Degradation Efficiency and Mechanism of Antibiotics by Sodium Hydroxide-Activated Hydrogen Peroxide Driven by Alkaline Environment

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Abstract. Ciprofloxacin (CIP), a typical fluoroquinolone antibiotic, exhibits strong environmental persistence, easy accumulation and biological toxicity. Its long-term residual in aquatic environments may induce microbial drug resistance and threaten the safety of ecological systems. Aiming at the problem that traditional Fenton/photo-Fenton reactions are limited to acidic pH, this study developed a high-efficiency novel photo-Fenton system based on Cu-C_3N_5 catalyst activating hydrogen peroxide (H_2O_2) under alkaline conditions for the degradation of CIP in water. By systematically investigating the effects of key parameters such as pH, H_2O_2 concentration and catalyst dosage, it was found that a strong alkaline environment (pH 10.3) could significantly accelerate the degradation kinetic rate of CIP. Under the optimal conditions of catalyst dosage 0.3 g·L-1, CIP concentration 0.5 mg·L-1, H_2O_2 concentration 20 mM and pH 10.3 (adjusted by 0.1 mL NaOH), the reaction showed the highest normalized rate constant. Mechanism studies indicated that the alkaline environment played a dual regulatory role. On the one hand, it induced the deprotonation of CIP molecules, altered the local electron cloud distribution of the target pollutant, and reduced the cleavage energy barrier of key chemical bonds, making them easier to break. On the other hand, OH^- contributed an additional negative charge (about 8%) to the hydrogen bond network of water, which significantly enhanced the interfacial electron transfer efficiency. This process synergistically promoted the activation of the O-O bond in H_2O_2 to form a high-energy transition state, extended the lifetime of reactive oxygen species such as singlet oxygen, and drove the directional collision of reaction molecules. This work not only reveals the key regulatory mechanism of alkaline microenvironment in heterogeneous Fenton-like reactions, but also breaks the dependence of traditional Fenton systems on acidic conditions. It provides a new theoretical basis and regulatory strategy for the development of universal advanced oxidation technologies suitable for neutral to alkaline wastewater, and has important scientific significance for promoting the efficient treatment of refractory pollutants in complex water bodies.

Keywords: Ciprofloxacin; Alkaline activation; Hydrogen peroxide; Advanced oxidation

1. Introduction

China is a major country in the production and consumption of antibiotics with a huge annual emission[1-5], leading to the widespread residual of various antibiotics in aquatic environments. As a typical third-generation fluoroquinolone drug, ciprofloxacin (CIP) has the characteristics of strong chemical stability, poor biodegradability and easy bioaccumulation. Its long-term existence in the environment not only poses an ecotoxicological threat to aquatic organisms, but also continuously induces the spread of antibiotic resistance genes (ARGs), seriously endangering public health and ecological security. Advanced oxidation processes (AOPs) are effective means[6] for the deep degradation of such persistent organic pollutants. Among them, hydrogen peroxide (H_2O_2) has attracted much attention due to its advantages of greenness, safety and no secondary pollution[7]. However, traditional H_2O_2-based Fenton-like technologies rely heavily on acidic pH conditions to maintain the activity of transition metal catalysts such as iron and the high yield of hydroxyl radicals (·OH)[8], which greatly limits their application in actual wastewater and natural water bodies that are generally neutral or alkaline. Therefore, developing a novel high-efficiency and stable H_2O_2 activation system that can operate in a wide pH range (especially alkaline conditions) is a core bottleneck to be broken through in the field of water pollution control at present.

Yan Xuanxuan[9] confirmed that the UV/H_2O_2 system could accelerate the aging of microplastics, but H_2O_2 activation depends on light, which is difficult to apply to water bodies with poor light penetration. Guo Huanyun[10] constructed a modified MIL-101(Fe)/H_2O_2

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system to achieve efficient degradation, but the activation mechanism completely relies on iron-based MOF materials, without involving the research on the regulation of solution chemical environment on H_2O_2 activation path and reaction kinetics.

