25 g in 1 L of MG solution did not lead to an
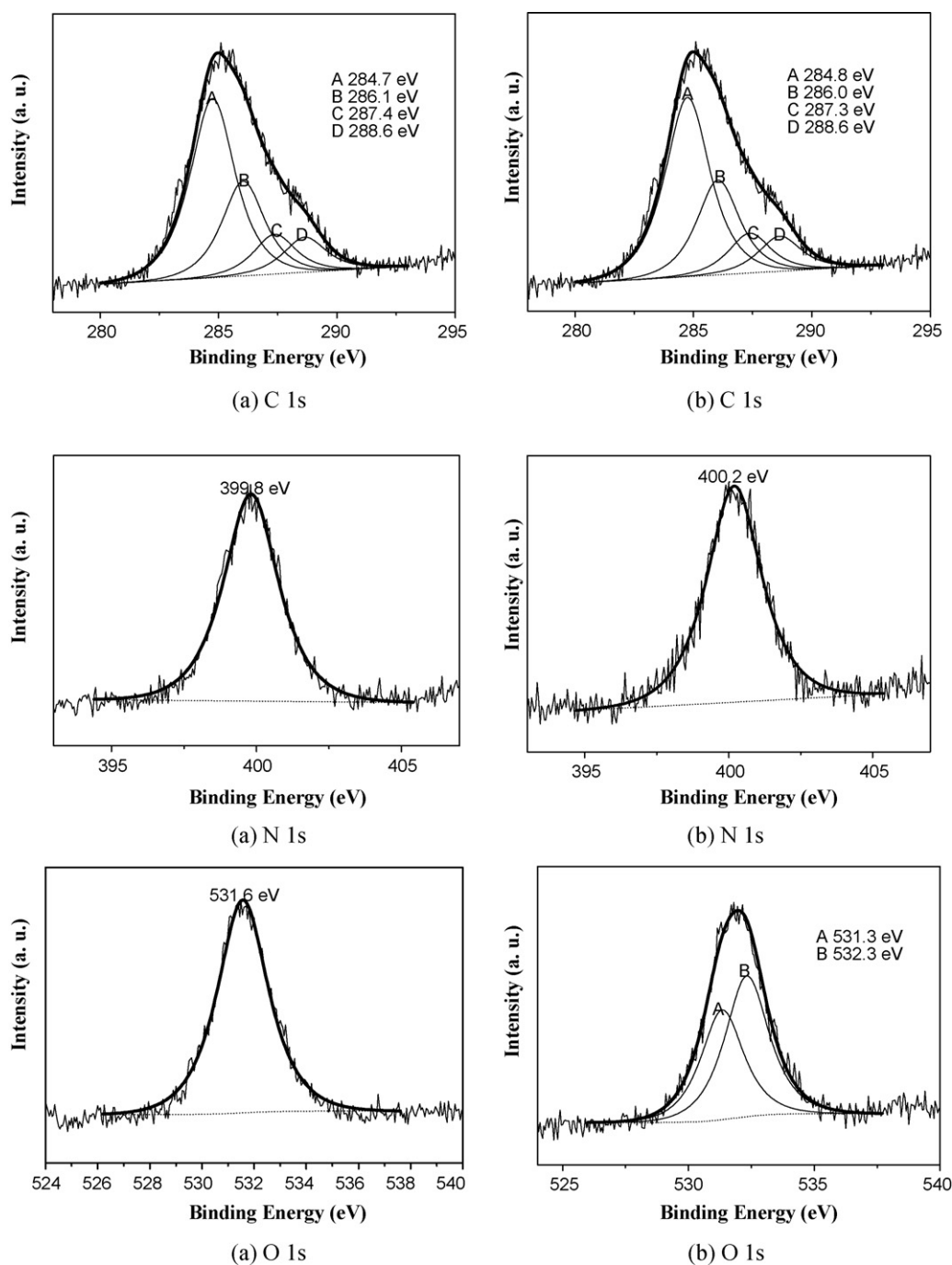
Fig. 2. XPS spectra of C 1s, N 1s and O 1s on (a) collagen fiber and on (b) Fe-CF.

increased TOC removal during the decomposition reaction. An optimal decomposition/mineralization of MG solution (0.1 mM) was achieved in the presence of 1.0 g/L of Fe-CF, where 55% of TOC was removed in 120 min.

