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Efficiency and mechanism of ciprofloxacin hydrochloride degradation in wastewater by $\text{Fe}_3\text{O}_4/\text{Na}_2\text{S}_2\text{O}_8$

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ABSTRACT

The nanosized Fe_3O_4 catalyst was synthesized via a modified reverse coprecipitation method and characterized by means of a scanning electron microscope (SEM) and an X-ray diffraction (XRD) analysis instrument. The degradation efficiency and reaction rate of Fe_3O_4 in activating sodium persulfate used to degrade ciprofloxacin were determined from the catalyst dosage, oxidant concentration, and initial pH. The results showed that under the optimum conditions of a catalyst dosage of $2.0 \text{ g}\cdot\text{L}^{-1}$, a sodium persulfate concentration of $1.0 \text{ g}\cdot\text{L}^{-1}$, and an initial pH of 7, the degradation rate of ciprofloxacin was 93.73%, the removal rate of total organic carbon was 78%, and the first-order reaction constant was 0.06907 min^{-1} within 40 min. It was also demonstrated that the reactive oxygen species in the Fe_3O_4 /sodium persulfate catalytic system were mainly composed of $\text{SO}_4^{\cdot-}$ and supplemented by $\text{OH}\cdot$ and $\text{HO}_2\cdot$ using probe compounds such as ethanol, tertiary butanol, and benzoquinone.

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Catalytic Oxidation;
Ciprofloxacin Hydrochloride;
 Fe_3O_4 ; Sodium Persulfate

Introduction

Pharmaceutical wastewater usually contains complicated components and belongs to wastewater that is more difficult to process due to its high chemical oxygen demand (COD) concentration, high biotoxicity, and unfriendliness to biochemical degradation. Moreover, due to the inhibiting and toxic effects of pharmaceutical wastewater on microbial growth, methods such as traditional biotreatment and physical absorption, conventional physical and biological tools, cannot be performed technically and economically. As a result, an advanced oxidation technology based on free radical reactions emerged (Zhao et al. 2015).

Because of its mild reaction conditions and high reaction rate, the advanced oxidation technology has become a research hotspot. During the application of the traditional advanced oxidation technology, the Fenton reagent may generate hydroxyl radicals ($\text{OH}\cdot$), which have the following properties: huge consumption of H_2O_2 oxidant, low utilization, easy decomposition at room temperature, high transportation cost, and poor economic efficiency. In recent years, an advanced oxidation technology based on sulfate

radical $\text{SO}_4^{\cdot-}$ has caught more attention. It generates new sulfate radical $\text{SO}_4^{\cdot-}$ with high redox potential through activation of sulfate to remove organic pollutants (Sharma, Chen, and Zboril 2016; Hu et al. 2011; Sun et al. 2011). Sodium persulfate of high stability and low price has been widely used and since it is stable, its reaction rate with organic matters at room temperature is low, requiring acticarbon in practical applications. The ongoing research studies have been focused on inspecting the degradation effect and influence factors of the technology against specific substances by using multiple activation methods (heat, light, wave, transition metal, acticarbon etc.), but these methods have shortcomings such as high energy consumption or poor catalytic reproducibility (Wojciech and Konrad 2017). However, by replacing Fe^{2+} and other transition metal elements with iron oxides, the organic matters can not only be effectively degraded but also be easily recycled (Xue et al. 2009). And Fe_3O_4 , with its unique paramagnetism, greatly simplifies the separation and recycling steps of the catalyst, facilitating the promotion and application of the experiment (Silveira, Garcia-Costa, and Cardoso 2017; Yan et al. 2011).

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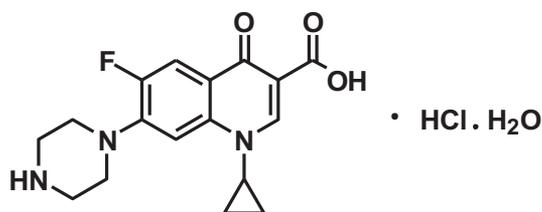


Figure 1. Ciprofloxacin hydrochloride (CIP) molecular structure.