In view of this, this study innovatively constructed an alkaline Fenton-like system driven by Cu-C_3N_5 heterogeneous catalyst, aiming to utilize the molecular bridge and dual regulatory mechanism of alkaline OH^-, break the dependence on traditional catalytic materials, and realize the efficient activation of H_2O_2 and rapid degradation of ciprofloxacin under neutral to alkaline conditions. The effects of initial solution pH, H_2O_2 concentration and catalyst dosage on degradation efficiency were systematically investigated through experimental research, and the reaction kinetics analysis was carried out. The results showed that the alkaline environment (pH 10.1–10.5) had a decisive promoting effect on the degradation reaction. Under the optimized conditions (Cu-C_3N_5 dosage 0.3 $g\cdot L^{-1}$, $[H_2O_2]_0$=20 mM, $[CIP]_0$=0.5 $mg\cdot L^{-1}$, pH 10.3 adjusted by 0.1 mL NaOH), the removal rate of CIP exceeded 95% within 60 min. The degradation process conformed to the pseudo-first-order kinetic model, and the apparent rate constant increased significantly with the enhancement of system alkalinity[11]. Free radical quenching experiments showed that the main reactive species in this alkaline catalytic system were not traditional ·OH, but selective oxidative species such as singlet oxygen ($^1O_2$) and superoxide radical $O_2\cdot^-$ ($O_2\cdot^-$).

This study revealed the multiple effects of high concentration of OH^- provided by NaOH in the Cu-C_3N_5/H_2O_2 system: OH^- changes the CIP molecular form through deprotonation to weaken its chemical bond strength, and injects an additional negative charge (about 8%) into the hydrogen bond network of water to enhance the interfacial electron transfer efficiency, thereby promoting the polar activation of O–O bond in H_2O_2 and realizing the efficient generation of $^1O_2$. Meanwhile, its high activity under neutral to alkaline conditions and good adaptability to high turbidity water bodies endow this technology with engineering application potential for treating actual alkaline industrial wastewater such as pharmaceutical and printing and dyeing wastewater, and provide a theoretical basis and technical support for the development of wide pH adaptive advanced oxidation processes.

2. Experimental Materials and Methods

2.1 Reagents and Instruments

The main reagents used in this study were as follows: hydrogen peroxide (H_2O_2, Sigma-Aldrich, St. Louis, Missouri, USA), sodium thiosulfate ($Na_2S_2O_3$, Sigma-Aldrich, St. Louis, Missouri, USA), ciprofloxacin (CIP, H.M.K, Beijing, China), sodium hydroxide (NaOH, Codow, Guangzhou, Guangdong, China), methanol (CH_3OH, Aladdin, Shanghai, China), 3-amino-1,2,4-triazole ($C_2H_4N_4$, Sigma-Aldrich, St. Louis, Missouri, USA), copper acetylacetonate ($C_{10}H_{14}CuO_4$, Sigma-Aldrich, St. Louis, Missouri, USA), argon (Ar, ≥99.999%, Niuruide, Wuhan, Hubei, China) and catalyst (Cu-C_3N_5). Deionized water was used as experimental water.

The experimental instruments used in this study included: ultrasonic cleaner (KQ2200DE, Shumei, Kunshan, Jiangsu, China), electric heating blast drying oven (DHG-9070, Yiheng, Shanghai, China), single temperature zone tube furnace (OTF-1200X-80, Kejing, Hefei, Anhui, China), water quality analysis acidity meter (ST3100CF, Ohaus, New Jersey, USA), high performance liquid chromatography (UItiMate3000, Thermo, Waltham, Massachusetts, USA), electric heating digital display constant temperature water bath (LC-WB-8+, Lichen, Shanghai, China), double suction circulating water vacuum pump (SHZ-D, Huichuang, China), magnetic stirrer (Topolino, IKA, Hanover, Germany), planetary ball mill (PM100, Retsch, Hahn, Germany), liquid chromatography-mass spectrometry (Thermos TSQ quantum Ultra, LC-MS, Thermo Fisher, USA).

2.2 Catalyst Preparation Method

5.0448 g of 3-amino-1,2,4-triazole (60 mmol) and 2.094 g of copper acetylacetonate (4 mmol) were used as precursors and co-ground in a planetary ball mill at a rotating speed of 400 rpm for 5 min to achieve full mixing. The uniformly mixed powder was transferred to a corundum crucible and placed in a tube furnace. Under the protection of continuous high-purity argon (Ar, ≥99.999%) atmosphere, the temperature was raised from room temperature to 500 °C at a heating rate of 5 $°C\cdot min^{-1}$, and calcined at this temperature for 3 h. After the pyrolysis, the reactor was naturally cooled to room temperature. The obtained black solid product was repeatedly washed with deionized water to remove soluble impurities. Then, the sample was dried overnight in a blast drying oven at 60 °C to finally obtain the target catalyst.

