Article

A Novel Reduced Graphene Oxide-Attapulgite (RGO-ATP) Supported Fe_2O_3 Catalyst for Heterogeneous Fenton-like Oxidation of Ciprofloxacin: Degradation Mechanism and Pathway

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Abstract: Ciprofloxacin, a third-generation fluoroquinolones (FQs) antibiotic, is observed to increasingly pollute the environment. In this study, a three-dimensional reduced graphene oxide-attapulgite-based catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ was prepared and used to analyze the degradation of ciprofloxacin in a heterogeneous Fenton reaction. The heterogeneous catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ was prepared by a one-step hydrothermal method, and the samples were characterized using BET (Brunauer-Emmett-Teller) surface area, Raman spectroscopy, X-ray diffraction (XRD), Fourier infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The effect of reaction time, temperature, pH, initial concentration, H_2O_2 dosage and reuse time on the degradation of ciprofloxacin by the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ was investigated. The optimum conditions of degradation of ciprofloxacin are observed to be 60 °C, pH 5, H_2O_2 concentration of 2.9724 mmol/L, and initial ciprofloxacin concentration of 50 mg/L. The catalyst could be reused several times with a decline in catalytic capacity. Fourier-transform ion cyclotron resonance mass spectrometer (FT) was also employed to study the degradation products of ciprofloxacin in the aqueous solution. The results show that the heterogeneous catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ possessed an excellent ability for the catalytic degradation of ciprofloxacin. Direct hydroxyl oxidation is noted to be the main pathway of degradation of ciprofloxacin, and no defluorination reaction is observed during the degradation process.

Keywords: graphene; ciprofloxacin; catalytic degradation; hydroxyl oxidation

1. Introduction

Antibiotics are chemicals that can interfere with the development of living cells. They are often used to prevent or treat diseases in humans or animals [1,2]. China is a large exporter of antibiotics, along with a major user of antibiotics [3,4]. The abuse of antibiotics in China is especially obvious as excessive use of antibiotics has stimulated the rapid emergence of drug-resistant bacteria (ARB) and drug-resistant genes (ARGs), thus reducing the therapeutic potential for human and animal pathogens [1,5]. Studies have shown that the consumption of antibiotics-containing meat, milk and other substances for a long period by humans results in a reduction in immune function. Likewise,

long-term exposure to low concentrations of ciprofloxacin in water leads to a chronic poisoning effect on aquatic plants. Thus, this poses a significant threat to human health and the safety of the entire ecosystem [6–8].

Ciprofloxacin (CIP) is widely used in human and veterinary medicines due to its broad-spectrum antibacterial activity and good oral absorption rate, classifying it as a third-generation fluoroquinolones (FQs) antibiotic. It is usually passed to animals or humans orally or through injection. However, it is considered to be one of the most important emerging pollutants due to the inhibition of the bacterial [9–13] DNA unwinding and replication to combat the bacterial infection caused by Gram-negative and Gram-positive bacteria. Ciprofloxacin is generally difficult to biodegrade and enters the environment in the form of prototypes or metabolites [14,15], thus posing a serious threat to the health of humans and aquatic organisms. Therefore, efficient and cost-effective strategies to deal with ciprofloxacin are the focus of the current research.

Current methods for the treatment of antibiotic-polluted water include biological processes and advanced oxidation technologies. A large number of research studies have demonstrated that the removal efficiency of ciprofloxacin by the activated sludge treatment method is negligible (<15%). The removal rate of ciprofloxacin by laboratory-scale membrane bioreactors is as high as 52.8% [16], but the residual extent of ciprofloxacin in the sludge is still very harmful to the environment and groundwater. A high ciprofloxacin concentration of 99 ng/L and 155 ng/L has been detected in recycled water and groundwater, respectively [17]. In Canada, ciprofloxacin was also detected in the final wastewater of eight sewage treatment plants, with a maximum concentration of 0.12 mg/L [18]. At the same time, ciprofloxacin was also detected in the remaining sludge of the sewage treatment systems in different countries. The presence of ciprofloxacin in Sweden has been reported to be 9300–11700 mg/kg, whereas a value of 2.09 mg/kg has been observed in Italy [19]. Due to the low efficiency of the biological methods in treating antibiotics, advanced oxidation technologies, such as ozone oxidation, electrochemical oxidation, photocatalytic oxidation and Fenton oxidation, have often been used in antibiotics treatments. The aim of advanced oxidation processes (AOPs) is to generate hydroxyl radicals ($\bullet\text{OH}$), which can oxidize most chemical species, especially hard-to-degrade organics. However, the hydroxyl radicals are non-selective when used for the oxidization of organics [20–22]. Heterogeneous catalysis is one of advanced oxidation technologies, which has attracted considerable research interest for the degradation of persistent organic compounds due to its high efficiency, absence of secondary pollution and simple operating conditions [23–25]. Catalysts often employ porous materials as supports, and active components, such as metals or metal oxides, are coated on the surface of the supports to form the catalyst structures. In this study, reduced grapheme oxide-combined attapulgite (ATP) has been used as support and Fe_2O_3 as the active component for the development of an advanced catalyst system.

