

Article

Visible-Light-Driven Photocatalytic Degradation of High-Concentration Ammonia Nitrogen Wastewater by Magnetic Ferrite Nanosphere Photocatalysts

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Abstract: In this study, magnetic CuFe₂O₄, MgFe₂O₄, and ZnFe₂O₄ nanosphere photocatalysts were prepared by the sol–gel method at 300 °C, 400 °C, and 500 °C, respectively (named as CF300, CF400, CF500, MF300, MF400, MF500, ZF300, ZF400, and ZF500). The characterization by X-ray diffraction (XRD) revealed that the optimal calcination temperature was 400 °C. Then, CF400, MF400, and ZF400 were used to treat high-concentration ammonia nitrogen wastewater (HCAW, 1000 mg/L) at different pH levels. The result showed that the optimal pH for CF400, MF400 and ZF400 to degrade HCAW was 9.0, and CF400 required a shorter illumination time (80 min) than MF400 and ZF400 (120 min) to completely remove ammonia nitrogen from HCAW. However, CF400 was unstable and decomposed, and a blue substance was observed during the magnetic recovery experiment. The recovery rate of ZF400 (66.7%) was higher than MF400 (53.2%) with no decomposition phenomenon, and the ammonia nitrogen removal rate of ZF400 remained above 90% after five cycles. Additionally, the ammonia nitrogen removal rate of ZF400 could reach 80.2% when the ammonia nitrogen concentration was as high as 5000 mg/L. Therefore, compared with CF400 and MF400, ZF400 was more suitable for treating HCAW.

Keywords: high-concentration ammonia nitrogen; photocatalyst; ferrite; stability; recovery rate



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1. Introduction

Ammonia nitrogen refers to nitrogen in the form of ammonium salt or free ammonia, which is one of the primary pollutants in the water environment [1,2]. High-concentration ammonia nitrogen wastewater (HCAW) [3] could be generated by a wide range of sources, such as landfill leachate [4,5], the livestock and poultry industry [6,7], fertilizer industry wastewater [8,9], sludge digestion fluid [10], etc. The release of ammonia nitrogen into natural water without proper treatment could not only exacerbate water eutrophication [11,12] and influence the growth of plants and aquatic animals [4,13–15], but also severely suppress microbial activity [16]. In short, HCAW could potentially threaten human health and destroy the ecological balance [17,18]. Therefore, seeking economically viable, environmentally friendly, and highly efficient approaches to treat HCAW has become a focal point of attention in the environment.

The biological method is an economical and effective method to degrade low-concentration ammonia nitrogen wastewater [19]. However, using biological methods to treat HCAW is challenging due to the low C/N ratio and weak biodegradability [4,20]. As a result, the further application of the biological method to degrade HCAW is hindered. In recent years, the advanced oxidation method has been widely researched for removing pollutants as it has advantages of a high reaction rate, good removal performance and environmental friendliness [21,22]. Under the excitation of ultraviolet light or visible light, photocatalysts could produce strong oxidizing free-radical products, such as hydroxyl radical ($\cdot\text{OH}$) and superoxide radical ($\cdot\text{O}_2^-$), which show potential application value in the treatment of ammonia nitrogen wastewater. For instance, $\text{TiO}_2\text{-CuO/HSC}$ synthesized by Peng et al. [23] exhibited efficient ammonia nitrogen removal performance to treat 100 mg/L ammonia nitrogen wastewater with an ammonia nitrogen removal rate of 99.7% and 60.7% under UV and sunlight, respectively. Lou et al. [24] used an La/Fe/TiO_2 photocatalyst with a large specific surface area to treat ammonia nitrogen wastewater (100.67 mg/L). The results showed that a dosage of 1 g/L of the photocatalyst and 2 mmol/L of H_2O_2 could effectively remove 78.3% of ammonia nitrogen at a pH of 9.9. Sun et al. [25] found that palladium-modified nitrogen-doped TiO_2 nanoparticles could remove 90% of ammonia nitrogen from low-concentration ammonia nitrogen wastewater (25 mg/L).

To date, among the photocatalysts, magnetic ferrite nanosphere photocatalysts (MFNPs) have captured the considerable attention of researchers because of narrow band gap semiconductor materials with unique magnetic, electrical, structural and dielectric properties, which can facilitate the formation of active oxygen species and promote the pollutant decomposition [26,27]. The general chemical formula of MFNPs is MFe_2O_4 , where M represents different metal cations, such as Mg^{2+} , Zn^{2+} , Ni^{2+} , and Co^{2+} , etc. [28]. For the structure of MFNPs, M(II) and Fe(III) are located in the gaps of tetrahedra and octahedra surrounded by oxygen in the crystal structure, respectively, which maintains good stability and excellent magnetic properties [29]. Meanwhile, MFNPs possess diverse physicochemical properties, such as abundant surface active sites and high catalytic activity [30]. Presently, MFNPs are used to treat many pollutants, such as organic matter [31] and heavy metals [32]. It was found that the redox reactions involving $\cdot\text{OH}$, $\cdot\text{O}_2^-$ and hole (h^+) could remove 37% of tetracycline in wastewater, and uranium (VI) could be completely removed by photoelectron reduction. The $\text{ZnFe}_2\text{O}_4/\text{AC}$ synthesized by Ye et al. [33] could remove 90.0% of ammonia nitrogen (100 mg/L) under ultraviolet irradiation, and the photocatalytic product was N_2 . Ajeesha et al. [34] found that the magnetic MgFe_2O_4 photocatalyst could remove 86% of methylene blue after 180 min of illumination. Similarly, magnetic CuFe_2O_4 photocatalysts synthesized by K. Shetty et al. could remove 82% of malachite green [35]. To our best knowledge, few studies have been reported on the treatment of HCAW by MFNPs [36].

