Research Article

Enhanced Adsorption and Removal of Ciprofloxacin on Regenerable Long TiO₂ Nanotube/Graphene Oxide Hydrogel Adsorbents

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To improve the adsorption performance and regeneration ability of adsorbent, a simple method was designed to synthesize long TiO₂ nanotube/reduced graphene oxide (rGO-TON) hydrogel, which has good adsorption and regeneration capacity toward ciprofloxacin. rGO-TON hydrogel could form 3D structure, which makes the separation and regeneration of adsorbent easy. For comparison, commercial P25 particle is used to prepare composite hydrogel with rGO; the results showed that TiO₂ nanotube supports the graphene sheets better than P25 particles, which would reduce the agglomeration of graphene sheets. rGO-TON have larger specific surface area (138.2 m²/g) than rGO-P25 (79.4 m²/g). In this paper, ciprofloxacin was chosen as target pollutants, the rGO-TON obtain excellent adsorption capacity, and the maximum adsorption capacities of rGO-TON for ciprofloxacin calculated from Langmuir model are 178.6 mg/g ($R^2 = 0.9929$), 181.8 mg/g ($R^2 = 0.9954$), and 108.7 mg/g ($R^2 = 0.9964$) for graphene oxide (GO), GO-TON, and GO-P25, respectively. In regeneration, the adsorption capacity of rGO-TON and rGO-P25 has little reduced after 5 cycles, while the adsorption capacity of rGO decreases to below 100 mg/g. Results of this work are of great significance for environmental applications of regenerable long TiO₂ nanotube/graphene oxide hydrogel as a promising adsorbent nanomaterial for antibiotic pollutants from aqueous solutions.

1. Introduction

As the pharmaceuticals industry is blooming these years, more and more antibiotics are polluted into the environment. Moreover, they are usually deposited continuously and maintain stability for a long time in the ecosystem [1]. Ciprofloxacin is a kind of second generation fluoroquinolone antibiotic which has been commonly used in various areas; however, it has a high solubility in aqueous solution at various pH conditions and a high stability in soil and wastewater systems; thus the removal of ciprofloxacin from water is very important [2]. Various chemical and physical methods could be used to remove antibiotic from wastewater [3], such as membrane techniques [4], biodegradation [5], chemical oxidation [6–8], adsorption [9–12], and ion-exchange [13]. Among them,

adsorption is widely used in water treatment as it is easily operated with high removal efficiency. Thus, the adsorbent disposal is necessary after adsorption process [14, 15]. At present, there are two groups of regeneration methods [16]: wet reclamation and dry reclamation. Thermal regeneration, which is a kind of dry reclamation, is the most popular method. However, if not combusted, it could produce pollutant gas. For overcoming these defects, microwave irradiation has been increasingly investigated these years [17]. However, in microwave method, some organic pollutants may volatilize rather than mineralize, and it still could not be used for continuous regeneration.

As a semiconducting metal oxide, titanium dioxide (TiO₂) is widely used due to its excellent photocatalytic

property [8]. Electrons could be excited from the valence band to the conduction band while being irradiated by UV light; during this process, electron-hole pairs are created. Thus TiO_2 possesses photocatalytic character. However, the traditional photocatalytic degradation method has some defect, such as the low usage of the light and the high consume of the energy [18]. For TiO_2 , electron-hole pairs are easy to be recovered which may be faster than the pollutant degradation rate. To overcome the defects in which the electron-hole pairs are easy to be recovered which would reduce the photocatalytic efficiency, a combination of TiO_2 with carbon nanomaterials has been considered as an efficient way [19]. Graphene oxide (GO) has a single layer two-dimensional graphite structure with abundant oxygen functional groups [20, 21]. Through treatment by reduction, GO could form a reduced graphene oxide (rGO) hydrogel, which possesses high adsorption capacity toward antibiotics [22]. GO has great potential to promote fast electron transfer. Thus the photoexcited electrons from TiO_2 are transferred to GO to hinder electron-hole recombination and to enhance oxidative reactivity [23]. There have been many investigations which reported the developments in the preparation of TiO_2 /GO composites for the removal of organic pollutants in water [24, 25]. However, though GO has high adsorption capacity, the regeneration ability is not well for reuse [26]. After the addition of TiO_2 into GO, the composite could be better reused through photocatalytic degradation after adsorption.

