Hydrothermal synthesis of GO/TiO₂ composites with high performance as UV photocatalysts for degradation of parabens

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1. Introduction

The emerging contaminants present in wastewater and water sources are compounds used in a wide spectrum of pharmaceutical and personal care products. The increasing consumption of this kind of products results in their increasing presence in water sources. In recent decades, pharmaceuticals and personal care products (PPCPs), as contaminants, have become a new focus of attention for their persistent existence in aquatic environments [1]. Parabens are widely used as preservative and antimicrobial agents in food and cosmetics, and are currently considered as potential emerging contaminants in the environment [2]. Parabens, a group of alkyl esters of p-hydroxybenzoic acid, have some estrogenic activity, which might be an endocrine disruptor that could induce diseases. In addition, the skin could absorb parabens in the cosmetics, which might be the cause of skin allergy [3]. The main sources of parabens in the environment are the discharge of industrial sewage and domestic sewage. Therefore, it is very important to remove parabens from water to protect the human health and the environment. Certain technologies, including adsorption and biodegradation, gamma irradiation combined with other biological means, and electrochemical methods, have been used to remove parabens from water [4]. However, these technologies have limits in practical applications because of incomplete mineralization, poisonous by-products, or strict reactive conditions.

Advanced oxidation processes (AOPs) have been widely used to degrade organic pollutants into less complex by-products for mineralization into CO₂, H₂O and inorganic ions. These processes are based on the production of powerful/non-selective hydroxyl radicals. This oxidant radical can attack the organic pollutants present in water, break, and finally mineralize them. AOPs used to degrade parabens in waters include photocatalysis, ozonation, electrochemical oxidation, photodegradation, UV/H₂O₂, activated persulfate, and Fenton reagent [5].

Photocatalysis is currently considered to be one of the most effective methods for the degradation of organic contaminants due to its cleanliness and sustainability. Photoinduced holes (h⁺), hydroxyl radical (HO·), and superoxide radical (O₂⁻) induced by photocatalysts can promote the degradation of some refractory organics [4]. TiO₂ is one of the materials most widely applied as photocatalysts in water decontamination. TiO₂ has been extensively studied because of their good chemical and thermal stability, and high efficiency. However, this material has two inherent limitations, the low quantum yield and the poor light harvesting ability [6]. Accordingly, recent studies have centered on photocatalysis processes that reduce these disadvantages. A research line of particular interest in this field has been the preparation of semiconductors with large surface area or their deposition on porous carbon materials and more recently, graphene based materials. Furthermore, graphene oxide (GO) has good ability to transfer
electrons and generate electron holes, which could significantly enhance photocatalytic performance of TiO$_2$ [3].

In this study, ethylparaben (EtP) was selected as the target pollutant. GO/TiO$_2$ composites were prepared by hydrothermal method, and the GO in the composites was changed to reduced graphene (rGO) during preparation [3]. As far as we know, the use of GO/TiO$_2$ composites as heterogeneous catalysts in the degradation of EtP has not been tested so far. With this background, the main objective of this study was to determine the effectiveness of GO/TiO$_2$ composites in the degradation and removal of EtP from aqueous solution. For this purpose, we synthesized GO/TiO$_2$ composites with different graphene oxide content by a hydrothermal method. The composites were characterized and tested in the photodegradation of EtP under ultraviolet light.

2. Experimental

GO was synthesized from graphite power according to the modified Hummers method [7]. GO/TiO$_2$ composites were prepared using a hydrothermal method as described elsewhere [8]. Different GO/TiO$_2$ proportions were tested to reach the optimum composite.

The composites were characterized by X-ray diffraction (XRD), Fourier-transform infrared (FT-IR) spectroscopy, nitrogen physisorption (77 K), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM), in order to analyze the structure and morphology of the samples.

EtP degradation experiments were conducted in an ultraviolet laboratory reactor system 2 (UV Consulting Pesch), equipped with a medium-pressure mercury vapour lamp (TQ 150, nominal power 150 W). About 700 mL of EtP solution (0.3 mM) in the presence of 0.7 g/L of composite was poured into the reactor. EtP concentration was determined at different period of time using a high-performance liquid chromatograph (Thermo-Fisher) equipped with a UV800 photodiode detector (column: Hypersil GOLD 25×4.6 mm; mobile phase: 50:50 methanol: acidic water (0.01% HCOOH); flow rate: 1 mL min$^{-1}$, injection volume: 20 µL; UV detector wavelength: 254 nm).