Ciprofloxacin hydrochloride (CIP) is one of the broad-spectrum quinolone antibacterial agents, with its antibacterial properties ranking the highest among currently applied quinolone antibiotics. But, with its high ecological toxicity and the difficulty in removing it by conventional water treatment technologies, it poses certain threats to the ecosystem (Ouyang et al. 2017; Maryam et al. 2017; Zhao et al., 2015). Owing to its low solubility, ciprofloxacin is usually made into ciprofloxacin hydrochloride. Ciprofloxacin hydrochloride is a white or light yellow crystalline powder, soluble in water, slightly soluble in methyl alcohol, very slightly soluble in ethanol, and hardly soluble in chloroform. Its solubility in water (25 °C) is 10 g/L (Mizukoshi et al. 2009). The molecular structure of ciprofloxacin hydrochloride is Figure 1.

In this paper, a nanosized Fe₃O₄ catalyst was synthesized through an improved reverse coprecipitation, and Fe₃O₄-activating sodium persulfate was proposed to be employed to degrade ciprofloxacin-based pharmaceutical wastewater; much exploration had been done as to whether the factors such as the dosage of Fe₃O₄, initial concentration of sodium persulfate, and initial pH of the solution had influence on the degradation efficiency and reaction rate, providing references for the engineering application of advanced oxidation technologies in the treatment of ciprofloxacin-based pharmaceutical wastewater.

Materials and methods

Experiment reagents and instruments

Reagents

Ciprofloxacin hydrochloride, sodium persulfate, ferric trichloride hexahydrate, absolute ethyl alcohol, ferrous sulfate tetrahydrate, ammonium hydroxide, sulfuric acid, sodium hydroxide, tertiary butanol, sodium thiosulfate, and benzoquinone were purchased from Aladdin with analytical reagents. All the solutions in the experiments were prepared with ultrapure water.

Instruments

UV-5200 ultraviolet and visible spectrophotometer, thermal-arrest constant-temperature heating magnetic

stirrer, AL204 electronic balance, DELTA-320 pH meter, DZF-6020 vacuum drying oven, supersonic cleaner, high-speed desktop centrifuge, Hitachi S-4800 scanning electron microscope, and D8 advance X-ray diffraction analysis instrument were used.

Catalyst preparation

Fe₃O₄ nanoparticles were prepared through the improved reverse coprecipitation method. The specific preparation methods are as follows:

FeSO₄ · 4H₂O and FeCl₃ · 6H₂O with a molar ratio of 2:1 were dissolved in 50 ml of deoxygenated water, respectively. To prevent the oxidation of Fe₃O₄ during preparation as much as possible, deoxygenated water was used for preparation, i.e., ultrapure water was boiled for 20 min and then cooled to room temperature in an N₂ atmosphere. A drop of 0.01 mol·L⁻¹ HCl was added to prevent iron ions from hydrolysis. The above two solutions were mixed and heated to 70 °C. The Fe(II)/Fe(III) mixed solution was slowly added dropwise to the 40 ml 3.0 mol·L⁻¹ ammonia solution and put aside for 2-h aging after a 1-h ultrasonic reaction. The prepared Fe₃O₄ nanoparticles were collected by the magnet and washed with deionized water and absolute ethyl alcohol several times. After 6-h vacuum drying at 40 °C, they were taken out for grinding before the Fe₃O₄ nanoparticles were obtained (Chang et al. 2009).

Characterization and analysis of the catalyst

The crystal structure of the samples was determined with a D8 advance X-ray diffractometer. The test conditions were: Cu target, graphite monochromator, with a voltage of 40 kV and a current of 200 mA, a scanning speed of 8°/min, a scanning scope of 10–80°; a Hitachi S-4800 scanning electron microscope was used to observe the surface appearance of the catalyst.

Research on the degradation of ciprofloxacin wastewater

The concentration of ciprofloxacin hydrochloride was determined depending on the distinct absorption peak at a wavelength of 277 nm through the establishment of a standard curve.

