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Magnetic recyclable heterogeneous catalyst Fe₃O₄/g-C₃N₄ for tetracycline hydrochloride degradation via photo-Fenton process under visible light

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ABSTRACT

Antibiotic pollution of water resources is a global problem, and the development of new treatments for destroying antibiotics in water is a priority research. We successfully manufactured recyclable magnetic $Fe_3O_4/g-C_3N_4$ through the electrostatic self-assembly method. Selecting tetracycline (TC) as the target pollutant, using $Fe_3O_4/g-C_3N_4$ and H_2O_2 developed a heterogeneous optical Fenton system to remove TC under visible light. $Fe_3O_4/g-C_3N_4$ was systematically characterized by SEM, TEM, XRD, FTIR, XPS, DRS, and electrochemical methods. The removal efficiency of 7% $Fe_3O_4/g-C_3N_4$ at pH = 3, $H_2O_2 = 5$ mM, and catalyst dosage of 1.0 g/L can reach 99.8%. After magnetic separation, the $Fe_3O_4/g-C_3N_4$ photocatalyst can be recycled five times with minimal efficiency loss. The excellent degradation performance of the prepared catalyst may be attributed to the proper coupling interface between Fe_3O_4 and $g-C_3N_4$ which promotes the separation and transfer of photogenerated electrons. Photogenerated electrons can also accelerate the conversion of Fe^{3+} to Fe^{2+} , thereby producing more 'OH. The new $Fe_3O_4/g-C_3N_4$ can be used as a raw material for advanced oxidation of water contaminated by refractory antibiotics.



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1. Introduction

Antibiotics are used in the pharmaceutical industry, aquaculture, as well as agriculture because of their antimicrobial activity and low operational cost [1]. As a result, a large proportion of wastewaters laden with antibiotics are generated annually. The remnants of antibiotics in wastewater can leach into groundwater and soil systems, and they induce long-term hazards to the environment and human health [2]. In this study, tetracycline (TC) was selected as an index antibiotic because it is the second most used antibiotic in the world [3]. A large amount of TC was excreted directly into the environment, which will lead to ecological risk and the resistance genes spread into the water [4]. Various physical, chemical, and biological treatment methods such as adsorption [5], photocatalytic degradation [6], biodegradation [7], and advanced oxidation processes [8,9] are used to mitigate TC contaminated water with partial success. The treatment based on adsorption or precipitation merely transfers contaminants from one compartment to another without destroying them. Most of the antibiotics are recalcitrant;

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hence biological treatment methods are not efficient. The advanced oxidation processes hold a promise in the destruction of antibiotics; however, they require modifications to meet specific requirements. Therefore, the destruction of TC from the aqueous environment is a pressing need.

Fenton process is widely used in advanced oxidation to destruct organic pollutants non-selectively [10]. The Fenton oxidation process generates highly reactive OH⁻ radical by Fe^{2+} and H_2O_2 reaction [11]. But the conventional homogeneous Fenton process has the following shortcomings: (1) limited Fenton activity and low utilization efficiency of hydrogen peroxide; (2) production of high Fe^{3+} concentrations, typically over 50 mg/L often exceeding world discharge standards (EU 2 ppm, China, 2 ppm); (3) iron-enrich sludge generation; (4) high acid dosage to maintain solution pH 2.5–3.5. The Fe^{2+} form complexes with natural and synthetic chelates ubiquitous in wastewater thus inhibiting Fenton activity [12,13].

The graphitic carbon nitride $(q-C_3N_4)$ is a nonmetallic semiconductor that consists of only C and N. Its bandgap is about 2.7 eV that facilitates light absorption at the visible range. The q-C₃N₄ resists acids, alkali, and lightinduced dissolution, it has good stability, and the structure can be tuned to desired properties. Presently g-C₃N₄ research is at its forefront in photo-catalysts formulations [14-16]. However, investigations into the degradation of organic pollutants by g-C₃N₄ are somewhat limited, owing to the fast electron-hole recombination [17]. As reported earlier, metal or non-metal elements can be doped to tune the bandgap of $q-C_3N_4$ to prevent the recombination of electrons and holes [18-20]. Singh et al. [21] found that the synthesized magnetic $Fe_2O_3/g-C_3N_4$ can degrade rhodamine B (RhB) up to 94.7% under visible light. However, the material is only degraded by photocatalysis, and its degradation ability is limited. Huang et al. [22] found that the magnetic photocatalytic 41.4%CoFe₂O₄/g-C₃N₄ degrades MB by 97.3%, but the reaction time required is too long, requiring 3 h. After the photocatalytic reaction, it can be quickly separated from the water by an additional magnetic field. Song et al. [23] also conducted an on Fedoped q-C₃N₄, which can increase the light absorption bandwidth, which leads to improved photocatalytic degradation of RhB under visible light irradiation. Ma et al. [24] found that Fe-q-C₃N₄/GMC can remove 99.2% of acid red in a wide pH window 4-10, most of Fe is uniformly distributed in the form of Fe-N coordination. Iron oxide composites [25-27], Fe(III) [28,29], iron oxide [28] and single molecule iron complex [30,31] were combined with g-C₃N₄ photocatalysts for photocatalysis/photo-Fenton degradation of organic pollutants. These studies prove that the composite formed by metal oxide doping $g-C_3N_4$ has a strong photocatalytic performance. However, in most of these studies [32,33], little attention was paid to the separation and recycling of the catalyst from the treated water.

Presently we synthesized, magnetic $Fe_3O_4/q-C_3N_4$ by a simple electrostatic self-assembly method to degrade TC by the heterogeneous photo-Fenton process under visible light. Tuning of the bandgap of the Fe_3O_4/q -C₃N₄ composite was achieved by Fe₃O₄ doping. Besides, due to the magnetic properties of Fe₃O₄, the used catalyst can efficiently be removed by the reaction mixture. TC is ubiquitous in soils and water, and it is not removed efficiently by conventional treatment methods. Hence, we selected TC to represents recalcitrant antibiotics. Before pursuing TC degradation, the Fe₃O₄-g-C₃N₄ composite was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), electrical impedance spectroscopy (EIS), electron spin resonance (ESR) and diffuse reflectance spectroscopy (UV-Vis). The TC degradation efficiencies as a function of pH, H₂O₂, degree of Fe₃O₄ doping, Fe₃O₄/g-C₃N₄ dosage, and TC concentration were also examined. Besides, the reusability and stability of the Fe₃O₄/g-C₃N₄ were also evaluated. Finally, the mechanism of TC degradation by Fe₃O₄/g-C₃N₄ under visible light was proposed.

2. Experimental

2.1. Chemicals

Ferrous sulfate heptahydrate (FeSO₄·7H₂O, \geq 98%), sodium thiosulfate pentahydrate (Na₂S₂O₃·5H₂O, \geq 98%), sodium hydroxide (NaOH, \geq 98%), hydrochloric acid (HCl, 36.0–38.0%) were purchased from Sinopharm (China). Urea (CO(NH₂), \geq 98%), tetracycline hydrochloride (TC·HCl, \geq 98%), Humic acid (HA, \geq 90%), isopropyl alcohol (C₃H₈O, \geq 99%) and p-benzoquinone (BQ, \geq 99%), potassium dichromate (K₂Cr₂O₇, \geq 99%), ethylenediaminetetraacetic acid disodium sodium (C₁₀H₁₄N₂-Na₂O₈, \geq 99%) were purchased from Shanghai Maclin (China). Hydrogen peroxide (H₂O₂, 30%), were supplied from Shanghai Aladdin Chemistry, (China). All chemicals were analytical grade and used as received.

