Photo-Fenton Degradation of Ciprofloxacin by Novel Graphene Quantum Dots/α-FeOOH Nanocomposites for the Production of Safe Drinking Water from Surface Water

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Abstract: In the current work, novel graphene quantum dots (GQDs)-doped goethite (α-FeOOH) nanocomposites (GQDs/α-FeOOH) were prepared by following a feasible hydrolysis method and applied for ciprofloxacin (CIP) removal. Results showed that the CIP degradation efficiency was significant (93.73%, 0.0566 min⁻¹) in the GQDs/α-FeOOH + H₂O₂ + Vis system using much lower amounts of H₂O₂ (0.50 mM), which is 3.9 times the α-FeOOH + H₂O₂ + Vis system. It was found that •OH, O₂⁻, and ¹O₂ were mainly responsible for CIP degradation in the GQDs/α-FeOOH photo-Fenton system. GQDs/α-FeOOH demonstrated broad-spectrum UV–vis–IR responsiveness in the degradation of ciprofloxacin as a function of the doping of GQDs. Additionally, GQDs/α-FeOOH showed outstanding durability (recyclability up to 3 cycles with a lower iron leaking amount, 0.020 mg L⁻¹), a broad range of application pH, and a pretty acceptable catalytic efficacy in a variety of surface water matrices. Overall, GQDs/α-FeOOH have been shown to be an effective photocatalyst for the remediation of emerging contaminants via the workable exploitation of solar energy.

Keywords: GQDs; goethite; emerging contaminants; photo-Fenton-like reaction; water pollution

1. Introduction

Water pollution caused by emerging contaminants is considered a potential threat to human health and the ecosystem. Ciprofloxacin (CIP) is a common emerging contaminant and has been widely used in both veterinary and human medicine, resulting in its widespread presence in natural water sources. Studies have shown that even at low concentrations, CIP can cause harm to humans and the environment by causing drug resistance and biotoxicity to some probiotics. Available wastewater treatment technologies are not enough to eliminate CIP from effluent entirely because of its low biodegradability nature, persistence, and bioaccumulation [1–4]. Therefore, in order to protect human and ecological viability, it is critical to figure out how to remove CIP from wastewater effectively.

In recent years, the heterogeneous photo-Fenton process has been identified as a promising solution for organic pollutant degradation, given its easy application, high efficiency, and reusability. This combined process relies primarily on a sequence of active chemicals, including hydroxyl radicals (•OH), superoxide radicals (O₂⁻), and holes (h⁺) [5–8]. Generally, iron (hydr)oxides are widely used as a heterogeneous Fenton catalyst and may act as a photocatalyst since they exhibit a broad absorption ranging from 200 to 800 nm, favoring azo dyes degradation behavior under photoreaction to some extent [9,10]. Particularly, as a prevalent semiconductor, FeOOH shows a good response in visible light with a narrow bandgap of 2.06 eV and stabilities in the heterogeneous photo-Fenton system.
For example, Wei et al. [11] were successful in fabricating an efficient FeOOH quantum dot-loaded WO$_3$ microsphere and able to degrade 98.69% methylene blue and 92.55% acid red-18 in a short period (5 min) under UV light irradiation, but the catalyst failed to run under sunlight. FeOOH-reduced graphene oxide was found to degrade 4-chlorophenol in a visible-light-driven Fenton system by Liu et al. [12], achieving 80% removal efficiency in just 6 h and remaining active even after 10 cycles despite the use of large amounts of H$_2$O$_2$. UV light sources comprise 8–9% of the solar spectrum, ranging from 200–400 nm. They are most commonly used to activate conventional heterogeneous Fenton-like systems in degrading organic pollutants [13]. Traditional FeOOH, on the other hand, faces several challenges, including a tendency to aggregate and difficulty separating them from photogenerated carriers, both of which reduce their photocatalytic efficiency. Moreover, the pure FeOOH still has not been shown to be effective as a visible light catalyst since it can only be excited by the light (response to 43% of the solar spectrum with wavelengths ranging from 400–800 nm) at a wavelength below 560 nm, limiting the utilization of the entire solar spectrum. For this reason, FeOOH must be modified or combined with other efficient materials to achieve efficient solar energy harvesting while also improving electron transfer to increase its visible light-responsive characteristics.