Graphene, a 2-dimensional (2D) sheet structure of carbon atoms, has many desirable properties such as high mechanical strength, electrical conductivity and molecular barrier ability [26]. Graphene oxide (GO), a graphene derivative possessing a surface with functionalized oxygen groups, has received significant attention due to its availability in large quantities, ease of modification, good conductivity and excellent chemical stability [27]. GO can be treated by different methods to synthesize reduced graphene oxide (RGO) so as to minimize the number of oxygen groups and achieve properties closer to those of grapheme [26]. Compared to the GO structure, the RGO-based material exhibits higher surface area, chemical stability, and electrical conductivity, which makes it possible for RGO to provide more stable active sites for catalytic reaction [28–31]. Xiaoyu Wang et al. [27] chemically anchored RGO with triethylenetetramine (TETA) molecules via a nucleophilic reaction, and bonded with Fe_3O_4 nanoparticles by forming stable chelating bonds, resulting in a RGO-TETA- Fe_3O_4 nanocomposite, which exhibited remarkable catalytic ability and excellent reusability to degrade Acid Orange 7 dye (AO7). Xiangyang Xu et al. [32] synthesized RGO based $\text{NiFe}_2-x\text{Co}_x\text{O}_4$ nanocomposite ($\text{NiFe}_2-x\text{Co}_x\text{O}_4$ -RGO) to activate persulfate (PS) for the degradation of bisphenol A (BPA). Ying-Hua Zhou et al. [33] successfully immobilized ceria-doped CuNi nanoparticles on the surface of RGO by a simple co-reduction approach

in aqueous solution at room temperature, which were then employed as heterogeneous catalysts for the hydrolytic dehydrogenation of ammonia borane (NH_3BH_3 , AB), and the obtained in situ hydrogen from AB hydrolysis could be further applied to reduce 4-nitrophenol.

Clays such as montmorillonite, kaoline, bentonite, attapulgite, etc., have been used as a natural cost-effective supporter for heterogeneous catalysis in wastewater treatment [22,34–36]. Attapulgite (ATP), with a unique fibrous morphology, is a crystalline hydrated magnesium aluminum silicate [33]. Given its unique structure, ATP has a large surface area exhibiting excellent adsorption properties and catalytic activity, which make it possible to be widely used as an adsorbent and catalyst support [33,37]. Zhi Zhu et al. [38] firstly synthesized the intercalation structure $\text{g-C}_3\text{N}_4@\text{ATP}$ using a eutectic technique and calcination method and observed the enhanced separation of photogenerated electron holes. Ma et al. [33] synthesized well-spread Ag_3PO_4 particles on the surface of attapulgite (ATP) for the sunlight-driven catalytic removal of Orange II from water, and the photocatalytic activity and stability of Ag_3PO_4 were observed to be significantly improved by the loading on ATP.

Among the iron-based catalysts, Fe_2O_3 has been widely used in the heterogeneous Fenton reaction due to its simple preparation, good stability and nontoxicity [39]. Fe_2O_3 is often employed as a component to mix with other materials, for instance, mesoporous $\text{Fe}_2\text{O}_3\cdot\text{SiO}_2$ composite [40] or as an active part to be coated on supports, such as diatomite- Fe_2O_3 catalyst [41] or Fe_2O_3 -Kaolin composite [42]. Our research group has also synthesized Fe_2O_3 -coated heterogeneous catalysts for persistent organics degradation [43–45].