2.2. $Fe_3O_4/g-C_3N_4$ synthesis

Specific amounts of $FeSO_4$ ·7H₂O (1.39 g) and $Na_2S_2O_3$ -·5H₂O (1.24 g) were dissolved in 15 mL deionized water, and NaOH (0.4 g) was dissolved in 10 mL deionized water. The two solutions were mixed and stirred for about 5 min. The resultant solution was transferred into a 50 mL Teflon-lined autoclavable tube which was sealed and the solution was kept at 140 °C for 12 h and then cooled to room temperature. Finally, the resulted black residue was washed with deionized water 3–4 times and dried in a vacuum oven at 60 °C for 4 h. The g-C₃N₄ was synthesized via solid-state synthesis using urea as a starting material. A 15 g urea was placed in a crucible and heated in a muffle furnace at 550 °C at a heating rate of 5 °C/min for 2 h. The g-C₃N₄ was then cooled to ambient room temperature and powdered for further use.

An electrostatic self-assembly method was used to prepare the Fe₃O₄/g-C₃N₄ nanocomposites as detailed elsewhere [34]. Briefly, 93 mg of g-C₃N₄ was dispersed in 50 mL deionized water by ultrasonication for 30 min; 7 mg of Fe₃O₄ was dispersed in 10 mL deionized water was dispersed through ultrasonic for 15 min. Then, Fe₃O₄ was mixed with g-C₃N₄ suspension stirred for 24 h. The resultant product was centrifuged and washed thoroughly with distilled water and dried in a vacuum oven at 60 °C for 24 h.

2.3. Materials characterization

The crystal structure of the composites was identified by X-ray diffraction spectrometer (PANalytical X'Pert Pro) at 40 kV and 40 mA in the 2 θ range of 10–70° with 6° min⁻¹ scan rate. The size and morphology of catalyst particles were characterized by SU-8020 scanning electron microscopy (SEM; Hitachi model, Tokyo) and JEM-1400F transmission electron microscopy (TEM; JEOL model, Tokyo). The UV-vis diffused reflectance spectra



Figure 1. (a) SEM images of $g-C_3N_4$, (b) SEM images of 7% Fe₃O₄/ $g-C_3N_4$, (c) TEM images of $g-C_3N_4$, (d) TEM images of 7% Fe₃O₄/ $g-C_3N_4$.

(UV-vis DRS) of the samples were obtained (UV 3600 Agilent, USA). The infrared spectra of the catalysts were obtained by Fourier transform infrared spectroscopy (FTIR model; Bruker, German) under transmission mode. The X-ray photoelectron spectroscopy (XPS, Thermo, ESCALAB₂50Xi) was used to determine the atomic composition and oxidation states of the elements. The specific surface area of Fe₃O₄/g-C₃N₄ was determined by the Brunauer–Emmett–Teller (BET) analyzer (Autosorb-IQ₃, Quantachrome, USA).

2.4. Degradation experiments

TC degradation experiments were carried out in a photocatalytic multi-test tube reactor equipped with a vertically aligned 500 W Xe lamp (UV radiation < 420 nm). The reactor vessel was water-jacketed at $18 \pm 2^{\circ}$ C with a recycled cooling unit (XPA-7 Nanjing, China). First, 0.05 g Fe₃O₄/g-C₃N₄ was weighed into 50 mL TC solution, and the reaction solution was stirred for 30 min in the dark to achieve the adsorption equilibrium. After H₂O₂ addition, the photocatalytic reaction was started for 100 min, and 1 mL sample aliquots were taken at 20 min intervals. The samples were filtered using 0.22 µm PES filters. Then, the catalytic reaction was repeated for 100 min using H₂O₂ was added and light radiation. A 1 mL aliquots of the reaction suspension were collected every 20 min. The samples were filtered for the determination of TC and its degradation products by high-performance liquid chromatography.

2.5. Analysis methods

The residual TC concentrations were detected by highperformance liquid chromatography using oxalic acid, methanol, and acetonitrile mobile phase at 357 nm (HPLC; Agilent 1200 Series). The overall degradation efficiency of TC by the photoreactor system was determined by measuring total organic carbon (TOC) with TOC/TN analysis (Multi N/C 3100). H₂O₂ was measured spectrophotometrically by the KMnO₄ method at 400 nm [35] (UV-Vis; Hitachi, Japan). The total iron concentration in solution was measured by flame atomic absorption spectrophotometry (AAS; AA140, VARIAN). The degradation intermediates were analyzed by high-performance liquid chromatography-mass spectrometry (LC-MS; Agilent 1290/6460, USA). The free radicals generated during the degradation process were detected by electron paramagnetic resonance spectroscopy (ESR; JES-FA200, JEOL, Japan) using a 50 mM 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) scavenger.

3. Results and discussion

3.1. Characterization of the $Fe_3O_4/g-C_3N_4$

SEM and TEM analyses were carried out to characterize the morphology and microstructure of the 7% $Fe_3O_4/$ $g-C_3N_4$ catalyst (hereafter Fe₃O₄/ $g-C_3N_4$). As detailed in Section 3.2, the selection of Fe₃O₄/q-C₃N₄ made based on its degradation efficiency. The SEM and TEM images are shown in Figure 1a, and 1c show that $q-C_3N_4$ has a layered structure. As shown in Figure 1b (SEM), Fe₃O₄/ $q-C_3N_4$ also indicates a similar lavering, which suggests that doping Fe_3O_4 into $q-C_3N_4$ did not change its microstructural properties significantly. As shown in Figure 1d (TEM), the black spots on the lamellar are from Fe₃O₄, and the elemental mapping of $Fe_3O_4/g-C_3N_4$ shows that C, N, O, and Fe are evenly formed on the surface (Figure S2). The SEM-EDS results are shown in Figure S1. b, and the peaks correspond to C, N, O, and Fe are uniformly dispersed in g-C₃N₄ on Fe₃O₄, which proves that the Fe₃O₄/g-C₃N₄ composite was successfully prepared.

Figure 2a shows XRD patterns of $g-C_3N_4$, Fe_3O_4 , and $Fe_3O_4/g-C_3N_4$ doped with different iron contents. The diffraction peak of (002) crystal plane of $g-C_3N_4$ is located at $2\theta = 27.857^\circ$, and the crystal plane spacing is d (002) = 3.200 Å (PDF50–1512) [36]. As shown in Figure 2a the XRD pattern of $g-C_3N_4$ has a distinct diffraction peak at $2\theta = 27.4^\circ$, and the interplanar spacing d (002) = 3.253 Å. The values are consistent, which indicates our substrate is a layered graphite phase-carbon nitride ($g-C_3N_4$), and it has a reasonable degree of graphitization. In the XRD spectrum of Fe_3O_4 , distinct diffraction peaks are observed at $2\theta = 62.5^\circ$, 57.2° , 53.4° , 43.1° , 35.4° , and 30.1° , which correspond to (220),

(311), (400), (422), (511), (440) planes (JCPDS (75–0449) standard card of Fe₃O₄) [37]. In the XRD spectrum of Fe₃O₄/g-C₃N₄, the characteristic diffraction peaks at 27.8°, 57.2°, 53.4°, 35.4°, and 30.1° of g-C₃N₄ and Fe₃O₄ can be observed, and with the increase of Fe₃O₄ content, the intensity of Fe₃O₄ diffraction peaks become strong, and the peak of g-C₃N₄ weakened indicating g-C₃N₄ and Fe₃O₄ admixtures.