3. Results and Discussion

The crystallographic structures and phase composition of the materials were examined by XRD. Figure 1 shows the XRD pattern of graphite and GO. As expected, XRD pattern of raw graphite showed a very big peak at 20 = 26.56°. The XRD pattern of GO showed a major peak centered at 20 = 10.78°, corresponding to interlayer spacing (d$_{002}$) of 0.82 nm. This confirmed that most of the graphite powder was oxidized into graphene oxide by expanding the interlayer spacing from 0.34 to 0.82 nm [9]. The large interlayer distance of graphene oxide could be attributed to the presence of oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl, and epoxide [9]. The mean size of the graphitic crystal along the c axis (D$_{002}$) can be determined by the Scherrer’s equation and the number of graphene layer, N$_c$, was calculated as: N$_c$ = (D$_{002}$/d$_{002}$)+1. Thus, the number of estimated graphite layers is 118, much higher than that for GO which was 7.

The XRD patterns of TiO$_2$ and GO/TiO$_2$ composites at different GO content 4, 7, 10, 30 wt. % are shown in Figure 2. The XRD patterns of TiO$_2$ and xGO/TiO$_2$ composites revealed obvious peaks located at 20 = 25.26°, 37.80°, 47.95°, 53.92°, 62.60° and 75.05°, which correspond to TiO$_2$ anatase phase (JCPDS 21-1272). No rutile phase was detected due to the low reaction temperature employed in this work. However, there are no observable diffraction peaks of graphene oxide at 10.78° in the XRD pattern of the composites, which is probably induced by the reduction of GO into reduced graphene oxide (rGO) during preparation of the composite in the hydrothermal reaction. Moreover, the characteristic peak of rGO (20 = 24.5°) may be screened by the main peak of anatase TiO$_2$ at 25.26°.
The diffraction peak at 25.6° for the composite samples is broader than that of TiO$_2$ (Figure 2). Peak broadening indicate that the lattice structure of TiO$_2$ is distorted by the interaction with rGO. The average crystal sizes calculated using Scherrer equation for the GO/TiO$_2$ composites were in the range of 17.6-19.7 nm, which is smaller than that corresponding to TiO$_2$, 19.9 nm (Table 1).

Table 1. Structural parameters of the studied materials obtained from their XRD patterns. Position peak (2θ), full width at half-maximum of the peak (FWHM) and crystallite size (D$_{101}$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (°)</th>
<th>FWHM (°)</th>
<th>D$_{101}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>25.29</td>
<td>0.409</td>
<td>19.9</td>
</tr>
<tr>
<td>4%GO/TiO$_2$</td>
<td>25.24</td>
<td>0.426</td>
<td>19.1</td>
</tr>
<tr>
<td>7%GO/TiO$_2$</td>
<td>25.23</td>
<td>0.444</td>
<td>18.3</td>
</tr>
<tr>
<td>10%GO/TiO$_2$</td>
<td>25.25</td>
<td>0.414</td>
<td>19.7</td>
</tr>
<tr>
<td>30%GO/TiO$_2$</td>
<td>25.22</td>
<td>0.464</td>
<td>17.6</td>
</tr>
</tbody>
</table>

The structural properties of the xGO/TiO$_2$ composites and electronic coupling between GO and TiO$_2$ were studied by Raman spectroscopy. Figure 3 shows the Raman spectra of graphite, graphene oxide, bare TiO$_2$ and xGO/TiO$_2$ composites at 514.5 nm excitation. There are two characteristic peaks in the spectrum of raw graphite, namely, the D band at 1354 cm$^{-1}$ and the G band at 1582 cm$^{-1}$. The D band corresponds to the defects in the graphite structure and disordered carbon, whereas the G band is ascribed to ordered sp$^2$-bonded carbon atoms [6]. In the Raman spectrum of GO, the G band broadens and up-shifts (1597 cm$^{-1}$) in comparison to that observed in graphite (1581 cm$^{-1}$), while the intensity of the D band increases substantially. These phenomena can be attributed to the significant decrease in size of the in-plane sp$^2$ domains due to oxidation and ultrasonic exfoliation [10].
The intensity ratio of D bands and G bands (I_D/I_G) increased from 0.16 for graphite to 0.81 for GO. This is because the D band increased during oxidation since oxygen functional groups were introduced into the graphitic plane and confirms the oxidation of graphite.