In our previous work, we investigated the catalyst $\text{Fe}_2\text{O}_3/\text{ATP}$ in a Fenton system for degrading sodium dodecyl benzene sulfonate (SDBS), Methylene blue (MB) and Congo red (CR) [46,47]. It was observed that $\text{Fe}_2\text{O}_3/\text{ATP}$ possessed high catalytic reactivity in a wide pH range with possibility for repeated use. In order to enlarge the surface area of ATP support to further reinforce the catalytic performance of the catalyst for degradation of other organics, a one-step hydrothermal method was used in this study to prepare a three-dimensional reduced graphene oxide-attapulgite (RGO-ATP) based catalyst. The developed catalyst was applied for the catalytic degradation of ciprofloxacin, along with the study of the degradation mechanism and pathway.

2. Results and Discussion

2.1. Characteristics of Catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$

Electron micrographs of ATP, GO and $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ are shown in Figure 1. Figure 1a shows the rod-like fiber structure of attapulgite clay. As can be seen, the rod-like structures of ATP are interlaced with each other, and the rod crystal length is about 500 nm. The SEM image of GO is shown in Figure 1b, which presents a wrinkled sheet structure of GO. Figure 1c demonstrates the SEM image of the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$. Successful incorporation of RGO and ATP, to develop a three-dimensional pore structure of composite support (RGO-ATP), can be observed. The sheet structure of graphene oxide can also be seen in the upper right corner of Figure 1c, indicating that GO is not completely reduced after subjecting graphene to a high-temperature treatment.

Table 1 presents the BET (Brunauer-Emmett-Teller) analysis of $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ and ATP. As can be seen from Table 1, the BET surface area of ATP is not very high. After introducing RGO, the surface area of the sample is observed to significantly increase, which indicates the positive impact of RGO incorporation.

Figure 1. (a) Electron micrograph of attapulgite (ATP); (b) Electron micrograph of graphene oxide (GO); (c) Electron micrograph of $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$.

Table 1. BET (Brunauer-Emmett-Teller) measurement results of $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ and ATP.

Samples	BET Surface Area (m^2/g)	Total Pore Volume (cm^3/g)	Average Pore Diameter (nm)
$\text{Fe}_2\text{O}_3/\text{RGO-ATP}$	168.0802	0.446792	9.13365
ATP	123.7691	0.315779837	4.43788

The Raman characterization of the catalyst is presented in Figure 2a. The peak at 1342 cm^{-1} (D-band) is associated with the vibrations of the carbon atoms with dangling bonds in the plane terminations of the disordered graphite from the defects and disorders of the structures in the carbon materials [48]. The peak at 410 cm^{-1} represents the vibration of $\alpha\text{-Fe}_2\text{O}_3$ [49,50].

FTIR characterization of ATP, GO and $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ is shown in Figure 2b. It can be seen that GO has a broad absorption peak at 3450 cm^{-1} , which corresponds to the stretching vibration of the $-\text{OH}$ groups on the surface of graphene oxide. The peak at 1737 cm^{-1} corresponds to $\text{C}=\text{O}$ and $-\text{COOH}$ stretching vibration peaks, whereas the peak at 1627 cm^{-1} is the stretching vibration of $\text{C}-\text{C}$ in the sp^2 hybrid carbon skeleton network. The peaks at 1387 cm^{-1} and 1065 cm^{-1} are the stretching vibration peaks of $\text{C}-\text{OH}$ and $\text{C}-\text{O}-\text{C}$ [51,52]. From the FTIR spectrum of ATP, it can be observed that the weak absorption peaks at 3530 cm^{-1} and 3417 cm^{-1} result from the stretching vibrations of $-\text{OH}$ from the water molecules adsorbed on the surface as well in the mineral layer in the crystal structure of ATP clay. The absorption peak at 1650 cm^{-1} is the characteristic peak of water adsorbed in mineral as well as interlayer water, and the absorption peak near 1030 cm^{-1} is the result of the $\text{Si}-\text{O}$ bending vibration in the ATP clay crystal structure [53–55]. The obvious characteristic peaks appearing at 3530 cm^{-1} and 1650 cm^{-1} are consistent with the characteristic peaks of ATP, indicating that the ATP incorporation was successful. The characteristic peaks at 1737 cm^{-1} , 1387 cm^{-1} and 1065 cm^{-1} disappeared or weakened, illustrating that the oxygen-containing functional groups were significantly reduced after high-temperature reduction of graphene oxide. A weaker absorption peak at 585 cm^{-1} is noted to be the characteristic absorption peak of $\text{Fe}-\text{O}$ [56].