Providing TiO_2 with greater interracial contact with the GO surface with lower aggregation is important to improve the photocatalytic performance of GO- TiO_2 composites as this could promote the electron transfer and charge separation from TiO_2 to GO [25]. Comparing with TiO_2 nanoparticles, long TiO_2 nanotubes (TON) have a higher specific surface area and more active sites. Then, while TON and GO have a greater degree of interfacial contact, charge separation would be better; moreover, under higher aspect ratio of TON, the photocatalytic property would be improved [27]. Therefore, we put forward a simple way for the preparation of the rGO-TON hydrogel to remove ciprofloxacin from aqueous solution. Rather than the traditional simultaneous adsorption and photocatalytic degradation, the photocatalytic degradation is operated after adsorption in our study, which would acquire better light availability because the pollutant is more concentrated on the adsorbents after adsorption. The separation of adsorption and photocatalytic degradation would avoid the light scattering caused by external environment or the pollutants. For rGO-TON hydrogel with a 3D microstructure, the separation and regeneration are easy. The results of this work are of great significance for environmental applications of regenerable long TiO_2 nanotube/graphene oxide, as a promising adsorbent nanomaterial for ciprofloxacin pollutants from aqueous solutions.

2. Materials and Methods

2.1. Materials. All chemicals were purchased from Sino-pharm Chemical Reagent Co., Ltd. (Shanghai, China), in analytical purity and were used in the experiments without

any further purification. All solutions were prepared using deionized water.

2.2. Preparation. Graphite oxide was prepared using the modified Hummers' method [28–30]. To get GO solution, graphite oxide is dispersed in deionized water and sonicated in an ultrasound bath for 12 h. Commercial P25 (a mixture of 80% anatase and 20% rutile with an average surface area of $50 \text{ m}^2/\text{g}$, size 20–30 nm) was purchased from Degussa Company, Essen, Germany.

TON is prepared by hydrothermal method [31]. 2.7 g P25 powder is put into 300 mL sodium hydroxide solution (8 mol/L), ultrasonic stirred for 2 h, and then magnetic stirred for 5 h, so that the titanium dioxide was fully dissolved in sodium hydroxide solution; then, the solution was transferred into 150 mL polytetrafluoroethylene reactor, the reaction kettle was put into stainless steel jacket, the reaction kettle was assembled and put into the oil bath with the heat conduction oil, and the rotating speed is maintained at 400 rpm, heating up to 130 for 28 h; after the reaction, the reactor was naturally cooled to room temperature; the mother liquor was centrifuged at 4000 rpm for 20 min to obtain coarse product; the filter cake was put into the water to rinse 5 times, until the washing supernatant pH is 12; then hydrochloric acid was added until the pH value of the solution was 2; then the sodium titanate became a hydrogen titanate; the solution was washed 4 times until the supernatant pH was 6, and then the solution was put into the hydrochloric acid; the pH value of the solution was adjusted to 2; after 5 hours, the sodium type is converted into a hydrogen titanate type; through suction filtration and freeze-drying, TON could be obtained.

TON (or P25) and ascorbic acid were put into the GO solution and placed into an ultrasound bath for 5 h to form a uniform solution. The mass ratio of GO to TiO_2 was 2 : 1. The mixed solution was heated under 90°C for 12 h to prepare a hydrogel [2, 11]. The hydrogel without TiO_2 was named rGO.

2.3. Characterization Methods. The material surface morphology of the material was tested by a field-emission scanning electron microscopy (SEM, Hitachi, S-4800) and transmission electron microscopy (TEM, JEOL, JEM-2010). X-ray diffraction (XRD) was tested on a Bragg-Brentano diffractometer (Rigaku, D/Max-2200) under monochromatic $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) in a graphite curve monochromator, and the data was collected from $2\theta = 10^\circ - 50^\circ$ with a scan rate of $2^\circ/\text{min}$. The specific surface area and pore parameters were measured using an Accelerated Surface Area and Porosimetry system (Micromeritics, ASAP 2020), calculated from the N_2 adsorption/desorption isotherms at 77 K using BJH model.

2.4. Batch Sorption Experiments. To evaluate the ciprofloxacin adsorption on the adsorbents, batch experiments were operated. Ciprofloxacin (200 mg) is dissolved in 1 L deionized water 200 mg/L stock solution to obtain a 200 mg/L stock solution. The stock solution was diluted with deionized water to get the required concentrations. All the adsorption experiments were operated in 100 mL flasks containing 10 mg

SCHEME 1: Preparation, adsorption, and regeneration process of rGO-TON.

adsorbent and 20 mL ciprofloxacin solutions with required concentrations. The flasks were shaken in a thermostatic shaker at 150 rpm at 298 K for 24 h in the dark. All the adsorption experiments were made in duplicate and calculate the mean values. To ensure that the decrease in the concentration was actually due to the adsorbent rather than by the adsorption on the glass bottle wall, the blank experiments were conducted without the addition of adsorbent. After adsorption, the adsorbent was separated through a $0.45\ \mu\text{m}$ membrane. The ciprofloxacin concentration is analyzed by an ultraviolet spectrophotometer (Tianmei UV-2310(II)) at 270 nm for ciprofloxacin. After adsorption, the adsorbents were placed in distilled water UV light for 24 h for regeneration. The above process was repeated 5 times to study the ability of the photocatalytic technology to regenerate the adsorbents.