Figure 2b shows the FT-IR spectra of $q-C_3N_4$ and $Fe_3O_4/q-C_3N_4$. The sharp peaks at 810 cm⁻¹, 1247– 1637 cm⁻¹, 810 cm⁻¹ are attributed to respiration modes of the triazine unit [36]. The absorption band of 1247–1637 cm⁻¹ (with the characteristic band at 1247 cm^{-1} and 1637 cm^{-1}) can be attributed to tensile vibration of the -CN heterocyclic ring [38]. The peak at $3000-3600 \text{ cm}^{-1}$ is the tensile vibration absorption peak of NH [36]. When different amounts of Fe₃O₄ are doped into $q-C_3N_4$, the peak position does not shift; however, the intensity values are reduced. By the incorporation of Fe, the skeleton structure of q-C₃N₄ does not vary. In the spectrum of Fe_3O_4 , the strong characteristic peak at 572 cm^{-1} is due to vibrations of Fe-O bonds. However, we could not observe any bands correspond to Fe-N and Fe-C bond vibrations in $Fe_3O_4/q-C_3N_4$. Therefore, in agreement with TEM and XPS data, Fe ions are doped into the g-C₃N₄ framework.

Figure 3a shows survey XPS spectra of the g-C₃N₄ and Fe₃O₄/g-C₃N₄ catalysts. The peaks of C, N, O are found in the XPS spectrum of g-C₃N₄, and the peaks of C, N, O, and Fe are found in the XPS spectrum of Fe₃O₄/g-C₃N₄. According to the results of XPS measurement, the weight percentages of elements in 7% Fe₃O₄/g-C₃N₄ are 39.93%, 50.38%, 6.75%, and 2.94% of C, N, O, and Fe, respectively. Because of the small amount of Fe



Figure 2. (a) XRD patterns of g-C₃N₄, Fe₃O₄, and Fe₃O₄/g-C₃N₄, (b) FTIR spectra of g-C₃N₄, Fe₃O₄ and Fe₃O₄/g-C₃N₄.

doping, the Fe peak is very low. Figure 3b shows the C1s spectra of $q-C_3N_4$ and $Fe_3O_4/q-C_3N_4$. For both materials, the C1s spectrum can be deconvolved into three Gauss-Lorentz peaks, and the binding energy of the central peak is 284.88 (q-C₃N₄) and 288.21 eV (Fe₃O₄/q-C₃N₄). The peak at 284.88 eV (19.82%) is attributed to the C-C coordination of amorphous carbon; the peak at 288.21 eV (80.18%) is due to the C-N or C-(N)₃ groups [39]. The C1s spectrum of $Fe_3O_4/q-C_3N_4$ was similar to that of g-C₃N₄, but the peak of C-N shifted 0.02 eV towards high binding energy direction, and the peak of C-C shifted 0.05 eV towards low binding energy direction. In the N1s spectrum of $q-C_3N_4$ (Figure 3c), three peaks are observed after deconvolution. The peak at 398.69 eV(76.54%) is ascribed to sp²-hybridized aromatic N (C-N=C); the peak at 399.93 eV (10.46%) is attributed to tertiary nitrogen N-(C)₃; the peak at 401.14 eV (9.28%) is attributed to C-N-H groups [40]. In the N1s spectrum of $Fe_3O_4/q-C_3N_4$ (Figure 3c), these peaks have shifted to 0.03, 0.05, and 0.06 eV towards high binding energy direction. The O1s peak at 532.3 eV is associated with $Fe_3O_4/g-C_3N_4$ surface hydroxyl group or water molecules [41] (Figure 3d). Six peaks are observed for $Fe_3O_4/q-C_3N_4$ in the Fe2p spectrum (Figure 3e). The binding energies at 709.2 eV (35.47%), 711.4 eV (28.55%) and 724.8 eV (27.83%) correspond to



Figure 3. The XPS spectra of whole XPS spectra (a) and typical elements C1s (b), N1s (c), O1s (d), Fe2p (e).

Fe²⁺ 2p_{3/2}, Fe³⁺ 2p_{3/2} and Fe³⁺ 2p_{1/2}, respectively, manifesting that the catalyst consists of Fe²⁺ and Fe³⁺ species. And the other four are satellite peaks of Fe²⁺ or Fe³⁺ [42]. The characteristic diffraction peak of Fe-C or Fe-N is not found in the Fe₃O₄/g-C₃N₄ indicating that no chemical bond formed between the Fe₃O₄ and g-C₃N₄ [34,43]. Our results confirm that Fe was doped into the g-C₃N₄ framework. The XPS of Fe₃O₄/g-C₃N₄ after reusing three times is shown in Figure S6.

The ultraviolet–visible diffuse reflectance spectra of g- C_3N_4 and Fe₃O₄/g- C_3N_4 were measured to study the light absorption characteristics of the photocatalyst. As shown in Figure 4a, the Fe₃O₄/g- C_3N_4 has a wide absorption rate in the ultraviolet–visible region. According to the Kubeka-Munk function (Figure S3(a)), the absorption wavelength of g- C_3N_4 is about 455 nm with a 2.67 eV bandgap [44]. The bandgap of Fe₃O₄/g- C_3N_4 is about 2.33 eV. In comparison with g- C_3N_4 , the wavelength of Fe₃O₄/g- C_3N_4 absorption show a redshift due to charge transfer between the Fe₃O₄ and g- C_3N_4 [34]. Therefore, the Fe₃O₄/g- C_3N_4 photocatalyst can effectively use in the range of visible solar radiation.

The hysteresis loops of $g-C_3N_4$ and $Fe_3O_4/g-C_3N_4$ are shown in Figure 4b. The results show that $g-C_3N_4$ is non-magnetic, while $Fe_3O_4/g-C_3N_4$ is magnetic. Besides, the saturation magnetization of $Fe_3O_4/g-C_3N_4$ is sufficient for its separation from the solution by an external magnetic field (Figure 4b, inset). This property can be used to recover the $Fe_3O_4/g-C_3N_4$ composite for recycling.

To better understand the photo-induced current separation behaviour of $Fe_3O_4/g-C_3N_4$, electrochemical impedance spectroscopy (EIS) and transient (I-t) were measured (Figure S3 and Figure 4c). The arc of a typical EIS electrochemical impedance spectrum reflects the resistance of the charge transfer layer at the electrode/electrolyte interface. A small arc indicates a low resistance and high charge transfer efficiency [45]. The arc radius of the Fe₃O₄/g-C₃N₄ composite photocatalyst is smaller than that of g-C₃N₄, which indicates that the conversion and separation of electron-hole pairs at the interface of $Fe_3O_4/g-C_3N_4$ is effective. Figure 4c shows that the photocurrent response of $Fe_3O_4/g-C_3N_4$ is about three times larger than that of q-C₃N₄. Both EIS results and I-t results indicate that the charge separation and transfer efficiency of Fe₃O₄/g-C₃N₄ light-induced carriers is more increased than g- C_3N_4 [46]. The charge separation efficiency was further tested by PL measurement. Figure S3(c) shows that g-C₃N₄ produces a high-intensity fluorescence peak at 440 nm. Compared with g-C₃N₄, the fluorescence intensity of Fe₃O₄/g-C₃N₄ is reduced, indicating that the electrons and holes produced by g-C₃N₄ have higher fluorescence intensity, which indicates Fe_3O_4 doping



Figure 4. (a) UV-vis diffuse reflectance spectra of $g-C_3N_4$ and 7% $Fe_3O_4/g-C_3N_4$, (b) Magnetization curve of $g-C_3N_4$, $Fe_3O_4/g-C_3N_4$ at room temperature, (c) Transient photocurrent responses of $g-C_3N_4$ and 7% $Fe_3O_4/g-C_3N_4$, (d) Nitrogen adsorption-desorption isotherms of $g-C_3N_4$ and 7% $Fe_3O_4/g-C_3N_4$.

into $g-C_3N_4$ can effectively inhibit the recombination of photogenerated electrons and holes.