The XRD patterns of ATP, GO and $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ are shown in Figure 2c. The diffraction peaks at $2\theta = 8.495^\circ$, 13.979° , 16.463° , 19.891° , 20.835° , 21.498° , 26.586° , 34.673° and 35.365° corresponded to 21-0957 in the standard card library, indicating the diffraction peaks of the ATP clay crystal structure. It can be seen that the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ did not induce changes in the physicochemical properties of the ATP clay during preparation. The weak diffraction peaks at $2\theta = 30.416^\circ$, 41.909° , 45.117° , 49.928° , 63.492° and 69.707° in the $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ catalyst sample were analyzed by the Jade6 XRD software, which corresponded with 33-0664 in the standard card library, indicating the characteristic diffraction peaks of Fe_2O_3 . It confirmed that Fe_2O_3 was successfully loaded on the structure of the RGO-ATP support. At the same time, the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ shows a broader peak at $2\theta = 20\sim 30^\circ$ as compared to the ATP clay structure, which is attributed to the characteristic peak generated by graphene

after high-temperature reduction. GO exhibited a strong characteristic peak at $2\theta = 11.42^\circ$, indicating that the surface of GO contained plenty of oxygen-containing functional groups after oxidation of graphene [52,57]. However, the peak disappeared in the XRD pattern $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$, implying that most of the oxygen-containing functional groups were reduced after high-temperature treatment.

Figure 2. (a) Raman spectrum of $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$; (b) FTIR diagrams of ATP, GO, $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$; (c) XRD patterns of ATP, GO, $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$.

The chemical states of C, O, Fe, and N in $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ catalyst were analyzed by XPS, as shown in the overall spectrum in Figure 3a. The C1s spectrum in Figure 3b includes five peaks: the peak at 284.8 eV is attributed to the sp^2 bonded carbon (C–C) in graphene, the peak at 287.8 eV originated from the carbonyl group, the peak at 286.1 eV is attributed to the epoxy and hydroxyl (C–O) or C=O, and the peak at 288.4 eV results from the carboxyl group (O–C=O), demonstrating that the oxygen-containing functional groups on the graphene surface were not completely reduced after the high-temperature treatment [51,58–60]. It can also be attributed to the C=N and C–N bonding configurations, which means that the C–N species are formed in the composite material [55]. Figure 3c shows the spectrum of N1s with four main peaks: the peak at 401 eV represents the graphitic carbon [61,62] and the peak at 406 eV represents the nitro group. After long-term high-temperature heating of the ferric nitrate solution, nitrate ions undergo auto-oxidation to produce nitro moieties [63]. Furthermore, the peak at 400.35 eV represents pyrroleN [64]. Figure 3d presents the spectrum of O1s with three main peaks: the peak at 532.5 eV indicates C=O on graphene, whereas the peaks at 533.5 eV and 534.0 eV represent C–O [5,65]. Figure 3e shows the spectrum of Fe2p with two main peaks: the satellite peak of Fe 2p_{3/2} at 715 eV demonstrates Fe (II) 2p_{3/2} and the satellite peak of 729 eV represents Fe 2p_{1/2} [65,66].

Figure 3. XPS spectra of C1s (b), N1s (c), O1s (d), and Fe2p (e) in Fe₂O₃/RGO-ATP, (a) is the total spectrum.

2.2. Ciprofloxacin Degradation

Temperature is one of the important influencing factors for the effective removal of ciprofloxacin by the catalyst. Especially, the temperature is noted to have a significant effect on the catalytic degradation of ciprofloxacin in wastewater in the heterogeneous Fenton reaction system, as shown in Figure 4a. Figure 4a shows that in the reaction temperature range from 30 °C to 70 °C, the degradation ratio of ciprofloxacin increases at first and subsequently decreases. The degradation ratio is noted to be the maximum at 60 °C. The reason for the observed phenomenon is that as the temperature increases, the •OH groups produced by the reaction of H₂O₂ and iron oxides also increase, thus subsequently increasing the degradation ratio of ciprofloxacin in the heterogeneous reaction. As the temperature reaches 70 °C, it results in an ineffective decomposition of H₂O₂ into water H₂O and O₂ [51] owing to too high temperature, thus the degradation ratio of ciprofloxacin is reduced. At the same time, the excessively high temperature leads to a waste of reagents. Overall, too high or low temperature is not suitable for the degradation of ciprofloxacin by Fe₂O₃/RGO-ATP catalyst. Thus, 60 °C was selected as the optimal temperature in subsequent experiments.

