Insight into the performance and mechanism of magnetic Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} in activating peroxydisulfate for ciprofloxacin degradation

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ABSTRACT

Magnetic nickel-copper ferrite (Ni\textsubscript{x}Cu\textsubscript{y}Fe\textsubscript{2}O\textsubscript{4}) nano-catalyst was synthesized by co-precipitation method, and it exhibited excellent ability for activating peroxydisulfate (PDS) in the degradation of ciprofloxacin (CIP). As-prepared Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} properties were characterized by Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscope equipped with an energy-dispersive X-ray (SEM-EDX), transisions electron microscopy (TEM), N\textsubscript{2} adsorption-desorption isotherm plot of Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH), vibrating sample magnetometer (VSM). The maximum degradation efficiency is 80.2\% by using 0.500 g/L of Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} for activating 5.00 mmol/L of PDS to degrade CIP (20.0 mg/L) at 25 ± 2 °C for 50 min (pH = 6.00). The presence of interfering ions Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, and HCO\textsubscript{3}\textsuperscript{-} inhibited the reaction by producing reactive species with low oxidation potential, inducing the degradation efficiency decreased down to 60.0\%, 58.1\% and 21.5\% respectively. Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} displayed great magnetic separation characteristic for the satisfactory magnetization saturation value is ≈8.6 emu/g. The degradation efficiency of recycled samples is no significant difference after using for three times, which is about 60\%, indicating that Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} is a reusability catalyst in activating PDS for CIP degradation. This work might provide an efficient and promising approach to construct recyclable magnetic materials that can be used for wastewater treatment.

Key words: ciprofloxacin, magnetic nano-catalyst, Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4}, peroxydisulfate

HIGHLIGHTS

- Magnetic nano-catalyst was synthesized via co-precipitation.
- Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} displayed excellent ability in activating peroxydisulfate.
- Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} displayed great magnetic separation characteristic.
- Ni\textsubscript{0.5}Cu\textsubscript{0.5}Fe\textsubscript{2}O\textsubscript{4} is a reusability catalyst in activating PDS for CIP degradation.
1. INTRODUCTION

In recent years, the harm to human health and the environment caused by the abuse of antibiotics has attracted extensive attention (Qin et al. 2021). A large number of quinolone antibiotics, such as Norfloxacin, Ofloxacin, Ciprofloxacin and Enoxacin, coming from human excreta, wastes from agricultural food, animal production and aquaculture, industrial wastewater directly used in plants, pharmaceutical industry, have entered the environment and become one of the new important pollutants in the water environment. Ciprofloxacin is one of the third generation fluoroquinolones with the strongest antibacterial activity is widely used in aquaculture or animal feeding, and also a drug for prevention and treatment. However, after using this kind of drug, savings will generate in animals’ body and enter consumers through the food chains, and threaten human health. At the same time, the incomplete metabolism of the drug will enter the environment, resulting in environmental pollution and huge ecotoxicological effects (Avc et al. 2020; Chow et al. 2021).

Nowadays, various traditional technologies for the removal of organic pollution from aquatic environments, such as adsorption (Avc et al. 2020), coagulation/floculation (Zhao et al. 2020), photocatalysis (Tho et al. 2020), biodegradation (Li et al. 2021), etc., have been investigated. However, many shortcomings remain including poor efficiency, membrane clogging, high energy consumption, the transmission of pollution from one phase to another, and the production of secondary waste (Amini & Mengelizadeh 2020). In recent years, a popular method, Advanced Oxidation Technology (AOP) based on sulfate radical (SO₄⁻), for treating refractory organic pollutants in wastewater has emerged, where SO₄⁻ was produced by the transfer of peroxydisulfate electrons in the activation process. In contrast to the hydroxyl radicals produced during the Fenton reaction, SO₄⁻ has the following advantages: high redox potential (E₀ = 2.5–3.1 V); long half-life (30–40 μs); high stability in solution; wide pH application range and stronger ability to mineralize organic pollutants (Xia et al. 2020).