Nitrogen adsorption/desorption isotherms were constructed to determine the specific surface area and porosity of g-C₃N₄ and Fe₃O₄/g-C₃N₄. As in Figure 4d, based on the classification of the International Union of Pure and Applied Chemistry (IUPAC), the N₂ adsorption–desorption isotherm is type IV of the H₃ hysteresis cycle [47]. The specific surface areas of g-C₃N₄ and 7% Fe₃O₄/g-C₃N₄ are 59.25 and 53.14 m²/g, respectively. The reduced specific surface area of Fe₃O₄/g-C₃N₄ is due to the blocking of the Fe₃O₄ region, which occurs during the composite synthesis. Table S1 shows the detailed properties of g-C₃N₄ and Fe₃O₄/g-C₃N₄ based on N₂ adsorption–desorption isotherms.

3.2. Influences of experimental conditions on TC oxidation

Figure 5a shows the degradation efficiency of TC by $Fe_3O_4/g-C_3N_4$ under different experimental conditions. We used $Fe_3O_4/g-C_3N_4$ fabricated by varying dopant concentration (Fe_3O_4) to assess optimal TC degradation. In all instances, 100 min reaction time was chosen. The adsorption rate of $Fe_3O_4/g-C_3N_4$ alone for TC under dark

conditions is only 5.6%, and after 30 min of adsorption, the TC concentration no longer decreases (Figure S4(d)). The results show that only when H_2O_2 is used, about 12% TC is photodegraded. In the presence of visible light, when bare q-C₃N₄ is used, only 40.4% TC was degraded. In the presence of visible light and H_2O_2 , the degradation rate of TC by g-C₃N₄ was slightly increased to 43.4%. In the dark, the TC degradation efficiencies by Fe_3O_4 and $Fe_3O_4/g-C_3N_4$ were 50.1% and 45.2%, respectively. However, in the presence of visible light radiation, the TC degradation by $Fe_3O_4/g-C_3N_4$ reaches over 99%. Our data show that the $Fe_3O_4/q-C_3N_4$ at Fe_3O_4 doping shows highest TC degradation. When compared to g- C_3N_4 , in $Fe_3O_4/q-C_3N_4$ proper interfacial coupling between Fe_3O_4 and $g-C_3N_4$ accelerates efficient hole and electrons separation; second, photogenerated electrons can accelerate the conversion of Fe^{3+} to Fe^{2+} , thereby efficient production of 'OH. The synergy between the aforementioned processes enhances the photo-Fenton activity in Fe₃O₄/g-C₃N₄ composite.

The TC degradation rate can be interpreted by pseudo-first-order rate law when [TC]_{initial} << [catalyst]_{initial} as shown in Figure S4(a);

$$\ln(C_0/C) = K_{\rm app}t$$



Figure 5. (a) Different reaction systems to remove TC, (b) The effect of different TC concentration on the TC removal efficiency, (c) The effect of different Fe doping amounts of Fe₃O₄/g-C₃N₄ to the TC removal efficiency, (d) The effect of different H₂O₂ concentrations to the TC removal efficiency, (e) The effect of different pH to the TC removal efficiency, (f) The effect of different catalyst dosage to the TC removal efficiency. ($C_0 = 25 \text{ mg/L}$, H₂O₂ = 5.0 mM, catalyst = 1.0 g/L, P = 500 W Xenon lamp > 420, T = 20 ± 2 °C).

where ($C_0 t_0$) and (C, t) are initial and final reaction conditions used, and K_{app} is the pseudo-first-order rate constant (min⁻¹). According to Figure 5b, the K_{app} values of g-C₃N₄, Fe₃O₄, and Fe₃O₄/g-C₃N₄ are 0.00559, 0.00679,

and 0.03907 min⁻¹ respectively. Table S-2 shows K_{app} and R^2 for different reaction systems, which indicates that doping Fe₃O₄ g-C₃N₄ contributes to optimal photo-Fenton activity. Figure 5b illustrates the effect of

the initial [TC]_{initial} loading on its degradation efficiency. The TC degradation rate is inversely proportional to the [TC]_{initial}. When the [TC]_{initial} is 25 mg/L, the TC is completed degraded within 100 min, but when [TC]_{initial} increased from 65 to 85 mg/L, the degradation efficiencies have reduced from 72.7 to 57.9% due to covering catalyst sites by TC which inhibits OH⁻ generation [48]. At the same time, Fe₃O₄/g-C₃N₄ was reacted under sunlight for one hour, and the removal rate of TC could reach 99.7% (Figure S4(c)).

Figure 5c shows the effect of Fe₃O₄ doping in Fe₃O₄/ g-C₃N₄ on TC degradation. When the Fe₃O₄ doping on g-C₃N₄ increased from 1 to 7%, and the TC degradation efficiency from 75 to 99%, respectively. However, at 9% Fe₃O₄ doping on g-C₃N₄, the TC degradation reduced to 80% showing an optimal value at 7% Fe₃O₄. In the photo–Fenton process, as the solution iron concentration increases the 'OH production by H₂O₂ is enhanced. However, at excess concentrations of Fe²⁺, the electrons and holes may recombine reducing the activity in the photocatalysis-Fenton system [49]. Therefore, doping 7% Fe₃O₄ in g-C₃N₄ is the optimal value for the photo-Fenton activity of the catalyst.

Figure 5d shows the effect of $Fe_3O_4/q-C_3N_4$ with different H₂O₂ concentrations on the efficiency of TC degradation by the photocatalysis-Fenton reaction. When the H_2O_2 concentration increased from 1 to 5 mM, the TC removal efficiency increased from 86 to 99.9% within 100 min. But when the concentration of H_2O_2 increased further to 7 mM, the TC degradation efficiency decreased slightly. When the H₂O₂ concentration is below a critical value, the amount of 'OH radicals produced by the catalytic reaction increases with the H_2O_2 concentration. When the H_2O_2 concentration reaches a critical value, the generated 'OH can be converted into less reactive HO_2 by the excess H_2O_2 , thus reducing the TC reduction [50] (Equations (1) - (3)). When a large proportion of 'OH is consumed, it cannot react effectively to degrade TC. The generation of 'OH radicals by $Fe_3O_4/q-C_3N_4$ is shown in Figure S5(b).

$$H_2O_2 + \dot{OH} \rightarrow \dot{H}O_2 + H_2O \tag{1}$$

$$\dot{H}O_2 + \dot{OH} \rightarrow H_2O + O_2$$
 (2)

$$\dot{OH} + \dot{OH} \rightarrow H_2O_2$$
 (3)

Figure 5e shows the TC degradation efficiency by the photo-Fenton system as a function of initial pH. As the pH is decreased from 9.0 to 3.0, the TC degradation rate has increased from 73.4 to 98.7% due to the enhanced formation of 'OH radical in acidic conditions. However, there is a threshold pH. When the solution

pH = 2, the TC degradation rate has declined to 87.1% due to scavenging OH by H⁺ [51]. Also, the pH of the resultant solution decreases from 9.00 to 6.48, as shown in Table S-3. The observed reduction of pH is ascribed to the formation of acidic intermediates as a result of TC degradation [52].