The ability of the catalyst to degrade ciprofloxacin as a function of the reaction time is shown in Figure 4b. It shows that the degradation ratio of ciprofloxacin by the catalyst initially increased with reaction time, followed by its stabilization. Increasing the reaction time for the Fe₂O₃/RGO-ATP/H₂O₂ system leads to a gradual enhancement in the amount of •OH produced from H₂O₂ catalyzed by Fe₂O₃/RGO-ATP, thus the ciprofloxacin molecules degraded by •OH also enhanced correspondingly. The available amount of H₂O₂ is gradually consumed, and the amount of •OH is correspondingly decreased with time, thus the rate of catalytic degradation of ciprofloxacin gradually decreases. After reaction time of 60 min, the degradation ratio of ciprofloxacin is noted to reach 90%.

pH is another important factor affecting the catalytic performance of the catalyst. Figure 4c shows the ciprofloxacin degradation ability of the catalyst under different pH conditions along with the reaction time. It is observed that the degradation ratio at pH 1, 3, 5 and 7 is significantly higher than that at pH 9, 11 and 13, demonstrating that the catalyst Fe₂O₃/RGO-ATP has an excellent catalytic ability under acidic conditions. However, the degradation ratio of ciprofloxacin by the catalyst Fe₂O₃/RGO-ATP can still reach more than 70% under strong alkaline conditions, which shows that Fe₂O₃/RGO-ATP can achieve the degradation of ciprofloxacin in a wide pH range, which significantly expands the application of the catalyst for water treatment.

The initial concentration of ciprofloxacin has a vital influence on the ciprofloxacin degradation by $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$. $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ was added to the solutions with different ciprofloxacin concentrations and the concentration was measured as a function of the reaction time, as shown in Figure 4d. As the concentration of ciprofloxacin increased, the degradation ratio initially increased, followed by its decrease. The maximum degradation ratio was noted at the initial concentration of 50 mg/L. The reason for the observed phenomenon is the enhancement of the reaction rate between the ciprofloxacin molecules and $\bullet\text{OH}$ radicals on increasing ciprofloxacin concentration. As the concentration of ciprofloxacin reaches a certain extent, the amount of catalyst and H_2O_2 required for the reaction does not increase, thus resulting in an insufficient generation of $\bullet\text{OH}$ radicals in the aqueous solution. Furthermore, the adsorption sites on the catalyst did not increase with the initial concentration of ciprofloxacin [65], thus leading to a drop in the degradation rate of ciprofloxacin by the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$.

Figure 4. Effects of (a) temperature, (b) reacting time, (c) pH value, (d) initial ciprofloxacin concentration, and (e) H_2O_2 concentration on the degradation of ciprofloxacin by $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ catalyst. (f) The recyclability of $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ catalyst.

Figure 4e shows the ciprofloxacin degradation as a function of different H_2O_2 concentration conditions (from 0.2477 mmol/L to 2.9724 mmol/L). The absorbance intensity for ciprofloxacin was measured after 60 min reaction time by a three-dimensional fluorescence spectrometer. The intensity of ciprofloxacin was observed to decrease on increasing initial H_2O_2 concentration. The characteristic peak at 275 nm is observed to vanish at H_2O_2 concentration of 2.9724 mmol/L. The reason for this phenomenon is that the increasing amount of H_2O_2 leads to the generation of more $\bullet\text{OH}$ radicals in the solution, resulting in a high extent of catalytic degradation of ciprofloxacin. However, as the amount of H_2O_2 is enhanced, the side reaction process $\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2\bullet + \text{H}_2\text{O}$, $\text{HO}_2\bullet + \bullet\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2$ is significantly strengthened. Low activity of $\text{HO}_2\bullet$ during the side reaction reduces the possibility of $\bullet\text{OH}$ to attack the organic pollution molecules [43,56], and leads to a reduction in the degradation rate of ciprofloxacin.