It is reported that there are many ways to effectively activate persulfate (peroxymonosulfate/peroxydisulfate), heat (Hu et al. 2019), ultrasound (Kermani et al. 2020), transition ions (Guo et al. 2020), ultraviolet radiation (Hsieh et al. 2021), electrolysis-activated (Wang et al. 2021), but as a homogeneous activation system these methods require...
more energy consumption. It is found that magnesium ferrite lack of the above mentioned disadvantage and had enhanced catalytic performance for pharmaceutical products and organic dyes mineralization (Ivanets et al. 2020, 2021). Bimetallic and trimetallic iron-based systems belonging to the family of spinel with the molecular structure of MFe₂O₄ (M can be Ni, Zn, Mn, Cu, etc.) have been widely used (Gupta et al. 2020; Alhamd et al. 2021). Based on these studies and the high efficiency of bimetallic iron-based materials, researchers have recently paid more and more attention to trimetallic iron-based materials to ensure multifunctional, excellent stable catalysts, and high efficiency (Awad et al. 2019). NiₓCuᵧFe₂O₄ as a heterogeneous catalyst having many advantages of electronic properties, recyclability, easy separation, excellent photocatalytic activity, and the structure of polymeric NiₓCuᵧFe₂O₄ catalysts is more stable, and different metals can produce synergy to improve their catalytic performance. NiₓCuᵧFe₂O₄ nano-catalyst must show an excellent ability in activating peroxydisulfate, and can be used as a reusable catalyst in the advanced oxidation process based on sulfate radical in a wide range of pH value, for it has good magnetic separation performance. Despite the unique properties of NiₓCuᵧFe₂O₄, no study has been done on its catalytic performance for the activation of PDS to degrade ciprofloxacin.

Therefore, the main purpose of this study is to synthesize Ni₀.₅Cu₀.₅Fe₂O₄ by co-precipitation, an easy method to be operated, and investigate its catalytic performance in the oxidation of CIP by activated peroxydisulfate. The characterization of Ni₀.₅Cu₀.₅Fe₂O₄ was determined using different techniques. The effect of operating conditions including metal ratio, pH, catalyst dosage, PDS dosage, pollutant concentration, temperature, interference ions in the degradation process of CIP was investigated. The free radicals in the system were determined by capture experiments, and proposed a possible degradation mechanism. Finally, the stability and recyclability of the catalyst were proved by cyclic experiments.

2. EXPERIMENTAL

2.1. Reagents
Iron (III) chloride hexahydrate (FeCl₃·6H₂O, AR), Copper sulfate pentahydrate (CuSO₄·5H₂O, AR), Nickel sulfate hexahydrate (NiSO₄·6H₂O, AR), Ethanol (EtOH), Tertiary butanol (TBA), Sodium persulfate (Na₂S₂O₈), Hydrochloric acid (HCl) and Sodium hydroxide (NaOH), Sodium chloride (NaCl), Sodium nitrate (NaNO₃), Sodium bicarbonate (NaHCO₃) were purchased from Sinopharm Chemical Reagent Co., Ltd. Ciprofloxacin hydrochloride (C₁₇H₁₈FN₃O₃·HCl, AR) was obtained from Aladdin Reagent Co., Ltd. In addition, deionized water was used during the whole experiment.

2.2. Synthesis of catalyst
The experimental process of co-precipitation synthesis of Ni₀.₅Cu₀.₅Fe₂O₄ is shown in Figure 1. In brief, 0.540 g FeCl₃·6H₂O, 0.125 g CuSO₄·5H₂O and 0.131 g NiSO₄·6H₂O were weighed and dissolved in 10 mL of deionized water respectively, and stirred for 30 min. Then the above solution was transferred to a 250 mL three-neck flask and stirred constantly for 2 h at 80 °C. The pH value of the solution was maintained at 11 using 4.00 mol/L of NaOH. Then the mixture was aged at 100 °C. The solid was filtered with a filter membrane, washed to neutral with deionized water, and then dried and ground for standby. To better compare and investigate the catalytic activity of Ni₀.₅Cu₀.₅Fe₂O₄, CuFe₂O₄, NiFe₂O₄ and Fe₃O₄ were prepared through a similar process.

