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Enhanced Catalytic Degradation of Ciprofloxacin by Iron-doped Hydroxyapatite

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Abstract: In order to solve the problems in the iron-based Fenton-like catalytic oxidation system, a green, safe, efficient and stable Fe-hydroxyapatite (HAP) catalyst was developed and prepared for the Fenton-like catalytic oxidation reaction system in this study. We constructed the Fe-HAP /hydrogen peroxide system, systematically evaluated the synergistic effect between the Fe-HAP catalyst and hydrogen peroxide, and investigated the effect of the Fenton-like catalytic oxidation system on the removal of Ciprofloxacin(CIP), a hard-to-degrade antibiotic organic pollutant. We investigated the effect of this Fenton catalytic oxidation system on the removal of CIP, a difficult-to-degrade antibiotic organic pollutant, and revealed the mechanism of the reaction system and the main mechanism of the degradation of CIP. We also applied this catalyst material to the actual water body and explored the value of the application of this system, which provided scientific basis and reference value for the subsequent development of more efficient, stable, green and safe catalyst materials.

Keywords: Fenton-like Catalytic; Fe-hydroxyapatite; Ciprofloxacin.

1. Introduction

With the rapid development of the health and wellness industry, and due to the continuation of epidemics in recent years, the production and use of antibiotics has increased dramatically, which has led to the generation of large quantities of antibiotic wastewater [1,2]. Antibiotics in the protection of human life safety and health at the same time, a large proportion of antibiotics in the form of the initial molecular structure or hydrolyzed molecules into the wastewater treatment process, which is a catastrophic problem for the biological treatment system in the wastewater treatment process, it will inhibit microbial growth and thus lead to the deterioration of the effluent water quality[4,5]. Conventional wastewater treatment systems are not able to remove most of the antibiotics, which results in a portion of the antibiotics entering the soil and water bodies in various ways and re-entering the environmental water cycle[6]. Usually, various pollutants and antibiotics in water bodies coexist with each other, and they may form new types of composite pollutants through various interactions, and the resulting composite pollutants may have an effect on the morphology, structure, and biotoxicity of antibiotics[7,8]. The presence of antibiotics and their hydrolysis or metabolites in water bodies can easily induce the production of resistance genes, which will spread through the food chain in the environment, and ultimately cause cumulative toxic effects on organisms and humans, thus threatening biological and human health and safety[9]. Therefore, antibiotic contamination has become an urgent problem in the process of water treatment, and the treatment of antibiotic contamination in water bodies has also become one of the hot issues that scholars have been keen to study in recent years[10,11].

Due to the continuous innovation of technology and after years of research, various branches of advanced oxidation technology have been developed, including Fenton catalysis, photocatalysis, electrocatalysis and peroxynitrite-based catalytic oxidation, etc[12,13]. Among the many advanced catalytic oxidation technologies, Fenton catalysis stands out[14]. Hydrogen peroxide (H_2O_2) is a strong oxidizing agent with a redox potential of 1.78 eV, and the degradation effect of hydrogen peroxide by direct reaction with organic pollutants is very poor and the reaction rate is very low. Hydrogen peroxide can be sulfated, transition metals (e.g. Fe^{2+}, Cu^{2+}, Co^{2+}, Ag^{+}, etc.), alkali, heat, ultrasound and other activation, forming hydroxyl radicals with higher redox potentials, which are extremely oxidizing and can theoretically degrade and mineralize most organic pollutants[15]. Compared with other methods, Fenton catalysis improves the generation of hydroxyl radicals and reduces secondary pollution, which has a broader application prospect in antibiotic wastewater treatment. In recent years, domestic and foreign research in the use of Fenton catalytic oxidation technology to treat antibiotics in sewage wastewater has developed vigorously[16,17].

In recent years, more research and practice have been carried out on the use of Fenton catalytic technology to treat antibiotics in wastewater, focusing mainly on the joint use of Fenton catalytic oxidation technology and other technologies, the study of the removal effect of antibiotics and the factors affecting it, and exploring the degradation mechanism, etc, and there have been preliminary research results on the application of removing a variety of typical antibiotics in water, but these technologies are still faced with problems such as pH range of application is not wide, the catalyst recovery is difficult, and the catalyst activity is low, resulting in poor antibiotic removal effect[18]. Therefore, the development of a new efficient and stable Fenton-like catalyst is of great significance for water environmental protection[19,20].

