One-Step Synthesis of Metal-Modified Nanomagnetic Materials and Their Application in the Removal of Chlortetracycline

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ABSTRACT: Magnetic nanomaterials are promising heterogeneous catalysts for environmental applications. According to X-ray diffraction, Brunauer−Emmett−Teller method, scanning electron microscopy, high-resolution transmission electron microscopy, and vibrating-sample magnetometer, a kind of copper-modified nanomagnetic material (Cu-nFe₃O₄) was successfully prepared by a one-step synthesis method. Among them, compared with the two-step synthesis method of Cu/Fe₃O₄ and Cu/nFe₃O₄, Cu-nFe₃O₄ has the best effect on chlortetracycline (CTC) removal. The batch study results indicate that the maximum removal of chlortetracycline is 99.0% at a dosage = 2.0 g L⁻¹, copper loading = 0.8 mM, and C₀ = 100 mg L⁻¹ at the optimum conditions within 90 min. The effects of humic acids (HA), NO₃⁻, Cl⁻, CO₃²⁻, and PO₄³⁻ on the CTC removal by Cu-nFe₃O₄ are also investigated. Repeated experiments were performed on the prepared Cu-nFe₃O₄ indicating that Cu-nFe₃O₄ has good recyclability. The kinetics of the Cu-nFe₃O₄ removal of CTC was investigated, indicating that the reaction conformed to the double constant model and the reaction is mainly dominated by a chemical reaction with physical adsorption. Finally, the mechanism of the CTC removal by Cu-nFe₃O₄ in a heterogeneous environment was clarified. This study aims to provide an experimental basis for the environmental application of Cu-nFe₃O₄.

1. INTRODUCTION

As an important magnetic material, magnetite (Fe₃O₄) has attracted much attention because of its unique characteristics. It has also been widely used in the fields of batteries, sensors, targeted drug delivery, catalysts, and data storage. The problem with magnetic materials is that the particles interact with each other, thereby forming large aggregates. However, if the size of the magnetic nanoparticles is reduced to less than a few nanometers, they will become superparamagnetic. The particles will obtain a certain magnetization when the magnetic field is applied; however, when the magnetic field is removed, the long program will be lost because of the high thermal energy, and the particles have no remanence.

Small-sized nanoparticles have high specific surface area and reactivity, which contribute to their interaction with a variety of chemicals. The immobilization of nano-Fe₃O₄ on organic or inorganic supports can prevent the agglomeration of nano-Fe₃O₄, which is a promising heterogeneous catalyst with potential applications. The removal of metals by nano-Fe₃O₄ has achieved a series of good results. Accordingly, researchers have modified nano-Fe₃O₄ by polymethyl methacrylate (PMMA), silicon dioxide, carboxymethyl-β-cyclodextrin (CM-β-CD), and polyvinylimide (PVAm), such that the nano-Fe₃O₄ surface has abundant functional groups to efficiently adsorb heavy-metal pollutants, such as nickel(II), lead(II), mercury(II), cobalt(II), chromium(VI), or arsenic(V) in water.

Zeng et al. proposed a two-step synthesis of iron-nitrogen codoped mesoporous carbon spheres to activate PMS to remove organic pollutants in water. Due to the richness and unique mesoporous structure of double heteroatom doping, in situ conversion of porous Fe₃O₄ microspheres into macroporous M-Fe/NC materials has greatly improved the catalytic performance of PMS activation. Roto et al. synthesized a thiol-modified Fe₃O₄/SiO₂ core−shell nanoparticle magnetic adsorbent by a two-step method for chlorogold adsorption. The adsorption of [AuCl₄]⁻ ions by Fe₃O₄/SiO₂ core−shell nanoparticles follows the Langmuir isotherm model, and the maximum adsorption capacity is 115 mg/g. However, the reusability of the composite needs to be considered. Xu and Wang prepared nano-Fe₃O₄/CeO₂ magnetic composites by a two-step synthesis method. The catalytic performance of the nano-superparamagnetic nFe₃O₄/CeO₂ composite for the removal...
oxidation of 4-chlorophenol (4-CP) by hydrogen peroxide was studied. Because the combination of Fe₃O₄ and CeO₂ in the two-step process is not close enough, the activity of the catalyst decreases greatly after six consecutive runs. Further work is needed to reduce the loss of the active ingredients of the catalyst.