3.5. Effect of H_2O_2 concentration on the catalytic decomposition of MG

H_2O_2 plays an important role in Fenton reaction system, where it can recycle the produce of hydroxyl radicals (Eqs. (1) and (2)) which are capable of decomposing and mineralizing substrates. During the photo-assisted decomposition of MG, the hydroxyl radicals produced may attack and break the chromophoric groups in the molecule of the dye. Consequently, MG is decomposed into some

intermediates and the dye solution is decolorized. This decomposition process is followed by a mineralization process during which the intermediates may be further decomposed/mineralized into some small molecule substances such as H_2O and CO_2.

UV irradiation can lead to the reduction of Fe(III) on Fe-CF to Fe(II), and simultaneously produce hydroxyl radicals (Eq. (2)). Without the presence of H_2O_2, this irradiation effect is limited and can hardly lead to the decomposition of MG. In addition, the Fe leakage from Fe-CF may be considerable because, unlike Fe(III), the Fe(II) produced due to UV irradiation cannot be immobilized onto collagen fiber to form catalyst Fe-CF. As shown in Fig. 6, Fe-CF did not catalysed the photo-assisted decomposition of MG in the absence of H_2O_2, but its Fe leakage in solution increased to 8.2 mg/L in 120 min.
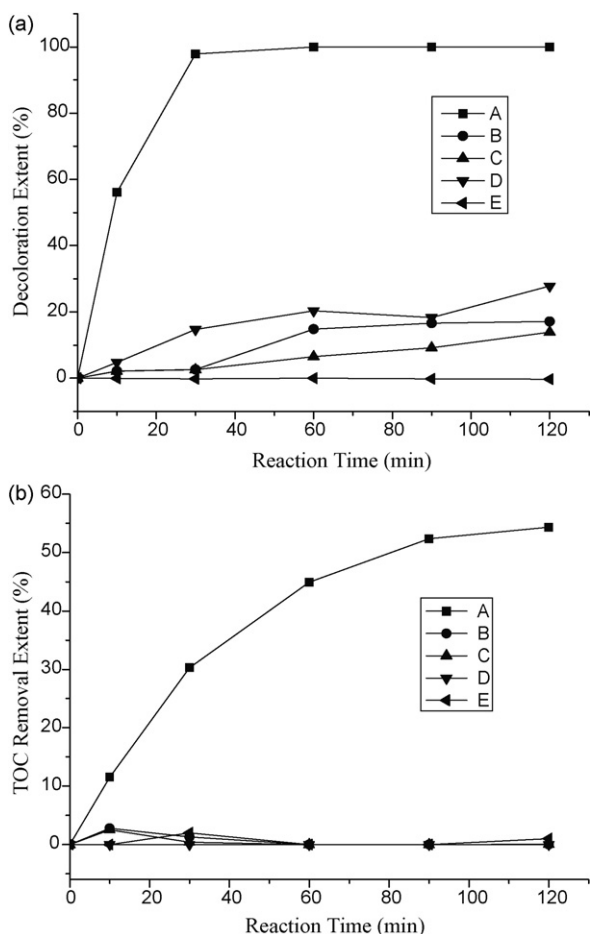
Fig. 3. Decoloration (a) and mineralization (b) extent of MG solution (0.1 mM, pH 3.0) under different experimental conditions. (A) Fe-CF 1.0 g/L, H_2O_2 5.0 mM, UVA 365 nm, 10 W; (B) Fe-CF 1.0 g/L, H_2O_2 5.0 mM; (C) H_2O_2 5.0 mM, UVA 365 nm, 10 W; (D) Fe-CF 1.0 g/L, UVA 365 nm; (E) Fe-CF 1.0 g/L.