Based on this, this experiment takes the antibiotic CIP (CIP), which exists in large quantities in the aquatic environment, as the target pollutant, and removes the experimentally formulated CIP solution through the preparation of a highly efficient and stable catalyst for the

Fenton-like reaction, and manually adjusts the experiments to achieve the optimal degradation efficiency, to explore the effects of the reaction system and the various influences on the target pollutant, and to explore the catalysts on the surface reaction mechanism of the target pollutant and the degradation mechanism.

2. Experimental

2.1. Synthesis of Catalysts

Fe-HAP was prepared by hydrothermal method. First, Calcium chloride, ferrous chloride and sodium hydroxide were used as raw materials, ethanol and oleic acid were added to synthesize the precursor solution under magnetic stirring. The product was separated by centrifugation, washed with Ultra-pure water and ethanol several times, and dried at 60℃. The product was used with the parent reaction solution for the subsequent catalyst synthesis. Sodium dihydrogen phosphate was added dropwise to the precursor solution, then transferred to an autoclave and heated at 180°C for 9 h. The product was collected by centrifugation after cooling to room temperature, washed with Ultra-pure water and ethanol several times, and dried at 60℃. The product was dispersed in ethanol, extracted and filtered, washed several times with ethanol and ultra-pure water, and dried at 60°C. The synthesized sample was denoted as Fe-HAP[21]. HAP was also synthesized without the addition of ferrous chloride as described above.

2.2. Characterization

The morphology and elemental composition of the catalyst was observed by using a field emission scanning electron microscope (FESEM, Hitachi SU8020), and the energy dispersion spectrum was scanned to detect the distribution of elements in the sample. The high resolution transmission electron microscopy (HRTEM) images of the samples were obtained using a FEI Tecnai G2 F20 TEM with an acceleration voltage of 200 kV. The structure and composition of the catalysts were characterized using powder X-ray diffraction (XRD) with a Scintag-XDS-2000 diffractometer (40kV, 40mA, 5°min^{-1} from 5° to 90°. The Brunauer-Emmett-Teller (BET) surface area of catalyst samples were determined by nitrogen adsorption/desorption experiments using a surface area and porosity analyzer (ASAP 2460). Fourier transform infrared (FTIR, Nicolet 8700) spectra were recorded to determine the surface functional groups of materials. The H_2O_2 concentration were acquired on an ultraviolet-visible spectrophotometer (UV-vis, Hitachi UV-3010). The composition and valence states of surface elements were recorded by X-ray photoelectron spectroscopy (XPS, AXIS-Ultra XPS) with Al Kα as the source (225 W, 15 kV, 15 mA). To compensate for surface charge effects, binding energies were calibrated using the C1s hydrocarbon peak at 284.8 eV. Ultra high-performance liquid chromatography & quadrupole time-of-flight mass spectrometer (UPLC-QTOF-MS) was used to analyze CIP intermediates. The electron spin resonance spectrometer (ESR, Bruker model ESP 300E) was used to determine the generation of radicals and non-radicals in the reaction system.

2.3. Procedures and Analysis

CIP (0.01mM) was selected as the target pollutant to evaluate the catalytic activity of the catalysts. Unless indicated otherwise, the optimal dosages of catalysts (1.0g L^{-1}) and H_2O_2 (10mM) were determined in view of the best performance and cost, and used for all the experiments. In the experiment, 1.0g L^{-1} of catalyst powders were added into pollutant aqueous solution and magnetically stirred for 60 min to establish an adsorption/desorption equilibrium. Then, 10mM of H_2O_2 was added into the above solution as oxidant under continuous stirring. At certain time intervals, 1mL of pollutant solution was immediately collected and filtered through 0.45μm Millipore filter for the next analysis. Subsequently, the samples were analyzed by high performance liquid chromatography (HPLC, 1200series; Agilent Santa Clara, CA) with Zorbax SB-Aq column (5μm, 4.6×250 mm). The total organic carbon (TOC) during the degradation of organic pollutants was analyzed using a Shimadzu TOC-VCPH analyzer. The leaching of metallic ions was detected by inductively coupled plasma-optical emission spectrometry (ICP-OES, OPTIMA 8300). The effect of initial pH on degradation of CIP, which was adjusted using 0.2M HCl or 0.2M NaOH solution, was detected under similar reaction conditions[22].