Because of the unreliable synthesis of active ingredients and Fe₃O₄ by the two-step method, the active ingredients combined with Fe₃O₄ will fall off due to hydraulic and collision effects. The active substances of the modified Fe₃O₄ composites prepared by the two-step method are easy to be lost, resulting in the rapid degradation of the properties of the composites. The active material of the modified Fe₃O₄ composite prepared by the one-step method combines with Fe₃O₄ more firmly, and the active ingredient is not easy to fall off, thus prolonging the service life of the composite. Moreover, the one-step process is simpler than the two-step process, avoiding the waste of raw materials caused by too many processes, and is more green and environmentally friendly. Composite materials have high catalytic activity for heterogeneous Fenton degradation of bisphenol A and synergistic enhancement after modification. Song et al. synthesized chitosan-coated Fe₃O₄ nanoparticles in one step from Fe₃O₄ and chitosan chemically modified with polyethylene glycol (PEG) and lactic acid (LA). The nanoparticles are stable and have no cytotoxicity and non-tissue toxicity. However, the existing one-step method is suitable for the modification of Fe₃O₄ by organic (such as PMMA, CM-β-CD, PVAm, PEG, and LA), graphene, and silicate. It is not suitable for the modification of Fe₃O₄ by metal (especially copper, silver, cobalt, nickel, etc.). This is mainly because the formation of Fe₃O₄ will be destroyed by copper, silver, cobalt, and nickel ions in one-step synthesis, leading to the failure of composite preparation.

In this paper, a feasible one-step method for doping metal to modify nano-Fe₃O₄ is proposed, which not only does not destroy the original structure of nano-Fe₃O₄ but also dredges the pore structure of nano-Fe₃O₄. At the same time, nano-Fe₃O₄ is firmly loaded with metal and has a specific catalytic effect. This study used chlortetracycline (CTC), one of the most representative tetracyclines, as the target pollutant. At the same time, it made nano-Fe₃O₄ loaded with metal, which has a certain catalytic effect. The nano-Fe₃O₄ modified by loading metal, dosage, and influencing factors was investigated to treat CTC. This study aims to develop more green and efficient antibiotic wastewater removal materials.

2. MATERIALS AND METHODS

2.1. Materials. Commercial Fe₃O₄ (CAS No: 1317-61-9), iron(II) sulfate heptahydrate (FeSO₄·7H₂O, CAS No: 7782-63-0), copper(II) sulfate pentahydrate (CuSO₄·5H₂O, CAS No: 7758-99-8), silver nitrate (AgNO₃, CAS No: 7761-88-8), sodium sulfate (Na₂SO₄·10H₂O, CAS No: 7770-41-9), magnesium sulfate heptahydrate (MgSO₄·7H₂O, CAS No: 7754-20-7), potassium nitrate (KNO₃, CAS No: 7758-49-3), anhydrous ethanol (C₂H₅OH, CAS No: 64-17-5), and manganese sulfate (MnSO₄·H₂O, CAS No: 1336-21-6), and manganese sulfate (MnSO₄·H₂O, CAS No: 7785-87-7) were purchased from Sinopharm Chemical Reagent Co., Ltd. Except for humic acid, which was chemically pure, all of the chemicals used were of analytical grade. Chlortetracycline (CTC, 98%) was purchased from Chengdu Aikeda Chemical Reagent Co., Ltd.

2.2. Synthetic Method. Coprecipitation is currently the most common method for preparing nano-Fe₃O₄ particles by adding a suitable precipitant to a salt solution containing various metal ions to promote sufficient precipitation and crystallization followed by precipitation. The particles were dried or thermally decomposed to produce nanoparticles. The basic principle of this method is as follows:

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\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- = \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}
\]

The basic steps of preparation are as follows: 1.39 g of FeSO₄·7H₂O and 2.7 g of FeCl₃·6H₂O were added to a 250 mL beaker. 100 mL of distilled water was added and rapidly heated at 80 °C. 30 mL of concentrated ammonia water was added at a slow rate. The solution gradually produced a black solid and reacted at a constant temperature for 10 min. The solid particles were washed several times with distilled water and ethanol. The supernatant was then discarded and dried at room temperature for 5 h to prepare n-nano-Fe₃O₄, which were stored in the dryer.