The presence of H_2O_2 from 2.5 mM to 10 mM favors the re-immobilization of leaked Fe(III) onto collagen fiber by oxidizing Fe(II) back to Fe(III) (Eq. (2)), and therefore, prevented Fe-CF from Fe leakage (Fig. 6b). Meanwhile, the oxidation reaction recycled the generation of hydroxyl radicals so that MG was continuously decomposed (Fig. 6a). The increase of H_2O_2 usage can speed up the generation of hydroxyl radicals and therefore, accelerate the decoloration and mineralization of MG solution. However, the generated hydroxyl radicals can also react with H_2O_2 besides MG, and convert into hydroperoxyl radicals (Eq. (5)) [29,30], whose oxidative-decomposing activity is much lower than that of hydroxyl radicals [27].

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + {}^\bullet OOH \tag{5}$$

Therefore, an over high concentration of H_2O_2 may reduce the catalytic efficiency of Fe-CF, that is, a proper offer of H_2O_2 is necessary for Fe-CF to effectively catalyse the photo-assisted decomposition of MG. As shown in Fig. 6a, 5 mM of H_2O_2 achieved an optimal mineralization of MG solution with 53.0% of TOC removal in 120 min.

3.6. Recycling tests

It is economically required for a heterogeneous catalyst to be reused effectively, whose recyclability is another significant property besides its photo-catalytic activity. So, the catalytic activity of recycled Fe-CF for the photo-assisted decomposition of MG was
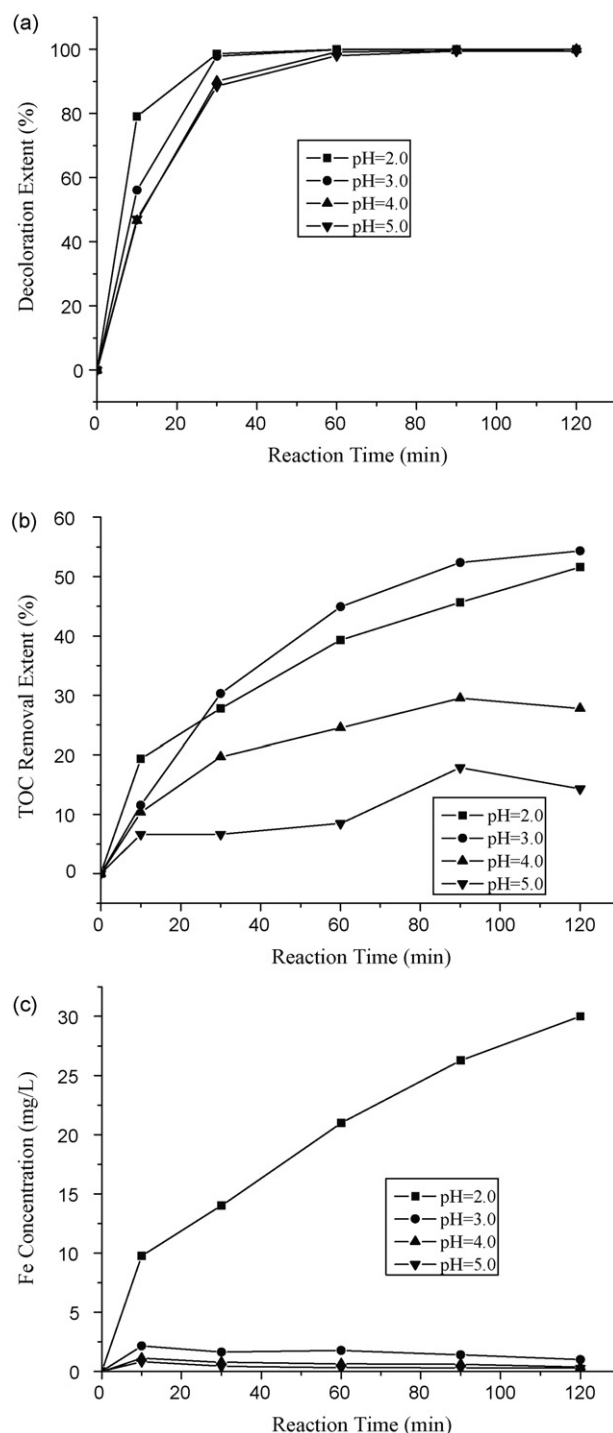