The recyclability of $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ catalyst was studied by continuous reusability experiments, as shown in Figure 4f. The catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ was reused after washing with distilled water, without any further treatment. The results are shown in Figure 4f. After four cycles, the degradation ratio of ciprofloxacin was decreased from 88.27% to 52.84%, indicating that the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$

can be reused several times. However, the degradation ratio decreased due to the decreasing active sites on the surface of $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$.

Ciprofloxacin has strong auto-fluorescence characteristics [67,68]; thus, its fluorescence intensity was measured before and after the 60 min reaction by three-dimensional fluorescence spectrophotometry, as shown in Figure 5. Figure 5a presents the three-dimensional fluorescence image of ciprofloxacin with initial concentration of 50 mg/L, and the red block clearly demonstrates the high concentration of ciprofloxacin. Figure 5b presents the fluorescence image of ciprofloxacin after 60 min catalytic degradation by the $\text{Fe}_2\text{O}_3/\text{RGO-ATP}/\text{H}_2\text{O}_2$ system. The red block could not be observed in Figure 5b which means that ciprofloxacin was truly catalytically degraded by $\text{Fe}_2\text{O}_3/\text{RGO-ATP}/\text{H}_2\text{O}_2$ system. Meanwhile, yellow and green blocks still can be seen because certain intermediate products are generated during the catalytic degradation of ciprofloxacin in the heterogeneous Fenton system, and the intermediate product also exhibits fluorescent characteristics.

Figure 5. (a) Three-dimensional fluorescence image of ciprofloxacin with concentration of 50 mg/L; (b) Three-dimensional fluorescence image of ciprofloxacin after 60 min degradation by $\text{Fe}_2\text{O}_3/\text{RGO-ATP}/\text{H}_2\text{O}_2$ system.

Several current methods for the degradation of ciprofloxacin were compared in the study, as shown in Table 2. It can be seen that the effect of the photocatalytic method is poor [69], but the degradation of ciprofloxacin by the Fenton oxidation and the ozone oxidation method in the advanced oxidation method is very good, and the degradation rate can reach more than 70%. The ozonation process even reached 98.7% [70,71]. However, many studies have been carried out under low ciprofloxacin concentration, and some of the catalysts cannot be recycled. In this study, the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ can effectively achieve the degradation of ciprofloxacin at a high ciprofloxacin concentration, over a wide pH range for several cycles.

Table 2. Degradation of ciprofloxacin by different methods

Methods	Process or Catalyst	Optimal Degradation Conditions	Degradation Ratio	Literature
Photocatalytic	3D $\gamma\text{-Fe}_2\text{O}_3/\text{ZnO}$	Surroundings: dark time = 30 min Initial concentration = 15 mg/L molar ratio ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) = 0.125, pH = 3.5 time = 45 min,	18.30%	[69]
Fenton oxidation	$\text{Fe}^{2+}/\text{H}_2\text{O}_2$	Initial concentration = 7.91 mg/L, time = 30 min, pH = 9	74.40%	[70]
Ozonation	Ozone	Initial concentration = 50 mg/L, time = 60 min, pH = 5, dosage of hydrogen peroxide = 0.2477 mmol/L	98.7%	[71]
Heterogeneous Fenton method	$\text{Fe}_2\text{O}_3/\text{RGO-ATP}$		88.27%	This study

