Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23326

138 (2019) 326–334
January

Removal of methylene blue in aqueous solution by a Fenton-like catalyst prepared from municipal sewage sludge

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Received 18 May 2018; Accepted 20 October 2018

ABSTRACT

Municipal sewage sludge and $FeSO_4·7H_2O$ were mixed and calcined at 350°C to prepare a catalyst (SS-Fe-350) via a one-step synthesis. The catalyst was used to degrade methylene blue (MB) in an aqueous solution. The influence of initial solution pH, catalyst dosage, H_2O_2 dosage and temperature on MB degradation was investigated. The MB removal mechanism was explored and the stability of the SS-Fe-350 was assessed. The results showed that MB removal could reach 98% under optimal conditions, that is, initial solution pH 4.0, catalyst dosage 1 g L^{-1}, H_2O_2 dosage 1 mL L^{-1}, and temperature 25°C. A multi-cycle experiment showed that the SS-Fe-350 had a good removal effect over several usage cycles. The MB removal efficiency remained >60% after three cycles. The main MB removal mechanism was free-radical reaction, in which hydroxyl radicals were generated between H_2O_2 and SS-Fe-350 through the heterogeneous Fenton reaction. Meanwhile, some Fe ions were dissolved during the MB degradation process and induced the homogeneous Fenton reaction. However, the heterogeneous Fenton reaction was the main mechanism for MB degradation. Therefore, municipal sludge can be used to synthesize an effective catalyst for the removal of dyes from wastewater through the heterogeneous Fenton reaction.

Keywords: Sludge-derived catalyst; Methylene blue; Heterogeneous Fenton reaction; Dye degradation; Free-radical reaction

1. Introduction

With widespread urbanization in China, many sewage treatment plants have been built to satisfy the need for wastewater treatment. Hence, large amounts of municipal sewage sludge are produced as the byproducts of wastewater treatment. Furthermore, the production of sewage sludge is increasing, from 30 million tonnes (at a moisture content of 80%) in 2012 to 34 million tonnes in 2015 [1]. The utilization/disposal of sludge can be a bottleneck for future economic development, and for expansion and upgrading of the wastewater treatment industry, as well as for environmental protection. Improperly treated municipal sludge can pose a serious risk to the ecological environment. Currently, the main approaches for sludge treatment include agricultural utilization, landfilling, pyrolysis and anaerobic digestion [2,3]. The sludge utilization methods include organic fertilizer preparation, energy recovery (methane, fuel, bio-oil), and adsorbent preparation (activated carbon). However, problems are associated with these utilization methods, such as low quality of fertilizer, low efficiency of energy recovery, high operation cost, and the need for complicated technology. Therefore, novel and more value-added approaches for

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integrated sludge utilization should be developed to maximize the recycling and reuse of municipal sewage sludge.

Currently, advanced oxidation technology is considered better than conventional methods for organic wastewater treatment due to advantages of low cost and effective pollutant removal. Among the advanced treatment technologies, the Fenton reaction has been widely investigated and utilized. However, the homogeneous Fenton reaction has many drawbacks: chromaticity is enhanced on account of degradation of wastewater, the reaction should be conducted at low pH, large amounts of iron sludge are produced, and separation of Fe^{2+} from solution is difficult [4]. Research has shown that Fe^{2+} ions can be fixed on a suitable carrier and participate in the degradation process during the heterogeneous Fenton reaction to overcome the disadvantages of the homogeneous Fenton reaction [5–7]. In previous studies, many new materials have been prepared and used to degrade methylene blue (MB) [8–19], a common contaminant in wastewater from the textile industry.

In recent years, sludge-derived catalysts have received increasing attention as a new pathway for utilizing sewage sludge as a resource. Sludge contains organic components and mineral elements (Fe, Ca, Al, Si, etc.) that determine the potential of the sludge to act as a catalyst. Yuan and Dai [20] prepared a novel catalyst from municipal sludge (at a preparation temperature of 350°C) and applied it to degrade the Rhodamine B dye in industrial wastewater. Zhou et al. [21] prepared a catalyst from paper mill sludge (at a preparation temperature of 400°C) and used it to degrade MB in wastewater. Tu et al. [22] produced a catalyst from sludge (at a preparation temperature of 800°C) and used it to degrade the Orange Yellow 2 dye in wastewater. Gu et al. [23,24] produced a catalyst from sludge (at preparation temperatures of 600°C, 800°C, and 1,000°C) and used it to degrade naphthalene dye, intermediate dye, and 1-diazo-2-naphthol-4-sulfonic acid in wastewater. These studies showed that sludge has the potential to be converted into excellent catalysts for the degradation of recalcitrant contaminants. However, the influence of operating conditions on the degradation of dyes in wastewater and the potential degradation mechanism remain unclear and require further research.