In this study, magnetic CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 nanosphere photocatalysts were prepared by the sol–gel method [37]. Then, the effect of temperatures on the property of magnetic nanosphere photocatalysts were studied to determine the optimal calcination temperature. Magnetic CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 nanosphere photocatalysts calcined at 300 °C, 400 °C, and 500 °C were named as CF300, CF400, CF500, MF300, MF400, MF500, ZF300, ZF400, and ZF500, respectively. It had been reported that the charge properties of the catalyst surface could be affected by pH as it could change the migration rate of h^+ and photogenerated electrons (e^-) [38]. Eventually, the ammonia nitrogen degradation performance would be significantly interfered with as the ammonia nitrogen redox in photocatalytic reactions involves the transfer of hydrogen ions [33]. Therefore, the effects of pH on the degradation of magnetic CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 nanosphere photocatalysts prepared at the optimum calcination temperature to treat HCAW were investigated. Finally, photocatalysts prepared at the optimum calcination temperature were separated by a magnetic field after photocatalytic degradation under an optimal pH, and photocatalytic recycling tests were conducted to assess the impact of recycling time on the ammonia nitrogen degradation performance of the photocatalysts.

2. Materials and Methods

2.1. Materials

The analytical reagents used in this study were provided by Sinopharm Chemical Reagent Co. (Damao Chemical Reagent Factory, Tianjin, China), including NH_4Cl , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NaOH , HCl , HgI_2 , KI-NaOH , $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ et al. NH_4Cl was added into ultrapure water to prepare HCAW (1000 mg/L). The initial pH of the HCAW was around 6.2.

2.2. Photocatalysts Synthesis

CF300, CF400, CF500, MF300, MF400, MF500, ZF300, ZF400, and ZF500 were synthesized using the sol-gel method [37]. A total of 10 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 5 mmol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 30 mL of deionized water. Subsequently, 15 mmol of $\text{C}_6\text{H}_8\text{O}_7$ was added to each vessel. Then, the mixed solution was stirred for 2 h at 60 °C with a stirring rate of 280 r/min to obtain a homogeneous solution. A ceramic crucible was used to contain the slurry after 80 min of evaporation in a water bath (95 °C). The slurry liquid contained in the ceramic crucibles were calcined for 2 h in the muffle furnace at 300 °C, 400 °C, and 500 °C, respectively. After cooling to room temperature, CF300, CF400, CF500, MF300, MF400, MF500, ZF300, ZF400, and ZF500 were obtained by grinding with agate. The optimum calcination temperature of different photocatalysts used as the preparation temperature of MFNPs in subsequent experiments was determined by photocatalyst characterization.

2.3. Characterization of CuFe_2O_4 , MgFe_2O_4 and ZnFe_2O_4 Nanosphere Photocatalyst

The composition and crystal structure of CF300, CF400, CF500, MF300, MF400, MF500, ZF300, ZF400, and ZF500 samples were analyzed by X-ray diffraction (XRD, Bruker, Karlsruhe, Germany). The morphology and size of the photocatalysts prepared at the optimum temperature were analyzed by a scanning electron microscope (SEM, SU8010, Hitachi, Tokyo, Japan). The elemental composition of photocatalyst composites was evaluated by X-ray Photoelectron Spectroscopy (XPS Escalab 250Xi, Thermo Fisher, Waltham, MA, USA). UV-vis absorption spectroscopy (DRS, JASCO, Tokyo, Japan) was used to investigate the optical properties of the photocatalyst samples. TiO_2 was used as the control sample in the experiment. The actual scanning wavelength range was 200–800 nm, and the scanning speed was 600 nm/min.

2.4. Photocatalytic Experiment of Magnetic Ferrite Nanosphere Photocatalysts

During the experiment, 0.15 g of CF400, MF400, and ZF400 was added into 100 mL of the ammonia nitrogen solution, respectively. The light source was supplied by a xenon lamp (CEL-S500L, Beijing Zhongjiao Jinyuan Technology, Beijing, China) with a voltage and current of 14 V and 15 A, respectively.

