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Fe_3O_4 and $Fe_3O_4/Fe^{2+}/Fe^0$ catalyzed Fenton-like process for advanced treatment of pharmaceutical wastewater

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ABSTRACT

Batch experiments were conducted for advanced treatment of pharmaceutical wastewater (after biological treatment) in a series of Fenton-like systems. Fe_3O_4-H_2O_2 system had the highest reactivity for COD removal comparing to classic Fenton and Fe^0-H_2O_2 systems. Effects of crucial experimental factors were investigated, including H_2O_2 and Fe_3O_4 dosage, pH, and reaction time. To reach 20% COD removal, the optimal conditions were pH of 3.0, Fe_3O_4 dosage of 1.0 g/L, and H_2O_2 dosage of 10 mg/L. Comparing with the classical Fenton's reaction, the Fe_3O_4-H_2O_2 system saved 75% H_2O_2, reduced 47% excess sludge, and slightly improved the COD removal. Furthermore, in order to meet the upcoming new local standard, Fe^{2+} and Fe^0 were introduced into Fe_3O_4-H_2O_2 system to form a hybrid system, $Fe_3O_4/Fe^0/Fe^{2+}$-H_2O_2 (pH of 3.0, Fe_3O_4 of 1.0 g/L, Fe^0 of 0.23 g/L, Fe^{2+} of 34 mg/L, and H_2O_2 of 40 mg/L). Fe^0 and Fe^{2+} not only improved the COD removal and decreased iron sludge, but also enhanced the reuse of catalysts. Compared to the classic Fenton process, 80% H_2O_2 dosage was saved and 94% iron sludge was decreased. Meanwhile, the cost decrease by 1.66 RMB/m^3-wastewater.

Keywords: Fe_3O_4; Fe^0; Pharmaceutical wastewater; Heterogeneous Fenton-like process

1. Introduction

High volume of wastewater is generated in the process of drugs production, which contains many pollutants including drug substances [1]. China is the biggest drug producer all over the world, and the resulting large volume of pharmaceutical wastewater imposes serious environmental pollution and public health threat [2]. The management of pharmaceutical wastewater is increasingly strengthened and the national discharge standard requires COD below 100 mg/L. Thus, advanced treatment is necessary.

The most frequently used advanced treatment in a typical pharmaceutical plant is the Fenton process where Fe^{2+} is used as the catalyst and hydrogen peroxide (H_2O_2) as the oxidant. Fenton process has many advantages such as high performance, simplicity for the treatment of organics [3] and non-toxicity [4]. However, it still has some disadvantages such as high operating cost, which is mainly caused by the high hydrogen peroxide dosage, large volume of iron sludge produced, and difficulties in recycling of the catalyst (Fe^{2+}) [5]. Iron sludge is increasingly regarded as hazardous waste in China and the disposal cost is 250–350 US $/t, which imposes great burden on the operator.

In order to overcome these disadvantages, heterogeneous Fenton-like process has attracted increasing attentions. In recent years, zero-valent iron [6], iron containing materials [7,8], and iron oxide minerals [6] as heterogeneous Fenton-like catalysts have been studied. Among these catalysts, iron oxides such as magnetite (Fe_3O_4), hematite (α-Fe_2O_3) and goethite (α-FeOOH), are of great importance because of their specific structural, magnetic and catalytic properties [9]. Taking into account the cost and non-toxicity, Fe^0 and Fe_3O_4 were selected as catalyst in this study for the treatment of pharmaceutical wastewater.

Wang et al. [10] investigated dechlorination of 3,3′,4,4′-tetrachlorobiphenyl (PCB77) in aqueous solution by hybrid Fe^0/Fe_3O_4 nanoparticle system, which removed 93.54% 3,3′,4,4′-tetrachlorobiphenyl. There was a synergy effect between Fe_3O_4 and Fe^0. Fe_3O_4 enhanced the PCB77 degradation with nanoscale Fe^0 by providing Fe^{2+} and

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Fe^{3+}. Fe^0/Fe_3O_4 system was also effective on decomposing trichloroethylene [11]. Heterogeneous Fenton system based on Fe^0/Fe_3O_4 composite was used to treat methylene blue [12]. HO· radicals generated from Fe^{2+}_{surf} species and H_2O_2 in a Fenton like mechanism. The number of Fe^{2+}_{surf} species was increased by an electron transfer mechanism from Fe^0 to Fe^{3+}_{surf} during the Fenton reaction. $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system was used in reduction nitrate [13]. Fe^{2+} improved the reductive efficiency of nitrate by Fe^0, and NO^{3-} and Fe^{2+} concentrations displayed a declining trend. Fe^{2+} accelerated the corrosion of iron surface, Fe_3O_4 accelerated the reductive denitrification rate of nitrate with Fe^0 and Fe^{2+} by acted as a great conductor which benefited to the electron transfer on iron surface.

In this study, $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid Fenton-like system was first time used to treat organic pollutants. The efficiencies of Fenton and Fenton-like processes were compared in treatment of pharmaceutical wastewater with the same H_2O_2 dosage. The feasibility and effects of experimental parameters in Fe_3O_4-H_2O_2 system were investigated. The enhancements of Fe^0 and Fe^{2+} on COD removal efficiency, iron sludge production and catalyst reuse time were studied in $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid Fenton-like system. Thus, a novel Fenton-like system ($Fe_3O_4/Fe^0/Fe^{2+}$ hybrid Fenton-like system) was proposed to treat the pharmaceutical wastewater. The aim of this study was to develop a novel Fenton-like process for the effective advanced treatment of pharmaceutical wastewater.