Hence, the objective of this study was to determine whether municipal sludge could act as a carrier for Fe^{2+} and serve as a resource to synthesize a catalyst through calcination treatment at the temperature of 350°C. The sludge-derived catalyst was used to degrade typical MB dyes in aqueous solution. The influence of various experimental conditions on MB degradation was assessed. Last, the potential MB removal mechanism was explored through ultraviolet-visible light (UV-Vis spectrum) analysis, free-radical quenching, and Fe leaching experiments. The investigation was designed to provide a reference for utilization of sludge as a resource and offer for a new alternative for treating dyes contained in wastewater.

2. Materials and methods

2.1. Materials

Municipal sludge was collected from a municipal wastewater treatment plant that used oxidation ditch technology. The sludge was dewatered through plate-frame pressure filtration equipment. The municipal sludge was dried in an oven at 105°C and was stored for further study.

Analytical grade reagents of methylene blue, $FeSO_4{\cdot}7H_2O$, 30%H_2O_2, HCl, NaOH, $FeCl_3$, methanol, and tert-butanol were purchased from Sinopharm Group Chemical Reagent Co., Ltd (Shanghai, China).

2.2. Preparation of sludge-derived catalyst

Sludge-derived catalyst was prepared according to previous studies with the modification of some steps [20,21]. Specifically, 10.0 g dried sludge was mixed with 30 mL $FeSO_4{\cdot}7H_2O$ (1.0 mol·L^{-1}) in a 250 mL Erlenmeyer flask. Then, the contents were stirred by magnetic stirring for 12 h to assure sufficient contact of sludge with Fe^{2+}. The mixed solution was dried in an oven at 105°C for 24 h. Then, the dried mixture was calcinated in a muffle furnace at 350°C for 2 h. When the sample was cooled to room temperature, it was washed with pure water until the eluent had a near neutral pH. After oven-drying at 80°C, the catalyst (named "SS-Fe-350") was ground and passed through a 100-mesh sieve (150 μm). Meanwhile, sludge material (named "SS-350") was prepared as control in the same way as SS-Fe-350 except without the addition of $FeSO_4{\cdot}7H_2O$.

2.3. Degradation experiment

A stock solution of 1 g L^{-1} methylene blue was prepared and diluted to different concentrations based on the requirements of the experiments.

In the degradation experiments, the influence of initial pH of MB solution, catalyst dosage, H_2O_2 dosage and temperature on the removal of MB was investigated. In these experiments, 100 mL of MB solution with an initial MB concentration of 100 mg L^{-1} was put into a 250-mL beaker. Then, HCl (0.1 M) or NaOH (0.1 M) was used to adjust the initial pH of the solution. Various amounts of catalyst (SS-Fe-350) were added to the MB solution, as well as a certain amount of H_2O_2 to initiate the reaction. Samples were collected at predetermined time intervals and passed through a 0.45 μm filter membrane. Then, the samples were analyzed using a spectrophotometer (722S, Shanghai Precision & Scientific Instrument Co. Ltd., Shanghai, China) at a wavelength of 665 nm. The MB removal efficiency was calculated using Eq. (1) as follows:

$$\text{MB removal efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{1}$$

where C_o is the concentration of MB solution at initial time (mg L^{-1}) and C_t is the concentration of MB solution at time t (mg L^{-1}).

2.4. Mechanism study

To explore the potential mechanism of MB removal, UV-Vis spectral analysis, free-radical quenching, and Fe leaching experiments were conducted.

(1) Fe leaching experiment: Leaching of the Fe ion was an important index to assess the stability of the sludge-derived catalyst. The Fenton reaction can be classified as heterogeneous or homogeneous. The measurement of Fe ions in solution was used to calculate the contribution of the homogeneous Fenton reaction. The Fe ion concentration was determined using an atomic absorption spectrometer (ZEEnit 700P, Analytik Jena AG, Jena, Germany).
(2) Free-radical quenching experiment: To reveal if the MB degradation process was a free-radical reaction, a certain concentration of tert-butanol (a free-radical inhibitor and known strong ·OH scavenger) was added to the reaction system.
(3) UV-Vis spectral analysis: The UV-Vis spectrum of MB during the degradation process was used to analyze the dynamic transformation of structural and molecular features of MB molecules. Samples were collected at predetermined time intervals and analyzed in the wavelength range of 200–800 nm.

2.5. Reusability and stability of SS-Fe-350

To investigate the stability and reusability of the sludge-derived catalyst, the SS-Fe-350 was separated from solution after a degradation process and triple-washed using pure water. Then, the sample was dried in the oven and again used to degrade the MB in aqueous solution. The experimental conditions were 100 mL of solution; MB concentration 100 mg L^{-1}; pH 4.0; solid-to-liquid ratio (catalyst-to-solution) 1 g L^{-1}, H_2O_2 dosage 1 mL L^{-1} (3%); and contact time 120 min. The catalyst was recycled and was used to degrade the MB solution under the same conditions three times.