2.3. Mechanism of Ciprofloxacin Degradation by $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ Catalyst

Based on previous studies focusing on advanced oxidation, ciprofloxacin is most likely to degrade at the quinolone moiety and piperazine ring, as shown in Figure 6 [72]. The product at $[\text{M}+\text{H}]^+ = 362$ should be attributed to the oxidation of piperazine. N15 and N18 of the piperazine ring are attacked by the hydroxyl radicals to form two ketogroups [73]. $[\text{M}+\text{H}]^+ = 344$ is formed by the CO loss of $[\text{M}+\text{H}]^+ = 362$ [74]. The product at $[\text{M}+\text{H}]^+ = 306$ is devinylciprofloxacin, caused by the net loss of C_2H_5 of the ciprofloxacin piperazinyl substituent or $[\text{M}+\text{H}]^+ = 334$. Intermediate products are formed by the secondary loss of $-\text{CO}$ [74], and literature studies have suggested that devinylciprofloxacin was formed directly from ciprofloxacin through an unknown mechanism involving an attack by the hydroxyl radicals [75]. The product at $[\text{M}+\text{H}]^+ = 263$ was aniline formed by the loss of $-\text{C}_2\text{H}_5\text{N}$ from devinylciprofloxacin [73]. The product at $[\text{M}+\text{H}]^+ = 362$ is also considered to result from the hydroxylation and carbonylation of an uncleaved piperazinyl ring [74] due to the initial attack on the carbon–carbon double bonds by the hydroxyl radicals [75]. According to the study of Cheng et al., the first addition of the hydroxyl radicals may take place on the atom with the highest FED2 HOMOb2FED2 LUMO value, observed on the quinolone ring. Thus, the most reasonable addition of the hydroxyl radicals can occur at the positions C4 and C11. The intermediate product $[\text{M}+\text{H}]^+ = 348$ is generated by the hydroxyl radical attacking the C4 atom [76]. Wang et al. also concluded that the hydroxyl group is most likely to attack the quinolone ring, and $[\text{M}+\text{H}]^+ = 348$ is considered to be the product of the hydroxylation process [72]. $[\text{M}+\text{H}]^+ = 322$ is the product of $[\text{M}+\text{H}]^+ = 348$ losing $-\text{C}_2\text{H}_2$, however, there is also a possibility that the quinolone ring in the ciprofloxacin structure loses $-\text{COOH}$ and is replaced by Cl [77]. Figure 7 shows a possible pathway for the catalytic degradation of ciprofloxacin by the $\text{Fe}_2\text{O}_3/\text{RGO-ATP}/\text{H}_2\text{O}_2$ system.

Figure 6. Structural formula of ciprofloxacin, where the blue box is the quinolone structure of ciprofloxacin and the red circle is the piperazine ring.

Figure 7. Possible pathways for catalytic degradation of ciprofloxacin (CIP) in $\text{Fe}_2\text{O}_3/\text{RGO-ATP}/\text{H}_2\text{O}_2$ system.

3. Materials and Methods

3.1. Preparation of Three-Dimensional Graphene-Based Catalysts

In order to obtain $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$, graphene oxide was first prepared by the Hummers method [78–80]. The procedures were as follows: 60 mL of concentrated sulfuric acid was taken in a flask, and 1 g of graphite powder and 1 g of sodium nitrate were added. The mixture was vigorously stirred in a low temperature water bath, followed by slow adding of 6 g potassium permanganate and stirring for 3 h. The reaction mixture was transferred to a water bath of 35 °C and stirred for another 3 h, and 140 mL of deionized water was added and stirred at room temperature for 12 h. A total of 200 mL of deionized water was added to the above mixture, followed by slow addition of 20 mL hydrogen peroxide. Subsequently, the mixture was stirred for 1 h and allowed to stand for 5 h. After precipitation, it was washed with 5% dilute hydrochloric acid, followed by deionized water to achieve neutral conditions. The contents were sonicated using an ultrasonicator at 100 Hz for 2 h to obtain the graphene oxide solution.

Then, 15 mL of 5 mg/mL graphene oxide solution was weighed, and 75 mg of ATP was added, followed by the addition of 3 mL of 0.005 mol/L ferric nitrate solution. The mixture was homogeneously mixed and ultrasonicated at room temperature for 20 min. Afterwards, the mixture was placed in a 50 mL reaction kettle at 170 °C for 12 h. Subsequently, the product was rinsed with an excess amount of distilled water, followed by freeze-drying for 24 h to obtain $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ aerogel.

3.2. Methods of Catalytic Degradation by $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ Catalyst

Fluoroquinolone (FQs) antibiotic ciprofloxacin was selected as a target pollutant to evaluate the catalytic degradation ability of the as-synthesized catalyst. For the determination of the catalytic degradation, 50 mL of ciprofloxacin solution with an initial concentration of 50 mg/L was added in a conical flask, followed by the dispersion of 50 mg of the catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ in the ciprofloxacin solution, along with a specific amount of H_2O_2 . The absorbance was measured by a three-dimensional fluorescence spectrometer at 0, 1, 2, 5, 10, 20, 30, 40, 50 and 60 min, and then the absorbance was converted into ciprofloxacin concentration based on its calibration curve. The degradation products of ciprofloxacin were determined by Fourier-transform ion cyclotron resonance mass spectrometer.