The removal rate of ciprofloxacin was the basis for catalytic performance evaluation and the specific experimental procedures were as follows: 100 mL ciprofloxacin solution of a certain concentration was put into a conical flask and added with a certain amount of catalyst. Magnetic stirring was performed to enable the preabsorption of the catalyst with pollutants for 30 min. The postabsorption concentration of pollutants was treated as the zero

concentration. With the addition of sodium persulfate, the diluted NaOH solution or diluted H₂SO₄ was used to regulate the pH value of the solution. At regular intervals, a 1-mL sample was taken, and 1 mL ethanol was added to it for quenching, and then it was shaken up and placed in a desktop centrifuge for 10000 r·min⁻¹ centrifugation for 5 min. Spectrophotometry was adopted to determine the residual concentration of ciprofloxacin (determination wavelength 277 nm).

Results and discussion

Analysis and characterization of the physicochemical properties of catalyst Fe₃O₄

Figure 2 shows the XRD pattern of nanosized Fe₃O₄ prepared via a reverse coprecipitation method. The

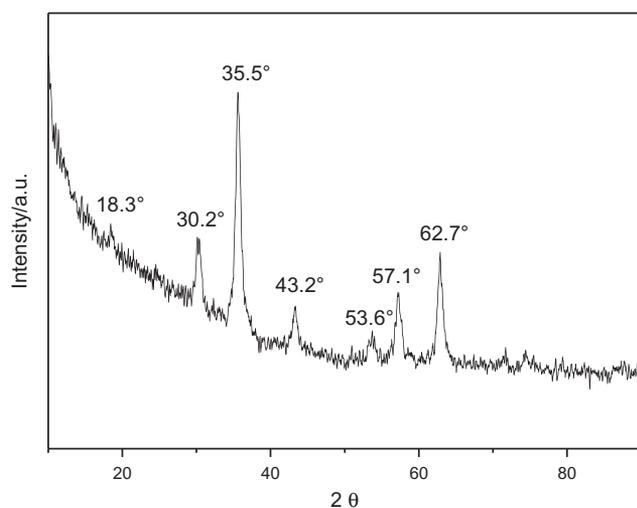


Figure 2. XRD pattern of the Fe₃O₄ catalyst.

pattern is consistent with the diffraction card of (JCPDS File No. 88-0315) standard Fe₃O₄. The characteristic diffraction peaks at 2θ values of 18.3°, 30.2°, 35.5°, 43.2°, 53.6°, 57.1°, and 62.7°, respectively, correspond to the (111), (220), (311), (400), (422), (511), (440), and (531) crystal facets of Fe₃O₄. The characteristic diffraction peaks of Fe₂O₃ were not observed in the pattern, indicating that the products were pure-phase Fe₃O₄, featured by an inverse spinel-type structure (Mizukoshi, Shuto, and Masahashi et al. 2009).

Figure 3 shows the SEM image of catalyst Fe₃O₄, and it can be seen that the particle size was evenly distributed and well dispersed, without significant agglomeration.

Effect of the Fe₃O₄/PM system on degrading ciprofloxacin hydrochloride wastewater

The changes in ciprofloxacin hydrochloride wastewater in relation to time under different conditions are shown in Figure 4. As indicated by the experimental results, Fe₃O₄ or PM alone could hardly degrade ciprofloxacin. Only when Fe₃O₄ and PM were coexistent, ciprofloxacin was almost completely degraded in 40 min, indicating that Fe₃O₄ and PM have a synergistic catalytic effect. After a 40-min reaction, the total dissolution amount of Fe²⁺ was 0.66 mg/L. The ciprofloxacin degradation rate was 11.65% with the same dissolution of Fe²⁺ in the Fe²⁺/PM system, which was much lower than the effects of the Fe₃O₄/PM system, indicating that the catalysis was mainly performed by heterogeneous catalysts themselves.