Figure 5f shows the TC degradation by $Fe_3O_4/g-C_3N_4$ as a function of catalyst dosing and the results are shown in Figure 5f. As the catalyst content increased from 0.5 to 1.0 g/L, the TC degradation rate increased from 83.8 to 98.7%. When the catalytic content is between 0.5 and 1.0 g/L, an optimal TC degradation was noted. When the concentration of the catalyst is greater than 1 g/L, TC degradation is decreased due to reduced intensity of light penetration as required for electron–hole pair generation. This result reduced OH⁻ generation thus reducing TC degradation efficiency [53].

Figure S4(b) shows a typical chromatogram of HPLC of the solution after the photo-Fenton process. The retention time of the TC peak is shown at about 6.3 min. As the reaction time increases, the peak gradually decreases, and after 100 min the peak disappeared.

Humic acid (HA) is a common macromolecular organic matter in natural water, accounting for about 50-90% of organic matter in natural water, which is mainly decomposed by natural organic matter [54,55]. Therefore, the application effect of Fe3O4/C3N4 catalyst in the treatment of real wastewater was investigated by adding different concentrations of HA to TC solution. When the concentration of HA is 5, 10, 15, and 20m/L, the degradation rate of TC is shown in Figure S4(e). When the concentration of HA gradually increased, the degradation rate of TC increased slightly at first and then decreased. When the concentration of HA is low, it can promote the conversion of Fe^{3+} to Fe^{2+} [56]. However, when the concentration of HA is too high, it has a certain inhibitory effect on the degradation of TC. This is because HA will be adsorbed on the surface of the catalyst to prevent effective contact between the catalyst and TC. On the other hand, HA and TC will compete for the OH radicals generated by the photo-Fenton, resulting in the decrease of TC degradation rate [55].

3.3. Reusability and stability of the $Fe_3O_4/g-C_3N_4$

The stability and reusability of the catalyst are important in the application of the proposed technology in real situations. To evaluate the chemical stability and reusability of $Fe_3O_4/g-C_3N_4$, five consecutive cycles of experiments were conducted to degrade TC under visible light. After each reaction cycle, the photocatalyst was separated from the system by applying an external



Figure 6. Removal efficiency of TC and TOC (Reaction conditions: $C_0 = 25$ mg/L, $H_2O_2 = 5.0$ mM, catalyst = 1.0 g/L, P = 500 W Xenon lamp > 420, $T = 20 \pm 2$ °C).

magnetic field, and then washed and dried for the commencement of the next cycle. The experimental results are shown in Figure 6a. After five cycles, the degradation efficiency of TC is reduced by only 11.2% (from 98.5 to 87.3%). The TOC degradation rate is only 10.1% (reduced from 67.2 to 57.1%). Besides, the amount of photocatalyst lost by magnetic separation is negligible. The stability of Fe₃O₄/g-C₃N₄ depends on the amount of iron leached. As shown in Figure S5(a), after five cycles, the leached iron concentration decreased from 0.17 to 0.11 mg/L. After the first cycle, the iron ions leaching was only 0.24%. This shows that iron ions are effectively fixed on the g-C₃N₄ framework. As shown in Table 1, Fe₃O₄/g-C₃N₄ shows excellent TC degradation efficiency when compared with different iron-doped photo Fenton catalysts. After five cycles, the Fe_3O_4/q_- C₃N₄ shows excellent stability and repeatability thus offer a potent material for pollution control.

The FTIR, SEM, BET, and XPS of the catalyst before and after the reaction was compared. As shown in Figure S7 (a), the functional groups of the catalyst did not change significantly before and after the reaction. As shown in Figure S7(b) and c, the catalyst maintains its original form after the reaction, and Fe_3O_4 is dispersed on

 $g-C_3N_4$. After the reaction, the specific surface area of the catalyst is only slightly reduced to 46.76 m²/g. As shown in Figure S6, the peaks of C, N, O, and Fe are found in the XPS spectrum of Fe₃O₄/g-C₃N₄ repeated three times. All the results show that the structure of Fe₃O₄/g-C₃N₄ after the reaction has not been damaged, and it has good stability and repeatability.

3.4. Reaction pathways of TC degradation

To study the mechanism of the photocatalysis-Fenton system, trapping experiments were carried out. Trapping experiments explored the generation of active species via the photocatalysis-Fenton system and their impact on TC removal efficiency. The trapping agents for the experiment were isopropyl alcohol ('OH), p-benzoquinone (O_2) , and EDTA-2Na (h^+) [61,62]. The experimental results are shown in Figure 7a. Without adding any trapping agent, the TC degradation efficiency reached 99.8%. After adding isopropanol to the reaction system, the TC degradation efficiency decreased significantly, only 34.6% (a reduction of 65.3%); after p-benzoquinone was added to the reaction system, the TC degradation efficiency was 62.7%; however, after adding EDTA-2Na, the TC degradation efficiency is slightly reduced. This shows that O_2^- , OH are the main active substances, and h⁺ is the secondary active substance. To further study the active free radicals in the photocatalysis-Fenton system, an ESR trap experiment with 5-dimethylpyrroline-N-oxide (DMPO) as a spin trap was carried out. The intensity ratios of the 1:1:1:1:1 quartet characteristic ESR signal and the 1:2:2:1 guartet pattern signal are respectively shown in Figure 7b. The results showed conclusively that 'OH and O_2^- were produced in the photo-Fenton system.

Through LC-MS analysis, these TC degradation intermediates were found including m/z = 461, 417, 374,401, 274, 236, 208, 150 (Figure S8). Based on the molecular structures of these compounds, Figure 8 suggests possible degradation pathways.

Table 1. Compare the degradation of pollutants by various iron-doped photo renton cata
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Materials	Pollutants	Conditions	Removal efficiency	Amount of iron leaching	References
rGS/Fe _x O _y /NCL	Rhodamine B. (10 mg/L, 60 mL)	Catalyst (30 mg); H_2O_2 (20 mM); 330 W Xe lamp with 420 nm cut-off filter; pH without adjustment; $t = 150$ min	100%	3.3 mg/L each cycle	[57]
Cu/Fe ₃ O ₄ @CRC	methylene blue (40 mg/ L, 100 mL)	Catalyst (20 mg); H_2O_2 (4 mM); 250 W Xe lamp with 420 nm cut-off filter; pH = 6; t = 40 min	97.5%	0.42 mg/L each cycle	[58]
Fe ₃ O ₄ @PBC	Metronidazole (300 mg/ L, 50 mL)	Catalyst (20 mg); H_2O_2 (3 mM); 300 W Xe lamp with UV cut-off filter; pH = 3; $t = 120$ min	95.1%	0.89~0.2 mg/L each cycle	[59]
Fe-modified rectorite (Fe-R)	TC (100 mg/L, 100 mL)	Catalyst (40 mg); H ₂ O ₂ (10 mM); 500 W LED visible-light lamp; pH = 3.81; <i>t</i> =120 min	95%	2.2–3.6 mg/L each cycle	[60]
$Fe_3O_4@g-C_3N_4$	TC (25 mg/L, 50 mL)	Catalyst (50 mg); H_2O_2 (5 mM); 500 W Xe lamp with 420 nm cut-off filter; pH = 3; $t = 100$ min	99.8%	0.17~0.11 mg/L each cycle	This work



Figure 7. (a) Effect of radical scavengers on the degradation of TC. (b) ESR spectra of DMPO- $^{-}O_{2}^{-}$ adducts.