2.3. Characterization of catalyst
Fourier-transform infrared (FT-IR, Nicolet Magna-IR 550) spectroscopy using KBr as the reference was collected within the wavelength range of 400–4,000 cm⁻¹. The crystal properties of the as-prepared samples are characterized by powder X-ray diffraction (XRD, Philips PW1730) with Cu Kα X-ray irradiation at 40 kV and 40 mA. The morphology and element analysis of Ni₀.₅Cu₀.₅Fe₂O₄ was observed and determined on a scanning electron microscope equipped with an energy-dispersive X-ray (SEM-EDX, MIRA3-XMU). The nanostructure was examined by Transmissions electron microscope (TEM, JEOL JEM 2100F). The specific surface areas are characterized via N₂ adsorption-desorption, the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The magnetic analysis is carried out by using a vibrating sample magnetometer (VSM, 7400, Lake Shore, USA).

2.4. Catalytic activity
The catalytic activity of the as-prepared catalysts is determined by the degradation efficiency of CIP (20.0 mg/L, 100 mL). The reaction begins at 25 ± 2 °C in a 250 mL round bottom flask. The pH of the system was adjusted using HCl and NaOH (pH =
3.00–10.0). Then the catalyst was suspended into the system with the dosage range 0.100–0.700 g/L, and stirred for 60 min to reach adsorption-desorption equilibrium. Then a certain dosage of PDS (2.00–9.00 mmol/L) was added to be activated for producing active free radicals. 4.00 mL samples were taken every 10 min, and the solid-liquid was filtered with a 0.45 μm filter membrane to obtain clear liquid to be determined.

To identify the free radicals in the reaction process, the capture experiments were carried out. The method is the same as mentioned above, besides adding additional Ethanol (EtOH, 10.0 mmol/L) or Tertbutanol (TBA, 10.0 mol/L) before the catalytic degradation process for trapping SO$_4^-$ and ·OH.

The degradation efficiency of CIP was calculated by the following Equation (1). Pseudo-first-order (PFO) was used to evaluate the degradation kinetics of CIP, and the reaction rate constant was determined at different CIP concentrations by the following Equation (2).

\[
\text{Degradation efficiency (100\%)} = 1 - \left( \frac{c_t}{c_0} \right)
\]

\[
\ln \left( \frac{c_t}{c_0} \right) = -kt
\]

where $c_0$ and $c_t$ are the initial and final CIP concentrations (mg/L), respectively.

The concentration of CIP during the reaction was measured by UV-Vis spectrophotometer at 272 nm wavelength. Total organic carbon (TOC) was determined by the TOC analyzer. The concentrations of released metals on the catalyst surface in the reaction solution were measured by inductivity coupled plasma-mass spectrometry (ICP-MS). A gas chromatograph/mass spectrometry (GC-MS) analysis was performed to determine the intermediates in CIP degradation process.

**Figure 1** | The schemes of synthesize Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ by co-precipitation method.
3. RESULTS AND DISCUSSION

3.1. Characterizations of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$

SEM-EDX and TEM were used to investigate the surface morphology, chemical composition and nanostructure of the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nano-particles, and the results are shown in Figure 2. As detected, the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ with a particle size <100 nm. The presence of Ni, Cu, Fe and O elements in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ catalyst were found in Figure 2(b).

FT-IR is shown in Figure 3(a), the peak around 3,400 cm$^{-1}$ can be attributed to the stretching vibration peak of O-H. Two main ferrite characteristic bands were detected: octahedral metal stretching inherent in the low-frequency band (415–455 cm$^{-1}$) and tetrahedral stretching vibration in the high-frequency band (570–630 cm$^{-1}$) (Wahaab et al. 2020).

XRD was further conducted to study the crystallinity of the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nano-particles, and Figure 3(b) indicate that the XRD patterns were indexed to pure cubic spinel structure with a change lattice parameter of ‘a’ and its space group: Fd-3 m (277). According to ICDD card for Ni and Cu ferrites, the peaks appeared at 2θ range of 31.22°, 35.81°, 38.70°, 43.51°, 53.52°, 57.44° and 63.20° can be attributed to the (220), (311), (320), (400), (422), (511) and (440) major lattice planes in the XRD patterns confirms the formation of spinel cubic structure.