Furthermore, the pH solution value plays an indispensable role in the photocatalytic degradation of ammonia nitrogen wastewater. The effect of pH (6.2, 8.0, and 9.0) on the ammonia nitrogen treatment performance of MFNPs was investigated. NaOH and HCl solutions were used to adjust the pH. Before the photocatalytic degradation experiment was conducted under the visible light source, the quartz reactor was initially placed on a magnetic stirrer (280 r/min). Subsequently, the reaction vessel was shielded with tin foil and left in the dark for 60 min to reach the adsorption and desorption equilibrium. Then, the reaction vessel was put on the magnetic stirrer (280 r/min) at 30 cm from the xenon lamp source for 160 min. Simultaneously, the circulating water-cooling system was used to control the temperature of the reaction chamber at about 17 ± 2 °C. Samples were collected every 40 min and filtered with filter paper. The ammonia nitrogen concentration of each sample was determined by an ultraviolet spectrophotometer according to the standard method [39] to investigate the performance of MFNPs treating HCAW. After confirming the optimal pH, a control experiment was conducted to evaluate the stripping rate of HCAW

without the addition of photocatalysts. The average values of triplicates were expressed as the results to minimize the variation.

2.5. Photocatalysts Recovery and Stability Tests

A magnet was used to recover CF400, MF400, and ZF400 after settling for 30 min at an optimal pH. Subsequently, the photocatalyst with the best stability and ammonia nitrogen treatment performance was washed 5 times by ultrapure water and ethanol. Then, the retrieved photocatalyst after centrifugation (5000 r/min) was dried in an oven at 80 °C and utilized in the subsequent degradation experiment.

3. Results and Discussion

3.1. Characterization of MFNPs

3.1.1. XRD of MFNPs

The X-ray diffraction patterns of CF300, CF400, CF500, MF300, MF400, MF500, ZF300, ZF400, and ZF500 calcined for 2 h are shown in Figure 1. No obvious characteristic diffraction peaks were observed in CF300, MF300, and ZF300, indicating that the structure developments were incomplete, and the substances mainly existed in an amorphous form. The continuous change in lattice spacing might be due to defects in nanocrystals, disordered intergranular structure, and the small size of CF300, MF300, and ZF300 photocatalysts formed at low calcination temperatures of 300 °C. In the preparation experiment of Fe-Ti-Ox catalysts at different temperatures, Song et al. [40] also found that the Fe-Ti-Ox catalyst mainly existed in an amorphous form at a low calcination temperature without prominent diffraction peaks. When the calcination temperature reached 400 °C and 500 °C, sharp and strong X-ray diffraction peaks appeared in this study. It could be suggested that the structure of CF400, CF500, MF400, MF500, ZF400, and ZF500 tended to be complete. Comparing the diffraction peaks of the obtained CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 photocatalysts with the standard card, it was observed that the diffraction peaks of these three groups correspond precisely to the crystal facets $\langle 111 \rangle$, $\langle 220 \rangle$, $\langle 311 \rangle$, $\langle 400 \rangle$, $\langle 422 \rangle$, $\langle 511 \rangle$ and $\langle 440 \rangle$ in the standard card JCPDS 25-0283 [41]; $\langle 220 \rangle$, $\langle 311 \rangle$, $\langle 400 \rangle$, $\langle 422 \rangle$, $\langle 511 \rangle$ and $\langle 440 \rangle$ in JCPDS 36-0398 [42]; and $\langle 220 \rangle$, $\langle 311 \rangle$, $\langle 400 \rangle$, $\langle 422 \rangle$, $\langle 511 \rangle$ and $\langle 440 \rangle$ in JCPDS No.22-1012 [33,43] without any additional impurity diffraction peaks, suggesting that the obtained three ferrite nanosphere photocatalysts had high purities. Similar XRD patterns of the three ferrite nanosphere photocatalysts were observed when calcination temperatures reached 400 °C and 500 °C, respectively. It could be concluded that calcination temperatures higher than 400 °C could barely affect the formation of reaction products. To reduce energy consumption, the ferrite nanosphere photocatalysts used afterwards were calcined at 400 °C in this study.

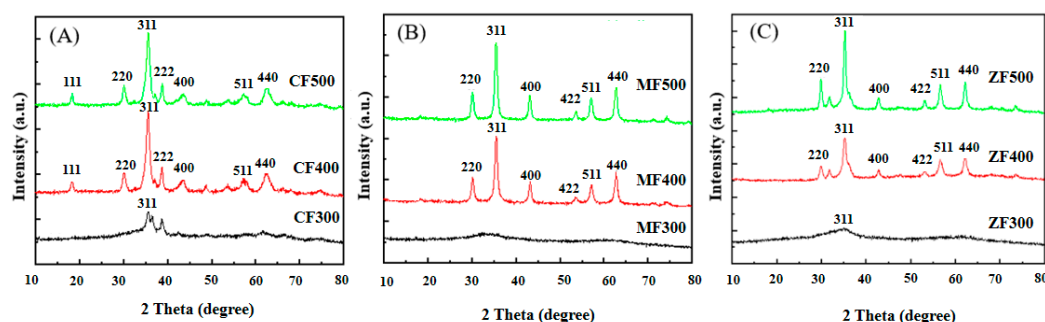


Figure 1. XRD diffraction patterns of CF300, CF400, CF500, MF300, MF400, MF500, ZF300, ZF400, and ZF500 at different calcination temperatures ((A): CuFe_2O_4 , (B): MgFe_2O_4 , (C): ZnFe_2O_4).