The adsorption isotherm was studied under initial concentration from 1 mg/L to 200 mg/L at pH = 7, 25°C. The adsorption capacity (mg/g) was calculated using

$$q_t = (C_0 - C_t) \times \frac{V}{m}, \quad (1)$$

where C_0 is the initial concentration, C_t is the concentration of time t (mg/L), V is the initial solution volume (L), and m is the adsorbent dosage (g).

Langmuir model, which assumes that the adsorbate forms a monolayer on the homogenous surface of the adsorbent and there is no interaction between the adsorbed molecules, is used to analyze the adsorption isotherms shown in

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{\alpha_L}{K_L} \right) C_e, \quad (2)$$

where K_L (L/g) and α_L (L/mg) are the Langmuir isotherm constants and α_L relates to the energy of adsorption. When C_e/q_e is plotted against C_e , a straight line will be obtained.

FIGURE 1: Optic image of rGO-TON.

3. Results and Discussion

3.1. Morphology Characterization. The preparation process of rGO-TON hydrogel for ciprofloxacin removal is shown in Scheme 1. GO and TON were mixed to form a uniform solution first, and then the composite hydrogel could be formed after hydrothermal treatment. The ciprofloxacin adsorption on GO/TON was operated in dark. Thus the ciprofloxacin was just adsorbed on GO/TON rather than being degraded. After adsorption, the rGO-TON was treated under UV, and the TON could degrade the ciprofloxacin. Thus the rGO-TON could be reused for adsorption. Optic image of rGO-TON is shown in Figure 1.

FIGURE 2: SEM images of rGO-P25 (a, b) and rGO-TON (c, d).

To investigate the morphology of rGO-P25 and rGO-TON, the SEM analysis is shown in Figure 2. Obviously, the structure of rGO-TON is totally different, the surface of rGO-P25 consists of thick blocks, while the surface of rGO-TON is fiber-like, as shown in Figures 2(c) and 2(d).

The TEM images of TON, rGO, rGO-P25, and rGO-TON are shown in Figure 3. In Figure 3(a), the as-prepared rGO is shown to have a typical layered structure. In Figures 3(c) and 3(d), it can be seen that both P25 and TON are anchored onto the rGO sheets after the hydrothermal reaction, the diameter of TON is ~ 30 nm, and the diameter of P25 is ~ 50 nm. The length of TON in rGO-TON is more than 500 nm, which is 10 times larger than its diameter. Both the P25 and TON tend to be distributed on the wrinkles and edges of the rGO sheets, which may help to prevent the rGO from agglomeration.

3.2. Composition and Structure Analysis. The specific surface area (SSA) and pore size distribution characterization of rGO, TON, rGO-TON, and rGO-P25 are shown in Figures 4(a) and 4(b). The SSA of rGO and TON are $119.2 \text{ m}^2/\text{g}$ and $139.8 \text{ m}^2/\text{g}$, while rGO-TON and rGO-P25 are $138.2 \text{ m}^2/\text{g}$ and $79.4 \text{ m}^2/\text{g}$, respectively. It can be seen that rGO-TON has larger SSA than rGO-P25, indicating that the tube-like structure of TON may support the graphene sheets better than the particles of P25. Moreover, it can be seen from the pore distribution analysis, as shown in Table 1, that rGO-TON has the highest pore volume among rGO, TON, rGO-TON, and rGO-P25, which indicate that the graphene sheets are well separated by TON. For further investigating the interaction between

TABLE 1: Physical properties of rGO, rGO-TON, and rGO-P25.