2. Experimental

2.1. Chemicals

Ferrous sulfate hexahydrate ($FeSO_4·7H_2O$), ferric chloride hexahydrate ($FeCl_3·5H_2O$) and other chemicals were of analytical grade. The concentration of ammonia water was 25–28%. These chemicals were used without further purification. Ferrous sulfate and ferric chloride were purchased from Tianjin Guangfu Technology Development Co. Ltd. Hydrogen peroxide (H_2O_2, 30%, V/V) and sulfuric acid (H_2SO_4, 98%) were obtained from Beijing Chemical Works, China. Chemical solutions were prepared with water purified by a Millipore Milli Q UV Plus system.

2.2. Pharmaceutical wastewater

Pharmaceutical wastewater was obtained from a major pharmaceutical manufactory. The treatment process for pharmaceutical wastewater was as following: pretreatments—UASB–UASB—aeration-Fenton–BAF shown in Fig. 1. The goal of the Fenton's process was 20% COD removal so the following BAF could further reduce the COD to meet the discharge standard. Pharmaceutical wastewater used for this study was taken at the outlet of the aeration tank, i.e., it was after conventional biological treatment and needed advanced treatment. The characteristics of the wastewater were as following: COD = 236 mg/L, pH = 6.86, Total dissolved solids (TDS) = 1784 mg/L, Electronic conductivity = 3.57 mS/cm, Electrical resistivity = 291 Ω cm. All data were the average value of multiple samples.

Two Fenton-like processes were examined in this study. The first was Fe_3O_4-H_2O_2 system to replace the in-use classic Fenton process in order to meet current discharge standard and the Fenton-like process needed a COD removal of 20%. The second was $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid Fenton-like system in order to meet the upcoming new local standard that needs a COD removal of 40%. The aim was to reduce H_2O_2 dosage and waste sludge, thus to reduce the wastewater treatment cost.

2.3. Synthesis of Fe_3O_4

Fe_3O_4 was prepared by reverse co-precipitation method [9]. $FeCl_3·5H_2O$ (0.02 mol) and $FeSO_4·7H_2O$ (0.02 mol) were dissolved in 100 mL deionized water under mechanical stirring. When $FeCl_3·5H_2O$ and $FeSO_4·7H_2O$ completely

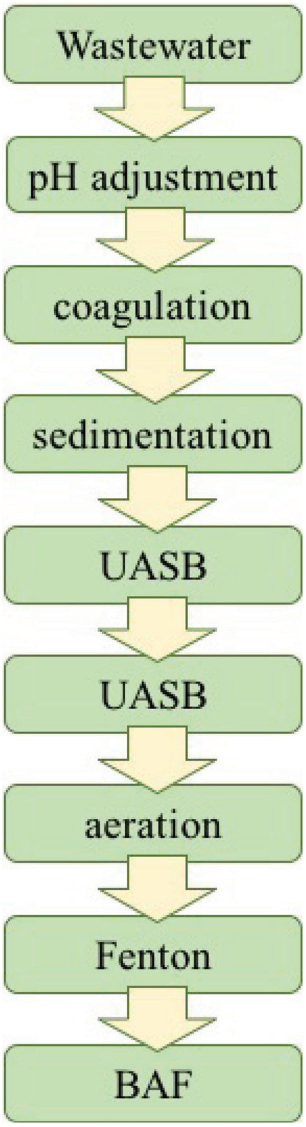


Fig. 1. Diagram of pharmaceutical wastewater treatment in the pharmaceutical manufactory.

dissolved in water, the solution was added into 100 mL ammonia water (concentration of 25–28%), and mixed at 300 rpm for 1 h. Then the product was separated by permanent magnet and cleaned for several times with ultrapure water till the supernatant was clear. The settled products were dried at 50ºC for 12 h.

2.4. Determination of COD removal

All experiments were conducted in 500 mL glass beakers. Each time, 300 mL of pharmaceutical wastewater was tested and the concentration of COD was about 236 mg/L. The solution of this experiment was adjusted with diluted H_2SO_4 to the desired initial pH. The desired dosage of catalyst and H_2O_2 was introduced into the reaction solution immediately. Then the beaker was placed in an electronic stirrer at an ambient temperature with continuous stirring at stirring rate of 250 rpm. At set intervals, supernatant was taken out immediately and the catalyst was separated by a permanent magnet. Part sample was used to test the residual H_2O_2. The pH of the remained sample was adjusted to 11.0 by adding $Ca(OH)_2$ solution and sludge was formed, thus remaining iron ion was removed. After 15 min settling, the supernatant was used to measure COD, the COD was named as COD_{test}. The residual H_2O_2 also contributed COD ($CODH_2O_2$). The actual COD was calculated by $COD_{actual} = COD_{test} - CODH_2O_2$ COD after reaction reported in this paper was all COD_{actual}. Control experiments were also performed under the same conditions.

2.5. Analytical methods

The COD was tested according to the national standard method (HJ/T 399–2007). The concentration of H_2O_2 was determined by iodometry [9]. The concentration of iron ion was measured by atomic absorption spectrometry (AAS).

At least three repetitive experiments were performed for every experimental condition, the average values of the experiments were used, and all the reported data were examined by T-test.