The preparation one-step synthesis method for M-nFe₃O₄ is as follows: 1.39 g of FeSO₄·7H₂O and 2.7 g of FeCl₃·6H₂O were added to a 250 mL beaker. 100 mL of distilled water was then added and rapidly heated at 80 °C. 30 mL of concentrated ammonia water was then added at a slow rate. The solution gradually produced a black solid and reacted at a constant temperature for 5 min. Subsequently, 0.2–0.8 mM of M (metal) salt solution was quickly added to the reaction solution, and the reaction was continued for 10 min. The solid particles were washed several times with distilled water and ethanol. Subsequently, the supernatant was discarded and dried at room temperature for 5 h to prepare n-M-nFe₃O₄ particles stored in the dryer.

2.3. Analysis Method. A certain amount of commercial Fe₃O₄, prepared nFe₃O₄, or M-nFe₃O₄ was added to a 250 mL conical flask. The initial concentration of the CTC solution was 50 mg L⁻¹. The conical flask was put into a constant temperature oscillator for continuous reaction at 25 °C and 200 rpm. The CTC concentration was measured by an ultraviolet–visible spectrophotometer after the 0.22 μm filter membrane was removed at different times. The detection wavelength was 276 nm. The residual CTC concentration was used as the measurement index to investigate the removal effect of the loaded metal, loaded amount, dosage, and initial concentration of the pollutants on CTC. Each experiment was parallel to three groups, and the mean was taken.

The commercial Fe₃O₄ prepared nFe₃O₄, and Cu-nFe₃O₄ were characterized by X-ray diffraction (XRD, Bruker AXS, D8 Advance) using copper–potassium alpha radiation (40 kV, 30 mA). The 2θ range was 20–100°, and the scanning speed was 10° min⁻¹. The adsorption–desorption isotherm of nitrogen was determined using a Micromeritics ASAP 2020 analyzer at a liquid nitrogen temperature (77 K) over a relative pressure range of 0 to 1. The specific surface area and pore structure characteristics of the materials were analyzed using the Brunauer–Emmett–Teller (BET) method and the Barrett–Joyner–Halenda (BJH) model. Scanning electron microscopy (SEM, XL-30ESEM FEG FEI scanning electron microscope
COMPANYTM) equipped with an Oxford Instruments X-max spectrometer (EDS) for studying the chemical composition and high-resolution transmission electron microscopy (HRTEM, Tecnai G2 F20) were used to observe the nanomaterial morphology and size. Magnetism was assessed using a magnetic measurement system (Squid-VSM, USA).

3. RESULTS AND DISCUSSION

3.1. Synthesis and Characterization. The compositional changes of the commercial Fe3O4, prepared nFe3O4, and 0.2–0.8 Cu-nFe3O4 were analyzed by XRD. Figure 1a1–a5 shows the XRD analysis of the five magnetic materials. The six peaks located at 2θ = 30.1, 35.5, 43.1, 53.5, 57.0, and 62.6°, which were correspondingly diffracted with (220), (311), (400), (422), (511), and (440) of Fe3O4, respectively, matched with the standard card (JCPDS no 65-3107).21 No other diffraction peaks were observed in Figure 1a, thereby ensuring a good purity of the samples with a cubic inverse spinel structure. A comparison of the letter-to-background ratios of the five XRD patterns in Figure 1 clearly shows that Figure 1a2–a5 had the lowest background ratio, indicating that its crystallinity was poor. In contrast, Figure 1a1 had the highest signal-to-background ratio, indicating its good crystallinity.22,23 The XRD peak widths of nFe3O4 and Cu-nFe3O4 prepared by the coprecipitation method were higher than those of the commercial Fe3O4, may be because of the non-crystalline structure properties of the nanomaterials prepared by the coprecipitation method15,24 and the modification with copper not changing the Fe3O4 composition.

The pore characteristics, surface area, and adsorption–desorption measurements of the samples were investigated with nitrogen. As shown in Figure 1b–d, Figures S1–S2, and Table 1, all samples showed a typical type-IV isotherm, illustrating the mesoporous structure. In addition, the appearance of H3 hysteresis loops indicated abundant mesopores in Cu-nFe3O4 after multiple reactions. The pore size distribution of the three samples was calculated by the density functional theory (DFT) method. As shown in Figure 1b–d, the micropores with a 1–2 nm diameter were present in all samples, but the commercial Fe3O4 had very few mesopores (2–50 nm) and macropores (>50 nm), while the prepared nFe3O4 and Cu-nFe3O4 did not only have abundant micro-pores but also had abundant mesopores and macropores. The mesopores were mainly concentrated at 30 nm. The differential pore volume of nFe3O4 and Cu-nFe3O4 was mainly attributed to the higher pores of 2–150 nm compared to the commercial Fe3O4, indicating that more mesopores and macropores were formed in the material by precipitation and modification. As shown in Table 1, compared with the commercial Fe3O4 (2.54 m² g⁻¹), the BET surface area of nFe3O4 (73.84 m² g⁻¹), 0.2 Cu-nFe3O4 (76.33 m² g⁻¹), 0.8 Cu-nFe3O4 (73.28 m² g⁻¹), and post-reaction 0.8 Cu-nFe3O4 (83.72 m² g⁻¹) significantly increased. Moreover, they were larger than nFe3O4 (55.72 m² g⁻¹)21 prepared by the precipitation method and the surfactant-modified nFe3O4 (30.18 m² g⁻¹),25 indicating that the precipitation method and the metal modification can improve the pore structure and

