Improved ciprofloxacin removal by a Fe(VI)-Fe₃O₄/graphene system under visible light irradiation

Shunping Fang, Zhengwei Zhou, Jinjuan Xue, Guangyu He and Haiqun Chen

ABSTRACT

In this paper, Fe₃O₄/graphene (Fe₃O₄/GE) nanocomposites were prepared by a co-precipitation method and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and UV-vis diffuse reflectance spectra (UV-vis DRS). The composites were used in combination with Fe(VI) to construct a Fe(VI)-Fe₃O₄/GE system in order to degrade ciprofloxacin (CIP) in simulated water samples. The photocatalytic properties of Fe(VI)-Fe₃O₄/GE were evaluated under visible light irradiation. The concentration of CIP in solution was detected by high performance liquid chromatography (HPLC). A series of results showed that Fe(VI), as a good electron capture agent, could significantly improve the treatment performance. Major determining factors during CIP degradation were also investigated, in which solution pH of 9, Fe(VI) to Fe₃O₄/GE dosage ratio of 1:25 and GE content in the Fe₃O₄/GE nanocomposites of 10 wt% were found to be the best experimental conditions. The results demonstrated that the Fe(VI)-Fe₃O₄/GE system could offer an alternative process in water treatment in addition to the current Fe(VI)-UV/TiO₂ process.

Key words | ciprofloxacin, ferrate, Fe₃O₄/graphene, visible light irradiation

INTRODUCTION

Every year, a great number of human and veterinary drugs are used globally (Rakić et al. 2015). Many pharmaceuticals are often not decomposed thoroughly in living bodies, resulting in the discharge of pharmaceutical residues and their metabolites into the aquatic environment (Ji et al. 2016). Ciprofloxacin (CIP), as an important quinolone antibiotic, is one of the most abundant drugs present in the environment, which poses a great threat to human health and the eco-system (Li et al. 2017). Therefore, many technologies have been developed with the intention of removing CIP from water and wastewater (Mahdi-Ahmed & Chiron 2014; Wang et al. 2015).

Fe(VI), as a dual-functional water treatment agent, has also been applied to the decontamination of many drug residues. For instance, more than 99% of diclofenac and naproxen were successfully removed from water samples (Yang et al. 2012), and the removal of carbamazepine was above 90% with Fe(VI) dosages of 6 mg·L⁻¹ as Fe (Hübner & Jekel 2013). However, there are some limitations of Fe(VI) technology (Sharma 2002; Lee et al. 2009). (1) The oxidation ability of Fe(VI) strongly depends on the solution pH. Acidic conditions benefit the oxidation ability of Fe(VI), but also speed the self-decomposition of Fe(VI), which sometimes leads to the incomplete removal of pollutants. (2) Fe(VI) is a selective oxidant, and its degrading ability for some refractory organic compounds without electron-rich moieties (ERMs) is limited. In recent years, a number of researchers (Yuan et al. 2008; Sharma et al. 2010; Ma et al. 2015) have combined Fe(VI) with photocatalysis to treat wastewater and obtained satisfying results, in which Fe(VI)-UV/TiO₂ was the most reported system. In this work, a Fe(VI)-Fe₃O₄/GE system was developed and its performance in the treatment of CIP was assessed. Also, the influence of major experimental conditions was investigated.

METHODS

Materials

Potassium ferrate(VI) (K₂FeO₄, ≥97%), CIP (≥98%) and acetonitrile (ACN, HPLC-grade) were purchased from...
Sigma-Aldrich (USA). The other chemicals and reagents were supplied by Sinopharm Chemical Reagent Co., Ltd (China).

**Preparation and characterization of Fe₃O₄/GE nanocomposites**

A typical preparation procedure for Fe₃O₄/GE nanocomposites with 10 wt% GE content was as follows: 4.5662 g of graphite oxide (GO) colloid (2.19 wt%) was dispersed into 100 mL of deionized water with ultrasonication. 1.2592 g of FeCl₃ · 6H₂O and 1.9412 g of FeSO₄ · 7H₂O were dissolved in 30 mL of deionized water under sonication. Then the solution was added slowly (10 mL · min⁻¹) into the GO dispersion with a vigorous stirring. NH₃ · H₂O was added to adjust the reaction mixture until the pH went up to 11 after the mixture was heated to 60 °C. Subsequently, the mixture was stirred for another 2 h before being cooled to room temperature. Finally, the as-obtained precipitate was separated from the mixture by vacuum filtration, washed several times with deionized water and ethanol until the redundant ions were removed, and dried in a vacuum oven at 60 °C.