The specific surface area and pore volume of the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nano-particles were analyzed by N$_2$ adsorption-desorption isotherm experiment in Figure 3(c) and 3(d). The specific surface area of the tested samples is 131 g/m$^2$. And through the BJH experiment results, we can see that the tested samples have mesoporous structure, of which the pore diameters are less than 10.0 nm. Meanwhile, the as-prepared catalysts showed H$_3$ hysteresis ring (P/P$_0 > 0.400$) and IV N$_2$ adsorption-desorption isotherms, which further proved that these samples had mesoporous structure, according to the IUPAC classification.

3.2. Removal of CIP

Figure 4(a) shows the degradation efficiency of CIP with different catalysts (Fe$_3$O$_4$, CuFe$_2$O$_4$, NiFe$_2$O$_4$, and Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$) to activate PDS. It is obvious that the degradation efficiency and kinetic rate are very low (6.50% and 1.30 × 10$^{-3}$ min$^{-1}$), without adding any catalyst, only PDS exists. When catalysts was added, the final degradation efficiency and kinetic data were 23.2% and 8.60 × 10$^{-3}$ min$^{-1}$ for Fe$_3$O$_4$; 61.8% and 1.60 × 10$^{-2}$ min$^{-1}$ for CuFe$_2$O$_4$, 65.8% and 2.05 × 10$^{-2}$ min$^{-1}$ for NiFe$_2$O$_4$, 80.2% and 2.98 × 10$^{-2}$ min$^{-1}$ for Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ respectively. These results indicated that Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ had the strongest catalytic efficiency.

Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ has redox cycles of Fe$^{3+}$/Fe$^{2+}$, Ni$^{2+}$/Ni$^{3+}$ and Cu$^{3+}$/Cu$^{2+}$. Therefore, the ratio between copper/nickel/iron Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ is an important variable to obtain the optimal efficiency. In theory, spinel with the molecular structure of MFe$_2$O$_4$(Fe$^{3+}$/M$^{2+}$ = 2:1). Changing the Fe$^{3+}$ will destroy the balance of Fe/Ni/Cu in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ and contribute a different effect on degradation efficiency (Pham et al. 2018). Figure 4(b) shows when the molar amount of Fe$^{3+}$ increased from 0.500 to 2.00 mol (with Cu$^{2+}$ and Ni$^{2+}$ quantified at 0.500 mol), the degradation efficiency increased from 57.2% to 80.2%, and the corresponding law appears in the kinetic rate, increased from 1.66 × 10$^{-2}$ min$^{-1}$ to 2.98 × 10$^{-2}$ min$^{-1}$. However, the continuous increase of the number of Fe$^{3+}$ (5.00 mol) will lead to an adverse impact on the degradation efficiency and kinetic rate: decreased down to 53.8% and 1.49 × 10$^{-2}$ min$^{-1}$. According to this result and analysis, the optimum ratio of the three metal ions can be determined at Fe$^{3+}$ : Cu$^{2+}$ : Ni$^{2+}$ = 2 : 0.5 : 0.5.

Figure 4(c) and the inset show two processes in the removal of CIP: adsorption and degradation. Adsorption-desorption equilibrium can be achieved in 60 minutes, and the adsorption and degradation rate is 56.1%, 80.2% (93.1% of CIP and 58.1% of CIP) at the range of pH 0.500 mol), the degradation efficiency and kinetic data are very low (6.50% and 1.30 × 10$^{-3}$ min$^{-1}$). According to this result and analysis, the optimum ratio of the three metal ions can be determined at Fe$^{3+}$ : Cu$^{2+}$ : Ni$^{2+}$ = 2 : 0.5 : 0.5.

Figure 4(c) and the inset show two processes in the removal of CIP: adsorption and degradation. Adsorption-desorption equilibrium can be achieved in 60 minutes, and the adsorption and degradation rate is 56.1%, 80.2% (93.1% of CIP and 55.4% total organic carbon were removed). Besides, the ratio of the dissolved iron of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ into solution was 0.0004 wt.% of Fe ions, 0.202 wt.% of Cu ions and 1.19 wt.% of Ni ions.