Recent progress on quantum dots (QDs)-derived materials has opened up a new avenue for treating wastewater with a photocatalytic system by virtue of its uniform sizes (less than 10 nm), chemical stability, optical property, electrical conductivity, water solubility, and nontoxicity [14–16]. Particularly, graphene quantum dots (GQDs) emerge as desired alternatives and advantageous photocatalytic substances with tunable bandgap (0–6 eV) and charge carrier tendency due to their strong edge effect and quantum confinement [17,18]. Crystalline GQDs with thickness of only one or a few layers of graphene are linked by chemical groups on their edges, giving them a larger diameter, more surface area, and improved surface-grafting properties thanks to the conjugated $\Pi-\Pi$ network. Conjugated $\Pi$ systems of GQDs also aid in enhancing transmission formally independent and diminishing electron–hole pair recombination. Accordingly, based on the abovementioned outstanding characteristics of GQDs, it may be used to increase metal oxide nanoparticles’ ability to respond to sunlight and execute photocatalysis. Currently, a number of GQDs-based photocatalysts have been documented, such as g-C$_3$N$_4$ [19,20], ZnO [21], TiO$_2$ [22], BiVO$_4$ [23], BiOBr [24], Bi$_2$MoO$_6$ [25,26], and so on, which showed that photocatalytic performances were significantly improved when exposed to a visible light source. GQDs/g-CNNR exhibited 3.46 and 2.03 times faster photocatalytic oxytetracycline degradation rates than the pristine graphitic carbon nitride (g-C$_3$N$_4$) and graphitic carbon nitride nanorods (g-CNNR), attributed to the high level of crystallization and engineered staggered band alignments [19]. Followingly, it was found that only 1.0 wt% GQDs loaded onto BiVO$_4$ achieved more than 95% mineralization degree of carbamazepine after 180 min, which is undoubtedly a potential implication of GQDs in a photocatalytic system. As of yet, however, there has not been any research focused on GQDs/$\alpha$-FeOOH nanocomposites and their catalytic removal of organic pollutants under the photo-Fenton oxidation system. Consequently, it is expected to eventually improve solar energy utilization by developing $\alpha$-FeOOH-based nanohybrid Fenton catalyst combined with the benefits of GQDs that will form good electron acceptors and donors, thereby overcoming the catalytic performance of pure $\alpha$-FeOOH. Additionally, it must be mentioned that the safety and environmental aspects of nanoparticles have been a matter of concern in recent workflow; for instance, a well-known photocatalyst such as TiO$_2$ is cytotoxic to human tissues in a variety of ways according to Kim’s study [27]. Hence, GQDs-modified $\alpha$-FeOOH nanocomposites for CIP removal under the photo-Fenton system are thought to be a promising photocatalyst, and it is advisable that before starting large-scale application of this nanocomposite, their reusability and actual effluent treatment ability should be investigated.

Therefore, this study uses a hydrothermal synthesis of graphene quantum dots doped with $\alpha$-FeOOH (GQDs/$\alpha$-FeOOH) and then catalyzes CIP degradation by hydrogen peroxide under visible light, which is the first time in the literature based on the authors’
knowledge. The main research objectives are as follows: to (1) investigate the photo-Fenton catalytic activity of GQDs/α-FeOOH; (2) study the degradation of organic pollutants with different structures by the reaction system; (3) through the analysis of the generation of free radicals in the reaction system, FTIR spectroscopy, etc., put forward the possible CIP degradation mechanism; and (4) explore the application potential of materials in surface water bodies.

2. Experimental

2.1. Chemicals

Ciprofloxacin (CIP, 331.346 g mol\(^{-1}\) and purity > 98.0%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Graphite (C) was bought from Guangfu Fine Chemistry Research Institute (Tianjin, China). Azo dye Orange II (OII) was purchased from Shanghai Yikang Chemical Co., Ltd. (Shanghai, China). Methylene blue (MB), concentrated sulfuric acid (H\(_2\)SO\(_4\)), concentrated nitric acid (HNO\(_3\)), ferrous sulfate heptahydrate (FeSO\(_4\)•7H\(_2\)O), hydrogen peroxide (H\(_2\)O\(_2\)), methanol (CH\(_3\)OH), and ascorbic acid (C\(_6\)H\(_8\)O\(_6\)) were all purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). Apart from that, all the other reagents were of analytical quality and were utilized without additional purification.

2.2. Synthesis of GQDs/α-FeOOH

At first, Hummer’s technique [28] was used to make graphene oxide (GO) by oxidizing graphite powder. After that, GQDs were prepared by following a previous method [29] with a slight modification. Briefly, about 150 mg of the as-prepared graphene oxide powder was loaded into a 500 mL single-necked flask and added a certain amount of concentrated HNO\(_3\) (32 mL) and H\(_2\)SO\(_4\) (8 mL). The mixture was mixed well and heated to reflux at 100 °C for 24–48 h. After the solution was cooled to room temperature, 0.1 M NaOH solution was added until the solution was neutral, left to stand for a while, the salt crystals were removed, and the solution was filtered with a 0.45 μm membrane. Then, the filtered solution was dialyzed for another 12 h (dialysis bag retention 3500 MWCO), whereby light yellow solution indicated the formation of GQDs, and the obtained GQDs powder was collected for the next step.

In the second stage, uniform dispersion of GQDs in 800 mL of distilled water was accomplished by sonicating the GQDs in a beaker with 9 mg, 12 mg, 13.5 mg, and 15 mg of GQDs in it for about 30 min. After that, 14.456 g FeSO\(_4\)•7H\(_2\)O was added to the mixture above and sonicated for 30 min. Finally, the mixture was heated to 95 °C for 1 h while agitated with a magnetic stirrer. The produced GQDs/α-FeOOH were rinsed with deionized water and then freeze-dried to be used in further applications.

2.3. Characterization

A Tecnai F30 high-resolution Transmission Electron Microscope (TEM, FEI Company, Hillsboro, OR, USA) was used to investigate the surface morphologies of the as-prepared GQDs/α-FeOOH samples. The crystallinity of samples was examined through the use of a D/Max-2500 X-ray diffractometer (XRD, Ultima IV, Rigaku, Japan) with a Cu-K\(\alpha\) radiation source. The scanning rate was 10° min\(^{-1}\) in the range of 5° to 70°. A DXR SmartRaman spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) was utilized to acquire the Raman spectra, and a 633-nm laser served as the instrument’s excitation source. The UV–Vis diffuse reflectance spectra were acquired using a U-4100 spectrophotometer (Hitachi, Chiyoda ku, Japan), in which BaSO\(_4\) was used as reference material. The surface functional groups of GQDs/α-FeOOH were analyzed by a Nicolet 8700 Fourier transform infrared spectroscopy (FTIR, PerkinElmer Inc., Waltham, MA, USA). In order to get the quantitative FTIR spectra, the samples were ground with potassium bromide powder in a mortar and pestle and then placed in front of the laser beam to be illuminated. The optical properties, i.e., photoluminescence (PL) spectra of samples, were measured using an F-4500 fluorescence spectrophotometer (Hitachi, Japan). As part of the Brunauer–Emmett–Teller
2.4. Photo-Fenton Degradation Test