All the above mentioned Raman bands are observed in the Raman spectra of GO/TiO_2. In addition, different bands appear at low frequencies located around 152 cm\(^{-1}\) (E\(_{\text{g}}\)), 201 cm\(^{-1}\) (E\(_{\text{g}}\)), 397 cm\(^{-1}\) (B\(_{1g}\)), 513 cm\(^{-1}\) (B\(_{1g}\) + A\(_{1g}\)) and 636 cm\(^{-1}\) (E\(_{g}\)), indicating the presence of anatase phase [6]. The intensity ratio I_D/I_G for GO was 0.81; however, this value increased around 1.00 in GO/TiO_2 composites. This change can be attributed to the decrease in the average size of the in-plane sp\(^2\) domains, through the reduction process of GO during a hydrothermal reaction [11].

Table 2 summarizes the surface areas and pore volumes of the composites. These materials have low microporosity. The results show that S\(_{\text{BET}}\) and micropore volume (W\(_0\)) increase with the amount of GO.

Table 2. Textural characteristics of composites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>S(_{\text{BET}}) (m(^2)/g)</th>
<th>W(_0) (cm(^3)/g)</th>
<th>L(_0) (nm)</th>
<th>W(_{0.95}) (cm(^3)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO(_2)</td>
<td>81.5</td>
<td>0.030</td>
<td>1.86</td>
<td>0.346</td>
</tr>
<tr>
<td>4%GO/TiO(_2)</td>
<td>89.1</td>
<td>0.032</td>
<td>1.89</td>
<td>0.258</td>
</tr>
<tr>
<td>7%GO/TiO(_2)</td>
<td>97.7</td>
<td>0.036</td>
<td>1.70</td>
<td>0.207</td>
</tr>
<tr>
<td>10%GO/TiO(_2)</td>
<td>106.3</td>
<td>0.039</td>
<td>1.69</td>
<td>0.282</td>
</tr>
<tr>
<td>30%GO/TiO(_2)</td>
<td>141.1</td>
<td>0.051</td>
<td>1.58</td>
<td>0.273</td>
</tr>
</tbody>
</table>

Figure 4 depicts EtP photodegradation kinetics by UV irradiation and by the simultaneous use of UV radiation and GO/TiO\(_2\) composites. In comparison with TiO\(_2\), the presence of composites increased the degradation of EtP. The rate constant of EtP photodegradation decreased in the order: 7\%GO/TiO\(_2\) > 4\%GO/TiO\(_2\) > 10\%GO/TiO\(_2\) > 30\%GO/TiO\(_2\); the percentage removal of EtP also decreased in the same order.
order, reaching 98.6 % for 7%GO/TiO₂ and 60.7 % for 30%GO/TiO₂ at 40 min of irradiation (Table 3).

Therefore, the photocatalytic efficiency of the composites for the photodegradation of EtP was found to depend on the GO content. Optimal results were obtained for 7%GO/TiO₂ composite, which exhibited the highest photocatalytic activity (Table 3). Further increase of the GO content results in a lower degradation efficiency, probably due to the fact that an excess of GO particles may cover the active sites TiO₂. The high efficiency of the composite containing GO was attributed to the efficient and uniform assembly of the TiO₂ nanoparticles on the reduced GO sheets, making the material to act simultaneously as electron-acceptor and electron-donor, thus reducing charge recombination.

![Figure 4. Photocatalytic degradation of EtP with different systems as a function of irradiation time.](image)

**4. Conclusions**

GO/TiO₂ composites were synthesized by a simple one-step hydrothermal method. TiO₂ is present in anatase phase in the composites. The obtained results confirmed the potential of GO to blend with TiO₂ and to produce effective composites for the photocatalytic treatment of wastewaters, in particular those polluted with parabens.

**5. References**