3. Results and discussion

3.1. Fe_3O_4-H_2O_2 process for 20% COD removal

Fenton-like systems were compared with the in-use classic Fenton process to meet the current discharge standard. The aim was to reduce the H_2O_2 dosage and thus to reduce the wastewater treatment cost. A COD removal of 20% was required for this step.

3.1.1. Comparative study: Fenton and Fenton-like process for treating pharmaceutical wastewater

The pharmaceutical manufactory used classic Fenton process while this study employed Fenton-like process, so the effectiveness of these two processes were compared firstly. COD removal efficiencies in different systems are illustrated in Fig. 2. The reaction conditions for the Fenton process were the same as in the pharmaceutical manufactory. The reaction conditions for Fe^0-H_2O_2 system were following our previous study (data in the supplementary material, Fig S1–S3). As shown in Fig. 2, the COD removal effectiveness varied largely among various systems. In these systems, the Fe_3O_4-H_2O_2 process had the highest reactivity for COD removal, achieving 28.87%. The removal effectiveness of COD in the classic Fenton system was slightly lower than 20%, which failed to meet the requirement of the pharmaceutical manufactory (sometimes the final effluent could not meet the national discharge standard in the pharmaceutical manufactory).

Then, the effectiveness of H_2O_2 oxidation was examined, Fe_3O_4 adsorption, and the Fe_3O_4-H_2O_2 Fenton-like reaction, and the results are shown in Fig. 3. H_2O_2 oxidization could hardly reduce COD from wastewater. Fe_3O_4 had a rapid adsorption in the first 15 min, which then fluctuated and then stabilized around 10%, the initial rapid adsorption might contribute to the initial quick COD removal in the Fe_3O_4-H_2O_2 reaction. The COD removal efficiency decreased

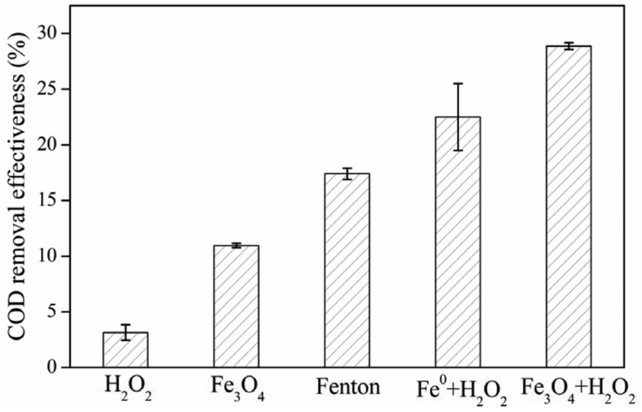


Fig. 2. COD removal effectiveness in different treatment systems with the same H_2O_2 dosage. pH = 3, H_2O_2 = 40 mg/L; Fe_3O_4+ H_2O_2: Fe_3O_4 = 2.5 g/L, reaction time = 2 h; Fe_0+ H_2O_2: Fe_0 = 0.23 g/L, reaction time = 2 h; Fenton: Fe^{2+} = 55.7 mg/L, reaction time = 30 min.

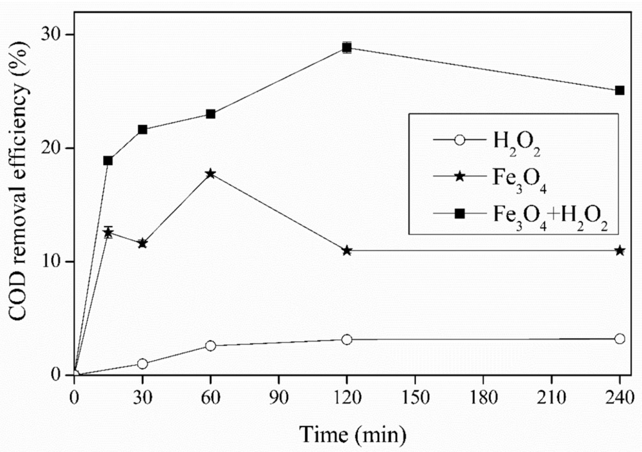


Fig. 3. COD removal efficiency in Fe_3O_4-H_2O_2 system. Reaction conditions: H_2O_2 = 40 mg/L, Fe_3O_4 = 2.5 g/L, pH = 3.

after 60 min for Fe_3O_4 system and 120 min for Fe_3O_4-H_2O_2 system. This phenomenon was because that some COD was be removed by the adsorption of Fe_3O_4, but a long period of intense agitation might result in the desorption of organic compounds adsorbed on Fe_3O_4 to the solution, resulting in the rise of COD in the solution and the decrease in COD removal rate. The Fe_3O_4-H_2O_2 system had a much higher COD removal, which is higher than the sum of H_2O_2 oxidation and Fe_3O_4 adsorption, therefore, it showed clearly the catalytic effect of Fe_3O_4. This phenomenon exhibited that Fe_3O_4 could catalyze H_2O_2 to generate hydroxyl free radicals. The ·OH can be formed in two ways in Fe_3O_4-H_2O_2 system. Firstly, H_2O_2 absorbed on Fe_3O_4 surface and reacted with $Fe(II)_{surf}$ [14]. Secondly, Fe^{2+} released to water and reacted with H_2O_2 to form ·OH [Eq. (1)] [15]. The best reaction time was 120 min and was used for following experiments.