The photo-Fenton activity test was carried out in a bowl-open glass reactor with a total capacity of 800 mL. The visible light source was a 350 W Xe lamp with a 420-nm cutoff filter placed 10 cm above the reaction chamber. To a 200 mL solution of CIP (10 mg L$^{-1}$), 50 mg GQDs/α-FeOOH (0.25 g L$^{-1}$) and 0.50 mM H$_2$O$_2$ were added and stirred at 25 ± 1 °C under neutral solution pH. A sample of 4 mL of the reaction solution was taken out and passed through a 0.45 µm cellulose esters membrane filter (Millipore, Burlington, MA, USA) to eliminate any remaining material after a predefined amount of time passed. Then, a commercial high-performance liquid chromatography (HPLC, SPD-20 A, Shimadzu, Japan) equipped with a C18 column (5 µm, 4.6 × 150 mm) was used to measure CIP concentration at 27°C in the wavelength of 276 nm. In this experiment, an aqueous solution of formic acid (0.1%) and acetonitrile (80:20, v/v) was utilized as mobile phases, injecting a volume of 30 µL under a flow rate of 0.3 mL min$^{-1}$. All reported results are based on the average of three experiments.

The effect of H$_2$O$_2$ on photo-Fenton degradation experiments was inspected by adding various dosages of H$_2$O$_2$ (0.125 mM, 0.25 mM, 0.50 mM, 0.75 mM) and 0.25 g L$^{-1}$ GQDs/α-FeOOH to 200 mL of an aqueous CIP solution (10 mg L$^{-1}$). Studying the effect of pH, adjusted the solution pH with 0.1 mol L$^{-1}$ HCl solution and NaOH solution to 3.01, 4.95, 7.00, 9.04, 10.40, 0.25 g L$^{-1}$ GQDs/α-FeOOH and 0.50 mM H$_2$O$_2$ was added to 10 mg L$^{-1}$ CIP solution with 200 mL. Studying the effects of different organic compound structures, the initial concentrations of Methylene blue (MB) and Orange II (OII) were 20 mg L$^{-1}$, and the initial concentrations of Bisphenol A (BPA) and Tetracycline (TC) were 10 mg L$^{-1}$. The concentration of MB and OII was obtained at 664 nm and 484 nm by using a UV–Vis spectrophotometer (UV-1102, Tianmei Techcomp Ltd., Shanghai, China), while the BPA and TC concentration was measured by HPLC. For all the above experiments, the reaction was stirred for 1 h, and samples were taken at predetermined time intervals. The change in H$_2$O$_2$ concentration during the reaction time was measured by the titanium (IV) oxalate method [30].

2.5. Recyclability

The recyclability of GQDs/α-FeOOH nanomaterials was examined over the course of three consecutive cycles. After the end of the cycle experiment, the solid phase catalyst was separated by centrifugation, and then eluted with distilled water to wash off the antibiotics and other reaction byproducts remaining on the catalyst’s surface. The total Fe concentration leaked in the reaction was measured using an OPTIMA8000 inductively coupled plasma spectroscopy (ICP-OES, Perkin-Elmer, Waltham, MA, USA). After one cycle of reaction, the solution was retained to prepare for the effect of a homogeneous experiment on the reaction system, and the other reaction conditions were the same.

2.6. Free Radical Inhibition Experiment

As a means of identifying the main oxidizing species in the GQDs/α-FeOOH + H$_2$O$_2$ + Vis catalytic system, the catalytic experiments were supplemented with a series of radical scavengers, namely 1.5 mM of methanol (MeOH) for the identification of hydroxyl radical (•OH), 1.5 mM of ascorbic acid (AA) for the superoxide radical (O$_2^•$), and 1.5 mM of sodium azide (NaN$_3$) for the singlet oxygen ($^1$O$_2$).

2.7. Actual Water Application

Practical application of the as-prepared catalyst is of paramount importance in the sense of their long-term common uses. To do so, we prepared five kinds of surface water samples: distilled water, Yangtze River water, Chongming Island river water, East China Sea water, and simulated seawater in order to study the effect of this reaction system on the...
treatment of antibiotics in actual water. A commercial 0.45 µm cellulose esters membrane filter (Millipore, USA) was used to filter the water samples from different surface water bodies and remove some insoluble solid impurities through the pretreatment. After that, the CIP sample was added to the filtered water sample and mixed evenly, controlling the CIP concentration at 10 mg L\(^{-1}\).