| composite          | BET surface area (m² g⁻¹) | pore volume (cm³ g⁻¹) | pore size (nm) |
|--------------------|----------------------------|-----------------------|---------------|
|                    | S_BET micro BJH total      |                       |               |
| commercial Fe3O4   | 2.54 0.42 0.009 0.005      | 8.31 23.75            |
| nFe3O4             | 73.84 2.70 0.475 0.334     | 18.09 24.76           |
| 0.2 Cu-nFe3O4      | 76.33 9.12 0.353 0.327     | 17.42 17.42           |
| 0.8 Cu-nFe3O4      | 73.28 14.38 0.443 0.297    | 24.94 24.94           |
| post-reaction 0.8 Cu-nFe3O4 | 83.72 -0.003 0.466 0.329 | 21.56 21.56         |

Figure 1. XRD spectra of the (a1) commercial Fe3O4 (a2) prepared nFe3O4 and (a3–5) 0.2–0.8 Cu-nFe3O4; (b) corresponding pore size distributions of the commercial Fe3O4 prepared nFe3O4 0.2, 0.8 Cu-nFe3O4 and post-reaction 0.8 Cu-nFe3O4 (c–d) N2 adsorption/desorption isotherms of nFe3O4 and 0.8 Cu-nFe3O4.
the specific surface area of nFe₃O₄. As shown in Figure S3, the specific surface area of the material can be increased by this precipitation method, and the number of micropore can be further increased by metal modification. The specific surface area increased and the micropore area sharply decreased after the reaction, indicating that the reactive sites were mainly concentrated in the micropore. Moreover, the specific surface area of the post-reaction 0.8 Cu-nFe₃O₄ after multiple reactions was 14.3% larger than that of the 0.8 Cu-nFe₃O₄ before being unreacted, which is also strong proof that the multiple reaction performance of the material is not reduced.

Figure 2a,b shows the SEM photographs of the nFe₃O₄ nanoparticles and the commercial Fe₃O₄ prepared by coprecipitation. Both of them had the same morphology and octahedron with an edge length of approximately 0.5−1.5 μm. According to the BET data, the specific surface area of the prepared nFe₃O₄ (73.84 m² g⁻¹) was 28 times larger than that of the commercial Fe₃O₄ (2.54 m² g⁻¹), indicating that an abundant pore structure can be obtained during coprecipitation, and the specific surface area of the material can be significantly increased. The morphology of the 0.2 Cu-nFe₃O₄ and 0.8 Cu-nFe₃O₄ nanoparticles prepared by the coprecipitation method was changed (Figure 2c,d). The surface formed a loose porous structure. However, the particle size of the sample can be hardly determined from the SEM photos. Therefore, HRTEM micrographs of the 0.8 Cu-nFe₃O₄ were collected, as shown in Figure 4 and Figure S6. The particle sizes of the 0.8 Cu-nFe₃O₄ nanoparticles prepared by coprecipitation were 15−20 nm. The loose structure with holes can be clearly observed in the HRTEM images of the single particles. The pore sizes were 20−50 nm. The structure shown in Figure 2d was formed by stacking these nanoparticles. EDX element mapping (Figure 3) showed the presence of oxygen, iron, and copper onto 0.8 Cu-nFe₃O₄. These mapping images showed that iron and copper were well dispersed throughout the sample. Approximately, 27.66 wt % oxygen, 70.22 wt % iron, and 2.12 wt % copper were detected in the sample through an elemental analysis. The atomic ratio of oxygen to iron given in this conclusion is about 1.22 < 1.33 (4:3), which indicates that the iron content on the surface of the material is higher than that of oxygen, which indirectly proves that there may be more reactive sites on the surface of the material.