The following experiments are the catalytic process after adsorption-desorption equilibrium, and the degradation rate is calculated with the adsorption-desorption equilibrium concentration as the initial concentration.

3.3. Effect of operational factors

The value of pH is a basic factor in AOPs. As shown in Figure 5(a), the degradation efficiency increased from 52.8% to 80.2%, the constant kinetic rate increased from 1.29 × 10$^{-2}$ min$^{-1}$ to 2.98 × 10$^{-2}$ min$^{-1}$ at the range of pH 3.00–6.00. For pH = 6.00–10.0, the degradation efficiency and constant kinetic rate decreased from 82.0%, 2.98 × 10$^{-2}$ min$^{-1}$ to 40.6%, 1.09 × 10$^{-2}$ min$^{-1}$. The degradation efficiency of CIP reached the highest at pH = 6.00. The inhibition of CIP degradation at pH < 6.00 may be due to scavenging reasons of H$^+$ on SO$_4^-$ and OH. And metal ion leaching will also affect the proportion of three metals in the catalyst and destroy the structure of the catalyst (Zhang et al. 2019). The degradation efficiency of CIP
Figure 2 | SEM-EDX (a) and (b), TEM (c) of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$. 
changed in pH = 3–10 can be made based on zeta potential of Ni_{0.5}Cu_{0.5}Fe_{2}O_{4} (pH_{zc} is about 6.7). Therefore, the surface of Ni_{0.5}Cu_{0.5}Fe_{2}O_{4} is positive at pH< pH_{zc}, while it will be negative at pH > pH_{zc}. Lower pH may promote the formation of hydrogen bond between H^{+} and O-O group in PDS, so the positive charge around PDS will hinder the electron transfer between PDS and positively charged catalyst (Wang et al. 2019). When the pH increases to alkaline, it can be inferred that the number of surface hydroxyl groups (OH⁻) of Ni_{0.5}Cu_{0.5}Fe_{2}O_{4} catalyst will increase, and the electrostatic repulsion force will reduce the opportunity of interaction between Ni_{0.5}Cu_{0.5}Fe_{2}O_{4} and PDS, resulting in a significant decrease in the degradation efficiency of CIP (Li et al. 2017). When the pH value increase, SO_{4}^{2−} could react with OH to form other mid-bodies, such as SO_{4}^{2−}, HSO_{4}^{−} and O_{2}, which could cut down the consistence of active free radicals and further debase the degradation efficiency of the system (Zhang et al. 2019).
Figure 4 | The effect of different catalysts (a) and the metal ions ratio of Fe$^{3+}$, Cu$^{2+}$, Ni$^{2+}$ in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ (b) on the degradation efficiency and kinetic rate of CIP. Removal process of CIP in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/PDS system (c).
Figure 5 | Factors affecting degradation efficiency and kinetic rate of CIP: (a) pH, (b) Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ dosage, (c) PDS dosage, (d) CIP concentration, (e) temperature and (f) inorganic anions.
The degradation of antibiotic CIP under different catalyst dosage was investigated in Figure 5(b). By increasing of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ dosage from 0.100 to 0.500 g/L, the degradation efficiency of CIP increased from 37.1% to 80.2%, the kinetic rate increased from $9.80 \times 10^{-3}$ min$^{-1}$ to $2.98 \times 10^{-2}$ min$^{-1}$. The reason for this phenomenon is that the catalyst can provide more active sites for CIP adsorption and PDS activation with the increase of dosage. However, when the dosage of catalyst was added to 0.700 g/L, a slight decline occurred in degradation efficiency and kinetic rate down to 77.1% and $2.70 \times 10^{-2}$ min$^{-1}$. As reported that related reactions (Equations (3) and (4)) occurred through the capture reaction between metal ions and radicals, which will consume SO$_4^{2-}$ and OH (Tian et al. 2020).

\[
\text{OH} + M^{2+} \rightarrow \text{OH}^- + M^{3+}
\]  

(3)

\[
\text{SO}_4^- + M^{2+} \rightarrow \text{SO}_4^{2-} + M^{3+}
\]  