3. Results and Discussion
3.1. Structural Analysis of GQDs/\(\alpha\)-FeOOH

Goethite (\(\alpha\)-FeOOH), which is classified as an orthorhombic iron oxyhydroxide mineral based on its crystalline structure, has played an essential role in the fundamental environmental catalytic process, among other applications \[31,32\]. However, in order to enhance the photocatalytic activity of \(\alpha\)-FeOOH, we synthesized GQDs/\(\alpha\)-FeOOH composite nanomaterials. Figure 1a shows the well-prepared crystalline structure of the freshly prepared GQDs/\(\alpha\)-FeOOH and \(\alpha\)-FeOOH samples, which was confirmed by the XRD pattern. Typical XRD patterns of GQDs/\(\alpha\)-FeOOH and \(\alpha\)-FeOOH are exhibited in sharp and characteristics peaks located around 2\(\theta\) = 21.2\(^{\circ}\), 33.2\(^{\circ}\), 36.6\(^{\circ}\), 41.3\(^{\circ}\), and 53.3\(^{\circ}\), assigned to the planes of (110), (130), (111), (140), and (221), where the pure orthorhombic phase \(\alpha\)-FeOOH can be accurately identified (JCPDS\#29-0713) \[33\]. The as-prepared GQDs/\(\alpha\)-FeOOH were found to be pure since no diffraction peaks shifted and no additional impurities were discovered, indicating that the incorporation of GQDs did not alter the diffraction of \(\alpha\)-FeOOH. This can also be correlated with the Raman spectra, as shown in Figure S1. In principle, it has D (1343 cm\(^{-1}\)) and G (1586 cm\(^{-1}\)) intense peaks, and a 2D flat region appears at a range of 2600–3000 cm\(^{-1}\), indicating the existence of graphene oxide \[34\].

The TEM images of GQDs/\(\alpha\)-FeOOH samples with various magnifications were used to examine their morphology (Figure 1b–d). The prepared GQDs were 3–5 nm with a mean diameter of 4.02 ± 0.22 nm, as shown in the particle size distribution histogram (Figure 1e). The GQD/\(\alpha\)-FeOOH formed by doping onto \(\alpha\)-FeOOH had a three-dimensional hollow flower-like structure with a clear crystal lattice, showing good crystallinity of GQDs/\(\alpha\)-FeOOH. Moreover, the presence of GQDs on the surface of \(\alpha\)-FeOOH allows the material to exhibit effective visible-light response characteristics.

![Figure 1](image-url)
Figure 1. X-ray diffraction spectra (a), TEM images of GQDs/α-FeOOH (b–d), (GQDs corresponding to the red circled area), and (e) particle size distribution histogram of GQDs.

In addition, N\textsubscript{2} gas adsorption and desorption investigation was carried out on GQDs/α-FeOOH (Figure S2) to examine the surface area. Type IVa isotherm curves were seen in the isotherm of GQDs/α-FeOOH, indicating the presence of mesoporous materials, and the specific surface area of the GQDs/α-FeOOH was calculated at around 107 m\textsuperscript{2} g\textsuperscript{-1}, which facilitates the photocatalytic efficiency [35].

3.2. CIP Degradation

The reaction performance of GQDs/α-FeOOH as a catalyst was investigated by the degradation of CIP under various experimental conditions. As shown in Figure 2, it is evident that GQDs/α-FeOOH has a poor affinity for CIP, as only 6.07% of CIP's dark adsorption was removed within 60 min of using GQDs/α-FeOOH. In addition, in the combined H\textsubscript{2}O\textsubscript{2} + Vis oxidation system, the degradation efficiency for CIP was only about 3.18%, basically, no degradation, which shows that under visible light conditions, H\textsubscript{2}O\textsubscript{2} is difficult to be excited to produce free radicals to degrade CIP, and under natural conditions. The existence of CIP is relatively stable. Under the GQDs/α-FeOOH-based Fenton system and visible light catalytic system, the degradation of CIP in the Fenton-like system is 52.50% higher than that of the photocatalytic system, indicating that this catalytic material has a more significant degradation effect in the Fenton system, mainly because of the ability GQDs to convert electrons rapidly [36].
photocatalysts in terms of the degradation percentage of CIP throughout the same period in Table 1. May be attributed to the inclusion of GQDs. The heterogeneous photo-Fenton system has a considerably improved CIP degradation, which may be attributed to the inclusion of GQDs. A visible light-responsive system (Table 2). The synergistic GQDs/\(\alpha\)-FeOOH system (0.0143 min\(^{-1}\)) was superior to that of previously reported photocatalysts in terms of the degradation percentage of CIP. As seen, the first-order kinetic constant of GQDs/\(\alpha\)-FeOOH + H\(_2\)O\(_2\) + Vis system (0.0291 min\(^{-1}\), \(R^2 = 0.838\)) and GQDs/\(\alpha\)-FeOOH + Vis (0.0055 min\(^{-1}\), \(R^2 = 0.925\)) systems were 1.9 times and 10.2 times, which shows that this can only be played in the presence of GQDs/\(\alpha\)-FeOOH, H\(_2\)O\(_2\), and visible light. Overall, our synthesized GQDs/\(\alpha\)-FeOOH photocatalytic efficiency was superior to that of previously reported photocatalysts in terms of the degradation percentage of CIP throughout the same period in a visible light-responsive system (Table 2). The synergistic GQDs/\(\alpha\)-FeOOH + H\(_2\)O\(_2\) + Vis heterogeneous photo-Fenton system has a considerably improved CIP degradation, which may be attributed to the inclusion of GQDs.

**Figure 2.** Degradation of CIP under different experimental conditions.

The Fe ions in \(\alpha\)-FeOOH activated H\(_2\)O\(_2\), reaching the maximum degradation of CIP to 93.73% in the GQDs/\(\alpha\)-FeOOH + H\(_2\)O\(_2\) + Vis system. This system combines a Fenton-like system and a visible light catalytic system to produce more activity, thus enhancing the degradation percentages of CIP. This system can achieve the purpose of effective oxidation of CIP by supporting the idea of GQDs incorporation into \(\alpha\)-FeOOH to improve its catalytic activity.