2.6. Physical characterization

Surface functional groups of SS-Fe-350 and SS-350 were characterized by Fourier-transform infrared (FTIR) spectroscopy (Nicolet™ iS50, Thermo-Fisher Scientific, Waltham, MA, United States) using the KBr pellet technique in the range 400–4,000 cm^{-1}. Crystalline compounds in SS-Fe-350 and SS-350 were determined by X-ray diffraction (XRD) (D8 ADVANCE, BrukerOptik GmbH, Ettlingen, Germany).

3. Results and discussion

3.1. Characterization of sludge-derived catalyst

The FTIR spectra of SS-Fe-350 and SS-Fe are displayed in Fig. 1(a) and show that SS-350 and SS-Fe-350 contained –OH, –CH, Si–O–Si, and Fe–O functional groups. In addition, SS-Fe-350 possessed the Si–O–Fe functional group, which indicated that SiO_2 in the sludge formed a chemical bond with Fe during the calcination process and that Fe was successfully loaded on the sludge-derived catalyst.

The XRD spectra of SS-Fe-350 and SS-Fe are presented in Fig. 1(b) and show that the main compound in the SS-350 and SS-Fe-350 was SiO_2. Furthermore, SS-Fe-350 also contained Fe_2O_3, which demonstrated that sludge-derived catalyst contained at least one Fe compound after calcination treatment, which was consistent with findings in previous studies [20,21].

3.2. Degradation of MB under different systems

The degradation of MB under different systems is shown in Fig. 2. The different systems included SS-350, SS-Fe-350, H_2O_2, SS-350/H_2O_2, and SS-Fe-350/H_2O_2. As shown in Fig. 2, MB removal under various systems exhibited different tendencies.

When only SS-350 was added in MB solution (without H_2O_2), the removal efficiency of MB was less than 30%. When SS-Fe-350 was added to MB solution (without H_2O_2), the removal efficiency did not reach 15%. The removal of MB mainly depended on the adsorption capacity of SS-350 or SS-Fe-350, and the adsorption mechanism involved electrostatic interaction, hydrogen bond interaction, π–π stacking, and surface complexation [25]. The SS-350 and SS-Fe-350 contained functional groups and minerals, which contributed to the adsorption capacity for MB molecules. However, due to the small surface area of sludge [25], the adsorption capacity for MB removal was limited.

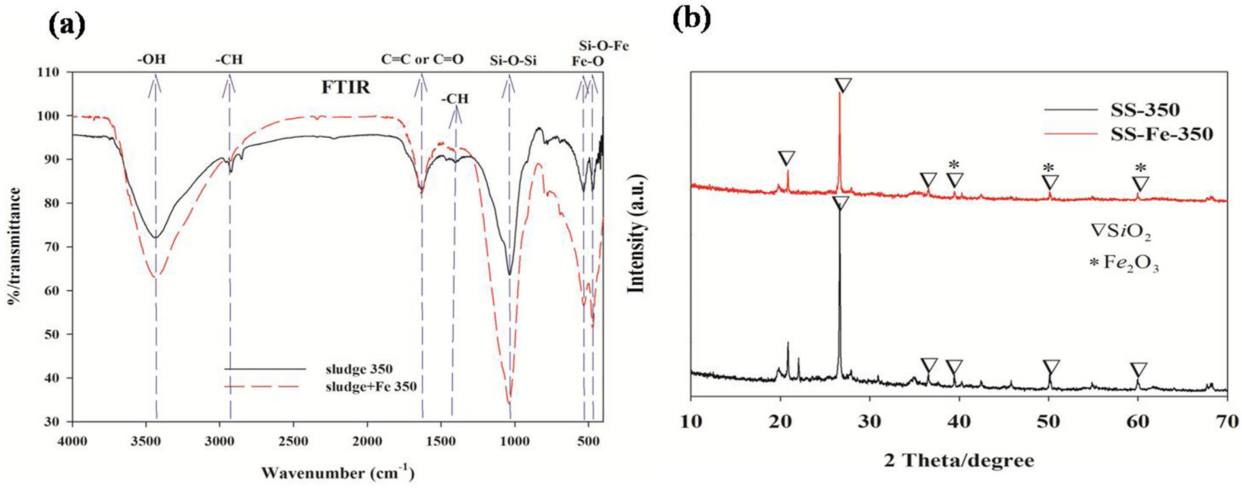

Fig. 1. (a) FTIR spectra of sludge-derived catalyst; (b) XRD spectra of sludge-derived catalyst.