(4)

Figure 5(c) shows the effects of different PDS concentrations on CIP degradation efficiency. With the increase of PDS concentration from 2.00 to 5.00 mmol/L, the degradation efficiency and kinetic rate of CIP increased from 65.3%, 2.03 \times 10^{-2} \text{ min}^{-1} \text{ to } 80.2\%, 2.98 \times 10^{-2} \text{ min}^{-1} respectively, which was aroused by the high amount of SO$_4^{2-}$ and OH production through more reaction between Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ and PDS. Nevertheless, when the dosage of PDS was further increased, the degradation efficiency and kinetic rate of CIP decreased down to 68.0% and $2.20 \times 10^{-2}$ min$^{-1}$. This reason can be explained by following radical quenching reactions (Equations (5) and (6)) (Dong et al. 2017).

\[
\text{SO}_4^- + \text{SO}_4^- \rightarrow 2\text{SO}_4^{2-} \text{ or } \text{S}_2\text{O}_5^{2-}
\]  

(5)

\[
\text{OH} + \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2
\]  

(6)

The initial CIP concentration on its degradation process in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/PDS system was evaluated in Figure 5(d). Under the condition of constant catalyst and oxidant dosage, the degradation efficiency and the kinetic rate increased from 62.4% and $1.95 \times 10^{-2}$ min$^{-1}$ to 84.2% and $3.23 \times 10^{-2}$ min$^{-1}$ with the increase of initial concentration in the low concentration range (10.0–100 mg/L). But with the initial concentration of CIP increased to 300 mg/L, the degradation efficiency and the kinetic rate decreased to 63.8% and $1.72 \times 10^{-2}$ min$^{-1}$. It can be explained that the amount of SO$_4^{2-}$ produced in the system is constant, so the number of CIP molecules that can be decomposed by these amounts of SO$_4^{2-}$ is also certain. In addition, the formation of intermediates produced by CIP decomposition occupies the catalyst surface and has competitive behavior with the target pollutants. At lower concentration, the active sites of the catalyst are sufficient, and this competition is not enough to inhibit the degradation of CIP, but when the concentration increases, the degradation efficiency and kinetic rate of CIP are significantly inhibited.

Figure 5(e) shows the distinction on CIP degradation caused by temperature variation (10 °C, 25 °C, 50 °C). The degradation efficiency reached 42.6%, 51.8%, 57.9% in 10 min, and the kinetic rate increased from $5.55 \times 10^{-2}$ min$^{-1}$ to $8.65 \times 10^{-2}$ min$^{-1}$. In general, the temperature can promote the degradation of CIP, for heating can decompose PDS into SO$_4^{2-}$ and OH through thermolytic cleavage of O-O bond (Hu et al. 2019).

Inorganic anions widely exist in actual water and have a significant impact on AOPs. Therefore, the influence caused by existing anions should be considered. Simulate the real system and test the influence of 10.0 mmol/L Cl$^-$, NO$_3^-$ and HCO$_3^-$, and the results are shown in Figure 5(f). In the presence of NaCl and NaNO$_3$, the degradation efficiency decreased slowly down to 60.0% and 58.1% respectively, and the kinetic rates decreased down to $1.45 \times 10^{-2}$ min$^{-1}$ and $1.39 \times 10^{-2}$ min$^{-1}$, compared with the blank group is 80.2% and $2.98 \times 10^{-2}$ min$^{-1}$. Considering that the pH changes little in these two systems, according to previous studies, the reasons for the decrease in efficiency may be caused by the following Equations (7)–(10) (Chen et al. 2020). When NaHCO$_3$ present in the system, the pH value changes significantly from 6.00 to 8.90. The degradation efficiency and kinetic rates decreased to 21.5% and $4.90 \times 10^{-2}$ min$^{-1}$, which are much lower than 40.6% and $1.09 \times 10^{-2}$ min$^{-1}$ at pH = 10.0. Therefore, there must be other reasons for inhibition of efficiency caused
by HCO$_3^-$ and can be explained by Equations (11) and (12) (Alhamd et al. 2021).