The X-ray diffraction (XRD) was analyzed by a Bruker D8 Advanced diffractometer (Rigaku, Japan) with Cu Ka radiation (λ = 1.54056 Å) at a scan rate of 0.02°/s (2θ) from 5° to 80°. Transmission electron microscopy (TEM) image was taken by JEM-2100 microscope (JEOL, Japan) with an acceleration voltage of 200 kV. A UV-2700 spectrophotometer (Shimadzu, Japan) was used to record the UV-vis diffuse reflectance spectra of the samples over a measurement range from 200 to 800 nm, and BaSO₄ was used as the reflectance standard.

**Photocatalytic tests**

All experiments were carried out in a photocatalytic reactor at room temperature (25 °C) by circulating water. An 800 W Xe lamp equipped with a UV cutoff filter (λ > 420 nm) was used as the light source to establish only visible light illumination. Water samples containing CIP were treated by Fe(VI)-Fe₃O₄/GE, Fe₃O₄/GE alone and Fe(VI) alone, respectively. In detail, as for the Fe(VI)-Fe₃O₄/GE process, Fe₃O₄/GE nanocomposites (GE wt% = 10%, 250 mg · L⁻¹) were firstly added into 40 mL of CIP solution (20 mg · L⁻¹) in a quartz tube. Prior to irradiation, the suspensions were magnetically stirred for 120 min in the darkness to reach the adsorption-desorption equilibrium, with 1 mL solution collected and analyzed every 30 min. Then, solution pH was adjusted to 9 using 0.01 M HCl or NaOH. After that, Fe(VI) (10 mg · L⁻¹ as Fe) was added and the light was immediately turned on to initiate the photocatalytic process. 1 mL of reaction solutions were collected and centrifuged at 5, 10, 20, 30, 60, 120, and 180 min to detect remaining CIP. In order to prove whether a synergistic effect between Fe(VI) and Fe₃O₄/GE existed in terms of CIP removal, controlled experiments using Fe₃O₄/GE alone and Fe(VI) alone were conducted following the above steps without adding Fe(VI) and Fe₃O₄/GE, respectively. In addition, the performance of CIP removal by all three processes without illumination was tested.

In the next stage, the influence of major experimental parameters in the Fe(VI)-Fe₃O₄/GE process was investigated. Specifically, solution pH, Fe(VI) to Fe₃O₄/GE dosage ratio and GE content in the Fe₃O₄/GE nanocomposites were adjusted from 5 to 9, from 1:250 to 1:12.5 and from 5% to 15%, respectively.

The comparison of the Fe(VI)-Fe₃O₄/GE process and the Fe₃O₄/GE-H₂O₂ process in the treatment of CIP was also studied through the following methods: Fe₃O₄/GE nanocomposites (GE wt% = 10%, 250 mg · L⁻¹) were added into 40 mL of CIP solution (20 mg · L⁻¹), and then the suspensions were magnetically stirred 120 min in the darkness to reach equilibrium. After, Fe(VI) (10 mg · L⁻¹ as Fe) and H₂O₂ (12.5, 25.0 mmol · L⁻¹) were added to the solutions, respectively. After 180 min of reaction under darkness or irradiation, the concentrations of remaining CIP in the solutions were detected.

**Analytical methods**

All samples were filtered by 0.45 μm membrane filters (Millipore, USA) after centrifugation. Chromatographic separation was achieved on a C18 column (Inertsil ODS-SP, 250 mm × 4.6 mm × 5 μm) at 25 °C. The quantification of CIP was analyzed by a high performance liquid chromatograph (HPLC, Shimadzu LC-20A, Japan) equipped with a UV/Vis detector (Shimadzu, Japan) at 270 nm (detection limit of CIP: 25 μg · L⁻¹). Deionized water (0.2% formic acid) and ACN was used as the mobile phase (25:75, V/V) at a flow rate of 0.8 mL · min⁻¹, and the sample injection volume was 8 μL.