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \cdot OH + H_2O \qquad (1)$$

3.1.2. Effects of experimental parameters in Fe_3O_4-H_2O_2 process

Results in Section 3.1.1 show that Fe_3O_4 had a beneficial catalytic activity for H_2O_2 and the Fe_3O_4-H_2O_2 reaction could achieve 28.87% COD removed for the advanced treatment of the pharmaceutical wastewater. However, the consumption of Fe_3O_4 and H_2O_2 was still high, and the COD removal was unnecessarily high (the required level was 20% for advanced treatment), so the operational conditions were further optimized for the purpose of saving cost.

The pH level of wastewater may be the most important parameter in Fenton's reaction which significantly influences the treatment efficiency [16]. In various Fenton-like reactions, pH also had a significant effect on the formation of free radicals [16], surface binding-sites of the catalysts and chemical form of reactants and products [17]. Generally, the optimal pH was 2.0–4.0 for Fenton's reaction. A low pH favors the generation of ·OH [18], and ·OH has higher oxidation potential in acidic conditions, relative to neutral and alkaline conditions [19]. As shown in Fig. 4a, pH significantly influenced the reaction efficiency, and the lower the pH value was, the higher COD removal efficiency was. The pH value of 4 gave a COD removal efficiency barely above 20% (the required efficiency), which left little room for catalyst and H_2O_2 dosage reduction. The wastewater itself was slightly acidic, addition of Fe_3O_4 and H_2O_2 further reduced its pH value to around 5.0, the cost of acid addition to achieve pH of 3 was much lower comparing to the cost of oxidant and catalyst, so pH of 3 was selected for following experiments.

Previous study showed that moderate increase in the catalyst dosage was beneficial to improve the pollutant removal efficiency from wastewater [20]. However, if the catalyst exceeded the optimum range, ·OH in solution would be consumed by the excess catalyst [21]. Results in Fig. 4b also show the same trend, the highest COD removal occurred at Fe_3O_4 dosage of 2.5 g/L and then decreased with more Fe_3O_4. The catalyst dosage of 1.0 g/L was selected since it could meet the requirement of 20% COD removal and save 60% catalyst (compared to Fig. 3), which would further reduce the waste sludge production. The remaining H_2O_2 after the catalytic oxidation was further examined, and the data are shown in Fig. 4b. Interestingly, the H_2O_2 consumption (added dosage–remain) was about 10 mg/L with different Fe_3O_4 dosages.

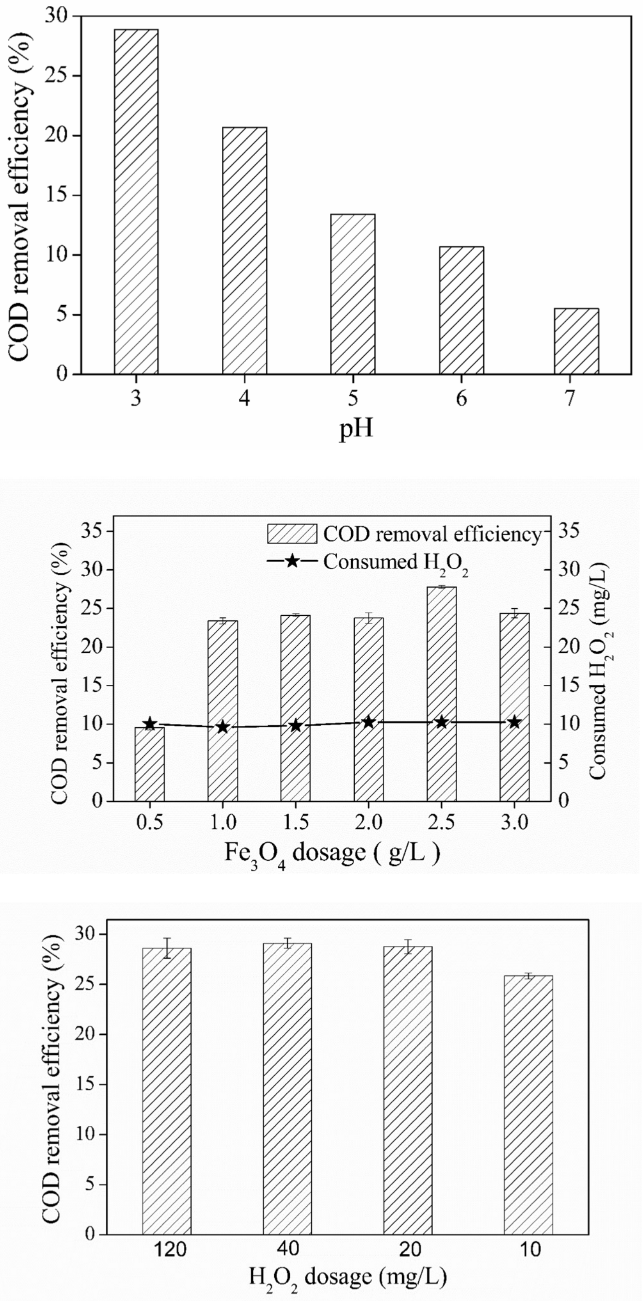


Fig. 4. Effects of important parameters for pharmaceutical wastewater treatment in Fe_3O_4-H_2O_2 process: (a) Fe_3O_4 dosage (b) pH (c) H_2O_2 dosage. Reaction conditions: (a) pH = 3, 4, 5, 6, 7, Fe_3O_4 = 2.5 g/L, H_2O_2 = 40 mg/L, reaction time = 2 h; (b) Fe_3O_4 = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, H_2O_2 = 40 mg/L, pH = 3, reaction time = 2 h; (c) H_2O_2 = 10, 20, 40, 120 mg/L, Fe_3O_4 = 1.0 g/L, pH = 3, reaction time = 2 h.