2.3 Experimental Procedure

Firstly, a 5 $mg\cdot L^{-1}$ CIP solution was accurately prepared for later use. 5 mL of CIP solution and 45 mL of ultrapure water were mixed in a 100 mL beaker respectively (the CIP concentration after mixing was 0.5 $mg\cdot L^{-1}$). Different volumes (0, 10, 25, 100, 300 and 3000 μL) of sodium hydroxide solution (0.1 $mol\cdot L^{-1}$) were added to each beaker, followed by the addition of 15 mg of catalyst (Cu-C_3N_5). The mixture was ultrasonicated for dispersion, and then the beaker was transferred to a constant temperature water bath at 30 °C and stirred at a rotating speed of 500 rpm for 15 min to mix the solution uniformly.

H_2O_2 solution was added to each beaker. At the 5th, 10th, 20th, 30th, 45th and 60th min of the reaction, 1 mL of the solution was drawn into a liquid phase vial, and 21 μL of $Na_2S_2O_3$ solution (0.1 $mol\cdot L^{-1}$) was added to terminate the reaction. Then, high performance liquid chromatography was used to detect the CIP concentration.

2.4 Analytical Methods

A SHIMSEN Superb II C18 chromatographic column (5 μm×4.6 mm×250 mm) was used for sample analysis. The mobile phase was a mixed solution of methanol and ultrapure water with a volume ratio of 8:2, and the flow rate was set to 1.0 mL·min^{-1}. The temperature of the column oven was maintained at 35 °C, and the detection wavelength was 260 nm. The temperature of the solution was measured by a thermometer and recorded after the reading was stable. The pH value of the solution was measured by a pH meter calibrated with standard buffer solution and recorded after the reading was stable.

The degradation rate of CIP was calculated by the following formula:

$$\eta(\%) = \frac{C_0 - C_t}{C_0} \times 100$$

Where:

η – Degradation rate (%);

C_0 – Initial concentration of CIP (mg·L^{-1});

C_t – Residual concentration of CIP at reaction time t (mg·L^{-1}).

3. Results and Discussion

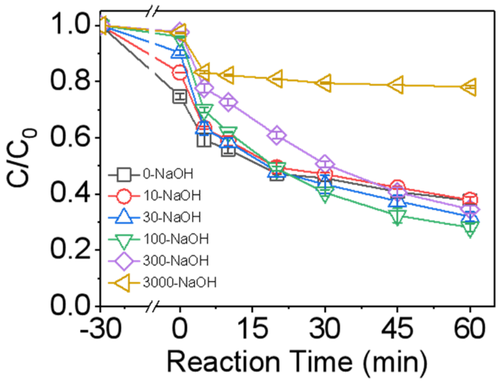
3.1 Degradation Effect of CIP by Cu-C_3N_5

3.1.1 Comparison of CIP Removal Effects in Different Systems

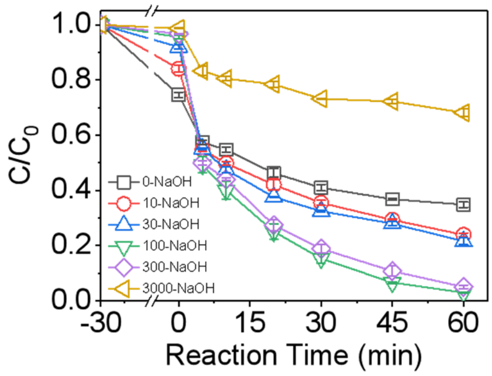
The initial H_2O_2 dosage and pH value of the system are key factors regulating the Fenton-like reaction process. This study systematically investigated the effects of H_2O_2 dosage and pH value on the degradation of CIP by the Cu-C_3N_5/H_2O_2 system. As shown in Figure 1, in the H_2O_2 concentration gradient experiment (5-30 mM), the degradation efficiency of CIP showed a significant concentration-dependent improvement. When the H_2O_2 concentration was 5 mM (Figure a), the degradation curves under various NaOH dosages were relatively gentle, and a high residual of CIP still existed after 60 min of reaction. With the gradual increase of H_2O_2 concentration to 10 mM (Figure b) and 20 mM (Figure c), the slope of the degradation curve increased significantly, and the reaction rate accelerated remarkably. When the H_2O_2 concentration was further increased to 30 mM (Figure d), a slight increase in CIP degradation rate was only observed under a few pH conditions compared with 20 mM. However, in most pH ranges, the removal efficiency had no significant difference with that at 20 mM, and the rapid CIP removal capacity was still maintained overall, with C/C_0 dropping to the lowest level at 60 min. The above results indicated that H_2O_2 was the key oxidant in this system, and the increase of its concentration could effectively enhance the overall oxidation capacity of the system, thus accelerating the degradation of CIP.