It is widely observed that the pseudo-first-order reaction could accurately describe the heterogeneous catalytic pollutants degradation process [37]. The corresponding first-order kinetic rate constants of CIP degradation under various experimental processes are listed in Table 1. As seen, the first-order kinetic constant of GQDs/\(\alpha\)-FeOOH + H\(_2\)O\(_2\) + Vis was 0.0566 min\(^{-1}\) (\(R^2 = 0.952\)), which is \(\alpha\)-FeOOH + H\(_2\)O\(_2\) + Vis 3.9 times that of the system (0.0143 min\(^{-1}\), \(R^2 = 0.940\)). This shows that the successful doping of GQDs can significantly improve the photocatalytic performance of \(\alpha\)-FeOOH, and the GQDs/\(\alpha\)-FeOOH + H\(_2\)O\(_2\) (0.0291 min\(^{-1}\), \(R^2 = 0.838\)) and GQDs/\(\alpha\)-FeOOH + Vis (0.0055 min\(^{-1}\), \(R^2 = 0.925\)) systems were 1.9 times and 10.2 times, which shows that this can only be played in the presence of GQDs/\(\alpha\)-FeOOH, H\(_2\)O\(_2\), and visible light. Overall, our synthesized GQDs/\(\alpha\)-FeOOH photocatalytic efficiency was superior to that of previously reported photocatalysts in terms of the degradation percentage of CIP throughout the same period in a visible light-responsive system (Table 2). The synergistic GQDs/\(\alpha\)-FeOOH + H\(_2\)O\(_2\) + Vis heterogeneous photo-Fenton system has a considerably improved CIP degradation, which may be attributed to the inclusion of GQDs.

**Table 1.** CIP degradation kinetic constants under different experimental conditions.

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>First-Order</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>(K) (min(^{-1}))</td>
</tr>
<tr>
<td>GQDs/(\alpha)-FeOOH + H(_2)O(_2) + Vis</td>
<td>0.0566</td>
</tr>
<tr>
<td>GQDs/(\alpha)-FeOOH + H(_2)O(_2)</td>
<td>0.0291</td>
</tr>
<tr>
<td>(\alpha)-FeOOH + H(_2)O(_2) + Vis</td>
<td>0.0143</td>
</tr>
<tr>
<td>GQDs/(\alpha)-FeOOH + Vis</td>
<td>0.0055</td>
</tr>
<tr>
<td>H(_2)O(_2) + Vis</td>
<td>0.0021</td>
</tr>
<tr>
<td>GQDs/(\alpha)-FeOOH</td>
<td>0.0005</td>
</tr>
</tbody>
</table>
Table 2. Comparison of CIP degradation performance in a photocatalytic system.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Light Source</th>
<th>CIP Conc. (mg L(^{-1}))</th>
<th>Catalyst Amount (g L(^{-1}))</th>
<th>CIP Degradation (%)</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi/Bi(_3)NbO(_7)</td>
<td>Xe lamp (300 W with 400 cutoff filter)</td>
<td>10</td>
<td>0.5</td>
<td>86 (120 min)</td>
<td>[38]</td>
</tr>
<tr>
<td>BiOCl/NGQDs</td>
<td>Xe lamp (300 W with 400 cutoff filter)</td>
<td>10</td>
<td>0.5</td>
<td>82.5 (60 min)</td>
<td>[39]</td>
</tr>
<tr>
<td>CQDs/BiOBr</td>
<td>Xe lamp (300 W with 420 cutoff filter)</td>
<td>10</td>
<td>0.3</td>
<td>~70 (240 min)</td>
<td>[40]</td>
</tr>
<tr>
<td>NCQDs/Bi(_2)O(_2)CO(_3)</td>
<td>Xe lamp (240 W with 420 cutoff filter)</td>
<td>10</td>
<td>0.04</td>
<td>91.1 (60 min)</td>
<td>[41]</td>
</tr>
<tr>
<td>CQDs/PbBiO(_2)Cl</td>
<td>Xe lamp (300 W with 400 cutoff filter)</td>
<td>10</td>
<td>0.03</td>
<td>78.9 (75 min)</td>
<td>[42]</td>
</tr>
<tr>
<td>GQDs/(\alpha)-FeOOH</td>
<td>Xe lamp (350 W with 420 cutoff filter)</td>
<td>10</td>
<td>0.25</td>
<td>93.73 (60 min)</td>
<td>This work</td>
</tr>
</tbody>
</table>

3.3. Influencing Factors on Degradation Performance

When preparing composite nanomaterials, a reasonable ratio can make the photocatalyst achieve the best results in the treatment of pollutants. As shown in Figure 3a, we used 9.0 mg, 12.0 mg, 13.5 mg, and 15.0 mg of GQDs dispersion solution and \(\alpha\)-FeOOH for doping. The separate \(\alpha\)-FeOOH material under the visible light catalyzed the Fenton system, after 60 min, the degradation efficiency of CIP reached 52.6%. As the amount of GQDs doped in \(\alpha\)-FeOOH increased from 12.0 mg to 13.5 mg, the removal rate of CIP gradually increased from 91.4% to 93.7%. Compared with the treatment of \(\alpha\)-FeOOH alone, as the amount of GQDs increased, this system had faster charge transfer efficiency, which effectively enhanced the degradation efficiency of CIP. However, when the amount of GQDs doped was increased from 13.5 to 15.0 mg, the CIP degradation efficiency after 60 min could still reach more than 90%, but the degradation rate of the reaction process was significantly slower. This result shows that the appropriate amount of GQDs improves CIP degradation by GQDs/\(\alpha\)-FeOOH. This phenomenon is related to previous studies [21,43]. This experiment finally determined that the optimal doping amount was 13.5 mg, and the GQDs/\(\alpha\)-FeOOH used in subsequent experiments were all prepared with 13.5 mg GQDs.