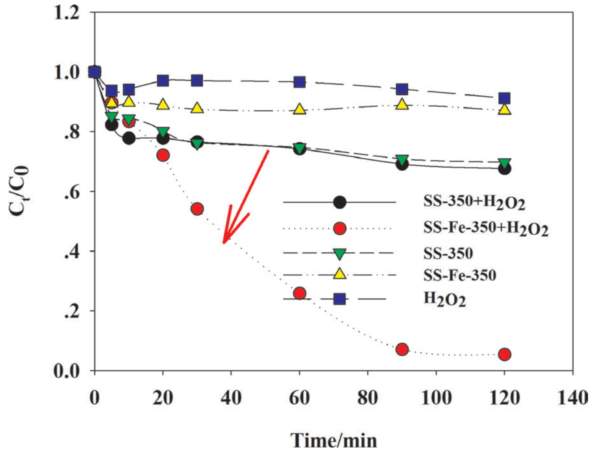

Fig. 2. Removal of MB under different systems. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, catalyst dosage 1 g·L^{-1}, 3% H_2O_2 dosage 1 mL·L^{-1}, temperature 25°C.

When only H_2O_2 was added to MB solution (without SS-350 or SS-Fe-350), the removal efficiency of MB was less than 10% because of the weak oxidative activity of H_2O_2. Therefore, the degradation of MB by H_2O_2 acting alone was restricted.

When SS-350 and H_2O_2 were added to the solution, the MB removal efficiency reached 35% after 120 min. The SS-350 derived from municipal sewage sludge contained a low content of transitional metals, including Fe, which accounted for the degradation of MB in the presence of H_2O_2.

When SS-Fe-350 and H_2O_2 were added to the solution, the removal efficiency of MB exceeded 97% after 120 min, suggesting that SS-Fe-350 possessed a high potential to remove MB dyes wastewater. In short, compared with the MB removal efficiency achieved in the different systems examined, the SS-Fe-350 catalyst derived from municipal sewage sludge, together with H_2O_2, provided an approach for treating wastewater containing dyes.

3.3. Removal of MB as a function of different factors

The optimal parameters were investigated to determine the MB degradation effect. The result could provide an important reference for insight into removal mechanism and practice application of the catalyst. The optimal parameters included initial pH of solution, catalyst dosage, H_2O_2 dosage, and system temperature.

3.3.1. Effect of initial solution pH on MB removal

The initial pH of the MB solution had a significant effect on MB removal by SS-Fe-350 (Fig. 3).When the initial pH was in the range of 2.0–3.0, the removal of MB by the catalyst was rapid and 60% removal efficiency was achieved in the first 5 min. The final MB removal efficiencies achieved by SS-Fe-350 were 80% (at initial pH 2.0) and 96% (at initial pH 3.0).

When the initial pH of the MB solution was in the range 4.0–5.0, MB removal was significantly slower than at pH 2.0–3.0; the removal efficiency was less than 10% in the first 5 min. However, the final MB removal efficiency exceeded 90% when the initial pH of MB solution was between 4.0 and 5.0.

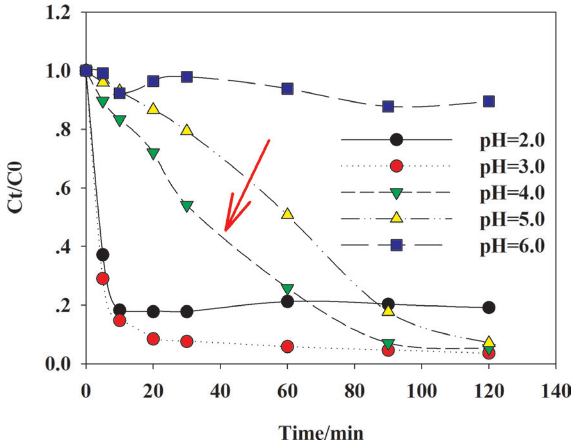

Fig. 3. Removal of MB as a function of initial pH. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, catalyst dosage 1 g·L^{-1}, 3% H_2O_2 dosage 1 mL·L^{-1}, temperature 25°C.

When the initial pH of the MB solution was 6.0, the removal of MB was negligible (<5%). The removal effect could be attributed to the adsorption of MB by SS-Fe-350.

Generally, ·OH could be generated under acidic conditions, and the MB removal efficiency increased with the decrease in initial pH of the MB solution. Fe easily precipitated when the pH of the solution increased, resulting in the decrease of ·OH generation and reduced removal of MB [26].

These results showed that when the initial pH of MB solution was in the range 3.0–4.0, MB removal was acceptable. The difference in MB removal at initial pH 3.0 and pH 4.0 was small. Considering cost-effectiveness, the optimal pH value of the MB solution should be adjusted to 4.0. This would widen the range of pH for effective MB removal in practical applications [27].