Under a certain H_2O_2 dosage, the degradation efficiency and rate of CIP both increased significantly with the increase of the initial pH value of the system. Under nearly neutral and weakly alkaline conditions, the removal rate of CIP was lower than 50% after 60 min of reaction, indicating that the catalyst had low activity in the dominant pH range of traditional Fenton-like reactions. However, when 100 µL of NaOH was added (corresponding to the system pH increased to 10.3), the degradation efficiency of CIP showed a turning improvement. This phenomenon could be attributed to the generation of a large amount of HO_2^- from the reaction of OH^- and H_2O_2 under alkaline conditions. As a key reactive intermediate, HO_2^- could further generate singlet oxygen ($^1O_2$) efficiently through disproportionation reaction or electron transfer pathway, thus significantly accelerating the oxidative degradation of CIP[12]. Under the strong alkaline condition of pH=10.1-10.5, the removal rate of CIP exceeded 95% within 30 min of reaction, showing extremely high catalytic activity.

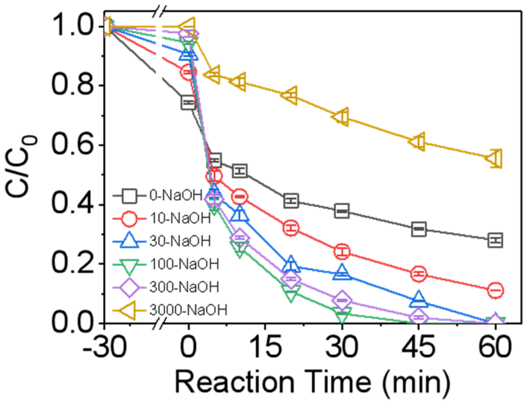
This phenomenon is completely different from the optimal pH range of traditional iron-based Fenton reactions, revealing the unique alkaline-driven mechanism of this system. We believe that the presence of high concentration of OH^- plays multiple roles: firstly, OH^- promotes the deprotonation of the piperazine group in CIP molecules (pKa~8.7), changes their electrical properties and adsorption behavior on the catalyst surface, and may make their active sites more vulnerable to attack. More importantly, according to recent studies, OH^- can reconstruct the hydrogen bond network of aqueous solution, significantly enhance the interfacial charge transfer efficiency, thus greatly promoting the electron transfer process between the catalyst surface and H_2O_2, and creating a favorable microenvironment for the efficient activation of H_2O_2.



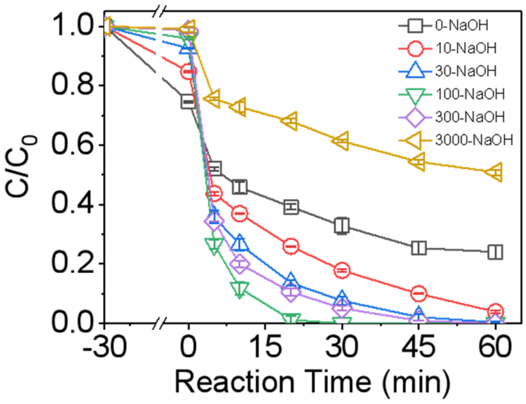
(a) H_2O_2-5 mM



(b) H_2O_2-10 mM



(c) H_2O_2-20 mM



(d) H_2O_2-30 mM

Reaction condition: Cu-C_3N_5[catalyst]0=0.3 g·L-1, [H_2O_2]0=5/10/20/30 mM, [CIP]0=0.5 ppm, [NaOH]0=0/10/30/100/300/3000 μl