During the treatment process, the TC intermediates are mainly formed via three routes: the loss of functional groups, ring-opening, and hydroxylation reactions via the addition or substitution by 'OH [63,64]. For pathway 1, when C11a-C12 reacts with 'OH, a hydroxyl and a ketone group at C11a-C12 are formed, resulting in the generation of a compound with TC 1 (m/z = 461). For pathway 2, TC 2 (m/z = 417) was formed by the demethylation of the diethylamino group by low N–C bond energy at C4 [65]. Then, 'OH radicals continued to attack TC 2, leading to two decomposition pathways of TC 2. On the one hand, TC 3 (m/z = 374) was formed by the loss of acylamino groups in C2. On the other hand, 'OH attacks the hydroxyl group in C3, leading to the generation of a compound with TC 4 (m/z = 401) [65]. TC 4 was further degraded led to the generation of TC 5 (m/z = 274) via loss of amino groups, because of breakage of naphthalene ring A [66]. The intermediates with TC 6 (m/z = 236) and TC 7 (m/z = 208) are generated through ruptures of rings



Figure 8. Proposed degradation pathways of TC in the photo-Fenton system.



Figure 9. (a) Acute toxicity of Fathead minnow, (b) developmental toxicity of TC and degradation intermediates.

B. TC 6 (m/z = 236) generates TC 8 (m/z = 150) by forming carboxyl groups and dissociating hydroxyl groups.

The acute toxicity, developmental toxicity of the 8 intermediates of TC was analyzed by Toxicity Estimation Software Tool (TEST) [67]. As shown in Figure 9a, the LC₅₀-96 h of Fathead minnow (the concentration of the chemical that causes 50% of Fathead minnow to die in 96 h) was 0.90 mg/L TC, which can be categorized as 'very toxic'. Except for TC 2 and TC 5, the toxicity of other intermediates is reduced. TC 1 and TC 3 are still toxic. As the number of benzene rings decreases, the toxicity of the intermediates gradually decreases. For example, TC 6, TC 7, and TC 8 are classified as 'harmful'. Figure 9b displayed the developmental toxicity, except for TC 2 and TC 4, the developmental toxicity of other degradation intermediates is reduced.

Based on experimental results and related literature (including physical and chemical properties, photocatalytic properties, and detected active groups) [20,68], a possible photo-Fenton TC degradation mechanism by $Fe_3O_4/g-C_3N_4$ composites under visible light is proposed



Scheme 1. The plausible mechanism of the photo-Fenton system with $Fe_3O_4/g-C_3N_4$.

as shown in Scheme 1. The g-C₃N₄ can generate electron-hole pairs by the excitation from visible light (Equation (4)). Because the conduction band of $q-C_3N_4$ (CB, -1.12 eV) is more negative than O_2/O_2^- (O_2/O_2^- , -0.33eV vs NHE) [69], it can reduce O₂ yielding O_2^- (Equation (5)). The holes in the VB of $q-C_3N_4$ (VB, 1.53 eV) cannot oxidize OH⁻ to give 'OH (OH⁻/'OH, 2.38 eV vs NHE) [70]. The holes in CB of g-C₃N₄ will transfer to the Fe₃O₄ surface, the electrons from $q-C_3N_4$ will be captured by Fe^{3+} to form Fe^{2+} (Equation (6)). Subsequently, the generated and original Fe²⁺ reacts with H_2O_2 to form Fe³⁺ and OH [71] (Equation (7)). The H_2O_2 in the system will also react with holes to form O_2^- (Equation (8)). After a series of reactions, the generated O_{2}^{-} , OH and h⁺ react with TC to mineralize into inorganic compounds (Equation (9)).

$$g - C_3 N_4 + hv \rightarrow g - C_3 N_4 (h^+ + e^-)$$
 (4)

$$O_2 + e^- \rightarrow \dot{O}_2^- \tag{5}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$
 (6)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \dot{OH} + OH^-$$
 (7)

$$h^+ + H_2O_2 \rightarrow O_2^- + 2H^+$$
 (8)

$$\dot{O}_2^- + \dot{OH} + h^+ + TC \rightarrow smallmolecules/ions$$
 (9)

4. Conclusions

We synthesized magnetic $Fe_3O_4/g-C_3N_4$ photocatalyst by electrostatic self-assembly method to design a heterogeneous Fenton process that operates under visible light irradiation. The TC degradation efficiency by the new Fenton process is 50% higher than the convention Fenton method. The photo-Fenton system completely destructs 25 mg/L of TC within 100 min. At 7% of Fe₃O₄ doping, the Fe₃O₄/g-C₃N₄ shows an optimized bandgap and 'OH generation rate. Therefore, Fe₃O₄/g-C₃N₄ shows a great promise as a photo-Fenton catalyst when compared to conventional Fenton analogs. Besides, the five experimental parameters namely Fe₃O₄/g-C₃N₄ are pH, H₂O₂, catalyst content, reaction time, and substrate loading, play a pivotal role in the TC degradation and the stability and reusability of the photo-catalyst. The Fe₃O₄/g-C₃N₄ can be recycled five times in the reduction of TC, and the leaching of iron is also reduced. This provides new ideas for the current treatment of antibiotic contamination.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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References

- [1] Wang S, Wang H. Adsorption behavior of antibiotic in soil environment: a critical review. Front Environ Sci Eng. 2015;9:565–574.
- [2] Milic N, Milanovic M, Letic NG, et al. Occurrence of antibiotics as emerging contaminant substances in aquatic environment. Int J Environ Health Res. 2013;23:296–310.
- [3] Sun J, Xu W, Yang P, et al. Enhanced oxytetracycline removal coupling with increased power generation using a self-sustained photo-bioelectrochemical fuel cell. Chemosphere. 2019;221:21–29.
- [4] Chen Y, Su JQ, Zhang J, et al. High-throughput profiling of antibiotic resistance gene dynamic in a drinking water river-reservoir system. Water Res. 2019;149:179–189.
- [5] Yu F, Li Y, Han S, et al. Adsorptive removal of antibiotics from aqueous solution using carbon materials. Chemosphere. 2016;153:365–385.
- [6] Palominos RA, Mondaca MA, Giraldo A, et al. Photocatalytic oxidation of the antibiotic tetracycline on TiO2 and ZnO suspensions. Catal Today. 2009;144:100– 105.
- [7] Xiong H, Zou D, Zhou D, et al. Enhancing degradation and mineralization of tetracycline using intimately coupled photocatalysis and biodegradation (ICPB). Chem Eng J. 2017;316:7–14.
- [8] Wu W, Huang Z-H, Lim T-T. Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water. Appl Catal, A. 2014;480:58–78.