The room-temperature hysteresis curve of 0.8 Cu-nFe₃O₄ was measured by a vibrating-sample magnetometer (Figure 5) and was found to have room-temperature ferromagnetism. The saturation magnetization (Ms) was 63.85 emu g⁻¹. The magnetic properties of the materials are generally affected by many factors, such as size, structure, and morphology. As far as we know, the Ms value of 0.8 Cu-nFe₃O₄ was higher than those of many metal-modified nFe₃O₄. In addition, almost zero coercivity and remanence demonstrated the super-paramagnetism of the composite, which allowed the magnetic properties of the nanoparticles to be separated from the solution using an applied magnetic field while avoiding aggregation after removal of the applied magnetic field.
Figure 8f2,3 demonstrates that, by applying an external magnetic field, the composite can be easily separated and reused from the solution, which was a particularly important advantage for nanoparticles. The magnetic properties make them easily controlled by the external magnetic fields, which is important for their application.16 A more detailed research on magnetism is still in progress.

3.2. Comparison of One-Step and Two-Step Synthesis. As shown in Figure 6, nFe3O4 is obtained by the coprecipitation method, Cu/Fe3O4 and Cu/nFe3O4 are obtained by a two-step method, and Cu-nFe3O4 is obtained by a one-step method. Here, we compare the effects of different synthetic methods on CTC removal, as shown in Figure 6d. It can be seen that the removal efficiencies of Cu/Fe3O4 and Cu/nFe3O4 synthesized by a two-step method are similar to those of Fe3O4 and nFe3O4 for 90 min, only 12.4 and 67.6%, respectively. This indicates that the two-step metal modification has not made the catalytic activities of Cu/Fe3O4 and Cu/nFe3O4 remarkable and thus cannot improve their removal efficiency of CTC. Compared with Cu/Fe3O4 and Cu/nFe3O4, the removal of CTC by one-step modification has improved significantly, reaching 89.2%. It shows that the one-step synthesis of Cu-nFe3O4 can significantly enhance the removal of CTC in water. This is mainly due to the larger specific surface area and stronger reactivity of nanosized Cu-nFe3O4 than that of Cu/Fe3O4. One-step synthesis of Cu-nFe3O4 has more active catalytic sites than two-step synthesis of Cu/nFe3O4 and has the characteristics of large specific surface area and strong reactivity of nanomaterials.

3.3. Effect of Loading Metals. Precious, transition, and rare-earth metals have excellent catalytic properties because of their unique physical and chemical properties. In this experiment, the one-step method was used to prepare different metal elements (i.e., Mn, Co, Ni, Cu, Ce, Zn, Bi, Ag, Al, and Mg) to modify nFe3O4 and explore the effect of different loading metals on the CTC removal. As shown in Figure 7a, the removal effect of the commercial Fe3O4 on CTC was far less than that of the prepared nFe3O4 and M-nFe3O4 after a 90 min reaction. The removal rate with a difference of 50.4–70.4% was observed. M-nFe3O4 prepared by the modification method
of the transition metals (Mn, Co, Ni, Cu, Zn, and Ag) and the Mg element can improve the CTC removal effect of nFe3O4. Cu-nFe3O4 was the most prominent, with a removal rate reaching 82.72%. The M-nFe3O4 prepared by the modification of Ce, Bi, and Al can inhibit the CTC removal by nFe3O4.

Compared with the commercial Fe3O4 (2.54 m² g⁻¹), the BET surface area of the prepared nFe3O4 (73.84 m² g⁻¹) material significantly increased, indicating that precipitation and metal modification can significantly improve the pore structure and the specific surface area of nFe3O4. These structures fully exposed the active sites, facilitated the adsorption and migration of the matrix, and improved the material’s ability to remove contaminants.¹⁵

3.4. Effect of Copper Loadings. An investigation on the effect of loading metals on the CTC removal showed that Cu-nFe3O4 prepared by the Cu element modification had the most outstanding effect on the CTC removal by nFe3O4. Compared with the commercial Fe₃O₄ (2.54 m² g⁻¹), the BET surface area of the prepared nFe₃O₄ (73.84 m² g⁻¹) material significantly increased, indicating that precipitation and metal modification can significantly improve the pore structure and the specific surface area of nFe₃O₄. These structures fully exposed the active sites, facilitated the adsorption and migration of the matrix, and improved the material’s ability to remove contaminants.¹⁵