Fig. 4. Effect of pH on the decoloration (a) and TOC removal (b) of MG solution, and on the Fe leakage (c) from Fe-CF (MG 0.1 mM, Fe-CF 1.0 g/L, H_2O_2 5.0 mM, UV 365 nm, 10 W).

investigated in this research. As shown in Fig. 7a, Fe-CF almost exhibited the same efficiency, in three runs, to catalyse a complete decoloration of MG solution in 30 min. In the first run, 55.0% of TOC was removed within 120 min of photo-assisted decomposition of MG (0.1 mM) in the presence of H_2O_2 (5.0 mM) and Fe-CF (1.0 g/L). A few Fe ions may leak from Fe-CF and some active sites of the catalyst may be enclosed by decomposition products in each run, which may deactivate Fe-CF to some extent. Thus, the mineralization rate of MG solution slowed down a little during following decomposition runs. But even so, the recycled Fe-CF still achieved
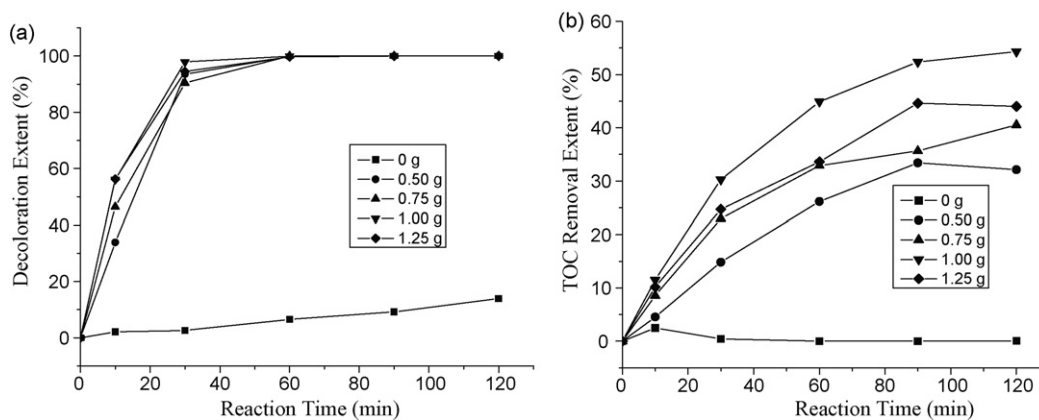
Fig. 5. Effect of Fe-CF dosage on the decoloration (a) and TOC removal (b) of MG solution (MG 0.1 mM, H_2O_2 5.0 mM, pH 3.0, UVA 365 nm, 10 W).
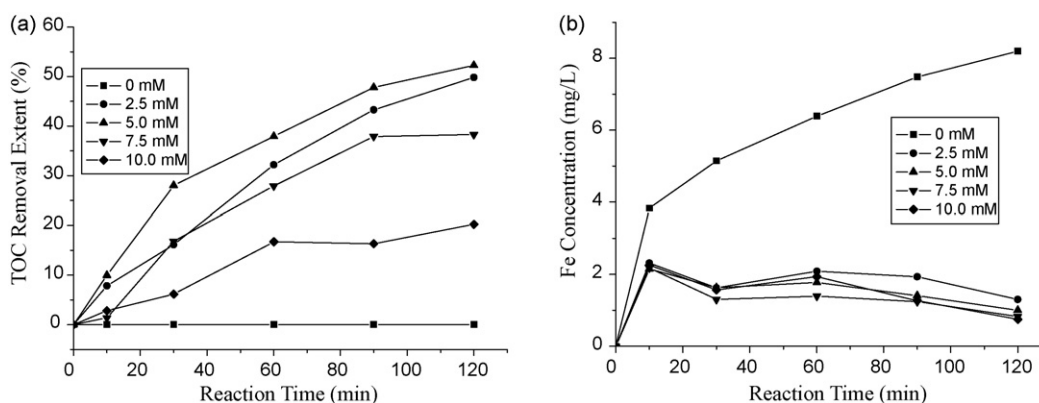