For the identification of CIP degradation intermediates in Fe-HAP suspension, sample solutions at different time points were filtered and the filtrates were concentrated by solid phase extraction (SPE) method consisting of an Oasis HLB hydrophilic-lipophilic cartridges (200mg/6mL) (Waters Oasis). The cartridges were initially conditioned with 4mL of methanol and 4mL of ultra-pure water. Then, 50mL sample solutions were loaded onto the cartridges at a 15mL min^{-1} flow rate. The compounds were eluted off the cartridges with 5 mL methanol and 5 mL ultra-pure water. The eluate was evaporated to 1 mL under a gentle stream of nitrogen, resulting in 50-fold concentration of analytes. The samples after concentration were analyzed by ultra high-performance liquid chromatography & quadrupole time-of-flight mass spectrometer (ACQUITY UPLC/Xevo G2 Q-TOF, Waters), using electrospray ionization (ESI) in positive mode. An ACQUITY UPLC® HSS T3 column (1.8 μm, 2.1 × 50 mm) was used with a mobile phase containing water (0.1% formic acid) as eluent A and acetonitrile (0.1% formic acid) as eluent B. The linear gradient was from 5% B to 70% B in 20 min, 70% B to 95% B in 20-22 min, and then kept isocratic up to 28 min.

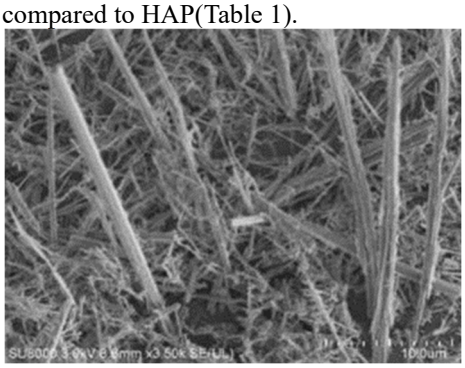
To test the stability and recyclability of Fe-HAP, the catalyst was filtered, washed with ultra-pure water thoroughly, and dried at 60℃ for reuse under similar experimental conditions. This process was repeated five times [23].

3. Results and Discussion

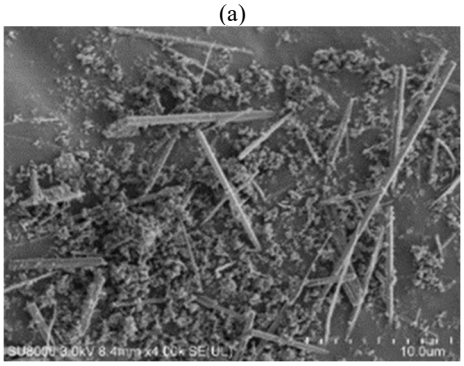
3.1. Characterization of Catalysts

In order to study the morphology and microstructure of the prepared catalyst materials, SEM examination of the homemade HAP and Fe-HAP catalysts was carried out in this study. The SEM images are shown in Fig.1.The SEM images show that the structure of the homemade HAP in accordance with the previous study shows a large number of rod-like fibers stacked and densely packed, and the rod-like fibers consist of a number of elongated fibers, so the flexibility of the material is extremely strong due to its very high aspect ratio. The morphology of the Fe-HAP catalyst material doped with ferrous ions has a large change relative to that of the HAP base material, which also contains a part of fibrous material within its structure, but more nanoparticles are piled up together in an irregular arrangement. The BET specific surface area of Fe-HAP (62.44 $m^2 \cdot g^{-1}$) was slightly larger

than that of HAP (15.85 $m^2 \cdot g^{-1}$), probably due to the flake structures and the existence of a large number of cracks on Fe-HAP compared to HAP(Table 1).