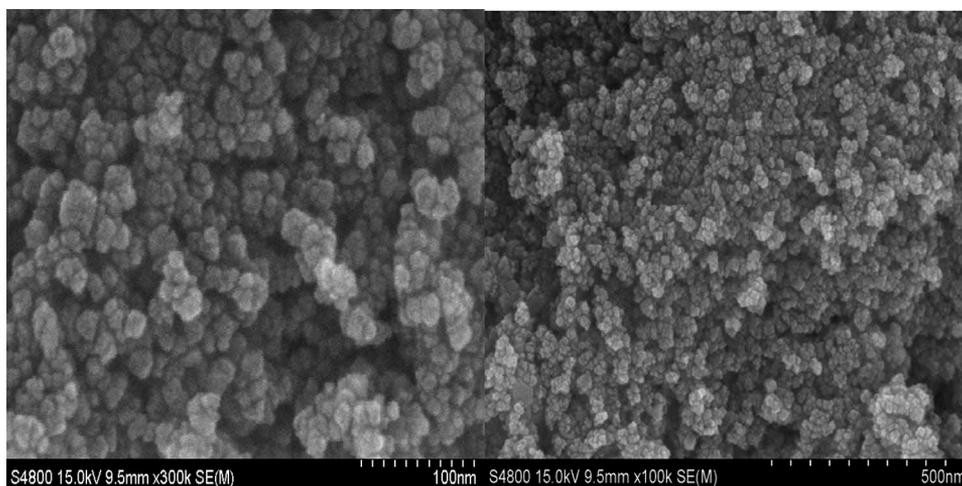


Figure 3. Typical SEM image of the Fe₃O₄ catalyst.

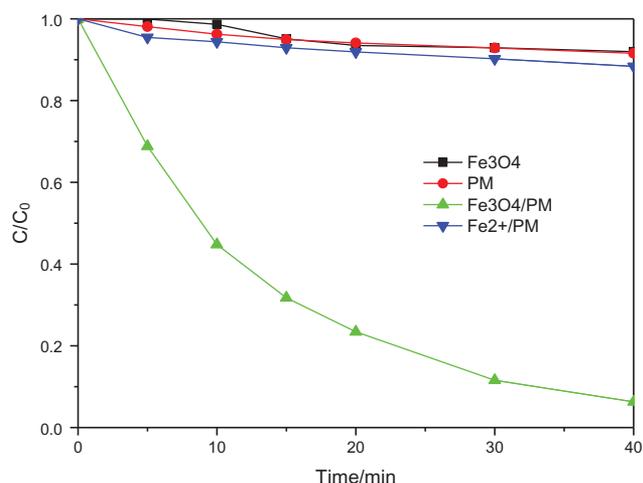


Figure 4. Effect of Fe₃O₄, PM, Fe₃O₄/PM, and Fe²⁺/PM technology degradation pollutant.

Impact of the initial pH value on the degradation of ciprofloxacin hydrochloride wastewater

It can be learned from Figure 5 (a) that when the pH was 2, 3, 4, 5, 7, 9, and 11, the degradation of ciprofloxacin hydrochloride wastewater was 26.76%, 45.67%, 56.85%, 69.64%, 93.73%, 64.58%, and 36.68% separately. This implies that under neutral conditions, the Fe₃O₄/PM system has the highest removal rate against ciprofloxacin. Neither acidic nor alkaline conditions are the best for CIP degradation. When the pH value was high, the sulfate radicals under alkaline conditions might react with hydroxyl ions, consuming the SO₄^{-•} in water and generating OH⁻. OH⁻ had less oxidation capacity than SO₄^{-•}, so under alkaline conditions, the oxidative degradation capacity of Fe₃O₄/PM was impaired more visibly