3.3.2. Effect of catalyst dosage on MB removal

The influence of catalyst dosage on MB removal is displayed in Fig. 4. When the SS-Fe-350 dosage increased from 0.5 to 4 g L^{-1}, the final MB removal efficiency increased from 90% to 99%. Meanwhile, a higher catalyst dosage led to a faster MD degradation rate. With the increase of catalyst dosage, more reaction sites were provided in the degradation process, which resulted in rapid degradation of MB molecules [28,29]. However, a high catalyst dosage could introduce more Fe in the system and accelerate the degradation of H_2O_2. Thus, fewer ·OH radicals had sufficient time to decompose the MB molecules.

Catalyst dosages from 1 to 4 g L^{-1} all achieved final MB removal efficiencies exceeding 95%. Considering both MB removal efficiency and economic efficiency, an optimal catalyst dosage for MB removal was 1 g L^{-1}.

3.3.3. Effect of H_2O_2 dosage on MB removal

The removal of MB at different H_2O_2 dosages is shown in Fig. 5. When the H_2O_2 dosage increased from 1 to 5 mL L^{-1}, the final removal efficiency of MB was effectively 100%. When the H_2O_2 dosage was 2 and 4 mL L^{-1}, the reaction with MD was rapid; however, when the dosage was 3 and 5 mL L^{-1}, the reaction was relatively slow.

Because ·OH radicals were generated under the catalytic reaction of SS-Fe-350 with H_2O_2, the dosage of H_2O_2 significantly affected the degradation process and reaction rate. With the increase of H_2O_2 dosage, more ·OH was generated, resulting in a more rapid reaction rate.

However, when the H_2O_2 dosage increased from 3 to 5 mL L^{-1}, the MB removal rate actually decreased. When the concentration of H_2O_2 was high, more H_2O_2 was available to react with ·OH, suggesting the quenching of ·OH [27,30,31]. As a result, the subsequent availability of H_2O_2 decreased, indicating a reduced reaction rate and degradation effect. Therefore, the optimal dosage of H_2O_2 for MB removal was 1 mL L^{-1}.

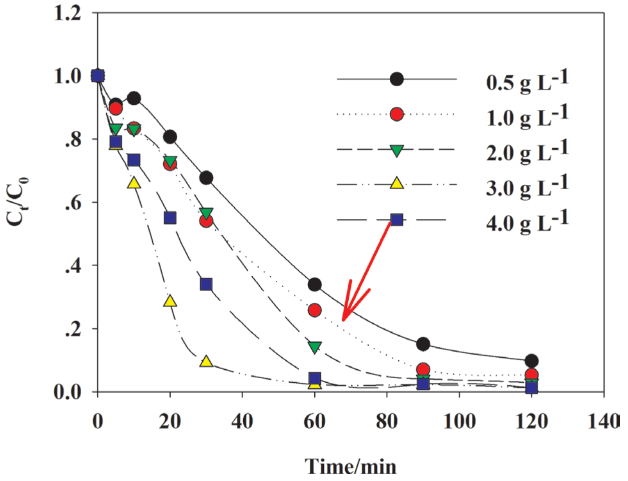

Fig. 4. Removal of MB as a function of catalyst dosage. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, 3% H_2O_2 dosage 1 mL·L^{-1}, temperature 25°C.

3.3.4. Effect of system temperature on MB removal

The removal of MB at different system temperatures is shown in Fig. 6. The system temperature clearly influenced the removal of MB. When the system temperature increased from 25°C to 45°C, the final MB removal efficiency exceeded 96%. Furthermore, the MB degradation rate accelerated at a higher temperature.

On one hand, with the increase of temperature, MB molecules absorbed heat and more were activated in a unit volume. Effective collision between MB molecules increased and accelerated the degradation of MB. On the other hand, higher system temperatures generated more ·OH in the reaction system [29].

Although increased system temperature was beneficial for the degradation of MB, most of the reaction process occurred at room temperature. Considering the application of the catalyst in practical applications, the optimal temperature for MB removal should be 25°C.

3.3.5. Reusability and stability of SS-Fe-350

Together with pollutant removal effectiveness, the reusability and stability of a catalyst determine its actual application potential. The reusability performance of SS-Fe-350 is shown in Fig. 7. The MB removal efficiency of SS-Fe-350 reached 95% after the first recycle. After the second and third recycle, the MB removal efficiency decreased to 77% and 60%, respectively. Obviously, MB removal by SS-Fe-350 decreased after several usage cycles.