\[
\begin{align*}
\text{SO}_4^{2-} + \text{Cl}^- & \rightarrow \text{SO}_4^{2-} + \text{Cl}^- \\
\text{OH} + \text{Cl}^- & \rightarrow \text{ClO}^- \\
\text{SO}_4^{2-} + \text{NO}_3^- & \rightarrow \text{SO}_4^{2-} + \text{NO}_3^- \\
\text{OH} + \text{NO}_3^- & \rightarrow \text{OH}^- + \text{NO}_3^- \\
\text{SO}_4^{2-} + \text{HCO}_3^- & \rightarrow \text{SO}_4^{2-} + \text{HCO}_3^- \\
\text{OH} + \text{HCO}_3^- & \rightarrow \text{CO}_3^- + \text{H}_2\text{O}
\end{align*}
\]

3.4. Degradation mechanism of CIP

It is found that Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ has superior activating ability in this study. The mechanism of CIP degradation in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/PDS system is proposed as following Equations (13)–(21) (Li et al. 2017). Firstly, CIP molecules will be adsorbed to the reaction site on the surface of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$. Then PDS is activated by electron transfer between redox pairs on the catalyst surface to form SO$_4^{2-}$, and then SO$_4^{2-}$ can be transferred into OH by the reactions with OH$^-$ and H$_2$O. Finally, the degradation reaction took place on the catalyst surface and produce intermediate products, CO$_2$ and H$_2$O. Intermediates from CIP degradation were identified by GC-MS, and possible degradation pathways were suggested in Figure 6, Pathway I: SO$_4^{2-}$ and OH attack on the piperazine ring and P1 (m/z = 334) was found. Followed by the ‘CO’ and ‘CH$_2$CH$_2$NH$_2$’ lose, the P2 (m/z = 334) was generated. Pathway II: The ‘C-F’ bond on the quinolone ring is hydroxyl substituted to form P5 (m/z = 330), and then further decarboxylated to form P6 (m/z = 285). Pathway III: Decarboxylation occurred and P5 formed (m/z = 288). Pathway IV: a hydroxylation process, hydroxyl radical attacked the quinolone ring of CIP to produce P4 (m/z = 348). Finally the above intermediates could be decomposed into other smaller products even CO$_2$ and H$_2$O.

As previously reported (Alhamd et al. 2021), TBA used as the scavenger for OH, can react at a very high rate with OH (k OH = 3.80–7.6 × 10$^8$ mol·L$^{-1}$·s$^{-1}$), compared to SO$_4^{2-}$ (k SO$_4^{2-}$ = 4.0–9.1 × 10$^5$ mol·L$^{-1}$·s$^{-1}$). EtOH can react with OH and SO$_4^{2-}$ at a constant kinetic rate of 1.2–2.8 × 10$^9$ mol·L$^{-1}$·s$^{-1}$ and 1.6–7.7 × 10$^9$ mol·L$^{-1}$·s$^{-1}$ respectively. TBA and EtOH were used in this trapping experiments, and Figure 7 shows that in the presence of 10.0 mmol/L TBA and EtOH, degradation efficiency and kinetic rate decreased down to 65.8%, 1.94 × 10$^{-2}$ min$^{-1}$ and 60.9%, 1.82 × 10$^{-2}$ min$^{-1}$ respectively.

**Figure 6** | Possible CIP degradation pathway in Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/PDS system.
results show that both SO₄²⁻ and ·OH play an important role in the process of CIP degradation.