Figure 1 Degradation efficiency of CIP in different systems

3.1.2 Effect of NaOH Concentration

The concentration of NaOH has a decisive effect on the degradation efficiency of CIP by the Cu-C_3N_5/H_2O_2 system. Experiments showed that the degradation activity of the system was very low when no NaOH was added. With the increase of NaOH dosage to 0.1 mL, the degradation rate constant of CIP reached the maximum, which was increased by more than an order of magnitude compared with the neutral condition. This was because the appropriate OH^- concentration could effectively promote the heterolysis of the O-O bond in H_2O_2, and dominate the generation of highly reactive species mainly including singlet oxygen ($^1O_2$) [13]by enhancing the interfacial electron transfer efficiency. However, with the increase of NaOH dosage from 0.1 mL to 3.0 mL, the degradation efficiency of CIP showed a trend of first increasing and then decreasing. Especially under the strong alkaline condition with pH reaching 12.1, the excessive OH^- and H_2O_2 had a strong competitive adsorption on the active sites of the Cu-C_3N_5 surface, and formed a solvation coating layer at the catalyst interface. On the one hand, this coating layer occupied the active centers required for H_2O_2 activation; on the other hand, it significantly increased the mass transfer resistance of H_2O_2 to the catalyst surface, leading to a sharp increase in the mass transfer resistance of H_2O_2 to the catalyst surface and seriously inhibiting the catalytic generation path of reactive oxygen species[14]. Therefore, the optimal dosage of NaOH in this system was determined to be 0.1 mL, and the corresponding pH value was used as the optimal reaction condition for subsequent experiments.

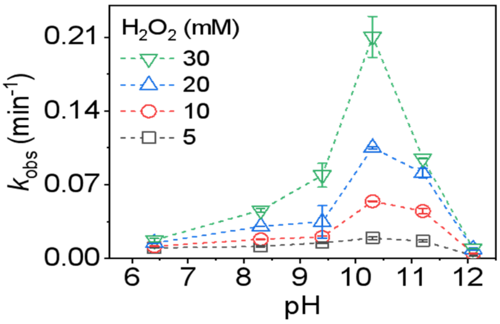


Figure 2 Normalized k values for the initial pH at different pHs

Table 1. k_{obs} values at varying pH and H_2O_2 concentrations

$K_{pH}/K_{pH}6.4$	5mM	10mM	20mM	30mM
pH 6.4	1	1	1	1
pH 8.3	1.1	1.6	2.1	2.6
pH 9.4	1.5	1.8	2.4	4.5
pH 10.3	1.9	4.7	7.2	12.1
pH 11.2	1.7	3.9	5.6	5.4
pH 12.1	0.2	0.4	0.6	0.5

Reaction condition: Cu-C_3N_5[catalyst]$_0$=0.3 g·L^{-1}, [H_2O_2]$_0$=5/10/20/30 mM, [CIP]$_0$=0.5 ppm, [NaOH]$_0$=0/10/30/100/300/3000 μl

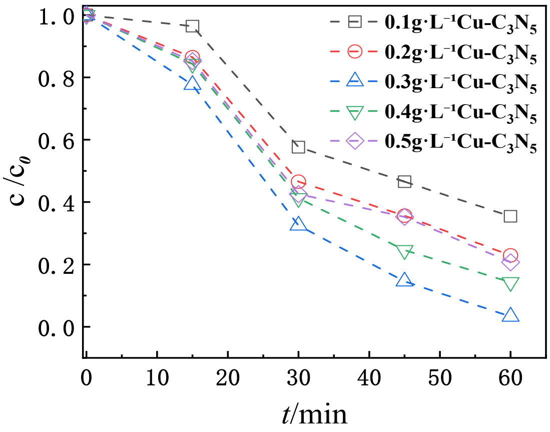
3.1.3 Effect and Optimization of H_2O_2 Concentration on Reaction Kinetics

As the precursor of reactive oxygen species, the dosage of H_2O_2 directly affects the degradation efficiency and operation cost. Figure 1 compared the degradation kinetic curves under different initial H_2O_2 concentrations (5-30 mM). The results showed that under any given pH condition, the degradation rate of CIP accelerated with the increase of H_2O_2 concentration from 5 mM to 20 mM. When the H_2O_2 concentration was 20 mM, the degradation rate of CIP reached nearly 85% within 15 min of reaction under the condition of pH 10.3, showing a rapid pollutant reduction capacity.

However, when the H_2O_2 concentration was further increased to 30 mM, the degradation rate tended to be gentle under some pH conditions. This was because the excessive H_2O_2 could not only act as a quencher for reactive species (such as ·OH and $^1O_2$) (H_2O_2+·OH=HO_2·+H_2O) to cause invalid decomposition, but also undergo homogeneous self-decomposition to generate O_2 in a strong alkaline medium, thus significantly reducing the effective utilization rate of H_2O_2. It is worth noting that the generation of $^1O_2$ in the system mainly depends on the disproportionation reaction of an appropriate amount of $^1O_2$ on the catalyst surface ($2O_2\cdot^- + 2H_2O = H_2O_2 + 2OH^- + ^1O_2$). The double quenching effect of excessive H_2O_2 on ·OH and $^1O_2$ further destroyed the synergistic balance between free radical and non-free radical pathways. Therefore, determining the optimal dosage of H_2O_2 is crucial for balancing the treatment efficiency and economy.