Figure 7. (a) Effects of M-nFe₃O₄ on the CTC removal (T = 298.15 K, C₀ = 50 mg L⁻¹, m = 1.5 g L⁻¹, l = 0.2 mM); (b) effects of copper loading on the CTC removal (T = 298.15 K, C₀ = 50 mg L⁻¹, m = 1.5 g L⁻¹); (c) kinetic process of the double constant model fitting for the CTC removal by 0.2–0.8 Cu-nFe₃O₄; (d) effects of the 0.8 Cu-nFe₃O₄ dose on the CTC removal (T = 298.15 K, C₀ = 50 mg L⁻¹); (e) kinetic process of the double constant model fitting for the CTC removal with dosage; (f) effects of the initial concentration on the CTC removal (T = 298.15 K, m = 2.0 g L⁻¹).

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3.4. Effect of Copper Loadings. An investigation on the effect of loading metals on the CTC removal showed that Cu-nFe₃O₄ prepared by the Cu element modification had the most outstanding effect on the CTC removal by nFe₃O₄. Therefore, the Cu-nFe₃O₄ loading was also investigated herein. Figure 7b shows that the removal efficiency of Cu-nFe₃O₄ to CTC also gradually increased with the load increase, which was significantly improved when the load was 0.8 mM, indicating that the load increase can improve the removal efficiency of Cu-nFe₃O₄ for CTC. The dynamic process was also studied, and the data were fitted according to the double constant model²⁰ (Figure 7c, Table S1). Comparing the correlation coefficient (R²) of the CTC removal kinetics model under different loadings, the removal kinetics was found to be in accordance with the two-constant reaction kinetics model, indicating that the reaction is mainly dominated by a chemical reaction with physical adsorption. R² exceeded 0.97, indicating that ln(C/C₀) had a good linear correlation with ln t. The reaction rate constants (k) of the CTC removal were 0.3982, 0.4075, 0.4698, and 0.6161 ln⁻¹ min at 0.1, 0.2, 0.4, and 0.8 mM loadings, respectively.

3.5. Effect of the Dosage. The active site of the reaction was closely related to the dosage. This study investigated the effect of the Cu-nFe₃O₄ dosage on the CTC removal under the conditions of 0.5, 1.0, 1.5, and 2.0 g L⁻¹. A better CTC removal effect was observed as the Cu-nFe₃O₄ dosage increased (Figure 7d). The CTC removal efficiency was only 47.18% at 90 min when the dosage was 0.5 g L⁻¹. Accordingly, the removal efficiency of CTC can reach 98.04% at 90 min when the dosage was 2.0 g L⁻¹. The active site of the reaction increased with the dosage increase; hence, the removal effect of Cu-nFe₃O₄ on the CTC treatment was improved. As shown in Figure 7e and Table S1, a comparison of the correlation coefficients (R²) of the CTC removal kinetics model at different dosages showed that the removal kinetics was in accordance with the double constant reaction kinetics model, and R² exceeded 0.96, indicating that ln(C/C₀) had a good
linear correlation with ln $t$. The reaction rate constants for the CTC removal at 0.5, 1.0, 1.5, and 2.0 g L$^{-1}$ were 0.1530, 0.5464, 0.6161, and 0.5399 ln $^{-1}$ min, respectively.

3.6. Effect of the Initial CTC Concentrations. In the case of a certain amount of Cu-nFe$_3$O$_4$, the active site was limited; hence, the effect of the initial CTC concentration on the Cu-nFe$_3$O$_4$ removal must be investigated. At initial concentrations of 5, 25, 50, and 100 mg L$^{-1}$, the removal rates were 91.4, 97.7, 98.0, and 99.0% at 90 min, respectively. The results showed that the CTC removal by CO-Cu-nMET was almost independent of the CTC concentration (Figure 7f). The main reasons were as follows: the driving force provided by CTC was indispensable for overcoming the resistance of the adsorbed material between the water and solid phases. The total available active sites will not limit the CTC removal under a certain Cu-nFe$_3$O$_4$ dosage.

3.7. Effect of Common Anions. The actual wastewater contained not only the target pollutants, but also a variety of anions and humic acids (HA), which may promote or inhibit the removal effect. Nie et al. reported a chlorine concentration of 2.0−3.7 mM in a wastewater treatment plant. Lie et al. reported that HCO$_3^-$ in the aquatic environment was usually present at a 1−5 mM concentration. Ghaitidak and Yadav reported that the chloride concentration in the gray waters of Israel was 20 mM, while that in the gray waters of Yemen was 1.6 mM. The effects of 0.1, 1.0, and 2.0 g L$^{-1}$ HA and 1, 10, and 100 mM anions (Cl$^-$, CO$_3^{2-}$, NO$_3^-$, CO$_3^{2-}$, and PO$_4^{3-}$) on the CTC removal in 0.8 Cu-nFe$_3$O$_4$ were studied herein.