In the light-assisted Fenton reaction system, the amount of H\(_2\)O\(_2\) also greatly influenced CIP degradation. As shown in Figure 3b, the degradation efficiency of CIP showed a gradual upward trend as the molar concentration of H\(_2\)O\(_2\) increased from 0.125 mM to 0.50 mM. This is because, with the increase of H\(_2\)O\(_2\), more \(\bullet\)OH was also produced in the solution. When H\(_2\)O\(_2\) was 0.75 mM, the degradation effect of CIP was not significantly improved. This may be because H\(_2\)O\(_2\) will self-clear once it is excessive. Similarly, the use of excessive H\(_2\)O\(_2\) will also increase the actual operating cost. Therefore, the oxidant concentration in the reaction system was set at 0.50 mM H\(_2\)O\(_2\), and the molar ratio of H\(_2\)O\(_2\) to CIP was 12. Compared with the amount of H\(_2\)O\(_2\) in other similar Fenton-like reactions, the H\(_2\)O\(_2\) consumption in our system was much less. For example, when the Fe\(_2\)O\(_3\)-supported graphene aerogel removed methyl orange, the molar ratio of H\(_2\)O\(_2\) to methyl orange was 5068 [44]. For the composite material, \(\alpha\)-FeOOH-supported mesoporous carbon, the molar ratio of H\(_2\)O\(_2\) to phenol was 30 [45].
Different initial pH values of the solution have an impact on the existence of the pollutant CIP and active oxygen radicals in the Fenton catalytic system. As shown in Figure 3c, the degradation of CIP was better under acidic and neutral conditions. CIP has two dissociation constants (pKa1 = 6.05, pKa2 = 8.37). The surface zero charge of α-FeOOH is between 8.5–9.0. When the pH of the reaction solution was less than 7, the degradation efficiency of CIP was 93.7%, 93.7%, and 79.78%, respectively. This is mainly because acidic conditions are more conducive to the protonation of H2O2 to produce •OH. At pH > 9, CIP decreased significantly to 58.7% and 22.0% under alkaline conditions. At this time, the surface of the material is negatively charged. •OH- and CIP in the solution compete for the active site on GQDs/α-FeOOH. In terms of pollutants and GQDs/α-FeOOH, electrostatic repulsion also exists, which prevents CIP from adsorbing onto the material’s surface for catalytic degradation [46,47]. Therefore, the degradation efficiency of CIP under alkaline conditions was reduced. In previous reports, the optimal pH of the Fenton reaction system was about 3.0. In the system described in this article, the emergence of GQDs/α-FeOOH as a heterogeneous photo-assisted Fenton catalyst can overcome this shortcoming and further expand the suitable pH range, which is the processing taking another important step.

In addition, when CIP is degraded at different initial pH values, the decomposition of H2O2 in the GQDs/α-FeOOH + H2O2 + Vis system is shown in Figure 3d. The trend of the decomposition rate of H2O2 at different pH is almost consistent with the corresponding trend of the CIP degradation efficiency in this system. This phenomenon indicates that CIP is mainly oxidatively degraded by free radicals obtained by the activation of H2O2 rather than the self-decomposition process. It can also be seen from Figure 3d that when the pH value rose from 3.01 to 10.40, the decomposition of H2O2 also decreased from 67.2% to 12.5%. This indicates that H2O2 is more likely to produce a large amount of •OH under acidic conditions, thus promoting CIP removal efficiency by this system.

Figure 3e describes the broad applicability of the photo-Fenton catalytic degradation of the prepared GQDs/α-FeOOH materials by degrading five organic pollutants with different surface charges, including MB (pKa, 3.8) [48], OII (pKa, 11.4) [49], BPA (pKa, 10.29) [50], CIP (pKa1 = 5.0 and pKa2 = 9.0) [51], and TC (pKa1 = 3.3 and pKa2 = 7.7 pKa3 = 9.7) [52]. The results show that the degradation efficiency of GQDs/α-FeOOH for these five pollutants was: CIP ≈ TC ≈ MB > OII ≈ BPA. The GQDs/α-FeOOH catalyst is...
easier to oxidize and remove positively charged organics, and the coupling effect between
the monomer excitation of MB dye and GQDs influence the degradation of MB [53]. CIP
is positively charged at natural pH, so CIP has a good processing effect. In general, the
optical Fenton system based on GQDs/α-FeOOH can remove more than 75% of the organic
substances with different structures, indicating that the system has wide applicability.

3.4. Recyclability

The CIP degradation efficiency and durability in the GQDs/-FeOOH + H2O2 + Vis
system were evaluated through three consecutive catalytic cycle experiments with the goal
of figuring out the catalyst’s recycling and stability. The results are shown in Figure 4. After
three repetitive experiments, the degradation efficiency of CIP decreased from 93.7% to
47.7%. The reasons for the decrease in the degradation efficiency of the experiment may
be as follows: First, in the circulation experiment, some GQDs fell off when the GQDs/α-
FeOOH material was eluted; second, when the experiment was repeated, there was a certain
loss of GQDs/α-FeOOH, of byproducts adhered to the surface of the GQDs/α-FeOOH
complex, and the reactive sites decreased; and thirdly, the reduction in iron leakage to the
reaction solution during the consecutive cycles directly affected the removal efficiency of
CIP under the photo-Fenton process. In repeated use, it can be considered further improved
by increasing the amount of oxidant.