3.1.4 Effect of Cu-C₃N₅ Dosage

To explore the effect of catalyst dosage on the system efficiency, the degradation of CIP under different $Cu\text{-}C_3N_5$ dosages (0.1–0.5 $g\cdot L^{-1}$) was investigated in the experiment. Figure 3 shows the effect of different $Cu\text{-}C_3N_5$ dosages on the degradation efficiency of the target pollutant. As shown in the figure, when the catalyst dosage increased from 0.1 $g\cdot L^{-1}$ to 0.3 $g\cdot L^{-1}$, the pollutant degradation rate increased significantly, and the group with 0.3 $g\cdot L^{-1}$ could achieve almost complete removal of pollutants within 60 min. This phenomenon could be attributed to the increase of catalyst dosage providing more surface active sites, thus promoting the effective activation of H_2O_2 and the generation of reactive oxygen species (such as ·OH and $^1O_2$), and accelerating the oxidative degradation process of the target pollutant.



Reaction condition: $Cu\text{-}C_3N_5$[catalyst]0=0.1/0.2/0.3/0.4/0.5 g·L-1, $[H_2O_2]$0=20 mM, [CIP]0=0.5 ppm, [NaOH]0=100 µl

Figure 3 Effects of different $Cu\text{-}C_3N_5$ dosages on degradation effects

However, with the further increase of $Cu\text{-}C_3N_5$ dosage to 0.4 $g\cdot L^{-1}$ and 0.5 $g\cdot L^{-1}$, the degradation efficiency decreased to different degrees. This was mainly because the excessive catalyst particles were prone to agglomeration at high concentration, leading to the reduction of effective specific surface area and the accessibility of active sites. At the same time, the excessively high catalyst concentration might induce quenching reactions between reactive species (such as the combination of ·OH and ·OH to generate H_2O_2), or cause too fast invalid decomposition of H_2O_2, thus inhibiting the overall oxidation efficiency[15].

In summary, under the experimental conditions of this study, the optimal dosage of $Cu\text{-}C_3N_5$ was 0.3 $g\cdot L^{-1}$. This dosage could provide sufficient active sites and effectively avoid the negative effects caused by excessive catalyst, thus achieving the optimal catalytic degradation performance.

3.2 Reaction Mechanism of CIP Removal

3.2.1 Free Radical Quenching Experiments

Hydrogen peroxide activation usually generates reactive species mainly including ·OH, but other reactive substances such as $^1O_2$ and $O_2\cdot^-$ are also produced during the reaction. Therefore, furfural (FFA) was selected as the quencher for $^1O_2$; methanol (MeOH) as the quencher for ·OH and $O_2\cdot^-$; p-benzoquinone (PBQ) as the quencher for $O_2\cdot^-$; and tert-butanol (TBA) as the quencher for ·OH.

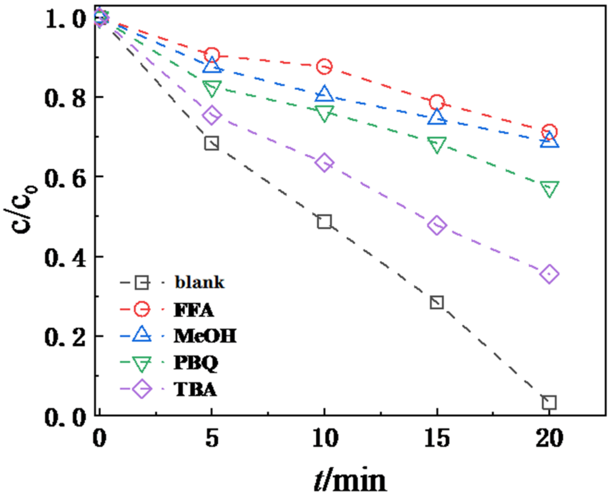
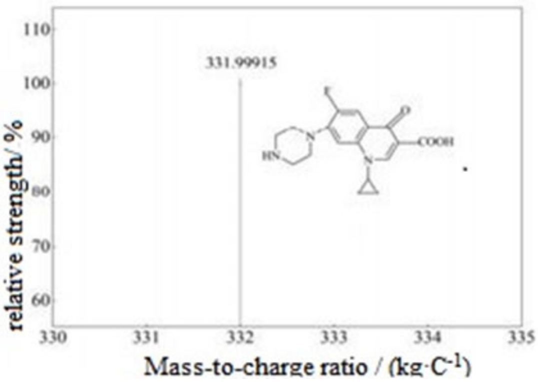