(a)



(b)

Fig 1. FESEM images of different samples: (a) HAP, (b) FE-HAP.

Table 1. BET specific surface area data of pure HAP and Fe-HAP catalysts

Sample	HAp	Fe-HAp
BET Surface Area	15.85m²/g	62.44m²/g

The crystal structures and phase compositions of HAP and Fe-HAP catalyst materials before and after the reaction were revealed by XRD patterns. As shown in Fig.2, the diffraction peaks of the laboratory-prepared catalyst materials have a high match with $Ca_8FeH_{21}O_{35}P_6$ powder diffraction data card No. 19-0575 and $Ca_{10}H_2O_{26}P_6$ powder diffraction data card No. 74-0565. Strong diffraction peaks can be seen at 2θ = 13.72°, 25.96°, 27.95°, 31.25°, 34.61°, 44.83°, and 53.21° corresponding to (1 1 1), (3 1 1), (1 3 1), (-4 2 2), (0 4 0), (-1 5 2), and (0 2 9) crystal planes. These evidences indicate that after hydrothermal, the catalyst material Fe-HAP after addition of iron is structurally stable and well dispersed, and the crystallization process is better, and the structural stability of its reaction is also better.

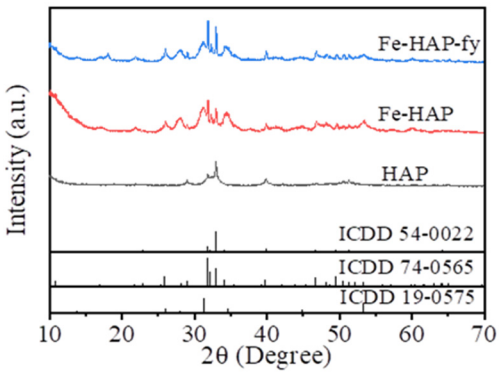
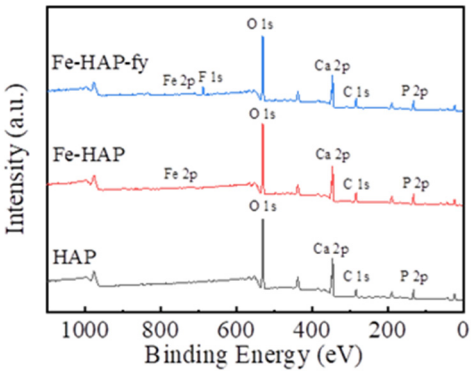
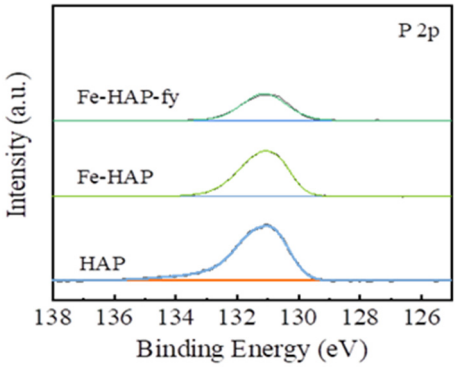


Fig 2. XRD patterns of different samples: HAP,Fe-HAP, (c)Fe-HAP-fy





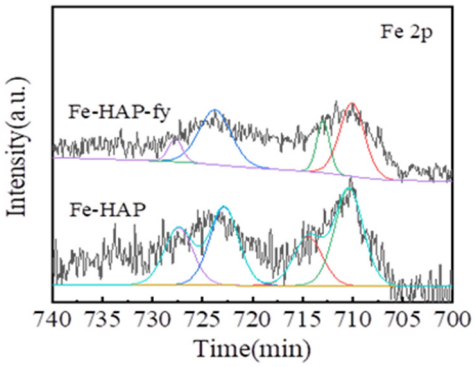


Fig 3. XPS spectra of pure HAP, Fe-HAP catalyst before and after degradation of CIP: (a) Total spectrum; (b) P 2p; (c) Fe 2p