3.1.2. SEM Analysis of CF400, MF400, and ZF400

The morphology of the CF400, MF400, and ZF400 sample were characterized by SEM. The surfaces and profiles of CF400, MF400, and ZF400 are depicted in Figure 2. Figure 2a–c demonstrate that CF400 had a nano-spherical raspberry-like structure with a

relatively uniform particle size (Figure 2d). Each nanosphere with a large particle size of approximately 100 nm comprised multiple 10–20 nm CF400 sub-nanospheres. Figure 2e–g show that MF400 was formed by many nanoparticles with a rough surface. The particle size fluctuated between 15 nm and 30 nm (Figure 2h). ZF400 had a small size (15–20 nm) and spherical surface, as illustrated in Figure 2i–l, and the grains aggregated with plenty of gaps. Table 1 shows the particle size information of CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 photocatalysts prepared by the sol–gel method in previous studies, which were similar to the MFNPs obtained in this study.

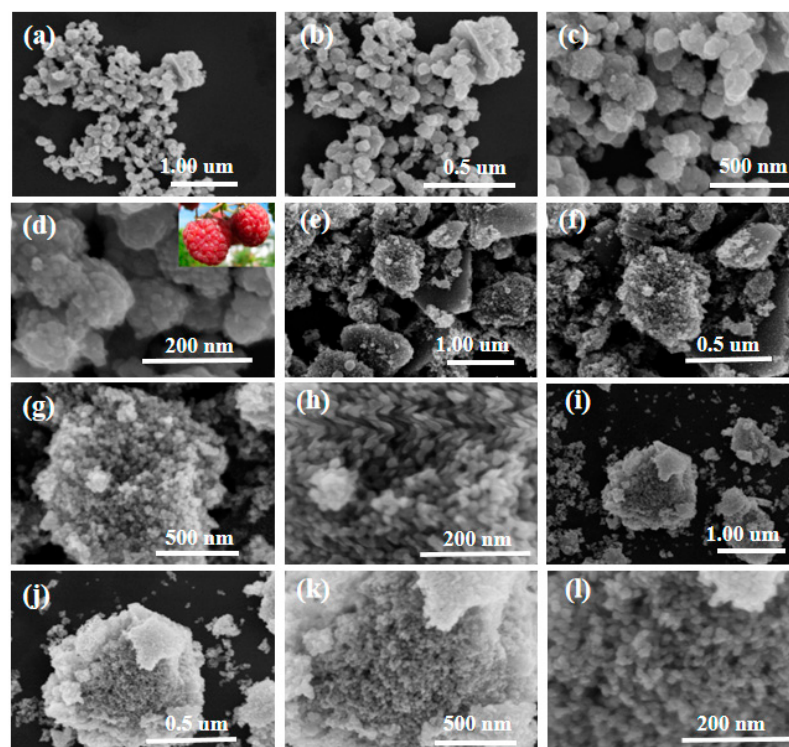


Figure 2. SEM images of CF400, MF400, and ZF400 (CF400: (a–d), MF400: (e–h), ZF400: (i–l)).

Table 1. Particle sizes and shapes of CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 photocatalysts prepared by the sol–gel method.

Material	Precursor Metal	Temperature (°C)	Particles Size (nm)	Shape	References
CuFe_2O_4	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	150	56	spherical	[44]
MgFe_2O_4	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_2\text{H}_4(\text{OH})_2$, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	350	12.63	spherical	[45]
MgFe_2O_4	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_2\text{H}_4(\text{OH})_2$, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	600	33.32	spherical	[45]
ZnFe_2O_4	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $(\text{C}_6\text{H}_{10}\text{O}_5)_n$	400	5–30	spherical	[46]
ZnFe_2O_4	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{C}_2\text{H}_4(\text{OH})_2$, $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$	450	10–20	spherical	[47]

3.1.3. XPS Analysis of CF400, MF400, and ZF400

XPS was used to further analyze the chemical states of atoms and surface composition in CF400, MF400, and ZF400 (Figure 3). The CF400 sample contained Cu, Fe, O and C elements. The MF400 sample contained Mg, Fe, O and C elements, and the ZF400 sample contained Fe, Zn, O and C elements, indicating that magnetic CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 nanosphere photocatalysts were successfully prepared in this study. The C1s signal peak detected in the XPS might be due to the adsorption of some gaseous impurities on CF400, MF400, and ZF400 surfaces or the introduction of exogenous substances during instrument testing.