Fig. 6. Effect of H_2O_2 concentration on the TOC removal (a) of MG solution and on the Fe leakage (b) from Fe-CF (MG 0.1 mM, Fe-CF 1.0 g/L, pH 3.0, UV 365 nm, 10 W).
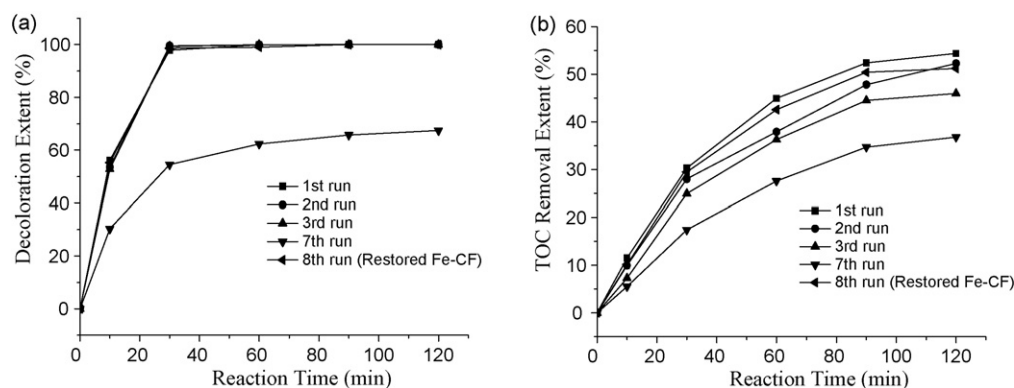

Fig. 7. The decoloration (a) and TOC removal (b) of MG solution by using recycled Fe-CF (MG 0.1 mM, Fe-CF 1.0 g/L, H_2O_2 5.0 mM, pH 3.0, UV 365 nm, 10 W).

52.6% and 46.0% of TOC removal in 120 min in the second and third runs, respectively (Fig. 7b). 1.2 mg/L of Fe leakage was determined in solution after 120 min of catalytic decomposition of MG in the first run, and the recycled Fe-CF showed similar Fe leakage (<1.0 mg/L) during following decomposition runs. After seven runs, the Fe-CF was deactivated to some extent due to the leakage of Fe, and the decoloration and mineralization extent of MG were greatly reduced. The lost catalytic activity of Fe-CF after being used for seventh runs was restored simply by re-immobilizing Fe(III) onto it, according to the same procedure as for the preparation of fresh Fe-CF. The TOC removal of MG solution in 120 min was recovered to 51% by using the regenerated catalyst.

Malachite Green is an un-biodegradable dye and hard to be treated by conventional wastewater-disposal methods; however,

all the results above indicate that Fe-CF can be repeatedly used with a high efficiency to catalyse its photo-assisted decomposition, which allows a practical treatment of the dye.

4. Conclusions

A heterogeneous catalyst, Fe-CF, for the photo-assisted decomposition of Malachite Green (MG) can be prepared by immobilizing Fe(III) onto collagen fiber. The Fe-CF effectively catalysed the decoloration and decomposition of MG solution. Furthermore, the catalyst exhibited high activity in reuse tests and can be easily regenerated through re-immobilizing Fe(III), which shows a potentially industrial application. As an abundant natural biomass, collagen fiber is biodegradable. So, Fe-CF would be an

environment-friendly and cost-effective catalyst for the photo-assisted decomposition of MG and for similar Fenton reaction systems.

Acknowledgements

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