Figure 4 Effects of each quenching agent on the degradation effect of CIP

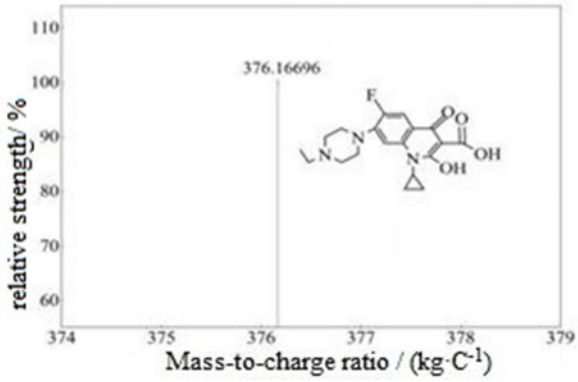
As shown in Figure 4, the degradation rate of CIP in the control group without quencher was 96.8%. After adding FFA, MeOH, PBQ and TBA, the degradation rates of CIP were 28.7%, 31.2%, 42.6% and 64.4% respectively. This confirmed that $^1O_2$, ·OH and $O_2\cdot^-$ jointly participated in the oxidative degradation of CIP in the reaction system. Based on the calculation results, $^1O_2$ was dominant, and the order of their relative contributions was: $^1O_2 > O_2\cdot^- > \cdot OH$.

3.3 Degradation Mechanism of CIP

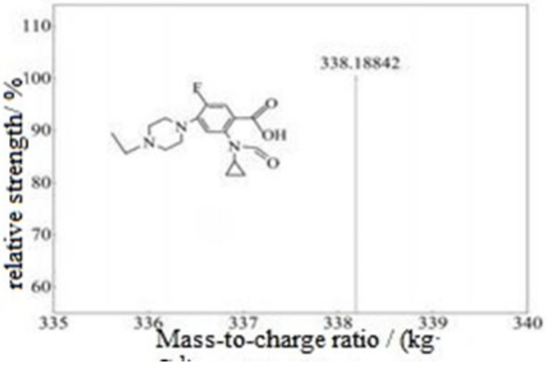
Liquid chromatography-mass spectrometry (LC-MS, electrospray ionization ESI mode) was used to determine the reaction intermediates. Based on the ion mass spectrum of CIP, the chemical formulas and structures of 6 possible degradation products were inferred as shown in Figure 5.



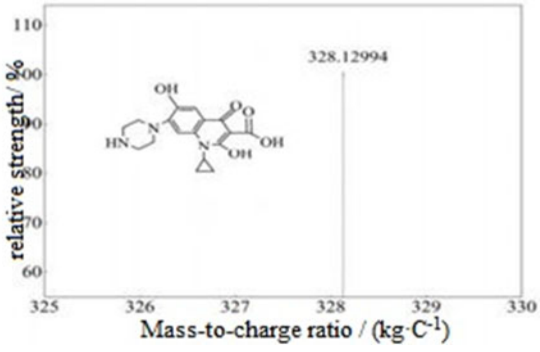
(a) Product 1;



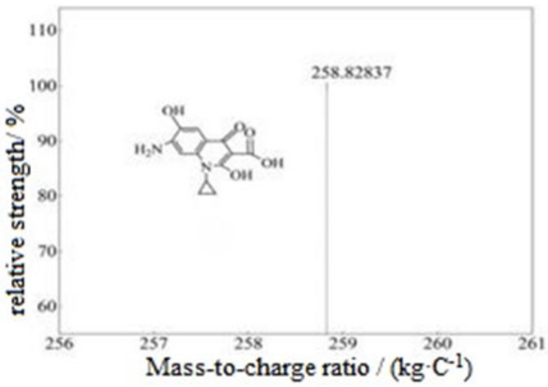
(b) Product 2;



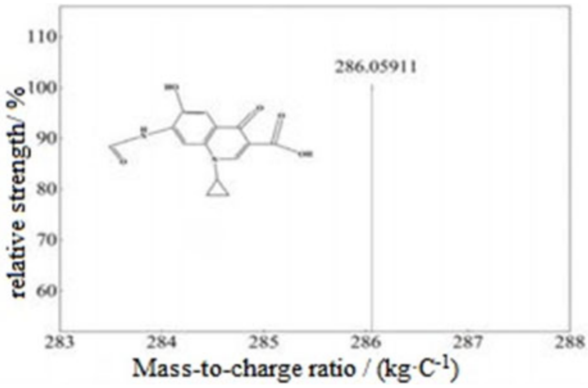
(c) Product 3;