In order to directly characterize the changes in the composition of each element on the surface of the Fe-HAP catalyst material, the chemical states of the surface elements of the prepared catalyst material were further explored by X-ray photoelectron spectroscopy analysis. In order to further confirm the information on the valence and electronic interactions of each element in the Fe-HAP catalyst material, the elemental spectra of the catalyst material were split-peak fitted to the XPS spectra of the elements of C 1s, Fe 2p, P 2p elemental spectra of the catalyst material were processed by split-peak fitting, as shown in Fig. All the XPS electronic spectra in Fig.3 were charge corrected at C 1s = 284.8 eV. From the full spectra in Figs. 3, it can be seen that there are five main peaks in the Fe-HAP catalyst material: C 1s, O 1s, Fe 2p, Ca 2p, P 2p, and no other impurity peaks are seen, but the peaks of iron are very weak, which is mainly attributed to the low content of iron in the catalyst material. However, it can be shown that the iron is uniformly distributed in the catalyst material in all the other characterization techniques, and this also can prove that the Fe-HAP catalyst material is composed of the above five elements. In Figs. 3, it can be seen

that there are three characteristic peaks in the high-resolution elemental spectra of Fe 2p, which are Fe 2p1/2 (724.48 eV), Fe 2p3/2 (711.28 eV), and satellite companion peaks, which proves that Fe exists in the catalyst material in the +3 valence state. The spectrum of P 2p has a characteristic peak at 132.7 eV, which is in agreement with the study in the literature[24,25]. The above XPS electron spectroscopy results indicate the successful synthesis of Fe-HAP catalyst material.

3.2. Fenton-like Catalytic Performance of Catalysts

In the pure HAP/H_2O_2 system, CIP was degraded by 40% in 180 min, which showed a weak catalytic ability and weak H_2O_2 activation ability. The weak catalytic ability of pure HAP may be due to the self-contained hydroxyl groups on the surface of the material, which will activate hydrogen peroxide to produce a certain amount of hydroxyl radicals, but the reaction process is very slow and the amount of hydroxyl radicals produced is small, so it has a weak catalytic ability. Therefore, its catalytic ability is weak. In the Fe-HAP/H_2O_2 system, the removal of CIP reached about 80% in 180 min, which is twice as much as that of the pure HAP/H_2O_2 system, and the removal of total organic carbon reached about 60% in 180 min, and the fluoride ions of the CIP were further removed, and the CIP was mineralized into small molecule acids (formic and acetic acid, etc.), which are described in later sections. be described in later sections. The above results indicate that Fe-HAP accelerated the activation of H_2O_2 and the generation of hydroxyl radicals, thus accelerating the degradation of CIP. In order to further investigate the catalytic activity and general applicability of the Fe-HAP/H_2O_2 Fenton-like system for the degradation of a variety of antibiotics,10 antibiotics, including tetracycline hydrochloride,erythromycin,norfloxacin,ofloxacin,diclofenac,sulfadiazine,sulfamethoxazole,azithromycin, clarithromycin, and rosithromycin, were selected as the target antibiotic pollutants and subjected to adsorptive degradation experiments. Before the addition of H_2O_2 for the Fenton-like catalytic reaction, the adsorption of these antibiotic pollutants by the Fe-HAP material was about 15-40%, and a large amount of pollutants were adsorbed on the surface of the catalyst material, which helped the Fenton-like catalytic oxidation reaction according to the previous studies. As can be seen in Figs. 4, the degradation effect of the Fe-HAP/H_2O_2 reaction system for sulfonamide antibiotics was extremely weak, and its removal effect for tetracycline hydrochloride was very significant, which could be completely removed in 180 min, and the mineralization rate reached 63%. In the antibiotic family, macrolide antibiotics belong to one of the antibiotic species that are extremely difficult to treat. In the Fe-HAP/H_2O_2 system, the catalysts removed 15%-30% of erythromycin antibiotics, and 40% of total organic carbon for clarithromycin, and these results indicate that the Fe-HAP catalyst material has a better effect on the removal of specific antibiotics, and this may be due to the fact that Fe-HAP catalyst materials are more effective in removing specific antibiotics, which may be used for the removal of tetracycline hydrochloride. This may be due to the specific binding ability of Fe-HAP catalysts to the chemical structure of certain types of antibiotics. The catalytic activity of Fe-HAP catalyst is excellent as the catalyst has the ability to remove macrolide antibiotics and the catalyst has significant effect on the total organic carbon of clarithromycin.