(FT). The initial pH of the ciprofloxacin solution was 5, which was adjusted with sulfuric acid (1:9) or sodium hydroxide (0.1 mol/L). The degradation ratio of ciprofloxacin by Fe₂O₃/RGO-ATP can be calculated using the following equation,

$$\eta = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

where C_0 is the initial concentration of ciprofloxacin and C_t is the concentration at contact time t .

3.3. Materials

Attapulgite clay was obtained from Xuyi, Jiangsu, China (specific surface area 150 m²/g), with ATP content of 90%, hydromica and montmorillonite content of 5%~8%, dolomite and quartz content of 1%~5%, dolomite and montmorillonite content of trace; nano graphite powder was purchased from Aladdin, Los Angeles, Southern California, USA; iron nitrate was purchased from Tianjin Kaixin Chemical Industry Co, Ltd, Tianjin, China; concentrated hydrochloric acid, concentrated hydrochloric acid, hydrogen peroxide, and ethanol were purchased from Sinopharm Chemical Reagent Co, Ltd, Shanghai, China; and potassium dichromate was purchased from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. Sodium nitrate was purchased from Tianjin Kaixin Chemical Industry Co, Ltd, Tianjin, China; ciprofloxacin was purchased from Aladdin, Los Angeles, Southern California, USA. All chemical reagents were of analytical grade and were not further purified before use.

3.4. Characterization

Scanning electron microscopy (SEM, JSM-5500, Tokyo, Japan) was used to characterize the microstructure of Fe₂O₃/RGO-ATP. The samples were treated with gold spray before observation, and the acceleration voltage was 20 kV. Fourier infrared spectrometer (FTIR, Nicolet AVTAR 360, Madison, Wisconsin, USA), with a scanning range of 4500 cm⁻¹–400cm⁻¹, was used to characterize the chemical composition of the three-dimensional graphene-based catalysts. X-ray diffraction (XRD, Panalytical X Pert PRO, Heracles Almelo, Holland) was used to characterize the structure of the catalyst, and the operating voltage and current were 40 KV and 150 mA respectively, with diffraction angle range of 5°–75° and scanning step of 0.02°/s. Three-dimensional fluorescence spectrum was measured using a three-dimensional fluorescence spectrum analyzer (HORIBA Scientific-Aqudog). Fourier-transform ion cyclotron resonance mass spectrometer(FT, Solarix X 7.0 T, Bremen, Germany) was used to determine the intermediate products of ciprofloxacin degradation by the catalyst. Prior to the test, the solution was first enriched and subsequently eluted. Thermo Scientific Escalab 250Xi photoelectron spectrometer (XPS, Massachusetts, USA) was used to analyze the chemical composition of the prepared catalyst surface. The obtained data was subjected to peak fitting by XPSpeak41 software for analysis of functional groups contained on the surface. The Raman detection was performed on parable Raman Spectroscopy (BWS465-785H, BWTEK, Ltd., Bremen, Germany).

4. Conclusions

This study demonstrates the preparation of a three-dimensional reduced graphene oxide-attapulgite-based (RGO-ATP) supported Fe₂O₃ catalyst for the degradation of ciprofloxacin. The catalyst was characterized by BET surface area, SEM, FTIR, XRD and XPS, which prove that Fe₂O₃/RGO-ATP catalyst possessed higher adsorption capacity and smaller pore sizes than ATP. Overall, a stable three-dimensional porous structure of RGO-ATP with successful loading of the iron oxide was confirmed. The effect of variables such as temperature, reacting time, pH and the amount of H₂O₂ on the catalytic degradation of ciprofloxacin by Fe₂O₃/RGO-ATP was studied. The results confirmed that the catalyst could degrade ciprofloxacin by more than 90% under the optimal conditions of 60 °C, pH 5, H₂O₂ concentration 2.9724 mmol/L and initial ciprofloxacin concentration 50 mg/L. The catalyst could be reused several times with a reduction in the catalytic capacity. Possible mechanism and pathways of ciprofloxacin degradation by using the Fe₂O₃/RGO-ATP/H₂O₂ system were proposed based on

the observed findings. Direct hydroxyl oxidation was noted to be the main pathway of ciprofloxacin degradation, and no de-F reaction was observed during the degradation process. The results showed that the heterogeneous Fenton catalyst $\text{Fe}_2\text{O}_3/\text{RGO-ATP}$ can effectively degrade ciprofloxacin, thus presenting a promising approach for the degradation of antibiotics in wastewater.

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