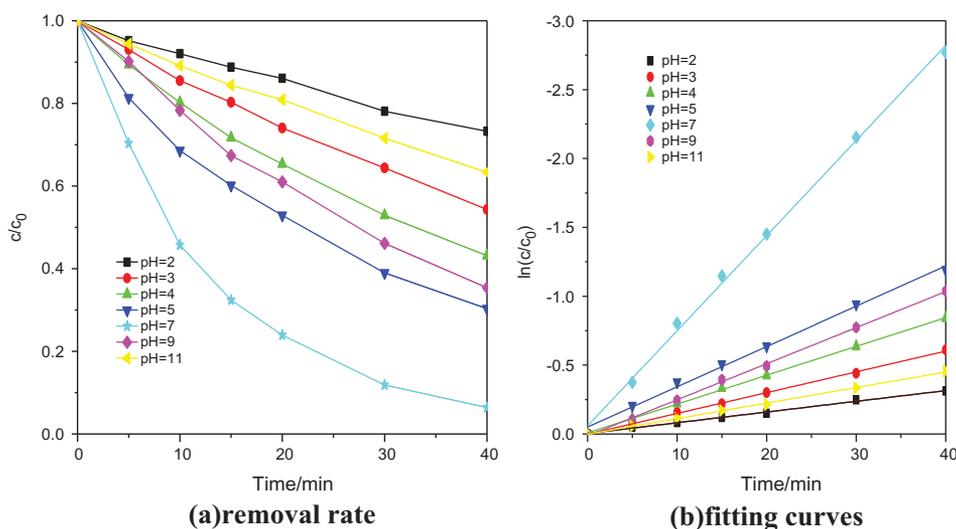


Figure 5. Effect of pH on the degradation efficiency of CIP (Na₂S₂O₈: 1 g/L; CIP: 50 mg/L; Fe₃O₄: 2 g/L; pH: 7.0; 25°C).

(Yan et al. 2017; Chen et al. 2017; George, Rassy, and Chovelon 2001; Maurino et al. 1997).

It can be learned from Figure 5 (b) and Table 1 that $\ln(C_t/C_0)$ was in a good linear relationship with time t , and the linear fitting coefficient R^2 was high, well demonstrating the features of first-order kinetics. The pH changes of the solution exerted a distinct influence on the reaction. When the pH was 2, the reaction rate was 0.00778 min⁻¹ and along with a gradual increase of pH, the reaction was faster; when the pH was 7, the reaction was the fastest, with a reaction rate of 0.06907 min⁻¹; then, with decreasing pH, the reaction slowed down and when the pH was 11, the reaction rate was only 0.01128 min⁻¹.

Impact of sodium persulfate concentration on the degradation of ciprofloxacin hydrochloride wastewater

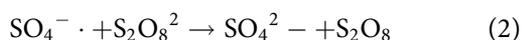
It can be seen from Figure 6 (a) that when the dosage of sodium persulfate increased from 0.1 to 2.0 g·L⁻¹, the increasing oxidants would provide more free radicals for the system and after a 40-min reaction, the removal rate of ciprofloxacin hydrochloride was raised from 69.68% to 93.73%.

It can be seen from Figure 6 (a) and Table 2 that $\ln(C_t/C_0)$ was in a good linear relationship with time t , and the linear fitting coefficient R^2 was high, well demonstrating the features of first-order kinetics. Within 40 min, when the dosage of sodium persulfate was raised from 0.1 to 1.0 g·L⁻¹, the reaction rate of ciprofloxacin hydrochloride was raised from 0.00284 to 0.06907 min⁻¹. The more the dosage of sodium persulfate, the greater the mass-transfer power of catalysis on the catalyst surface. And more and

Table 1. Kinetic parameters of CIP by Fe₃O₄ at different pH.

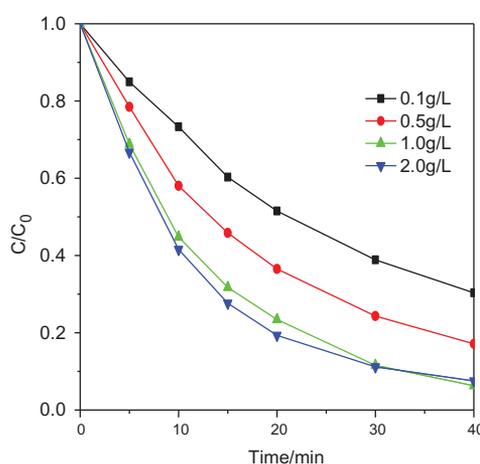
Initial pH	Pseudo-first-order reaction kinetic mode	Correlation R ²
2	$\ln(C_t/C_0) = -(0.00396 + 0.00778t)$	0.996
3	$\ln(C_t/C_0) = -(-0.00155 + 0.01508t)$	0.999
4	$\ln(C_t/C_0) = -(0.00396 + 0.00778t)$	0.996
5	$\ln(C_t/C_0) = -(0.05016 + 0.02925t)$	0.994
7	$\ln(C_t/C_0) = -(0.05871 + 0.06907t)$	0.997
9	$\ln(C_t/C_0) = -(0.01337 + 0.02618t)$	0.999
11	$\ln(C_t/C_0) = -(-0.00113 + 0.01128t)$	0.998