(e) Product 4



(f) Product 5;

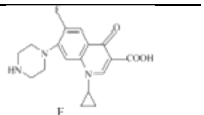
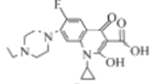
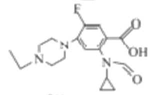
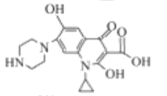
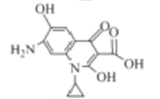
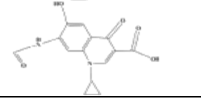


(g) Product 6

Figure 5 Mass spectrum of CIP degradation products

Based on the identification results of LC-MS intermediates and combined with the reports in relevant literatures, the degradation of CIP in the Cu-C_3N_5/H_2O_2/alkaline system mainly followed three parallel paths: first, the oxidative ring-opening and gradual cleavage of the piperazine ring to generate monohydroxyl, dihydroxyl and carbonylated intermediates, which were further cracked into small molecule amines or carboxylic acids; second, the hydroxyl ring-opening decomposition of the quinolone parent nucleus, where reactive oxygen species preferentially attacked the aromatic ring to undergo hydroxyl substitution, and the aromatic ring structure was destroyed and ring-opened with the deepening of oxidation degree, generating chain carboxylic acid or aldehyde intermediates; third, the defluorination reaction of the C-F bond, where the carbon-fluorine bond was polarized and broken under strong oxidation conditions to release fluoride ions. Under the synergistic effect of the above paths, CIP was gradually degraded into short-chain organic acids, and finally mineralized into inorganic ions such as CO_2, H_2O and F^-, realizing the deep removal of the target pollutant.

Table 2 Products of CIP degradation

Name	Chemical formula	LC-MS mass-to-charge ratio	m/z	Retention time/min	Structural formula
1	$C_{17}H_{19}FN_3O_3$	331.99915	332.14	4.71	
2	$C_{19}H_{23}FN_3O_4$	376.16696	376.17	10.14	
3	$C_{17}H_{25}FN_3O_3$	338.18842	338.18	11.70	
4	$C_{17}H_{18}N_3O_4$	328.12994	328.13	3.25	
5	$C_{13}H_{11}N_2O_4$	258.82837	259.07	9.72	
6	$C_{14}H_{10}N_2O_5$	286.05911	286.06	8.33	

4. Conclusions

1.This study successfully constructed and verified a novel Fenton-like system of Cu-C_3N_5 catalyzing and activating hydrogen peroxide (H_2O_2) under alkaline conditions. The system exhibited excellent catalytic activity and stability in the range from neutral to strong alkaline.

2.Under the optimized reaction conditions of catalyst dosage 0.3 $g \cdot L^{-1}$, initial CIP concentration 0.5 $mg \cdot L^{-1}$, H_2O_2 concentration 20 mM and pH 10.3 (adjusted by 0.1 mL NaOH), the degradation rate of CIP could reach 96.8% within 60 min of reaction, and the degradation process conformed to the pseudo-first-order kinetics. The alkaline environment had a decisive promoting effect on the reaction, but excessively high pH (> 12) would lead to a decrease in activity due to the invalid decomposition of H_2O_2 and the passivation of the catalyst surface.

3.Free radical quenching experiments and mechanism studies showed that the system mainly played a role through the non-free radical pathway under alkaline conditions, in which singlet oxygen ($^1O_2$) was the main reactive species with the contribution of superoxide radical ($O_2\cdot^-$), and the effect of hydroxyl radical ($\cdot OH$) was limited. This revealed the key mechanism of OH^- directing the generation of $^1O_2$ by promoting interfacial electron transfer and inducing the heterolysis of H_2O_2.

4.Based on LC-MS analysis, it was inferred that the degradation of CIP mainly included three paths: oxidative ring-opening and gradual cleavage of the piperazine ring, hydroxyl ring-opening decomposition of the quinolone parent nucleus and defluorination reaction of the C-F bond, with the final products being small molecule organic acids, CO_2 and inorganic ions.

In conclusion, this study not only provides a feasible catalytic system for the efficient removal of CIP under alkaline conditions, but also deepens the understanding of the mechanism of non-free radical advanced oxidation processes. It provides a theoretical and experimental basis for the development of advanced oxidation technologies adapted to the pH fluctuation of actual water bodies.

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