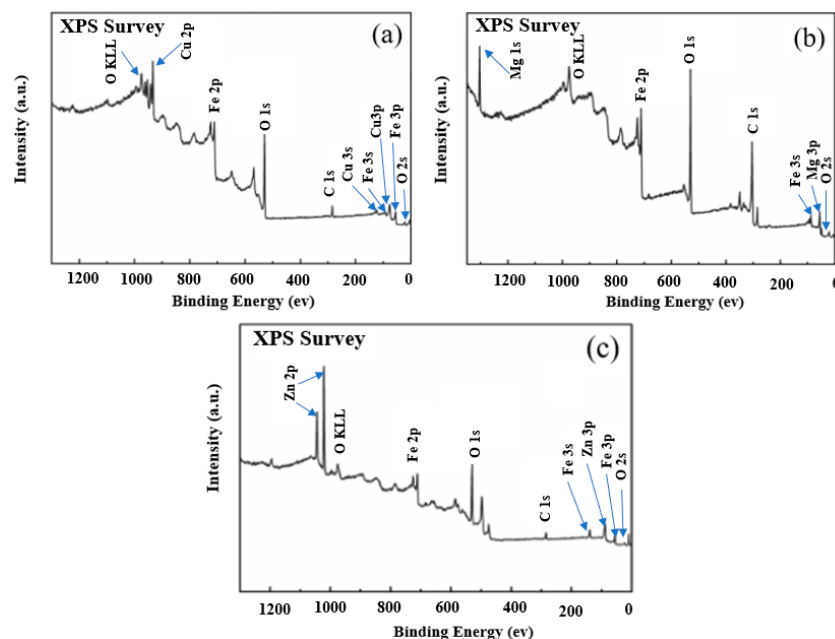


Figure 3. XPS full spectrum of CF400 (a), MF400 (b) and ZF400 (c) samples.

High-resolution XPS spectra experiments were conducted to further determine the chemical states of Cu, Mg, Fe and O elements in CF400, MF400, and ZF400 (Figure 4). In the Cu2p spectrum (Figure 4a), two characteristic peaks detected at binding energies of 953.0 eV and 933.0 eV corresponded to $\text{Cu}2p_{1/2}$ and $\text{Cu}2p_{3/2}$, respectively, suggesting that the Cu element presented in the form of Cu^{2+} [48,49]. Figure 4b displays the Fe2p XPS spectrum of CF400 with binding energies of $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ observed at 723.1 eV and 709.9 eV, respectively. After a comparison with the standard spectrum, it could be determined that the Fe element mainly existed in the form of Fe^{3+} [50,51]. Figure 4c shows the XPS spectrum of O1s in the CF400, which exhibited a single peak at a binding energy of 529.4 eV, indicating that oxygen (O) primarily presented as O^{2-} [52].

Figure 4d displays the Mg1s spectrum of the MF400 sample. An obvious peak was observed at a binding energy of 1303.3 eV, indicating that the predominant presence of the Mg element was Mg^{2+} [53,54]. Figure 4e represents the XPS spectrum of Fe2p. The binding energies of $\text{Fe}2p_{1/2}$ and $\text{Fe}2p_{3/2}$ were measured as 724.3 eV and 711.6 eV, respectively [55,56]. It could be concluded that the Fe element also existed in the form of Fe^{3+} within the MF400. Figure 4f displays the XPS spectrum of O1s. The two conspicuous feature peaks at 528.7 eV and 530.2 eV binding energies corresponded to the oxygen element and adsorbed oxygen, respectively, in the MF400 sample [57]. The above analysis revealed that Mg and Fe elements existed as Mg^{2+} and Fe^{3+} , respectively, and the O element existed as O^{2-} and adsorbed oxygen within the synthesized MF400 sample.

In Figure 4g, characteristic peaks with binding energies of 1021.17 eV and 1044.26 eV corresponded to $\text{Zn}2p_{3/2}$ and $\text{Zn}2p_{1/2}$, respectively, indicating that the zinc element existed as Zn^{2+} (a typical oxidation state) in the ZF400 sample [31,58,59]. Figure 4h displays

the XPS spectrum of Fe2p. Two distinct peaks detected at binding energies of 709.9 eV and 723.1 eV corresponded to the Fe2p_{3/2} and Fe2p_{1/2} characteristic peaks, respectively, demonstrating the presence of Fe³⁺ [60,61]. Figure 4i presents the XPS spectrum of O1s. The characteristic peaks at 529.8 eV and 531.4 eV were attributed to the oxygen element and adsorbed oxygen, respectively, in the ZF400 sample, which were consistent with those reported in other literature [60]. The XRD, SEM, and XPS analysis suggested that CF400, MF400, and ZF400 were successfully obtained in this study.