more SO₄⁻· would be generated so as to enhance the reaction rate and catalytic degradation effect of ciprofloxacin hydrochloride. However, since the concentration of nano-sized Fe₃O₄ in the solution was a constant value and only a certain amount of sodium persulfate could be activated, after the concentration of sodium persulfate in the solution exceeded 1.0 g·L⁻¹, the degradation rate of ciprofloxacin showed a downward trend instead. The reason was that, along with the increased concentration of SO₄⁻· in the reaction system, the amount consumed by its own reaction also increased (formula 1 and formula 2), leading to the decreased degradation rate of ciprofloxacin.



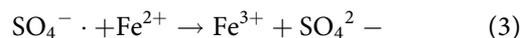
Impact of Fe₃O₄ dosage on the degradation of ciprofloxacin hydrochloride wastewater

Figure 7 (a) shows that when the dosages of the catalyst were, respectively, 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0g·L⁻¹, after a 40-min reaction, the removal rates of ciprofloxacin

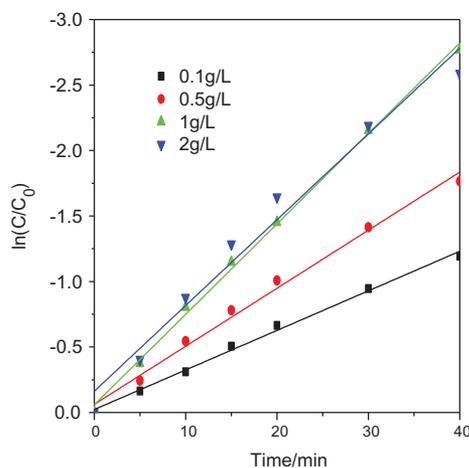
**(a)removal rate****Table 2.** Kinetic parameters of CIP by Fe₃O₄ at different Na₂S₂O₈ concentration.

Na ₂ S ₂ O ₈ concentration (g/L)	Pseudo-first-order reaction kinetic mode	Correlation R ²
0.1	$\ln(C_t/C_0) = -(0.02242 + 0.03021t)$	0.995
0.5	$\ln(C_t/C_0) = -(0.06191 + 0.04433t)$	0.990
1	$\ln(C_t/C_0) = -(0.05871 + 0.06907t)$	0.997
2	$\ln(C_t/C_0) = -(0.02242 + 0.03021t)$	0.971

hydrochloride were, respectively, 51.97%, 70.69%, 83.93%, 93.73%, 92.49%, and 93.12%. It shows that along with the increased dosage of Fe₃O₄, the removal rate of ciprofloxacin was accordingly raised, mainly because the increased dosage of the catalyst could increase the contact area between the catalyst and sodium persulfate, and more active sites participated in the reaction to generate more SO₄⁻· in catalysis and, therefore, enhance the removal rate of the system. When the consumption of the catalyst exceeded 2.0 g·L⁻¹, there was no significant increase in the removal rate, or even a decrease instead. On one hand, with a constant dosage of sodium persulfate, the generation amount of SO₄⁻· would not increase when a certain degree was reached, and the excessive SO₄⁻· would be consumed by its own quenching reaction; on the other hand, Fe²⁺ on its surface of excessive nano-sized Fe₃O₄ would also react with SO₄⁻·. These two side reactions would prevent SO₄⁻· from further contact with ciprofloxacin, so the degradation rate was reduced (Long et al. 2016; Silveira et al. 2017; Guan et al. 2011).