**RESULTS AND DISCUSSION**

**Characterization of Fe₃O₄/GE nanocomposites**

The XRD diffraction patterns of the Fe₃O₄/GE and Fe(VI)-Fe₃O₄/GE nanocomposites are displayed in Figure 1(a). The sharp peak at
2θ = 11.2° of the GO disappeared in the XRD pattern of Fe3O4/GE, indicating that the orderly stack of GO was exfoliated by the loading of Fe3O4. The diffraction peaks of Fe3O4 at 2θ = 30.04°, 35.38°, 43.10°, 53.44°, 56.90°, and 62.46° are all assigned to standard hcp-type Fe3O4 (JCPDS Card No. 88-0315), respectively. In the meantime, it indicated that the as-prepared Fe3O4/GE composites had a better particle crystal type and obvious characteristic peaks. The Scherrer formula was used to calculate the average particle size of Fe3O4/GE, which was 12.19 nm.

The microstructures of Fe3O4/GE nanocomposites examined by TEM are shown in Figure 1(b). Fe3O4 particles exhibited a uniform particle size distribution and were uniformly attached to the surface of graphene. The sheet-like and transparent GE could be clearly seen, demonstrating that GO was well stripped into a few layers. As shown in the HRTEM image, the lattice spacings of Fe3O4/GE nanocomposites was 0.25 nm, assigned to the crystal plane of Fe3O4 (311).

The pure Fe3O4 composites had a better absorption in the UV region (200–400 nm), as depicted in Figure 1(c). In contrast, the absorption in the visible region was very weak, which indicated that Fe3O4 can only use a small fraction of the solar energy. However, owing to the large specific surface area and excellent optical absorption property of GE, the Fe3O4/GE nanocomposites presented a strong absorption ability in the whole UV-vis light range, proving that Fe3O4/GE exhibits good photocatalytic properties theoretically.

**General performance**

The performance of the combined Fe(VI)-Fe3O4/GE process on CIP removal was initially assessed. For comparison, the removal of CIP by Fe(VI) alone and Fe3O4/GE alone were also investigated, and the results are depicted in Figure 2(a). In the Fe3O4/GE and Fe(VI)-Fe3O4/GE processes, Fe3O4/GE nanocomposites were added in the beginning of the experiments, and the equilibrium was achieved within
120 min. As observed, approximately 47% of CIP was adsorbed by the nanocomposites. Fe(VI) was then dosed into the solutions and various reductions of CIP were achieved. Generally, the combination of Fe(VI) and Fe₃O₄/GE improved the CIP removal, and the visible light irradiation did enhance the treatment performance to a certain extent. A few studies have reported that the UV illumination was able to enhance the Fe(VI) performance and sometimes even generated a synergistic effect (Chen et al. 2015; Aslani et al. 2015). For instance, up to 19.1% enhancement in the removal of profenofos by Fe(VI) was observed after the introduction of UV (Chen et al. 2015). Such enhancement could be attributed to the capturing of e⁻ by Fe(VI) to prevent their recombination with h⁺ (Winkelmann et al. 2008). In this study, visible light illumination could also enhance the performance of Fe(VI). This phenomenon might be attributed to the formation of a Fe(V) species, which is 10³–10⁵ times more reactive than Fe(VI) (Sharma et al. 2015). Meanwhile, Fe₃O₄/GE was demonstrated to be a visible light active catalyst (Boruah et al. 2016). Here, visible light illumination did improve the CIP removal by Fe₃O₄/GE, though not much (less than 10%). Nevertheless, the removal of CIP by either Fe(VI) alone or Fe₃O₄/GE alone was below 60%. However, in the combined Fe(VI)-Fe₃O₄/GE system, 98.5% of CIP was degraded with the light on.

Although a synergistic removal was not obvious in this study, in terms of the mathematical summary of the CIP removals by Fe(VI) alone and Fe₃O₄/GE alone, the performance of the combined Fe(VI)-Fe₃O₄/GE process should not be underestimated. Comparatively, a conventional Fe₃O₄/GE-H₂O₂ process was tested with two initial H₂O₂ concentrations (Figure 2(b)). A number of studies have demonstrated that the Fe₃O₄/graphene-H₂O₂ process was effective in degrading many organic pollutants, such as methyl orange and rhodamine B, which could be effectively degraded under a solar-driven Fenton reaction of the Fe₃O₄/RGO-H₂O₂ (Qiu et al. 2016). In this study, the proposed Fe(VI)-Fe₃O₄/GE system showed superiority both under dark and illuminated conditions.

**Effects of experimental conditions**

Solution pH, Fe(VI) to Fe₃O₄/GE dosage ratio and GE content in the Fe₃O₄/GE nanocomposites were three determining factors investigated in this study.