The decrease of MB removal efficiency may be due to the loss of Fe from the sludge-derived catalyst. The loss of Fe may have decreased the number of active reaction sites and reduced the generation of ·OH, which decreased the MB removal efficiency. In addition, during recycling and reuse of SS-Fe-350, the surface and pore structure of the catalyst retained abundant intermediate products from MB molecules. Thus, a number of active reaction sites of SS-Fe-350 may have been occupied by these intermediate

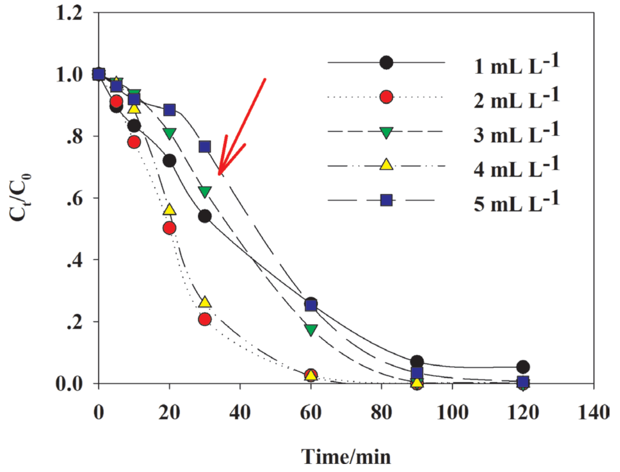

Fig. 5. Removal of MB as a function of H_2O_2 dosage. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, catalyst dosage 1 g·L^{-1}, temperature 25°C.

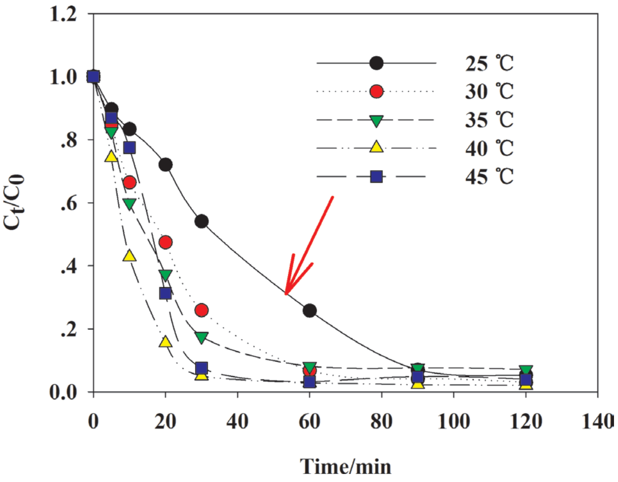

Fig. 6. Removal of MB as a function of system temperature. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, catalyst dosage 1 g·L^{-1}, 3% H_2O_2 dosage 1 mL·L^{-1}.

products, which affected the MB removal performance of SS-Fe-350 in subsequent usage cycles.

To assess the stability of SS-Fe-350, Fe ion leaching was analyzed during the MB removal process. As shown in Fig. 8, Fe ions were detected after 30 min when the MB removal efficiency exceeded 55%. These results implied that the main mechanism for MB removal was a heterogeneous catalyst reaction. However, with the leaching of Fe ions, a homogeneous catalyst reaction may have also occurred and promoted the degradation of MB molecules. Therefore, more research is needed on the reusability and stability of this sludge-derived catalyst.

3.4. Removal mechanism

3.4.1. UV-Vis spectral analysis of MB degradation process

To observe the molecular feature and the structural transformation of MB in the degradation process, changes in the UV-Vis spectrum of MB during the degradation process were examined. Fig. 9 shows that different structural features of MB presented various adsorption bands. Three spectral peaks were observed in the range of 200–800 nm at 229, 310, and 664 nm. As the reaction proceeded, the absorbance peaks gradually diminished, indicating that the benzene and naphthalene rings were degraded to smaller compounds, CO_2, and water.

As reaction time in the system that contained both SS-Fe-350 and H_2O_2 increased, the absorbance peaks gradually diminished and a "blue shift" in their location appeared, indicating the degradation of MB molecules. The chromophoric group in MB was destroyed and MB was transformed to byproducts [32]. After 120 min, the main absorption peaks nearly disappeared and MB was almost entirely degraded.

In contrast, in the system that contained SS-350 and H_2O_2, the position of the absorbance peaks did not change

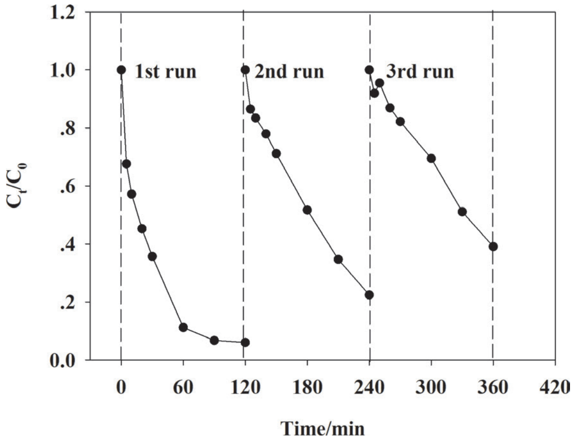

Fig. 7. Removal of MB as a function of SS-Fe-350 reuse. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, catalyst dosage 1 g·L^{-1}, 3% H_2O_2 dosage 1 mL·L^{-1}, temperature 25°C.