From Figure 7 (a) and Table 3, it can be concluded that (C_t/C₀) was in a good linear relationship with time

**(b)fitting curves****Figure 6.** Effect of Na₂S₂O₈ concentration on the degradation efficiency of CIP (Na₂S₂O₈: 1 g/L; CIP: 50 mg/L; Fe₃O₄: 2 g/L; pH: 7.0; 25°C).

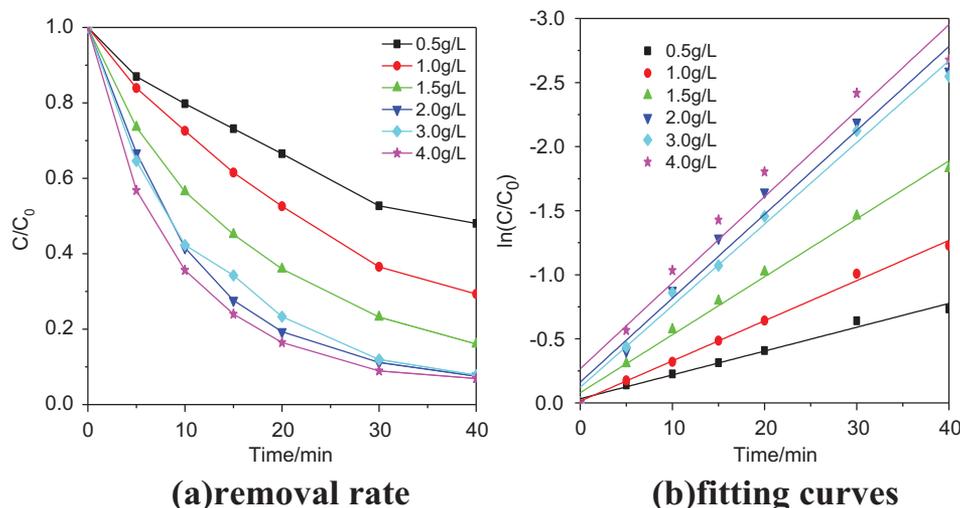


Figure 7. Effect of catalyst dosage on the degradation efficiency of CIP ($\text{Na}_2\text{S}_2\text{O}_8$: 1 g/L; CIP: 50 mg/L; Fe_3O_4 : 2 g/L; pH: 7.0; 25°C).

Table 3. Kinetic parameters of CIP by Fe_3O_4 at different catalyst dosages.

Catalyst dosage (g/L)	Pseudo-first-order reaction kinetic mode	Correlation R^2
0.5	$\ln(C_t/C_0) = -(0.03271 + 0.01859t)$	0.984
1	$\ln(C_t/C_0) = -(0.01412 + 0.03134t)$	0.995
1.5	$\ln(C_t/C_0) = -(0.07971 + 0.04524t)$	0.993
2	$\ln(C_t/C_0) = -(0.05871 + 0.06907t)$	0.997
3	$\ln(C_t/C_0) = -(0.1218 + 0.06369t)$	0.987
4	$\ln(C_t/C_0) = -(0.2664 + 0.06714t)$	0.949

t , and the linear fitting coefficient R^2 was high, well demonstrating the features of first-order kinetics. When the dosage of the catalyst was 0.5 $\text{g}\cdot\text{L}^{-1}$, the reaction rate of ciprofloxacin hydrochloride was only 0.01859 min^{-1} ; when the dosage of the catalyst was raised to 1.5 and 2.0 $\text{g}\cdot\text{L}^{-1}$, the reaction rate was raised to 0.04524 and 0.06907 min^{-1} . This indicates that the reaction rate would be raised along with the increased dosage of the catalyst.

Reaction mechanism

Under the conditions of catalyst consumption of 2 g/L, an oxidant concentration of 1 g/L, and pH of 7, 93.73% of 50 mg/L ciprofloxacin was degraded after a 40-min reaction. The total organic carbon test results showed that 78% organic matters were removed, indicating that ciprofloxacin was mostly decomposed into low-molecular weight organic matters.