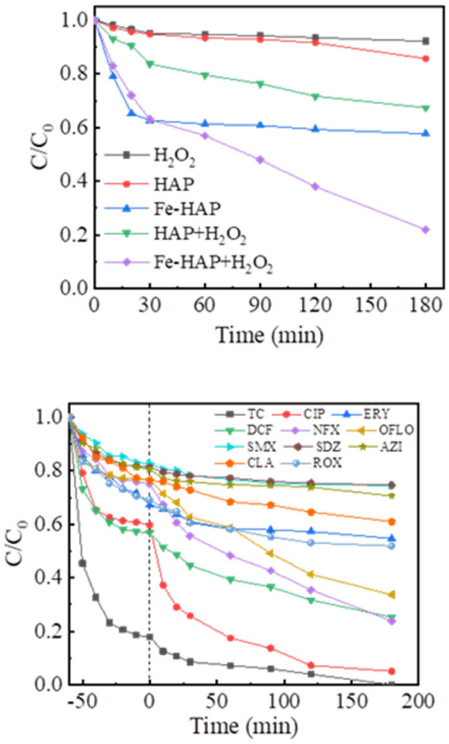


Fig 4. (a) Degradation effect of different systems for CIP;(b) Effectiveness of Fe-HAP catalysts for the removal of various antibiotics

The catalytic activity of the Fe-HAP catalyst material for repeated use was evaluated by cycling experiments. After five cycling experiments, the Fe-HAP was still able to remove about 65% of CIP in 180 min, and the removal rate of total organic carbon was still around 50%, and the dissolution rate of iron ions was under the detection limit, which fully proved the Fe-HAP Fenton-like catalyst material's Stability.

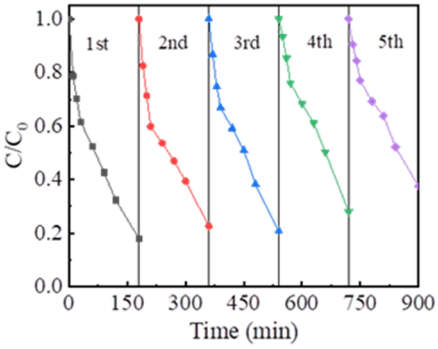


Fig 5. The effect of five cycles of material degradation

The pH value is one of the important influencing factors in the advanced oxidation process [5,7,26,27]. The system degraded CIP best when the pH of the solution was acidic, and CIP could be completely removed within 180 min at pH 3 and 4, which also proved that the catalytic oxidation efficiency of the iron-based Fenton catalyst was best in the acidic system. Further increasing the initial pH of the solution to neutral or alkaline, the efficacy of this system for degrading CIP gradually decreased, which was positively correlated with the increase in pH, because in alkaline environment, Fe^{2+} is difficult to activate H_2O_2 to produce -OH, and at the same time, some iron hydroxide precipitates are produced thus weakening the catalytic oxidation ability of the catalyst.

Therefore, the removal of CIP by Fe-HAP catalyst/hydrogen peroxide system was more favorable under acidic conditions(Fig.6).