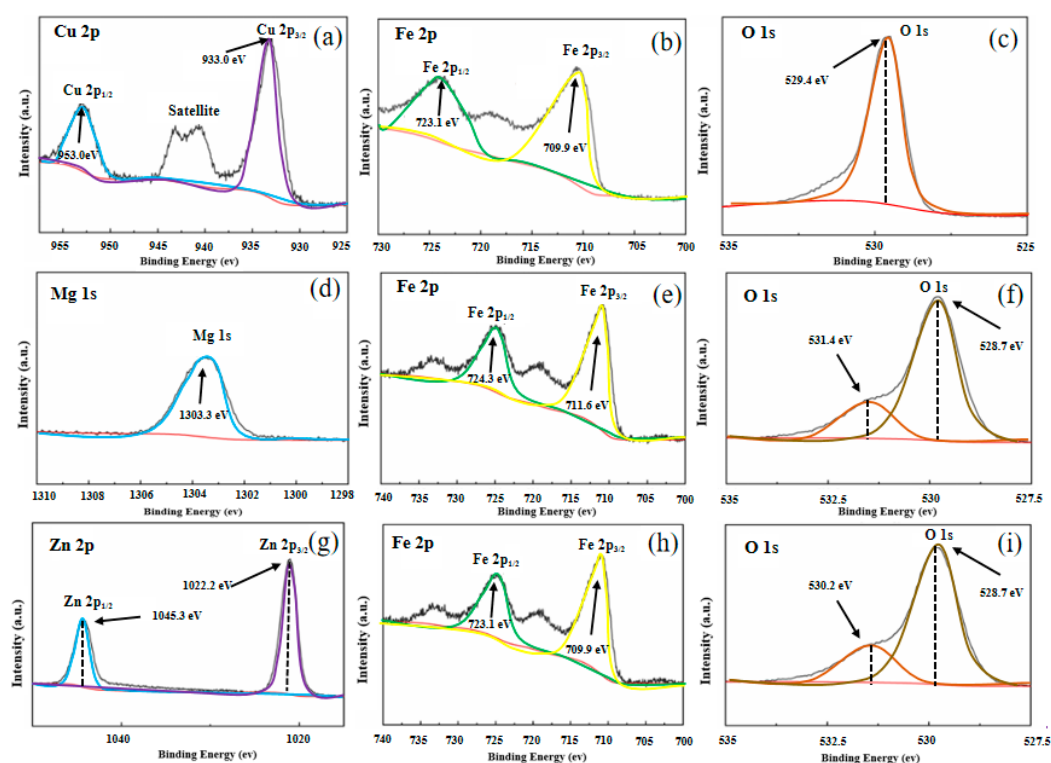


Figure 4. High-resolution XPS spectra of CF400, MF400 and ZF400 samples. (CF400: (a–c), MF: (d–f), ZF: (g–i)).

3.1.4. DRS Analysis of CF400, MF400, and ZF400

The difference in light absorption could have a significant impact on the photocatalytic performance of the sample. To assess the photocatalytic performance of CF400, MF400, and ZF400, DRS was conducted with a scanning wavelength range of 200–800 nm. The TiO₂ was employed as a control material. The results are shown in Figure 5. As a common semiconductor photocatalyst, TiO₂ could not absorb the visible light. Yoriya S et al. [62] confirmed that TiO₂ could only utilize 4% of the ultraviolet fraction of the solar spectrum and had low quantum efficiency, which significantly limited its solar energy utilization rate. Meanwhile, it was impossible to transport all photo-generated charge carriers to the surface for a reaction while increasing the recombination rate, which seriously restricted the application of catalysts. Compared to TiO₂ catalysts, CF400 could absorb the entire visible light region, MF400 exhibited distinct characteristic peaks within the range of 320–650 nm, and the absorption edge of ZF400 was 700 nm and displayed strong light absorption characteristics in the ultraviolet–visible region. The absorption band edge of the ZnFe₂O₄ photocatalyst obtained in this study was similar to that of the ZnFe₂O₄ photocatalyst synthesized by Liu et al. [63]. The above result indicated that the CF400, MF400, and ZF400 obtained in this study had better optical absorption properties than TiO₂ catalysts.

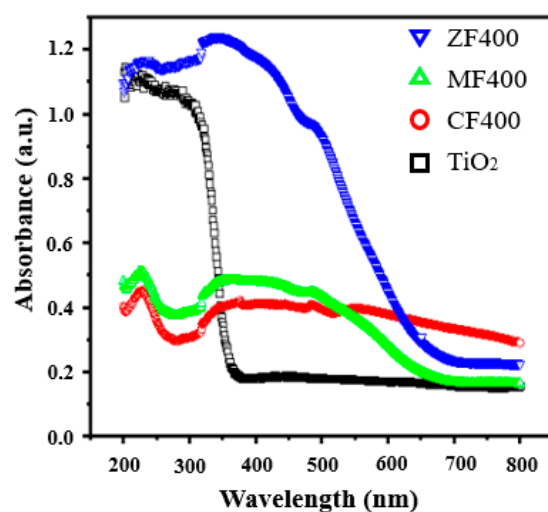


Figure 5. UV-vis diffuse reflection spectra of TiO_2 , CF400, MF400 and ZF400.