- [9] Pignatello JJ, Oliveros E, MacKay A. Advanced oxidation processes for organic contaminant destruction based on the Fenton reaction and related chemistry. Crit Rev Environ Sci Technol. 2006;36:1–84.
- [10] Giri AS, Golder AK. Fenton, photo-Fenton, H₂O₂ photolysis, and TiO₂ photocatalysis for dipyrone oxidation: drug removal, mineralization, biodegradability, and degradation mechanism. Ind Eng Chem Res. 2014;53:1351– 1358.
- [11] Hu J, Zhang P, An W, et al. In-situ Fe-doped g-C₃N₄ heterogeneous catalyst via photocatalysis-Fenton reaction with enriched photocatalytic performance for removal of complex wastewater. Appl Catal, B. 2019;245:130–142.
- [12] Miralles-Cuevas S, Oller I, Perez JAS, et al. Removal of pharmaceuticals from MWTP effluent by nanofiltration and solar photo-Fenton using two different iron complexes at neutral pH. Water Res. 2014;64:23–31.
- [13] Qian X, Wu Y, Kan M, et al. FeOOH quantum dots coupled $g-C_3N_4$ for visible light driving photo- Fenton degradation of organic pollutants. Appl Catal, B. 2018;237:513–520.
- [14] Akhundi A, Badiei A, Ziarani GM, et al. Graphitic carbon nitride-based photocatalysts: toward efficient organic transformation for value-added chemicals production. Mol Catal. 2020;488:110902.
- [15] Asadzadeh-Khaneghah S, Habibi-Yangjeh A. $g-C_3N_4/$ carbon dot-based nanocomposites serve as efficacious photocatalysts for environmental purification and energy generation: a review. J Clean Prod. 2020;276: 124319.
- [16] Akhundi A, Habibi-Yangjeh A, Abitorabi M, et al. Review on photocatalytic conversion of carbon dioxide to value-added compounds and renewable fuels by graphitic carbon nitride-based photocatalysts. Catal Rev. 2019;61:595–628.
- [17] Wen J, Xie J, Chen X, et al. A review on g-C 3 N 4 -based photocatalysts. Appl Surf Sci. 2017;391:72–123.
- [18] Kumar A, Kumar A, Sharma G, et al. Biochar-templated g- $C_3N_4/Bi_2O_2CO_3/CoFe_2O_4$ nano-assembly for visible and solar assisted photo-degradation of paraquat, nitrophenol reduction and CO2 conversion. Chem Eng J. 2018;339:393–410.
- [19] Kumar A, Sharma SK, Sharma G, et al. $Ceo_2/g-C_3N_4/V_2O_5$ ternary nano hetero-structures decorated with CQDs for enhanced photo-reduction capabilities under different light sources: dual Z-scheme mechanism. J Alloys Compd. 2020;838:155692.
- [20] Kumar A, Kumari A, Sharma G, et al. Carbon quantum dots and reduced graphene oxide modified self-assembled $S@C_3N_4/B@C_3N_4$ metal-free nano-photocatalyst for high performance degradation of chloramphenicol. J Mol Liq. 2020;300:112356.
- [21] Singh J, Basu S. Synthesis of mesoporous magnetic Fe₂O₃/g-C₃N₄ monoliths for Rhodamine B removal. Microporous Mesoporous Mater. 2020;303:110299.
- [22] Huang S, Xu Y, Xie M, et al. Synthesis of magnetic $CoFe_2O_4/g-C_3N_4$ composite and its enhancement of photocatalytic ability under visible-light. Colloids Surf, A. 2015;478:71–80.
- [23] Song X, Tao H, Chen L, et al. Synthesis of Fe/g-C₃N₄ composites with improved visible light photocatalytic activity. Mater Lett. 2014;116:265–267.

- [24] Ma J, Yang Q, Wen Y, et al. Fe-g-C₃N₄/graphitized mesoporous carbon composite as an effective Fenton-like catalyst in a wide pH range. Appl Catal, B. 2017;201:232–240.
- [25] Wang X, Wang A, Ma J. Visible-light-driven photocatalytic removal of antibiotics by newly designed C₃N₄@MnFe₂O₄-graphene nanocomposites. J Hazard Mater. 2017;336:81–92.
- [26] Kumari A, Kumar A, Sharma G, et al. Constructing Z-scheme LaTiO₂N/g-C₃N₄@Fe₃O₄ magnetic nano heterojunctions with promoted charge separation for visible and solar removal of indomethacin. J Water Process Eng. 2020;36:101391.
- [27] Kumar A, Kumar A, Sharma G, et al. Sustainable nanohybrids of magnetic biochar supported g-C₃N₄/FeVO₄ for solar powered degradation of noxious pollutantssynergism of adsorption, photocatalysis & photo-ozonation. J Clean Prod. 2017;165:431–451.
- [28] Zhou L, Wang L, Zhang J, et al. Well-dispersed Fe_2O_3 nanoparticles on $g-C_3N_4$ for efficient and stable photo-Fenton photocatalysis under visible-light irradiation. Eur J Inorg Chem. 2016;2016:5387–5392.
- [29] Hu JY, Tian K, Jiang H. Improvement of phenol photodegradation efficiency by a combined g-C₃N₄/Fe(III)/persulfate system. Chemosphere. 2016;148:34–40.
- [30] Lin KA, Lin JT. Ferrocene-functionalized graphitic carbon nitride as an enhanced heterogeneous catalyst of Fenton reaction for degradation of Rhodamine B under visible light irradiation. Chemosphere. 2017;182:54–64.
- [31] Li X, Pi Y, Wu L, et al. Facilitation of the visible lightinduced Fenton-like excitation of H_2O_2 via heterojunction of $g-C_3N_4/NH_2$ -iron terephthalate metal-organic framework for MB degradation. Appl Catal, B. 2017;202:653– 663.
- [32] Vesali-Kermani E, Habibi-Yangjeh A, Ghosh S. Visiblelight-induced nitrogen photofixation ability of $g-C_3N_4$ nanosheets decorated with MgO nanoparticles. J Ind Eng Chem. 2020;84:185–195.
- [33] Vesali-Kermani E, Habibi-Yangjeh A, Diarmand-Khalilabad H, et al. Nitrogen photofixation ability of g-C₃N₄ nanosheets/Bi₂MoO₆ heterojunction photocatalyst under visible-light illumination. J Colloid Interface Sci. 2020;563:81–91.
- [34] Liu CG, Wu XT, Li XF, et al. Synthesis of graphene-like g- C_3N_4/Fe_3O_4 nanocomposites with high photocatalytic activity and applications in drug delivery. RSC Adv. 2014;4:62492–62498.
- [35] Gallard H. Kinetic modelling of $Fe(III)/H_2O_2$ oxidation reactions in dilute aqueous solution using atrazine as a model organic compound. Water Res. 2000;34:3107– 3116.
- [36] Yan SC, Li ZS, Zou ZG. Photodegradation performance of $g-C_3N_4$ fabricated by directly heating melamine. Langmuir. 2009;25:10397–10401.
- [37] Akhundi A, Habibi-Yangjeh A. Codeposition of Agl and Ag_2CrO_4 on $g-C_3N_4/Fe_3O_4$ nanocomposite: Novel magnetically separable visible-light-driven photocatalysts with enhanced activity. Adv Powder Technol. 2016;27:2496–2506.
- [38] Liu L, Qi Y, Lu J, et al. A stable Ag₃PO₄@g-C₃N₄ hybrid core@shell composite with enhanced visible light photocatalytic degradation. Appl Catal, B. 2016;183:133–141.