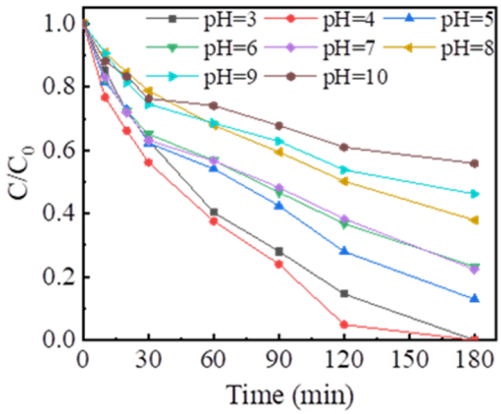


Fig 6. Effect of different initial solution pH on the degradation of CIP

In this experiment, the inorganic anion influence experiment used bicarbonate ions, sulfate ions and chloride ions as the main inorganic anion influences studied, and the anion concentrations added were all 5 mmol/L [28]. All other experimental variables were kept in line with the degradation experiments in the previous chapters as a means of investigating the stability and degradation effects of Fe-HAP catalyst materials in complex aqueous environments. The experimental results are shown in Figure.7. The three inorganic anions, bicarbonate ion, sulfate ion and chloride ion, affect the degradation of CIP in the Fe-HAP catalyst/hydrogen peroxide system, and the degradation efficiencies of the three inorganic anions decreased to different degrees when compared with the control group, which indicates that these anions inhibit the removal of CIP by this system to varying degrees, and the influences of the three inorganic anions in order of the results are: sulfate ion > chloride ion > hydroxyl radical reaction rate constants.

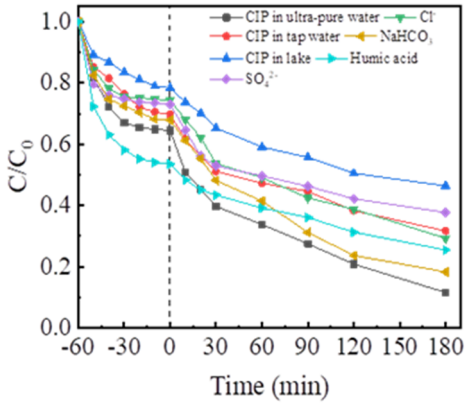


Fig 7. Effect of different inorganic anions on the degradation system of CIP

According to the experimental results, the influence of these three inorganic anions in order of magnitude is as follows: sulfate ions > chloride ions > bicarbonate ions, which is also consistent with the magnitude of the rate constants of the three inorganic anions and the hydroxyl radicals as described earlier [29]. This may be due to the fact that the presence of inorganic anions such as bicarbonate ions, sulfate ions, and chloride ions triggers side reactions in the system, which can burst the reactive substances such as hydroxyl radicals and superoxide radicals in the reaction system, and thus inhibit the removal effect of CIP by the catalytic oxidation system [30, 31].

3.3. Reaction Mechanism of Catalysts

In order to determine the types of reactive oxygen species in the system and to verify the conclusions of the free radical scavenging experiments, the generation of hydroxyl radicals and superoxide radicals in the Fe-HAP catalyst/hydrogen peroxide system was determined by electron paramagnetic resonance (EPR). 5,5-dimethyl-1-pyrrolidone-N-oxide (DMPO) was used to capture hydroxyl radicals to determine whether hydroxyl radicals were generated in the system. DMPO was added to the catalyst samples in methanol solvent as a superoxide radical capture agent to detect the generation of superoxide radicals [15,24,32]. The catalyst sample was added to the methanol solvent, and DMPO was used as a trap for superoxide radicals to determine whether superoxide radicals were generated in the reaction system. As shown in Figure.8, the 1:2:2:1 DMPO-hydroxyl radical spin signal captured in the system can be found after the start of the reaction; Figure.8 is the experimental data plot for the detection of superoxide radicals, and the superoxide radical signal peaks were not obviously detected, which requires further optimization of the experimental conditions. The experiments confirmed that the Fe-HAP catalyst/hydrogen peroxide system could produce a large number of hydroxyl radicals.

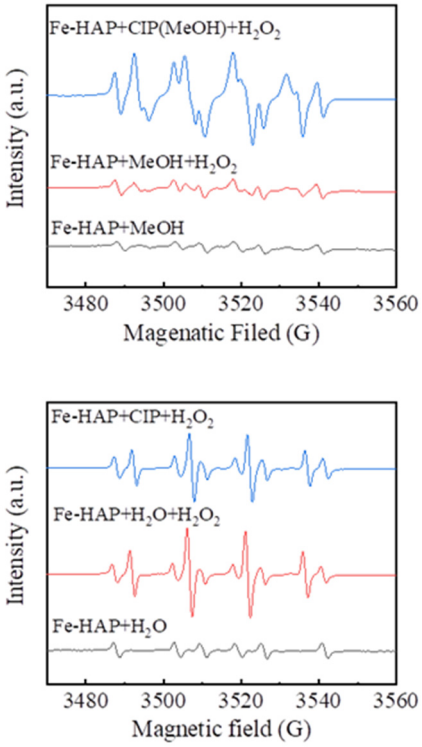


Fig 8. DMPO spin-trapping ESR spectra recorded in different suspensions under air:(a) DMPO-·O^{2-};(b) DMPO-·OH