The effects of H_2O_2 dosage were then determined and the results are shown in Fig. 4c. In the Fenton-like process, H_2O_2 plays a critical role in the treatment of wastewater, because it is the dominant source of ·OH under catalysis [21]. However, excess H_2O_2 could decompose to H_2O and O_2, which contributed little to pollutants reduction. Fig. 4c showed that when the H_2O_2 dosage was higher than 10 mg/L, the benefit of more oxidant became insignificant. This phenomenon could be explained by the H_2O_2 consumption. As shown in Fig. 4b, the largest consumption of H_2O_2 was 10.25 mg/L, therefore too much H_2O_2 did not improve COD removal, but consumed the produced ·OH [21]. Among the studied H_2O_2 range, the lowest dosage of 10 mg/L could meet the required COD removal of 20%. Since 87.25% H_2O_2 was consumed at 10 mg/L, further decrease was impractical. Thus, the H_2O_2 dosage of 10 mg/L was selected.

The optimized conditions for Fe_3O_4-H_2O_2 system were pH of 3.0, Fe_3O_4 dosage of 1.0 g/L, and H_2O_2 dosage of 10 mg/L. Compared to those conditions in Fig. 3, the dosage was reduced by 60% for Fe_3O_4, and 75% for H_2O_2. In comparison to the classic Fenton process used in the pharmaceutical manufactory (conditions in Fig. 2), the COD removal met the requirement, and the H_2O_2 consumption decreased by 75%. Furthermore, the sludge was only 66.88 mg/L, while the sludge from the classic Fenton process was 125.88 mg/L, showing a reduction of 46.88%.

3.2. Fe^{2+}/Fe^0/Fe_3O_4 hybrid Fenton-like process for advanced treatment of pharmaceutical wastewater

The above experiments provided a good solution to the existing problem in the pharmaceutical manufactory: sometime low efficiency, high H_2O_2 consumption, and large waste sludge. However, since environmental requirements are increasingly stringent in China, a new local discharge standard of COD of 60 or 70 mg/L will be imposed in the near future. Though legislation is still debating on the number (60 or 70 mg/L), the trend is unavoidable. The new local standard imposes a great pressure on the pharmaceutical wastewater treatment. Evaluation showed that COD removal in the AOP step should reach 40% under that scenario.

Therefore, the Fe_3O_4-H_2O_2 reaction was carefully examined to find out whether it could meet the new requirement. Fig. 4b shows that consumed H_2O_2 was about 10 mg/L. Too much Fe_3O_4 and H_2O_2 did not enhance the COD removal, but increased the costs. This phenomenon showed that the Fe_3O_4/H_2O_2 process had some limitations. Experiments (data not reported) showed that the classic Fenton reaction could achieve 40% COD removal with 204 mg/L H_2O_2 and 336 mg/L Fe^{2+}, accompanied by sludge generation of 642 mg/L; which consumed too much H_2O_2 and formed too much iron sludge. Thus, Fe^{2+} was introduced into the Fe_3O_4/H_2O_2 system, in hope to enhance the COD removal efficiency and control the H_2O_2 consumption and sludge generation.

3.2.1. Combination of Fe^{2+} into Fe_3O_4-H_2O_2 process

Section 3.1 shows that in order to achieve 20% COD removal, the experimental condition for Fe_3O_4-H_2O_2 was pH of 3.0, Fe_3O_4 of 2.5 g/L, and H_2O_2 of 10 mg/L. In order to enhance the COD removal, higher H_2O_2 was needed. Analysis showed that for the Fe_3O_4-H_2O_2 system, with 40 mg/L Fe_3O_4-H_2O_2, only 9.82 mg/L was consumed and 30.18 mg/L remained in the system. The remained H_2O_2 could react with Fe^{2+} to form ·OH Eq. 1. Thus, Fe^{2+} of difference concentrations was introduced into the Fe_3O_4-H_2O_2 system to form a hybrid system. The corresponding results are shown in Fig. 5.

Fig. 5 shows that addition of Fe^{2+} could improve the COD removal efficiency. In the Fe_3O_4-H_2O_2 system, only 17.3% of H_2O_2 was consumed, which was low. Addition of Fe^{2+} significantly improved the H_2O_2 utilization efficiency. About 30 mg/L H_2O_2 was consumed with Fe^{2+} dosage of 50 mg/L and H_2O_2 was consumed completely with 100 mg/L Fe^{2+}. As a result, more ·OH was formed in the hybrid system, which benefited the pollutants degradation.