![Figure 4](image-url)

**Figure 4.** Durability and concentration of iron leaking of GQDs/α-FeOOH after 3-times reuse cycles.

We also monitored the quantity of iron that leaked out of the solution after each cycle
of the experiment to further validate the material’s stability. Based on the results of the
experiment, as shown in Figure 4, after three cycles, the leakage of iron in the reaction
solution decreased from 0.121 mg L⁻¹ to 0.020 mg L⁻¹, which is lower than the 0.2 mg L⁻¹
in the European standard [54], and thus will not cause secondary pollution.

3.5. Degradation Mechanism

3.5.1. Generation of Free Radicals in the Reaction System

In order to explore the role of active oxygen species in the system of GQDs/α-FeOOH
+ H2O2 + Vis when degrading CIP, we conducted a series of free radical suppression
experiments, respectively using •OH, O2•−, free radical inhibitors MeOH, AA, and NaN3
corresponding to ¹O2. It can be seen from Figure 5 that the degradation of CIP significantly
decreased when MeOH, AA, and NaN₃ were present in the reaction solution compared to the case without a free radical inhibitor. This result indicates that OH, O₂⁻, and ¹O₂ intensely participated in the heterogeneous optical Fenton reaction. The inhibition of CIP degradation was most apparent after the addition of NaN₃, which shows that ¹O₂ had the highest contribution to CIP degradation and played an important role in this optical Fenton system. At the same time, adding MeOH also has a certain suppression performance for CIP, which shows that under visible light irradiation, H₂O₂ can decompose with the aid of GQDs/α-FeOOH composite materials to produce •OH, and strong oxidizing •OH will oxidatively decompose CIP. O₂⁻ is an important intermediary for the formation and conversion of •OH radicals during the superoxide-driven reaction and can also be obtained by the reduction of molecular oxygen on the catalyst surface.

Figure 5. CIP degradation in presence of various radical scavengers.

3.5.2. CIP Degradation Pathway

In order to understand more about the light absorption characteristics of α-FeOOH and GQDs/α-FeOOH, we tested the UV–Vis DRS of the two materials (Figure 6a). The absorption edge of α-FeOOH is around 604 nm, and the bandgap is 2.06 eV. GQDs/α-FeOOH is significantly stronger than α-FeOOH in the visible-to-near infrared region, that is, in the range of 450–800 nm, which is also the oxidation of CIP by GQDs/α-FeOOH in the visible light Fenton system. This is one of the reasons why degradation is much higher than that of α-FeOOH alone.

The measurement of the steady-state PL spectrum can further provide the light absorption characteristics of the two materials. In the presence of photo-excited electron-hole pairs, the measured PL's recombination probability is reflected in the relative strength of its intensity. It is evident that the emission shoulders of the two materials in this study are distinct at 400–415 nm (Figure 6b). The PL spectrum of the composite material GQDs/α-FeOOH is lower than that of α-FeOOH, which shows that GQDs as an electron storage body are very conducive to the rapid transfer of charge [55]. The electron and hole recombination was suppressed by using GQDs as both a source and a sink of electrons. Overall, it is reported that the slower electron–hole pair recombination is favorable to the Fe (III)/Fe (II) cycle, increasing the catalytic performance of the Fenton process [45].
In order to study the degradation of CIP over time in the GQDs/α-FeOOH + H₂O₂ + Vis system, we used UV–Vis to scan the absorbance changes of CIP at different intervals, and the results are shown in Figure 6c. After 5 min, the main UV–Vis absorption peak at 276 nm CIP showed a significant downward trend. The absorption approached zero at 60 min. The maximum absorption peak during the degradation process did not move, indicating that the system can remove CIP quickly and effectively.

In the homogeneous Fenton reaction, the Fe content is one of the key influencing factors. In order to evaluate the contribution of the homogeneous reaction in this system, we studied the degradation of CIP by homogeneous photo-Fenton at the maximum Fe leakage concentration, that is, in a solution containing 0.121 mg L⁻¹ Fe. As shown in Figure 7, 26.5% CIP was removed in the homogeneous Fenton reaction, which was significantly lower than the heterogeneous GQDs/α-FeOOH + Vis + H₂O₂ system (93.7%), but higher than the H₂O₂ + Vis system. This result indicates that the Fe dissolved in the reaction contributes less to the system, or the heterogeneous GQDs/α-FeOOH + Vis + H₂O₂ system plays a major role in degradation.
Through infrared spectroscopy analysis, information on the functional group structure of GQDs/α-FeOOH before and after the reaction can be obtained. As shown in Figure 8, for the GQDs/α-FeOOH before the reaction, the peak appeared at 3172 cm⁻¹ due to the stretching of the hydroxyl functional group on the α-FeOOH surface, and the absorption peak near 1633 cm⁻¹ corresponds to the deformation vibration of H₂O or OH. In addition, the peak in the range of 1700–1200 cm⁻¹ is due to C-O vibration. The absorption bands around 1141 cm⁻¹, 1047 cm⁻¹, and 976 cm⁻¹ are due to the stretching vibration and split stretching of SO₄. The absorption peaks at 887 cm⁻¹ and 793 cm⁻¹ and the shoulder peak at 631 cm⁻¹ are attributed to the results of Fe-O-H bond vibration and Fe-O stretching vibration, respectively. Compared with the GQDs/α-FeOOH before the reaction, there is no obvious difference in the characteristic peak of the material after the reaction, indicating that the GQDs/α-FeOOH material has good reaction stability.