\[
\text{CIP} + \text{NiCuFe}_2\text{O}_4 \rightarrow \text{CIP@Ni}_{0.5}\text{Cu}_{0.5}\text{Fe}_2\text{O}_4 \\
\text{H}_2\text{O} + \text{S}_2\text{O}_8^{2−} \rightarrow \text{HSO}_5^{−} + \text{HSO}_4^{0} \\
\text{Cu}^{2+} + \text{S}_2\text{O}_8^{2−} \rightarrow \text{Cu}^{3+} + \text{SO}_4^{−} + \text{SO}_2^{−} \\
\text{Ni}^{2+} + \text{S}_2\text{O}_8^{2−} \rightarrow \text{Ni}^{3+} + \text{SO}_4^{−} + \text{SO}_2^{−} \\
\text{Fe}^{2+} + \text{S}_2\text{O}_8^{2−} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{−} + \text{SO}_2^{−} \\
\text{Fe}^{3+}/\text{Cu}^{3+}/\text{Ni}^{3+} + \text{HSO}_5^{−} \rightarrow \text{Fe}^{2+}/\text{Cu}^{2+}/\text{Ni}^{2+} + \text{SO}_4^{−} + \text{H}^{+} \\
\text{SO}_4^{−} + \text{H}_2\text{O} \rightarrow \text{SO}_3^{2−} + \text{OH}^{−} + \text{H}^{+} \\
\text{SO}_4^{−} + \text{OH}^{−} \rightarrow \text{SO}_2^{−} + \text{OH}^{−} + \text{H}^{+} \\
\text{SO}_4^{−}/\text{OH} + \text{CIP} \rightarrow \text{Intermediates} + \text{CO}_2 + \text{H}_2\text{O}
\]

3.5. Reusability and stability study

The magnetic separation characteristics of the catalyst were further studied. From the magnetic hysteresis loops of Figure 8(a), Ni₀.₅Cu₀.₅Fe₂O₄ exhibits a distinctly symmetric hysteresis loop with a satisfactory magnetization saturation value (≅8.6 emu/g), so it can be easily separated by a magnet and the result was shown in the inset photograph of Figure 8(b). It is obvious that when the magnet exists, the system gradually becomes clear from turbidity, which implies that the catalyst has good magnetic retrievability.

As shown in Figure 8(b), the degradation efficiency and kinetic rate are reduced compared with the new catalyst after three cycles of experiments. The reason contributing to this phenomenon can be explained: On the one hand, the leaching of metal ions, the destruction of active surface, and the conglomeration of catalyst. On the other hand, the main contaminant and its intermediate will occupy the catalyst sites at the same time and competitive adsorption occur. However, there is no big gap between the three cycle runs, the degradation efficiency is almost maintained at 60.0%. From the FT-IR spectrometer comparison in Figure 3(a) before and after use, it can be seen that two main ferrite characteristic bands still exist, which proves that the structure of the catalyst has not changed significantly after three times of use. Base on the analysis above, Ni₀.₅Cu₀.₅Fe₂O₄ has excellent stability and recyclability for activating PDS in CIP degradation.
4. CONCLUSION

Utilizing a simple co-precipitation method to synthesize magnetic Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ nano-catalyst for activating PDS in degradation of CIP was studied. Two processes exist in the removal of CIP: adsorption and degradation. The experiments show that compared with heterogeneous systems (Fe$_3$O$_4$/PDS, CuFe$_2$O$_4$/PDS, NiFe$_2$O$_4$/PDS), the degradation efficiency of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/PDS is much higher (80.2%) at pH = 6.00, 0.500 g/L of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$, 5.00 mmol/L of PDS, CIP concentration of 20.0 mg/L at 25 $\pm$ 2°C for 50 min. Besides, the ratio of the dissolved iron of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ into solution was 0.0004% of Fe ions, 0.202% of Cu ions and 1.19% of Ni ions. The presence of Cl$^-$, NO$_3^-$, HCO$_3^-$ in the reaction solution can reduce the degradation efficiency. Free radical capture experiments emphasized that the two reactive species (SO$_4^-$ and ·OH) were produced in the present process, and the important reactive species in the degradation of CIP by Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/PDS. The Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ is proved a magnetic material, so the catalyst can be easily separated from the solution and used in recycling experiments after the reaction. The results show that with increasing the number of cycles from 1 to 3, the degradation efficiency decreased and was maintained near 60%. It should be noted that this work provides an easily prepared and practical catalyst for the development of magnetic retrievability catalyst for degradation organic pollutant molecules based on the practical needs.

Figure 8 | Hysteresis loops of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ (a) Cycle runs of Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$/PDS system, the inset shows the Ni$_{0.5}$Cu$_{0.5}$Fe$_2$O$_4$ attracted by a magnet (b).
CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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