The best Fe^{2+} dosage was 34 mg/L and the highest COD removal reached 35.25%. Higher dosage of Fe^{2+} did not always favor the COD removal. When less Fe^{2+} was added, less ·OH was formed. With too much Fe^{2+}, H_2O_2 was consumed fast by Fe^{2+}, and the formed ·OH might react with the excess Fe^{2+}, as shown in Eq. (2) [22]. Such side effect decreased the ·OH utilization efficiency. Besides, excessive Fe^{2+} might be adsorbed on the Fe_3O_4 surface, which decreased effective reaction sites [22]. Meanwhile, excessive Fe^{2+} on the surface of Fe_3O_4 might lead to Fe^{2+} agglomeration, which acted as colloid and had negative effects on the reactivity of Fe_3O_4 [23]. Thus, COD removal efficiency was decreased. In a summary, Fe^{2+} could enhance COD removal efficiency, and the best dosage of Fe^{2+} was 34 mg/L. Further results showed that 1 h reaction achieve the same result as 2 h when Fe^{2+} was added in the system.

$$\cdot OH + Fe^{2+} \rightarrow Fe^{3+} + HO^{-} \tag{2}$$

3.2.2. The enhancement of Fe_0 and Fe^{2+} in Fe_3O_4–H_2O_2 process

Though the COD removal efficiency was improved by Fe^{2+}, as demonstrated in Fig. 6, it still did not meet the

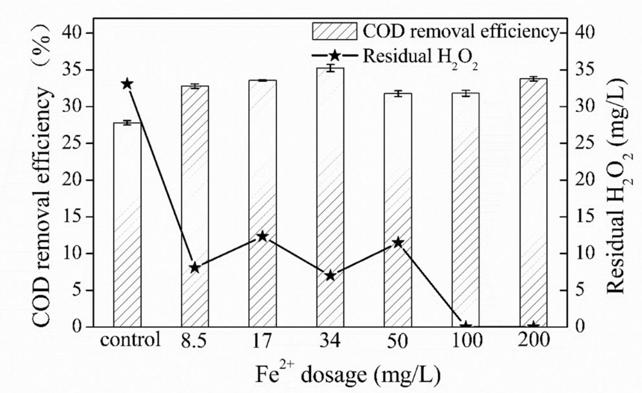
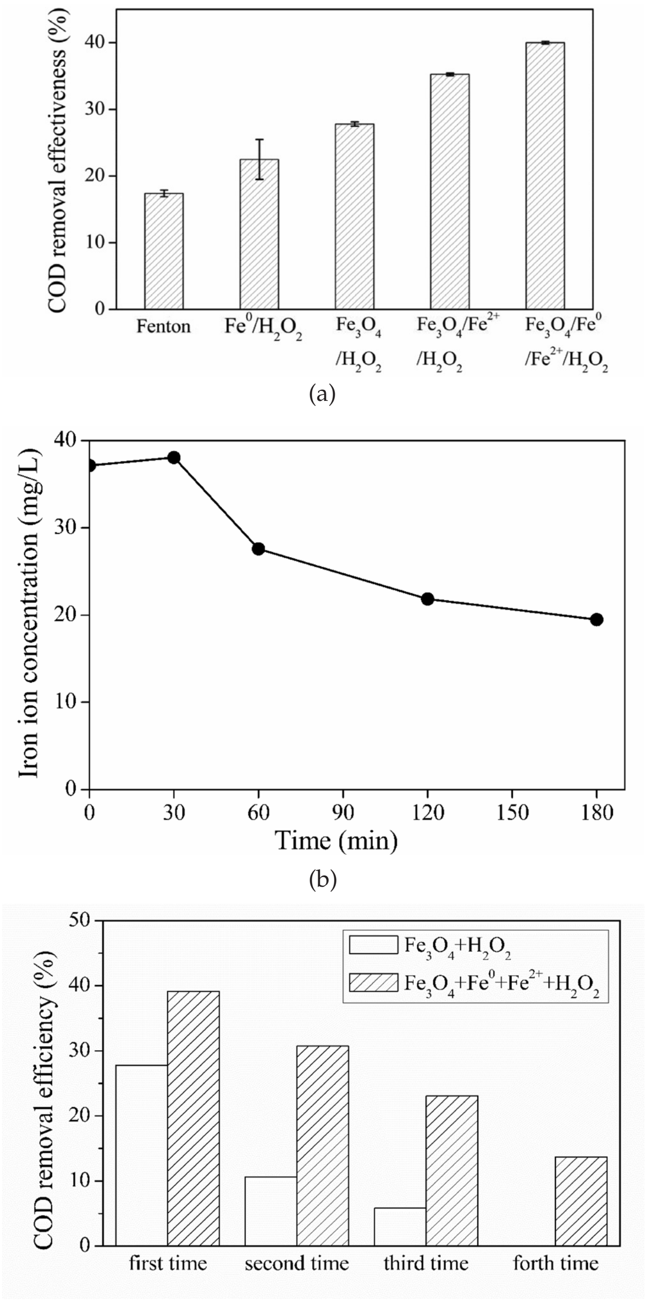


Fig. 5. COD removal efficiency in Fe_3O_4/Fe^{2+}/H_2O_2 system with different Fe^{2+} concentrations. Reaction conditions: Fe_3O_4 = 2.5 g/L, H_2O_2 = 40 mg/L, pH = 3, reaction time = 2 h.