3.1.5. Photocatalytic Decomposition of Ammonia Nitrogen by CF400, MF400, and ZF400 at Different pHs

Since the pH affects the photocatalytic performance of ammonia nitrogen significantly, the effects of the pH (6.2, 8.0, and 9.0) on the ammonia nitrogen removal performance of CF400, MF400, and ZF400 were investigated under visible light irradiation (Figure 6). During the photocatalytic process, the ammonia nitrogen concentration barely changed when the pHs were 6.2 and 8.0, respectively. Once the pH was adjusted to 9.0 and CF400 was introduced into the solution, ammonia nitrogen removal rates reached 100% after 60 min of adsorption–desorption and 80 min of exposure to visible light. MF400 and ZF400 could remove all ammonia nitrogen after 60 min of adsorption–desorption and 120 min of visible light illumination when the pH was adjusted to 9.0. The result of the control test demonstrated that ammonia-nitrogen-stripping contributed 15.1% to the total ammonia nitrogen removal rate, indicating that the ammonia nitrogen degradation from wastewater was dominantly attributed to the photocatalytic activity of CF400, MF400, and ZF400. Previous studies consistently highlighted a preference for relatively high pH levels in the catalytic oxidation of ammonia nitrogen as well [25,64–66]. To strike a practical balance between treatment efficiency and the associated cost of alkaline substances, the optimal pH for CF400, MF400, and ZF400 to treat HCAW was determined as 9.0 under visible light irradiation in this study.

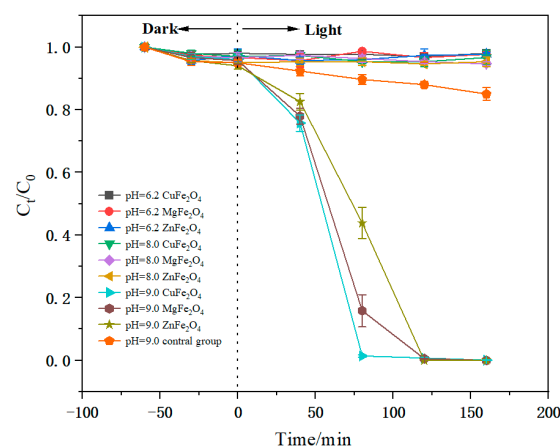


Figure 6. The influence of pH on the ammonia nitrogen removal efficiency of CF400, MF400, and ZF400 (C_0 : initial ammonia nitrogen concentration, C_t : ammonia nitrogen concentration at a certain time. pH = 6.2, 8.0, and 9.0; dark: 60 min, light: 160 min).

3.1.6. Stability and Recyclability Analysis of CF400, MF400, and ZF400

As is well known, stability and recyclability are important parameters for presenting the practical application of photocatalysts [31,67]. MFNPs possess excellent magnetic properties which are conducive to external magnetic recovery [68]. In this study, CF400, MF400 and ZF400 were collected and weighed after the photocatalytic degradation test at an optimum pH of 9.0. The recovery rate of CF400 and ZF400 was similar (66.7%), while MF400 had a relatively low recovery rate (53.2%). However, the solution turned pale blue when CF400 precipitated completely, as shown in Figure 7a. A small amount of blue and transparent crystalline solids were found at the bottom and surrounding the container after drying the post-reaction solution (Figure 7b). The blue solid accounted for approximately 16.6% of the total solids. XPS analysis (Figure 4a) confirmed that Cu^{2+} was presented in the blue crystals. As the Cu element in CF400 existed in the form of Cu^{2+} in the solution, the stability of CF400 prepared in this study was poor.

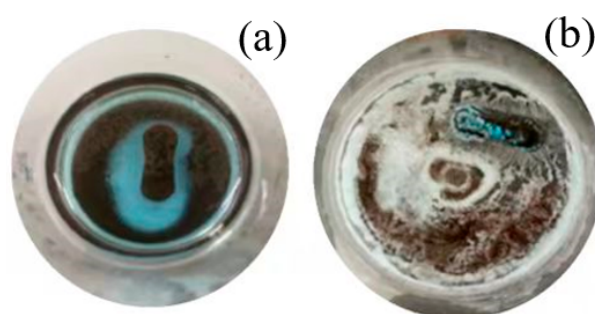


Figure 7. Stability analysis of CF400. (a) Solution after the degradation of CF400; (b) crystallization of the CF400 degradation solution after drying.

MF400 and ZF400 could completely remove ammonia nitrogen after 120 min of illumination. In addition, the recovery rate of ZF400 (66.7%) was higher than that of MF400 (53.2%). Therefore, ZF400 was determined to be the most suitable photocatalyst to degrade HCAW in this study.

To investigate the impact of recycling time on the ammonia nitrogen removal performance of ZF400, the photocatalyst was recycled and reused for five cycles at an optimal pH (9.0) during the photocatalytic experiment. The result showed that ZF400 could still remove 90% of ammonia nitrogen at the fifth cycle (Figure 8), which was similar to the findings of Guo et al. [69] and Cai et al. [70]. Hence, it could be concluded that the ZF400 obtained in this study had good recyclability under visible light irradiation.