As shown in Figure 8a, the effect of HA (inhibition or promotion) on the CTC removal depended on the HA dosage. The presence of HA within the HA concentration range of 0.1−1.0 g L$^{-1}$ can promote the removal efficiency, but the promotion efficiency decreased with the increase of the HA concentration. The inhibitory effect was observed at a HA concentration of 2.0 g L$^{-1}$ mainly because the HA can adsorb CTC (Figure S5) and react with the iron ions in the aqueous solution. The active sites of competitive reaction between HA and CTC will result in the decrease of the CTC removal rate. The adsorption was also dominant, showing a promotive effect. The complexation gradually became obvious, and the promotion efficiency was lowered with the increase of the HA concentration. The complexation effect was very significant when the HA concentration was 2.0 g L$^{-1}$, which made the adsorption sites of CTC on HA and the reaction sites on 0.8 Cu-nFe$_3$O$_4$ decrease, showing inhibition.

Figure 8b,c depicts the effects of NO$_3^-$ and Cl$^-$ on the CTC removal from 0.8 Cu-nFe$_3$O$_4$. The removal efficiency of CTC did not significantly change when the NO$_3^-$ and Cl$^-$ concentrations increased from 0 to 100 mM. The results showed that NO$_3^-$ and Cl$^-$ in water did not inhibit the CTC removal by 0.8 Cu-nFe$_3$O$_4$. However, NO$_3^-$ and Cl$^-$ were the
main anions in the surface water, and NO₃⁻ and Cl⁻ will not interfere with the CTC removal by 0.8 Cu-nFe₃O₄, indicating that 0.8 Cu-nFe₃O₄ was suitable for the removal of pollutants in the surface water.

Figure 8d,e shows that the removal rates of CTC by 0.8 Cu-nFe₃O₄ was reduced by 57.5 and 83.3%, respectively, when CO₃²⁻ and PO₄³⁻ were added at 10 mM. The removal rates of CTC decreased by 83.4 and 90.2%, respectively, when adding them to 100 mM. The addition of CO₃²⁻ and PO₄³⁻ will greatly inhibit the removal effect of 0.8 Cu-nFe₃O₄ on CTC.

The SEM diagram in Figure 8f (see Figure S4 for an enlarged version) showed that the porous structure on the surface of the post-reaction 0.8 Cu-nFe₃O₄ decreased with the addition of CO₃²⁻ and PO₄³⁻ but turned into dense layered structures, which will reduce the active sites on the surface of 0.8 Cu-nFe₃O₄ and inhibit the CTC removal by 0.8 Cu-nFe₃O₄.

3.8. Cyclic Experiments. The preparation of the magnetic nanomaterials aimed to achieve two main purposes: (1) provide more reactive sites using their high specific surface area and (2) make use of the magnetic properties of the materials to facilitate recycling utilization. Therefore, the activity of material reuse deserves attention. As shown in Figure 9a, four repeated experiments were performed using 0.8 Cu-nFe₃O₄ to remove CTC. The removal rates of CTC were 93.4, 94.2, 94.8, and 93.1% after a 30 min reaction. The prepared 0.8 Cu-nFe₃O₄ had good reusability. A comparison of the SEM images of 0.8 Cu-nFe₃O₄ before and after the reaction revealed that the number of spherical 0.8 Cu-nFe₃O₄ increased after the reaction (Figure 9b,c). This result is attributed to the friction between the cup wall and 0.8 Cu-nFe₃O₄ caused by the oscillating reaction. The core structure of 0.8 Cu-nFe₃O₄ did not significantly change before and after the reaction. The BET data also showed that the specific surface area of 0.8 Cu-nFe₃O₄ after the reaction was 14.3% larger than that of 0.8 Cu-nFe₃O₄ without the reaction, indicating that the spherical 0.8 Cu-nFe₃O₄ after the reaction had a larger specific surface area, which was also strong proof that the material’s multiple-reaction efficiency did not decrease. As shown in Figure 8d, the solid–liquid separation performance during the material recovery by the magnet was excellent before and after multiple reactions, indicating that the reaction did not weaken the magnetic characteristics of 0.8 Cu-nFe₃O₄ and it still had good recovery characteristics.