(a)

(b)

(c)

Fig. 6. (a) Comparison of COD removal effectiveness in various Fenton-like systems; (b) iron ion changes; (c) Reusability of catalysts in Fe_3O_4 and $Fe_3O_4/Fe^0/Fe^{2+}$ Fenton-like systems. pH = 3, H_2O_2 = 40 mg/L; Fe_3O_4+ H_2O_2: Fe_3O_4 = 2.5 g/L, 2 h; Fe^0+ H_2O_2: Fe^0 = 0.23 g/L, 2 h; Fenton: Fe^{2+} = 55.7 mg/L, 30 min; Fe_3O_4+ Fe^{2+}+ H_2O_2: Fe_3O_4 = 0.83 g/L, Fe^{2+} = 37.13mg/L, 1 h; Fe_3O_4+ Fe^0+Fe^{2+}+ H_2O_2: Fe_3O_4 = 0.83 g/L, Fe^0 = 0.23 g/L, Fe^{2+} = 18.57 mg/L, 1 h.

requirement of 40%. As depicted in Fig. 2, COD removal in the Fe^0-H_2O_2 system was better than Fenton system. Fe^0 reduces pollutants in wastewater, and reacts with H_2O_2 to produce free radicals Eqs. (1), (3)–(6). The pharmaceutical wastewater might contain some oxidizing pollutants, which could be reduced by Fe^0. Thus, Fe^0 was introduced into the $Fe_3O_4/Fe^{2+}/H_2O_2$ system. This system was named as $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system. The results are summarized in Fig. 6. The final COD removal reached 40%, meeting the new requirement. Compared to all other systems, the $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system had obvious advantages on COD removal effectiveness.

Inducing Fe^0 into the hybrid system successfully enhanced the COD removal efficiency, as illustrated in Fig. 6a. Fe^0 is an efficient catalyst, it is the primary electron source for redox transformations in $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system [23]. Fe^0 reacts with H_2O_2 through two electron transfer under acidic conditions, as given in Eqs. (3) and (4). Dissolved oxygen can lead to Fe^0 corrosion and generate H_2O_2 in-situ Eq. (5) [24]. Fe^0 can also be dissolved by the reduction of Fe^{3+}, as shown in Eqs. (6) and (20). These formed Fe^{2+} went on further Fenton reaction and produced ·OH [25], which could enhance the homogeneous Fenton reaction.

$$Fe^0 + H_2O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O \tag{3}$$

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + 2H_2 \tag{4}$$

$$Fe^0 + O_2 + 2H^+ \rightarrow Fe^{2+} + 2H_2O_2 \tag{5}$$

$$Fe^0 + Fe^{3+} \rightarrow 3Fe^{2+} \tag{6}$$

In acidic conditions, Fe^0 and Fe_3O_4 released some iron ions into water, leading to iron ion concentration increase. As the same time, some iron ions were adsorbed on Fe^0 and Fe_3O_4 particles, formed the adsorbed iron ion. Data in Fig. 6b is the iron ion concentration after treatment of $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system. The ion concentration was stable in the first 30 min and then decreased as the adsorption was dominated. Klausen [26] demonstrated that Fe^{2+} adsorbed on iron oxides played an important role in the process of removing organic pollutants.

Fe^0 and Fe^{2+} not only could improve the COD removal efficiency, but also enhance the reusability of the catalyst Fe_3O_4. Fig. 6c showed that the reusability of $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system was also improved. After each test, the treated pharmaceutical wastewater was poured out, then new pharmaceutical wastewater was poured into the beaker with used catalysts. In the $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system, the COD removal efficiency was still above 20% after three times reuse. However, the COD removal efficiency was very low after three times reuse in the control system (Fe_3O_4-H_2O_2 system). The improvement of reusability was caused by continue dissolving of Fe^0 and forming Fe^{2+} in the $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system. The aggregation property of Fe^0 is poorer compared with Fe_3O_4, so Fe^0 might weaken the aggregation in the $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system. Meanwhile, the surface of Fe^0 probably was oxidized by dissolved oxygen and formed a layer of iron oxides, covered the surface of Fe^0. Thus, the COD removal efficiency decreased with increasing of reuse time.

To achieve 40% of COD removal, 204 mg/L H_2O_2 was needed in the classic Fenton system, which contributed to a large cost. Further, the classic Fenton process formed

641 mg/L iron sludge, which demanded very expensive disposal. Compared to the classic Fenton system, $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid Fenton-like system needed 40 mg/L H_2O_2 and formed 52.69 mg/L iron sludge, which greatly decreased the cost of H_2O_2 and treatment cost of iron sludge. Table 1 reports the cost of these two methods and found that the hybrid method could save 1.66 RMB/m^3-wastewater. For 1 m^3 of pharmaceutical wastewater, the hybrid method could save 0.66 RMB by reduced H_2O_2 and 1.00 RMB by decreased iron sludge disposal. Fig. 6c shows that $Fe_3O_4/Fe^0/Fe^{2+}$ could be reused for several times, so the cost could be further reduced by using the recycled catalysts.

In summary, to meet the current requirement, Fe_3O_4-H_2O_2 system could be used to replace the classic Fenton in use. The optimal conditions were Fe_3O_4 dosage = 1.0 g/L, pH = 3, H_2O_2 dosage = 10 mg/L, and reaction time = 2 h. In comparison to the classic Fenton's reaction used in the pharmaceutical manufactory (conditions in Fig. 2), the H_2O_2 consumption decreased by 75%, and the sludge was reduced 46.88%.

To meet the upcoming new local standard, a hybrid $Fe_3O_4/Fe^0/Fe^{2+}$-H_2O_2 system was proposed. Compared to the classic Fenton system, $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system greatly decreased the cost of H_2O_2 and treatment cost of iron sludge. Furthermore, the catalysts could be reused for several times.