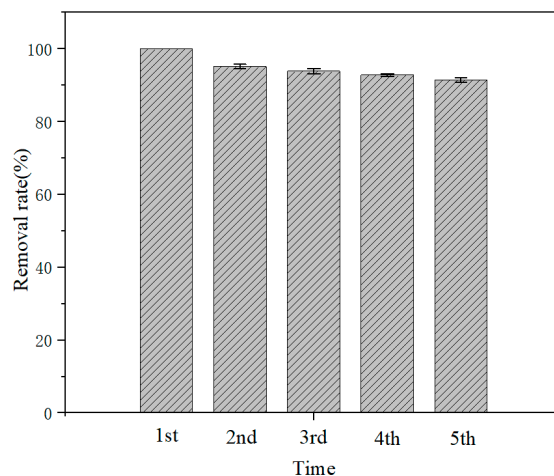


Figure 8. Ammonia nitrogen degradation performance of ZF400 after 5 recoveries (pH = 9.0).

3.1.7. Treatment of Ammonia Nitrogen Wastewater with Different Concentrations by ZF400

The experiment was investigated under the optimum pH of 9.0. A total of 0.15 g of ZF400 was added into the ammonia nitrogen solution with concentrations of 5000 mg/L, 1000 mg/L, 200 mg/L, and 20 mg/L, respectively. The results are shown in Figure 9. Ammonia nitrogen from wastewater with ammonia nitrogen concentrations of 20 mg/L, 200 mg/L, and 1000 mg/L could be completely removed by ZF400 after adsorption and desorption for 60 min in the dark, and 120 min under light. However, when the ammonia nitrogen concentration reached 5000 mg/L, the ammonia nitrogen could not be completely degraded under the above experimental condition. This could be attributed to the obstruction of active sites by pollutant molecules crowding on the surface of the photocatalyst at a high concentration. Eventually, the decreased concentration of active substances on the photocatalyst surface influenced the activity of photocatalysts to degrade ammonia nitrogen [71]. Nonetheless, the removal rate was still as high as 80.2%. Generally, the ZF400 could efficiently remove ammonia nitrogen from wastewater with a high ammonia nitrogen loading rate. Therefore, the ZF400 obtained in this study had a significantly practical value in the field of HCAW treatment.

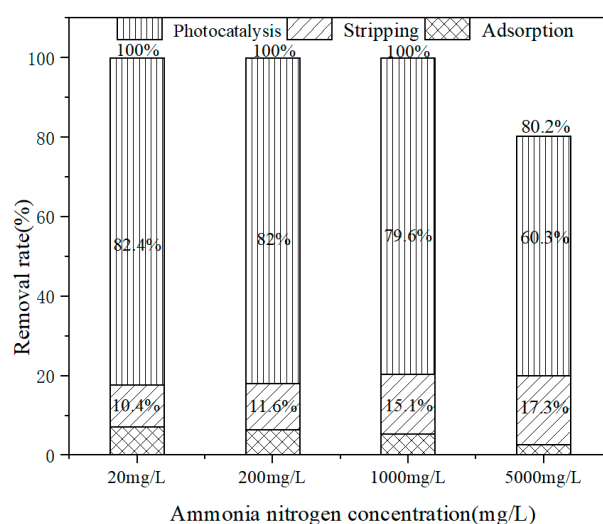


Figure 9. Removal rates of ammonia nitrogen at different concentrations by ZF400.

4. Conclusions

Magnetic CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 nanosphere photocatalysts were synthesized at different temperatures by the sol–gel method. The composition and structure of the synthesized photocatalysts determined by XRD revealed that the optimal calcination temperature was 400 °C. The economical temperature of 400 °C was employed to prepare CF400, MF400, and ZF400 to treat HCAW under varied pH conditions. Additionally, the stability and recyclability of the magnetic CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 nanosphere photocatalysts were examined.

(1) There was no discernible characteristic diffraction peak at a calcination temperature of 300 °C, suggesting that CF300, MF300, and ZF300 retained an amorphous structure. As the temperature increased to 400 °C, the diffraction peaks of the three photocatalysts became sharper and stronger without any impurity peaks, suggesting that the obtained photocatalysts at 400 °C had high crystallinity in this study.

(2) Different pHs significantly influenced the photocatalytic removal rate of CF400, MF400, and ZF400 to treat HCAW. When the pH was 9.0, magnetic CuFe_2O_4 , MgFe_2O_4 , and ZnFe_2O_4 nanosphere photocatalysts could completely remove HCAW (1000 mg/L) under visible light irradiation in this study.

(3) During the recovery process, CF400 showed poor stability. Both MF400 and ZF400 exhibited similar degradation performances after 120 min of illumination. The recyclability of ZF400 was higher than MF400. ZF400 had an excellent ammonia nitrogen degradation

performance even for high-concentration ammonia nitrogen wastewater (5000 mg/L). ZF400 was the most suitable magnetic ferrite nanosphere photocatalyst for treating HCAW wastewater.

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