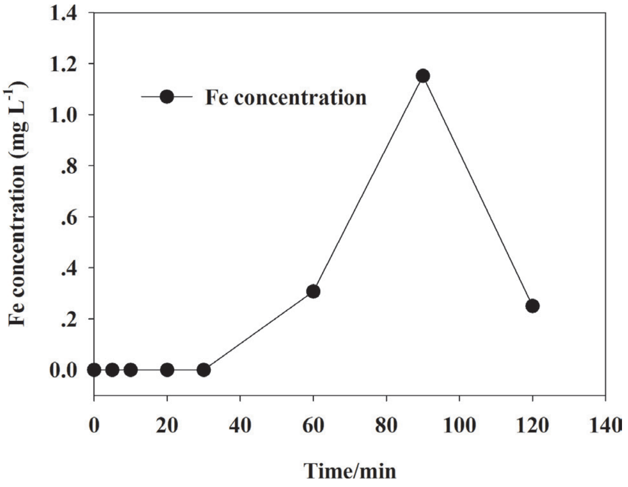

Fig. 8. Fe leaching during the MB degradation process. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, catalyst dosage 1 g·L^{-1}, 3% H_2O_2 dosage 1 mL·L^{-1}, temperature 25°C.

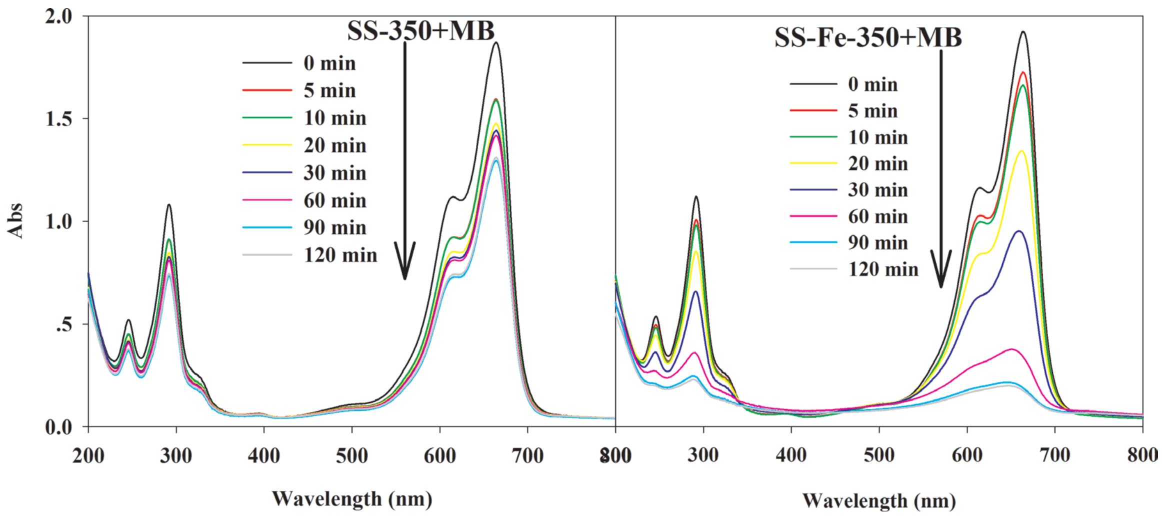

Fig. 9. UV-Vis spectra of a typical degradation process. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, catalyst dosage 1 g·L^{-1}, 3% H_2O_2 dosage 1 mL·L^{-1}, temperature 25°C.

and only the magnitude of the absorbance peaks diminished. The reduction of absorbance was attributed to MB adsorption on SS-350.

3.4.2. Influence of tert-butanol on the MB degradation system

The influence of tert-butanol on the MB degradation system is illustrated in Fig. 10. Tert-butanol is known to be a strong ·OH scavenger and was used to explore the potential mechanism of MB degradation by SS-Fe-350. Thus, tert-butanol was adopted as the indicator for the free-radical reaction [33,34]. As shown in Fig. 10, the MB removal efficiency achieved by the SS-Fe-350 catalyst reached 95% in the system without tert-butanol. When the concentration of tert-butanol was 0.1 mmol L^{-1} in the degradation system, MB degradation was slightly reduced and the final removal efficiency was 93%. However, when the concentration of tert-butanol was increased to 1.0 mmol L^{-1}, the final MB removal efficiency decreased to 30% and the degradation rate was also significantly slower. Based on the data presented in Fig. 2, the contribution of adsorption was 13%. Thus, because ·OH could be captured by tert-butanol in the system, the tert-butanol inhibited the free-radical reaction and reduced the MB removal efficiency. Therefore, the mechanism of MB degradation by SS-Fe-350 was dominated by the ·OH free-radical reaction.