3.9. Mechanisms of the CTC Removal by Cu-nFe₃O₄.

Fe(II)–Fe(III) is an important redox couple in the natural environment. The transformation between Fe(II) and Fe(III) can occur at various global aerobic—anoxic boundaries. In natural waters, most of the dissolved Fe(II) and Fe(III) exist in organic species through organic ligand complexation. Wang et al. and Bolobajev et al. found that under a homogeneous environment, neutral pH, and no light conditions, Fe(II) was easily oxidized by oxygen to form a stable Fe(III). TCs could interact with Fe(III) to further promote the TC oxidation and removal. Fe(II) and Fe(III) exist in nano-Fe₃O₄ (Figure 10).

According to Figure S7, the main existing forms of copper in the materials before the reaction are Cu (2p⁳), Cu₂O, and CuO, and the main existing forms of copper in the materials before the reaction are still Cu (2p⁳), Cu₂O, and CuO, indicating that the basic copper in the materials does not participate in the removal reaction with chlortetracycline, but from the removal experiment, it can be seen that copper plays a catalytic role in the reaction, accelerating the removal of chlortetracycline. This study described the mechanism of the...
CTC removal by Cu-nFe₃O₄ in a heterogeneous environment. The porous structure of Cu-nFe₃O₄ and the Fe(II) and Fe(III) redox systems existing inside the porous structure provided the possibility of CTC removal. First, CTC was rapidly adsorbed by the copper nanoporous structure attached to the surface of Cu-nFe₃O₄ to form ~CTC (reaction 2). Under a neutral or weak acid environment, the ~CTC reacted with Fe(III) to form CTC-Fe(III) and ~ (reaction 3). ~ continued the adsorption process in reaction 2, and CTC-Fe(III) was decomposed into CTC: free radicals and Fe(II) (reaction 4). Second, Cu~CTC reacted with Fe(II) to form CTC-Fe(II) and ~ (reaction 5). Furthermore, CTC-Fe(II) reacted with dissolved oxygen (O₂) in water to form CTC-Fe(III) and the reactive oxygen species (ROS) (reaction 6). Finally, CTC- and ROS reacted to degrade CTC (reaction 7). ROS is produced by the participation of dissolved oxygen in the reaction process.

4. CONCLUSIONS

In this study, a copper-loaded nanomagnetic material (Cu-nFe₃O₄) was prepared by a one-step synthesis method, which can effectively remove chlorotetracycline. The XRD and BET data showed that the Cu-nFe₃O₄ (73.28 m² g⁻¹) was 28 times larger than the commercial Fe₃O₄ (2.54 m² g⁻¹) and had a certain Fe₃O₄ crystal structure. Meanwhile, the SEM and HRTEM data depicted that the particle size of the 0.8 Cu-nFe₃O₄ nanoparticles ranges 15 to 20 nm, and a loose structure with pores can be clearly observed in the HRTEM image of a single particle. The batch study results indicated that the maximum removal of chlorotetracycline was 99.0% at dosage = 2.0 g L⁻¹, copper loading = 0.8 mM, and C₀ = 100 mg L⁻¹ at the optimum conditions within 90 min. At the same time, the effect of HA (inhibition or promotion) on the CTC removal depended on the HA dosage; NO₃⁻ and Cl⁻ would not interfere with the Cu-nFe₃O₄ removal of CTC; CO₃²⁻ and PO₄³⁻ would greatly inhibit the removal of CTC by Cu-nFe₃O₄. This result was attributed not only to the decrease in the porous structure of the Cu-nFe₃O₄ surface after their addition but also to the formation of a layered dense structure. The SVM characterization showed that 0.8 Cu-nFe₃O₄ had good magnetic properties. The solid–liquid separation performance before and after the Cu-nFe₃O₄ multiple reactions during the magnet recovery was good, indicating that the reaction did not weaken the magnetic characteristics of the material, and the material still had a good recovery characteristic. The mechanism of the chlorotetracycline removal by the Fe(II) and Fe(III) redox systems in the porous structure of Cu-nFe₃O₄ and the porous structure in the heterogeneous environment was elucidated.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04106.

Experimental conditions and materials and characterization data for one-step synthesis of metal-modified nanomagnetic materials (PDF)

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Notes

The authors declare no competing financial interest. The photos and pictures in this paper were taken or processed by one of the authors (Y.L.).

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