Sample	TON	rGO	rGO-TON	rGO-P25
Specific surface area (m^2/g)	139.8	119.2	138.2	79.4
Average pore size (nm)	7.9	6.2	6.5	5.3
Total pore volume (m^3/g)	0.28	0.27	0.48	0.22

graphene and TON or P25, XRD patterns of GO, rGO, TON, rGO-TON, and rGO-P25 are shown in Figure 5. The peak at 10.5° in GO indicates the interlayer space of 0.9 nm. However, in rGO, TON, rGO-TON, and rGO-P25, all the peaks at $2\theta = 10.5^\circ$ are obviously weaker than in GO, indicating that the GO has been reduced to rGO [32]. The disappearance of the rGO characteristic peaks in the rGO-TON indicates that the graphene sheets are separated by TON [33]; however, it can be seen that there is still a small peak around 27° in rGO-P25, indicating that the graphene sheets are better separated by TON than P25, which may be a benefit for SSA of rGO-TON. The peaks of rGO-TON and TON in 25.3° , 37.8° , and 48° correspond to the (101), (004), and (200) planes of the anatase TiO_2 (JCPDS 21-1272), respectively [31].

3.3. Adsorption and Regeneration Properties. Langmuir isotherm is used to fit the ciprofloxacin adsorption on rGO, rGO-TON, and rGO-P25, as shown in Figure 6(a); all the samples were operated in 3 duplicates with presented data equally ($R^2 > 0.9800$). The maximum adsorption capacities are 178.6 mg/g ($R^2 = 0.9929$), 181.8 mg/g ($R^2 = 0.9954$),

FIGURE 3: TEM images of TON (a), rGO (b), rGO-P25 (c), and rGO-TON (d).

FIGURE 4: N_2 adsorption/desorption isotherms (a) and BJH pore size distribution (b) of rGO, TON, rGO-TON, and rGO-P25.

and 108.7 mg/g ($R^2 = 0.9964$), respectively. The excellent adsorption capacity of rGO-TON is mainly attributed to its larger SSA. Besides physical adsorption, chemical adsorption also plays important role in this adsorption process. During ciprofloxacin adsorption on rGO, rGO-TON, and rGO-P25, the graphene provides π - π bond and hydrogen bond with ciprofloxacin. One of the driving forces for the organic chemicals adsorption on graphene is electron donor-acceptor interaction owing to the benzene rings. With -OH groups

on the surface, graphene could act as electron donors and enhanced adsorption significantly through forming π - π bond [34]. Figure 6(b) shows the regeneration of rGO, rGO-TON, and rGO-P25; all the samples were operated in 3 duplicates with presented data equally ($R^2 > 0.98$). Obviously, the rGO-TON and rGO-P25 have little reduction of adsorption capacity after 5 cycles, while the rGO decreases to below 100 mg/g . It can be seen that both TON and P25 promote the composite hydrogel with good regeneration

FIGURE 5: XRD of rGO, TON, rGO-TON, and rGO-P25.

ability. While under the UV irradiation, electron-hole pairs are generated in TiO_2 , which could move immediately from valence band to conduction band in the excited state, and the charge separation and hydroxyl radical formation occur in the regeneration process. Moreover, the electrons transfer from TiO_2 to rGO, and the photogenerated holes stay behind in the valence band. Therefore, the electrons and holes are separated immediately and then react with dissolved oxygen and water molecules to form hydroxyl radical, acting as a strong oxidant for ciprofloxacin degradation [35]. Therefore, the rGO has good adsorption capacity but low regeneration capacity; however, the rGO-P25 has good regeneration ability but the adsorption capacity is not well while the rGO-TON has both good adsorption capacity and regeneration ability.

4. Conclusion

To combine the adsorption of graphene and photocatalytic degradation of TiO_2 , TiO_2 nanotube-reduced graphene oxide (rGO-TON) hydrogel is prepared toward ciprofloxacin removal. Commercial P25 particle is used for comparison with long TON; graphene sheets are shown to be better separated by TON than P25. The resulting rGO-TON have a higher specific surface area, adsorption capacity, and regeneration ability than rGO-P25. Calculated from Langmuir model, the maximum adsorption capacities of ciprofloxacin on the hydrogels are 178.6, 181.8, and 108.7 mg/g, respectively, indicating the excellent adsorption ability of rGO-TON. The rGO has good adsorption capacity, but the regeneration ability is low while the rGO-P25 has good regeneration ability but the adsorption capacity is not well. However, the rGO-TON overcome the above-mentioned defects of rGO and rGO-P25; it has both good adsorption capacity and regeneration ability attributed to the combination of graphene and long TON. Therefore, results of this work are of great significance for environmental applications of regenerable long TiO_2 nanotube/graphene oxide hydrogel adsorbent for antibiotic pollutants.

(a)

(b)

FIGURE 6: Langmuir isotherm model (a) and regeneration properties (b) (initial concentration 200 mg/L) of rGO, rGO-TON, and rGO-P25.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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