Further comparison of the inhibitory effects of different radical scavengers revealed that when tert-butanol was added to the Fe-HAP catalyst/hydrogen peroxide system, the removal of CIP decreased from 85% to 15% in 180 min. This indicates that the addition of tert-butanol inhibits the degradation of CIP in this reaction system, suggesting that

hydroxyl radicals are present in the reaction system and have a major role in the degradation of CIP. When p-benzoquinone scavenger was added to the reaction system, the degradation effect of CIP decreased to 30%. It indicates that superoxide radicals in the system also contribute to the degradation of CIP, but according to recent studies, superoxide radicals are easily converted to hydroxyl radicals in aqueous systems. So in the Fe-HAP catalyst/hydrogen peroxide system hydroxyl radicals play the main role of oxidative degradation, and superoxide radicals also contribute partially, but in the electron paramagnetic resonance experiments in the next section, the peak signals of hydroxyl radicals were detected, and the peak signals of superoxide radicals were not detected (Fig.9).

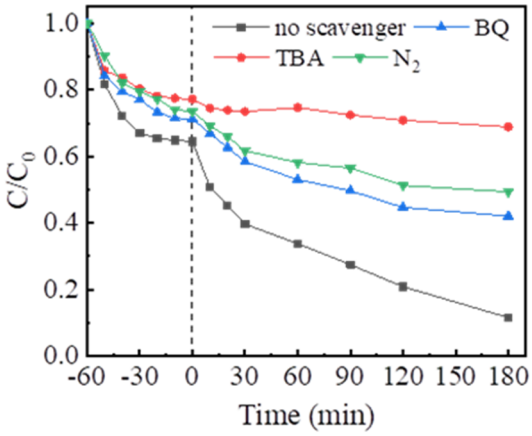


Fig 9. Effect of different radical scavengers and N_2 on CIP degradation in Fe-HAP/H_2O_2 system.

4. Conclusion

In this study, Fe-HAP was prepared as a catalyst material for activating hydrogen peroxide, and a series of characterization of the catalyst material was carried out; the Fe-HAP catalyst/hydrogen peroxide was constructed, and the degradation efficacies of the system for CIP were compared with those of other control experiments; the effects of the amount of catalyst material, the concentration of hydrogen peroxide, and the initial pH value of solution on the degradation of CIP in the Fe-HAP The effects of catalyst loading and initial pH of the solution on the degradation of CIP by Fe-HAP catalyst/hydrogen peroxide system were investigated. The intermediates and degradation pathways of CIP produced in the reaction system were also determined by ultra-high-performance liquid-phase time-of-flight mass spectrometry analysis. The specific findings of this study are as follows:

(1) In this study, Fe-HAP catalysts were prepared to achieve uniform dispersion of Fe, with a mostly granular and partly fibrous morphology, a porous structure, and a larger specific surface area compared with pure HAP, and the material surface was dispersed with functional groups, such as C-O, P-O, and Fe-O, and the functional groups on the surface of the material before and after the use of the material did not undergo any significant changes.

(2) Compared with other control systems, the Fe-HAP catalyst/hydrogen peroxide system has obvious superiority, and has a better removal effect on the target pollutant CIP.

(3) The degradation effect of the reaction system in the actual water body decreased, which was due to the inhibitory effect of various inorganic anions (bicarbonate ions, sulfate ions, chloride ions, etc.) and natural organic matter on the active substances in the reaction system; through the degradation experiments of catalyst cycling, it was found that the stability of the catalyst was higher, and the degradation efficiency of CIP was still high after five times of cycling. The degradation efficiency of the catalyst for CIP remained high after five cycles.

(4) The active substances generated in the Fe-HAP catalyst/hydrogen peroxide system included hydroxyl radicals and superoxide radicals, which were proved to play an important role in the degradation of CIP by free radical scavenging experiments and electron paramagnetic resonance analysis.

Acknowledgments

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