4. Conclusions

Fe_3O_4-H_2O_2 system was very efficient for the advanced treatment of pharmaceutical wastewater. Crucial factors were inspected to determine their effects on the COD removal efficiency and the optimal conditions were found to be: Fe_3O_4 dosage = 1.0 g/L, pH = 3, H_2O_2 dosage = 10 mg/L, and reaction time = 2 h. The COD removal efficiency reached 28.87%, which met the current need of advanced treatment.

Further, in order to meet the upcoming local discharge standard, Fe^{2+} and Fe^0 were introduced into the Fe_3O_4-H_2O_2 system to form a hybrid $Fe_3O_4/Fe^0/Fe^{2+}$-H_2O_2 system. Addition of Fe^0 and Fe^{2+} could not only improve the COD removal efficiency and decrease the iron sludge, but also enhance the reusability of catalysts. Compared to the classic Fenton process, 80% H_2O_2 dosage was saved and 94% iron sludge was decreased, which meant that 1.66 RMB/m^3-wastewater was saved. Generally, $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid system was the most efficient system for pharmaceutical wastewater treatment.

Table 1
Cost comparison between Fenton and $Fe_3O_4/Fe^0/Fe^{2+}$ hybrid Fenton-like system

		Fenton system	$Fe_3O_4/Fe^0/Fe^{2+}$ hybrid Fenton-like system
H_2O_2	Price (RMB/ton)	1100–1300	
	Dosage (mg/L)	204	40
	Cost (RMB/ton)	0.82–0.96	0.16–0.19
Iron sludge	Treatment price (RMB/ton)	1700	
	Yield (g/ton)	642	52.69
	Cost (RMB/ton)	1.09	0.09
Total cost (RMB/ton)		1.91–2.05	0.25–0.28

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Supplementary Data

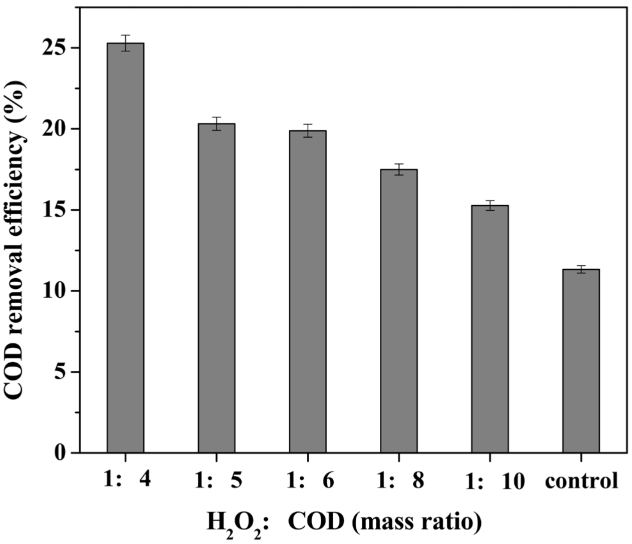

Fig. S1. H_2O_2 dosage optimization in treatment of pharmaceutical wastewater by Fe_0 Fenton-like process.

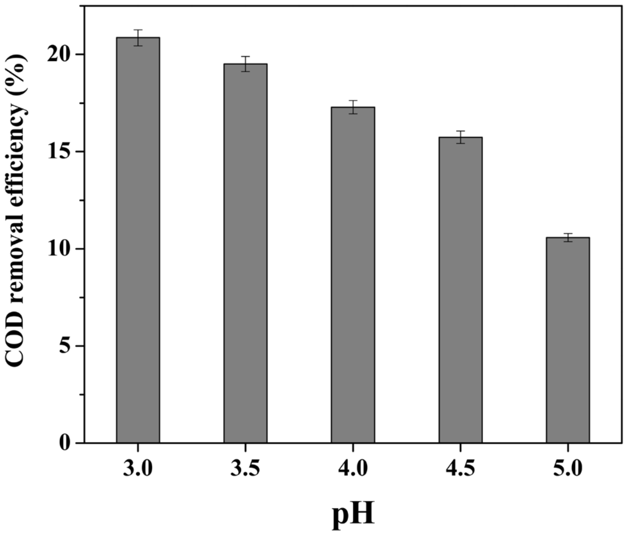

Fig. S3. pH optimization in treatment of pharmaceutical wastewater by Fe_0 Fenton-like process.

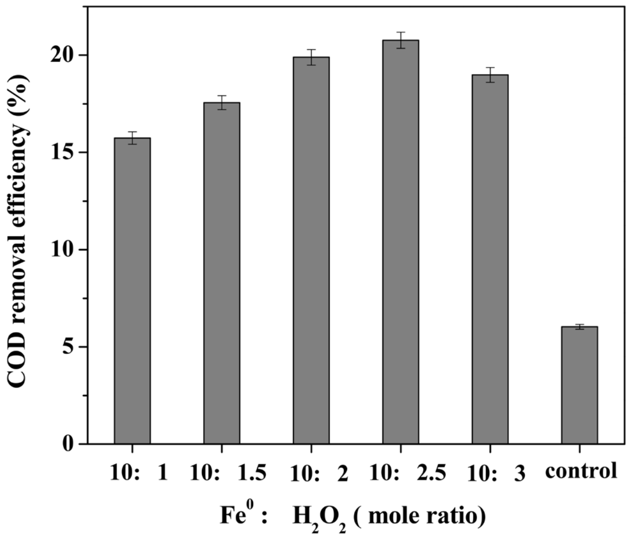

Fig. S2. Fe_0 dosage optimization in treatment of pharmaceutical wastewater by Fe_0 Fenton-like process.