- [39] Song X, Hu Y, Zheng M, et al. Solvent-free in situ synthesis of $g-C_3N_4/\{0\ 0\ 1\}$ TiO₂ composite with enhanced UV- and visible-light photocatalytic activity for NO oxidation. Appl Catal, B. 2016;182:587–597.
- [40] Tan Y, Shu Z, Zhou J, et al. One-step synthesis of nanostructured $g-C_3N_4/TiO_2$ composite for highly enhanced visible-light photocatalytic H2 evolution. Appl Catal, B. 2018;230:260–268.
- [41] Katsumata H, Sakai T, Suzuki T, et al. Highly efficient photocatalytic activity of $g-C_3N_4/Ag_3PO_4$ hybrid photocatalysts through Z-scheme photocatalytic mechanism under visible light. Ind Eng Chem Res. 2014;53:8018–8025.
- [42] Bhargava G, Gouzman I, Chun CM, et al. Characterization of the "native" surface thin film on pure polycrystalline iron: a high resolution XPS and TEM study. Appl Surf Sci. 2007;253:4322–4329.
- [43] Xie X, Liu Y, Dong X, et al. Synthesis and characterization of Fe₃O₄/BiOl n-p heterojunction magnetic photocatalysts. Appl Surf Sci. 2018;455:742–747.
- [44] Zhu Z, Tang X, Kang S, et al. Constructing of the magnetic photocatalytic nanoreactor MS@FCN for cascade catalytic degrading of tetracycline. J Phys Chem C. 2016;120:27250–27258.
- [45] Bu Y, Chen Z, Li W. Using electrochemical methods to study the promotion mechanism of the photoelectric conversion performance of Ag-modified mesoporous g- C_3N_4 heterojunction material. Appl Catal, B. 2014;144:622–630.
- [46] Ma TY, Cao JL, Jaroniec M, et al. Interacting carbon nitride and titanium carbide nanosheets for high-performance oxygen evolution. Angew Chem Int Ed. 2016;55:1138– 1142.
- [47] Sing KSW. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity (recommendations 1984). Pure Appl Chem. 1985;57:603–619.
- [48] Bel HadjItaief H, Da Costa P, Galvez ME, et al. Influence of operational parameters in the heterogeneous photofenton discoloration of wastewaters in the presence of an iron-pillared clay. Ind Eng Chem Res. 2013;52:16656– 16665.
- [49] Tonda S, Kumar S, Kandula S, et al. Fe-doped and -mediated graphitic carbon nitride nanosheets for enhanced photocatalytic performance under natural sunlight. J Mater Chem A. 2014;2:6772–6780.
- [50] Buxton GV, Greenstock CL, Helman WP, et al. Critical review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals (·OH/·O– in aqueous solution. J Phys Chem Ref Data. 1988;17:513–886.
- [51] Sun B, Li H, Li X, et al. Degradation of organic dyes over Fenton-like Cu_2O-Cu/C catalysts. Ind Eng Chem Res. 2018;57:14011–14021.
- [52] Li W, Wang Y, Irini A. Effect of pH and H₂O₂ dosage on catechol oxidation in nano-Fe₃O₄ catalyzing UV–Fenton and identification of reactive oxygen species. Chem Eng J. 2014;244:1–8.
- [53] Jiang J, Gao J, Li T, et al. Visible-light-driven photo-Fenton reaction with alpha-Fe₂O₃/BiOI at near neutral pH: boosted photogenerated charge separation, optimum

operating parameters and mechanism insight. J Colloid Interface Sci. 2019;554:531–543.

- [54] Yang Y, Hu X, Zhao Y, et al. Decontamination of tetracycline by thiourea-dioxide-reduced magnetic graphene oxide: effects of pH, ionic strength, and humic acid concentration. J Colloid Interface Sci. 2017;495:68–77.
- [55] Gómez-Pacheco CV, Sánchez-Polo M, Rivera-Utrilla J, et al. Tetracycline degradation in aqueous phase by ultraviolet radiation. Chem Eng J. 2012;187:89–95.
- [56] Vione D, Merlo F, Maurino V, et al. Effect of humic acids on the Fenton degradation of phenol. Environ Chem Lett. 2004;2:129–133.
- [57] Yao T, Jia W, Feng Y, et al. Preparation of reduced graphene oxide nanosheet/Fe_xO_y/nitrogen-doped carbon layer aerogel as photo-Fenton catalyst with enhanced degradation activity and reusability. J Hazard Mater. 2019;362:62–71.
- [58] Le VT, Doan VD, Tran VA, et al. Cu/Fe₃O₄@carboxylate-rich carbon composite: one-pot synthesis, characterization, adsorption and photo-Fenton catalytic activities. Mater Res Bull. 2020;129:110913.
- [59] Cai H, Zhao T, Ma Z, et al. Efficient removal of metronidazole by the photo-fenton process with a magnetic Fe₃O₄@PBC composite. J Environ Eng. 2020;146:04020056.
- [60] Guo S, Yang W, You L, et al. Simultaneous reduction of Cr (VI) and degradation of tetracycline hydrochloride by a novel iron-modified rectorite composite through heterogeneous photo-Fenton processes. Chem Eng J. 2020;393:124758.
- [61] Cui W, Wang H, Liang Y, et al. Microwave-assisted synthesis of Ag@AgBr-intercalated K₄Nb₆O₁₇ composite and enhanced photocatalytic degradation of Rhodamine B under visible light. Chem Eng J. 2013;230:10–18.
- [62] Wei Z, Liang F, Liu Y, et al. Photoelectrocatalytic degradation of phenol-containing wastewater by $TiO_2/g-C_3N_4$ hybrid heterostructure thin film. Appl Catal, B. 2017;201:600–606.

- [63] Cao M, Wang P, Ao Y, et al. Visible light activated photocatalytic degradation of tetracycline by a magnetically separable composite photocatalyst: graphene oxide/ magnetite/cerium-doped titania. J Colloid Interface Sci. 2016;467:129–139.
- [64] Ju Y, Yang S, Ding Y, et al. Microwave-assisted rapid photocatalytic degradation of malachite green in TiO₂ suspensions: mechanism and pathways. J Phys Chem A. 2008;112:11172–11177.
- [65] Niu J, Ding S, Zhang L, et al. Visible-light-mediated Sr-Bi₂O₃ photocatalysis of tetracycline: kinetics, mechanisms and toxicity assessment. Chemosphere. 2013;93:1–8.
- [66] Liu X, Lv P, Yao G, et al. Microwave-assisted synthesis of selective degradation photocatalyst by surface molecular imprinting method for the degradation of tetracycline onto ClTiO₂. Chem Eng J. 2013;217:398–406.
- [67] Zhou Y, He J, Lu J, et al. Enhanced removal of bisphenol A by cyclodextrin in photocatalytic systems: degradation intermediates and toxicity evaluation. Chin Chem Lett. 2020;31:2623–2626.
- [68] Habibi-Yangjeh A, Asadzadeh-Khaneghah S, Feizpoor S, et al. Review on heterogeneous photocatalytic disinfection of waterborne, airborne, and foodborne viruses: can we win against pathogenic viruses? J Colloid Interface Sci. 2020;580:503–514.
- [69] Gao N, Lu Z, Zhao X, et al. Enhanced photocatalytic activity of a double conductive C/Fe₃O₄/Bi₂O₃ composite photocatalyst based on biomass. Chem Eng J. 2016;304:351–361.
- [70] Akhundi A, Habibi-Yangjeh A. Graphitic carbon nitride nanosheets decorated with CuCr₂O₄ nanoparticles: Novel photocatalysts with high performances in visible light degradation of water pollutants. J Colloid Interface Sci. 2017;504:697–710.
- [71] Subramanian G, Madras G. Introducing saccharic acid as an efficient iron chelate to enhance photo-Fenton degradation of organic contaminants. Water Res. 2016;104:168–177.