3.4.3. Mechanisms

Combining the findings of previous research [21,29,31,35–41] with the experimental results from this study, the main mechanism of MB degradation by SS-Fe-350 involved several steps as follows:

(1) First, H_2O_2 was adsorbed on the SS-Fe-350 surface. The heterogeneous Fenton reactions were initiated.
(2) The site $\equiv Fe_{sur}^{III}$ was reduced to $\equiv Fe_{sur}^{II}$.
(3) $\equiv Fe_{sur}^{II}$ reacted with H_2O_2 to generate ·OH while $\equiv Fe^{II}$ was oxidized into $\equiv Fe_{sur}^{III}$ at the end of the reaction cycle.

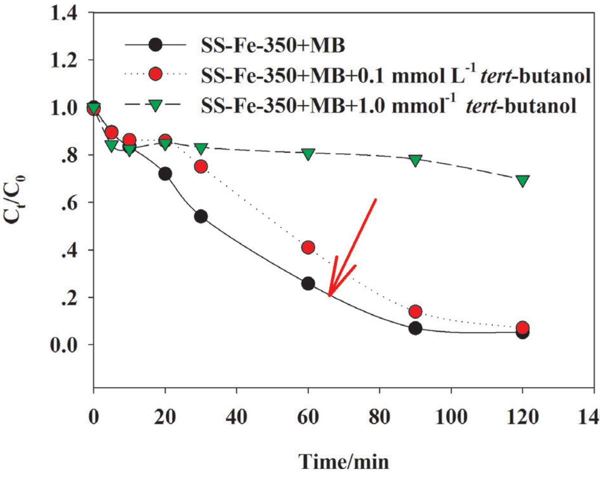

Fig. 10. Influence of tert-butanol on MB degradation. Experimental condition: MB concentration 100 mg L^{-1}, volume of solution 100 mL, initial pH of solution 4.0, catalyst dosage 1 g·L^{-1}, 3% H_2O_2 dosage 1 mL·L^{-1}, temperature 25°C.

(4) ·OH attacked MB molecules and produced reaction intermediates. Then, the reaction intermediates were degraded to H_2O, CO_2, and other small molecule substances.
(5) Meanwhile, ·OH reacted with H_2O_2 to generate HO_2. The HO_2· reacted very slowly with MB and reaction intermediates. The heterogeneous Fenton reactions occurred as described by Eqs. (2)–(7) as follows:

$$\equiv Fe_{sur}^{III} + H_2O_2 \rightarrow \equiv Fe_{sur}^{III}H_2O_2 \tag{2}$$

$$\equiv Fe_{sur}^{III}H_2O_2 \rightarrow \equiv Fe_{sur}^{II} + HO_2\cdot + H^+ \tag{3}$$

$$\equiv Fe_{sur}^{II} + H_2O_2 \rightarrow \equiv Fe_{sur}^{III} + \cdot OH + OH- \tag{4}$$

$$\cdot OH + MB \rightarrow \text{degradation products} \tag{5}$$

$$\cdot OH + H_2O_2 \rightarrow HO_2\cdot + H_2O \tag{6}$$

$$HO_2\cdot + MB \rightarrow \text{degradation products} \tag{7}$$

4. Conclusions

A catalyst (SS-Fe-350) was synthesized from municipal sewage sludge and was used to degrade MB in aqueous solution. The degradation mechanism was investigated. The main conclusions justified by the results of this study are as follows:

(1) The MB removal efficiency (concentration 100 mg L^{-1}, volume of solution 100 mL) of SS-Fe-350 could reach 98% under optimal conditions. In this study, the optimal conditions were initial pH 4.0, catalyst dosage 1 g L^{-1}, H_2O_2 dosage 1 mL L^{-1}, and contact time 120 min.
(2) The initial pH of solution, catalyst dosage, H_2O_2 dosage, and system temperature significantly influenced MB removal by the catalyst SS-Fe-350.
(3) The main mechanism for MB degradation was the heterogeneous catalyst Fenton reaction and free-radical reaction. Some Fe from the catalyst could induce the homogeneous catalyst reaction.
(4) The MB removal efficiency achieved by SS-Fe-350 decreased as the number of usage cycles increases. In this study, the efficiency decreased from 98% to 60% after three usage cycles. Further investigation on the stability and reusability of the catalyst is needed.
(5) The catalyst preparation provided an effective approach for the utilization of municipal sewage sludge as a resource and offers an alternative for the treatment of dyes contained in wastewater.

Acknowledgements

This study is supported by National Natural Science Foundation of China (51809001), Natural Science Foundation of the Education Department of Anhui Province (KJ2018A0125, KJ2018A0347), Fuyang Normal University Youth Fund Project (No. 204008134, 2018FSKJ07ZD), The Open Fund of State Key Laboratory of Tea Plant Biology and Utilization (SKLTOF20170117).

Conflicts of interest

The authors declare no conflict of interest.

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