To verify the radical type of Fe_3O_4 /sodium persulfate, a free radical quenching experiment was conducted by adding a certain amount of ethanol, tertiary butanol, and benzoquinone. The reaction rates of ethanol with the two free radicals, $\text{SO}_4^{\cdot-}$ and OH^{\cdot} , were basically the same. The reaction between tertiary

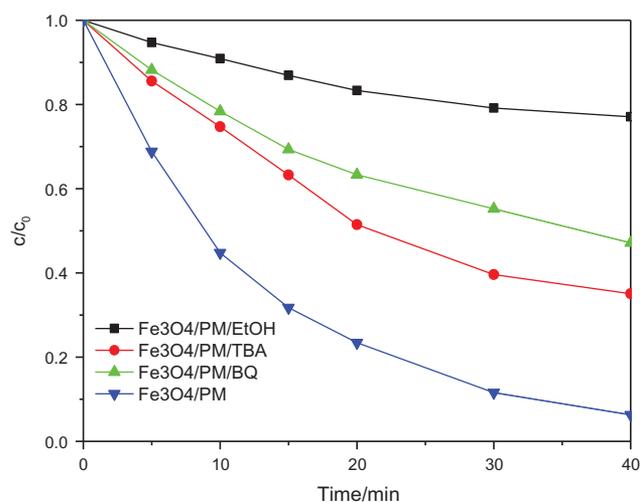


Figure 8. CIP degradation rate by activation of PM with and without radical scavengers of EtOH, TBA, and BQ ($\text{Na}_2\text{S}_2\text{O}_8$: 1 g/L; CIP: 50 mg/L; Fe_3O_4 : 2 g/L; MeOH: 10 mmol/L; TBA: 10 mmol/L; BQ: 10 mmol/L; pH: 7.0; 25°C).

butanol and OH^{\cdot} was faster while the combination of benzoquinone and HO_2^{\cdot} was faster (Muthukumari et al. 2009; Luo et al. 2010).

Figure 8 shows an experimental curve of free radical quenching in the Fe_3O_4 system catalyzing sodium persulfate for CIP degradation. When TBA was added to the system, the removal rate of CIP was reduced from 93.73% to 64.96% in 40 min. This indicates that OH^{\cdot} existed in the system, but the content was not much; when excessive EtOH was added, the removal rate of CIP was 22.92%, remarkably lower than when nothing was added. The reason was that EtOH reacted with OH^{\cdot} and $\text{SO}_4^{\cdot-}$ in the system, so that the content of free radicals participating in CIP degradation was reduced;

and compared with TBA, the removal rate of CIP has great difference, indicating that $\text{SO}_4^{\cdot-}$ in the reaction system played a dominant role in CIP degradation. Moreover, after the addition of excessive EtOH, the system still can effectively remove ciprofloxacin to some degree. After the trapping agent, benzoquinone of superoxide radicals (HO_2^{\cdot}), was added during the experiment, the removal rate of ciprofloxacin in the reaction system was decreased, demonstrating that the mechanism of Fe_3O_4 activating persulfate (PS) was that Fe_3O_4 generated superoxide radicals (HO_2^{\cdot}) which could activate PS to produce more sulfate radicals ($\text{SO}_4^{\cdot-}$), helping in the degradation of organic matters (Fang et al. 2013).

Conclusions

- (1) For ciprofloxacin hydrochloride wastewater with an initial concentration of 50 mg/L, under the conditions of a catalyst dosage of 2.0 g·L⁻¹, a sodium persulfate dosage of 1.0 g·L⁻¹, pH of 7, and room temperature of 25°, the degradation rate and reaction rate of ciprofloxacin hydrochloride reached the highest level, 93.73% and 0.6907 min⁻¹, respectively.
- (2) The catalysis of Fe_3O_4 /sodium persulfate is based on a solid-liquid interfacial reaction. Increasing the dosages of sodium persulfate and the catalyst could effectively enhance the removal rate and reaction rate of ciprofloxacin hydrochloride.
- (3) The reactive oxygen species in the Fe_3O_4 /sodium persulfate catalytic system was mainly composed of sulfate radicals ($\text{SO}_4^{\cdot-}$), supplemented by hydroxyl radicals (OH^{\cdot}) and superoxide radicals (HO_2^{\cdot}), and can be used to degrade ciprofloxacin through oxidation.

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