![FTIR spectra of GQDs/α-FeOOH before and after reaction.](image)

**Figure 8.** FTIR spectra of GQDs/α-FeOOH before and after reaction.

Through the above results, we proposed a possible GQDs/α-FeOOH photo-Fenton system degradation CIP reaction mechanism. The degradation mechanism of CIP is mainly that the presence of GQDs/α-FeOOH under visible light enhances the absorption intensity of visible light, which promotes that GQDs/α-FeOOH can separate more photogenerated carriers to react with H₂O₂, and GQDs can store more electrons and weaken the reorganization of electron-hole pairs. On the other hand, Fe (II) in GQDs/α-FeOOH also reacts with H₂O₂ to generate •OH, which in turn generates O₂•⁻ and ¹O₂. When GQDs transfer electrons to α-FeOOH, they can also react with oxygen in the solution to form O₂•⁻. These strong oxidizing groups oxidize CIP.

### 3.6. Actual Water Application

According to previous research findings, the actual wastewater has a more complex composition than the actual water body, which contains various complex salt ions and dissolved organic matter. It will weaken or inhibit the antibiotic treatment effect of the actual water body to a certain degree [56,57].
In order to further evaluate the application of GQDs/α-FeOOH in actual water bodies, under natural conditions and visible light irradiation, we used this system to carry out CIP degradation in different river water matrices. The results are shown in Figure 9. The CIP degradation of the GQDs/α-FeOOH + H₂O₂ + Vis (350W Xe, 420 nm filter) system was mainly investigated in several water matrices, such as distilled water and the East China Sea, Yangtze River water, Chongming River water, and simulated seawater, under visible light. The highest degradation of CIP in distilled water was 93.7%, mainly because there is no interference from other components; in the Yangtze River water and Chongming River water, the degradation of CIP decreased significantly to 16.4% and 32.0%, and the East China Sea dropped to 21.8%. In simulated seawater containing humic acid, the degradation of CIP was 44%, an increase of 22.2% over the actual seawater degradation, indicating that humic acid in seawater will have less influence on the degradation of antibiotics. In addition, the drop in the actual water sample is more obvious, mainly due to the dissolved organic matter present in the water matrix. The presence of the dissolved organic matter will hinder sunlight and compete with antibiotics for the active sites on the surface of GQDs/α-FeOOH, thereby consuming part of the active oxygen radicals [58].

![Figure 9](image)

**Figure 9.** The effect of real water matrix on CIP in GQDs/α-FeOOH + H₂O₂ systems under visible light irradiation.

As shown in Table 3, the presence of various inorganic salt ions in the simulated seawater quality index will also reduce the CIP degradation of the water body. There are also reports that the presence of microplastics above a certain amount will inhibit or weaken the removal of antibiotics in actual water. The above results show that the GQDs/α-FeOOH + H₂O₂ system performs well under the visible light conditions for CIP removal in actual water samples, but the oxidant content used in this system was low (0.5 mM H₂O₂). The improvement can also be achieved by increasing the amount of oxidant or catalyst or combining it with other technologies to treat antibiotic wastewater.

**Table 3.** Quality index of simulated seawater (mg L⁻¹).

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Salinity (%)</th>
<th>TOC</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>PO₄³⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS</td>
<td>7.8</td>
<td>3.4</td>
<td>–</td>
<td>1.03×10⁴</td>
<td>–</td>
<td>–</td>
<td>3.6×10³</td>
<td>1.6×10⁴</td>
<td>–</td>
<td>1.2×10³</td>
<td>–</td>
</tr>
</tbody>
</table>

SS: Simulated seawater.
4. Conclusions

In this study, GQDs/\(\alpha\)-FeOOH nanocomposites outperformed pristine \(\alpha\)-FeOOH on CIP degradation using a low amount of H\(_2\)O\(_2\) (0.50 mM) under a photo-Fenton catalytic system, which was attributed to the inclusion of GQDs. The degradation performance of antibiotic CIP by the GQDs/\(\alpha\)-FeOOH + H\(_2\)O\(_2\) + Vis system, including the influence of GQDs doping amount, H\(_2\)O\(_2\) concentration, initial pH, organics with different structures, and different river water bodies, were systematically explored. The experimental results showed that the optimized reaction system has a good degradation effect on antibiotics and other pollutants. The reaction system is relatively stable and can be further improved by increasing the amount of oxidant in repeated use. From the free radical inhibition experiment, it can be concluded that the main active oxygen species in the reaction system are \(\bullet\)OH, O\(\bullet\)\(_2\), and 1\(\bullet\)O\(_2\). Moreover, it was found that surface charges in the presence of UV-vis-IR irradiation, as well as remarkable durability. This system provides ideas for the effective use of light energy and the environmentally friendly treatment of emerging contaminants.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/w14142260/s1, Figure S1: Raman spectra of rGO; Figure S2: Nitrogen adsorption-desorption isotherms of GQDs/\(\alpha\)-FeOOH.

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References
15. Pervez, N.; Wei, Y.; Sun, P.; Qu, G.; Naddeo, V.; Zhao, Y. α-FeOOH quantum dots impregnated graphene oxide hybrids enhanced arsenic adsorption: The mediation role of environmental organic ligands. Sci. Total Environ. 2021, 781, 146726. [CrossRef]
28. Wang, H.; Liu, C.; Liu, Z.; Ren, J.; Qu, X. Specific oxygenated groups enriched graphene quantum dots as highly efficient enzyme mimics. Small 2018, 14, e1703710. [CrossRef]

34. Kaniyoor, A.; Ramaprabhu, S. A Raman spectroscopic investigation of graphite oxide derived graphene. AIP Adv. 2012, 2, 032183. [CrossRef]


49. Giraldo, S.; Robles, I.; Godínez, L.; Acenas, N.; Flores, E. Experimental and theoretical insights on methylene blue removal from wastewater using an adsorbent obtained from the residues of the orange industry. Molecules 2021, 26, 4555. [CrossRef]