As shown in Figure 3(a), solution pH obviously affected the CIP removal. When Fe(VI) and light source were added synchronously, the concentration of CIP in solution decreased rapidly within 30 min. Except for the obvious slow reaction at pH 10 (62.4%), the CIP removal increased gradually from pH 5 to pH 9, with CIP removal above 80%. It was in excellent agreement with the stability of Fe(VI) in aqueous solution; the most stable of Fe(VI) occurs at pH 9.4 (Mácová et al. 2009; Ma et al. 2015). At pH < 7, although Fe(VI) has strong oxidation capacity, it is also extremely unstable and easily self-decomposes (Sharma 2002; Zhang et al. 2015). Fe(VI) could not effectively play the role as an electronic capture agent to prevent electron/hole recombination under acidic conditions. It was worth noting that the degradation effect of CIP was lowest at pH 10. It was indicated that there were two Fe(VI) species (HFeO₄⁻/C₀ and FeO₄²⁻/C₀) at higher pH values (Sharma et al. 2010). The electrostatic repulsion between the negatively charged Fe₃O₄/GE
surface and HFeO₄⁻ or FeO₄²⁻ was increased, resulting in a slower photoreduction of Fe(VI) at higher pH values. And the product of Fe(VI) reduction is mainly Fe(OH)₃ in alkaline conditions, which was possibly adsorbed on the surface of Fe₃O₄/GE to reduce the available active sites (Yuan et al. 2017). Meanwhile, the experimental results were consistent with some other reports. Taking sulfonamides, for instance, the degradation of sulfonamides by Fe(VI) combined with ultrasound (Fe(VI)-US) reached its maximum efficiency at pH 9 (Zhang et al. 2018), and their removal was also highest at pH 9 in a UV-TiO₂-Fe(VI) system (Ma et al. 2018).

Besides, the Fe(VI) to Fe₃O₄/GE dosage ratio also affected CIP removal (Figure 5(b)). It could be clearly seen that the CIP removal increased along with the rising Fe(VI) to Fe₃O₄/GE dosage ratio until 1:25 (corresponding to 10 mg · L⁻¹ of Fe(VI) as Fe). Continuing increase of the dosage ratio to 1:12.5 did not contribute to any further CIP removal. Fe(VI) played a dual role in the photocatalytic degradation, in which one was to improve the photocatalytic efficiency as an electron acceptor and the other was to directly oxidize the organic matter. Hence, the oxidation of Fe(VI) was enhanced with the increase of Fe(VI) dosages (Zhang et al. 2018) until its dual role reached equilibrium.

In terms of the GE content, since GE has a large specific surface area, the adsorption of CIP by Fe₃O₄/GE would increase with the rising GE content in the nanocomposites. However, as depicted in Figure 3(c), the most CIP removal was observed when the GE content was 10 wt%. The main reason was that the introduction of graphene greatly influenced the photocatalytic activity of Fe₃O₄/GE by facilitating the separation of electron/hole pairs (Ni et al. 2018). Increasing GE content to 12 wt% and 15 wt% reduced CIP removal, which may be attributed to an excess of graphene decreased correspondingly the Fe₃O₄ content as well as hindered the exposure of active sites (Xie et al. 2017).
This phenomenon indicated that Fe$_3$O$_4$ played a significant role in the generation of reactive species during CIP degradation under illumination.

Altogether, solution pH, Fe(VI) to Fe$_3$O$_4$/GE dosage ratio and GE content have varying degrees of influence on the removal of CIP by playing different roles in Fe(VI)-Fe$_3$O$_4$/GE system. The optimal values are shown in Table 1. Experimental results showed 98.5% of CIP was degraded when the experimental conditions were at best values, respectively.

<table>
<thead>
<tr>
<th>Influencing factor</th>
<th>pH</th>
<th>Dosage ratio (Fe(VI):Fe$_3$O$_4$/GE)</th>
<th>GE content of Fe$_3$O$_4$/GE (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal value</td>
<td>9</td>
<td>1:25</td>
<td>10</td>
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In this paper, a Fe(VI)-Fe$_3$O$_4$/GE process was proposed to enhance CIP removal under visible light irradiation. Results showed a significant reduction of CIP by the proposed combination system. Solution pH, Fe(VI) to Fe$_3$O$_4$/GE dosage ratio and GE content in the Fe$_3$O$_4$/GE nanocomposites played important roles in the degradation process. The proposed Fe(VI)-Fe$_3$O$_4$/GE process can be considered as a promising water pollution control technology.

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