Fabrication and Characterization of Magnetic GQDs Using Green Tea Extract for Environmental Remediation

Tong Ye[1], Changsheng Peng[1,2*], Imran Ali[1], Jiwei Liu[1]
1. *The Key Lab of Marine Environmental Science and Ecology of Ministry of Education, Ocean University of China, Qingdao 266100, China*
2. School of Environment and Chemical Engineering, Zhaoqing University, Zhaoqing, 526061, China

Abstract: A graphene-based magnetic nanocomposite was synthesized and used as an effective adsorbent for crystal violet dye. The properties of the magnetic nanocomposite were characterized by X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and Vibrating Sample Magnetometer (VSM). This novel graphene-based magnetic nanocomposite showed great adsorptive ability towards the analytes and can easily separated from the water. When the amount of magnetic GQDs was 10 g/L, the removal rate of was more than 90%.
Keywords: graphene quantum dots（GQDs）; magnetic nanoparticles; iron oxide; adsorption

1. Introduction

Graphene, as a carbon nanomaterial, has drawn increasing attention for its unique properties such as large specific surface area, high carrier mobility, excellent mechanical flexibility, good chemical stability, and environmentally friendly features [1]. As a zero-dimensional nanomaterial, graphene quantum dots（GQDs） have quantum effects and boundary effects when their size is less than 10 nm [2,3]. GQDs have a large number of π-π interaction sites [4], and the surface is rich in hydroxyl, carboxyl and alkoxy oxygen-containing functional groups [5], which make it has great application prospects in electronic, biosensors, drug delivery, environmental water purification and other fields [6-9]. If we give carbon nanomaterial magnetic properties, the formed magnetic carbon nanomaterial will have both high adsorption properties and easy separation from final effluents. In this study, we used green tea extract for making nano-iron oxide as the solid phase carrier and further synthesized magnetic GQDs.

2. Materials and methods

2.1 Materials

All chemicals used were of analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd., China. The chemicals used in this study were ferrous chloride, ferric chloride, sodium hydroxide, ethanol and crystal violet. GQDs solution was kindly provided by Chemical Engineering Department of Ocean University of China (ref). Green tea was purchased at the local tea market.

2.2 Fabrication of magnetic GQDs

Preparation of green tea extract:

The collected green tea were thoroughly rinsed with distilled water to remove dust particles and dried at 85℃. Dried tea leafs were grounded into powder. An amount of 10g of dried powder were taken into 250mL flask, to this added 100mL distilled water and refluxed for 1h at 85℃. Then the resultant mixture is cooled to room temperature and filtered to be used for further experiments.

Synthesis of magnetic GQDs:

5.0g $FeCl_3 \cdot 6H_2O$, 5.0 g $FeCl_2 \cdot 4H_2O$ was dissolved in 10 mL of distilled water, then added 20 ml green tea extract into the solution. The above solution was added dropwise to 20ml of GQDs solution (2.9 mg/L) under magnetic stirring. A small amount of sodium hydroxide was added to the reaction system to completely darken the solution and reacted at 85℃ for one hour. The resultant black product was washed with distilled water and ethanol several times by centrifugation and was dried at 80℃ in a vacuum oven.

* Corresponding author. Tel.: +86 15853299827; fax: +86 532 66782011. E-mail: pcs005@ouc.edu.cn (Changsheng Peng)

3. Results and discussion

3.1 XRD analysis

X-ray diffraction (XRD) measurements were employed to investigate the phase and structure of the synthesized magnetic GQDs. As shown in Fig.1, the XRD peaks identified in the whole spectrum of 2è values of 21.2°, 35.0° are the characteristic peaks of ɤFe_2O_3 [10]. And the peaks of 35.5°, 53.7°, 57.3° and 62.5° corresponded to Fe_3O_4 [11]. It shows that the magnetic iron oxide particles were prepared.

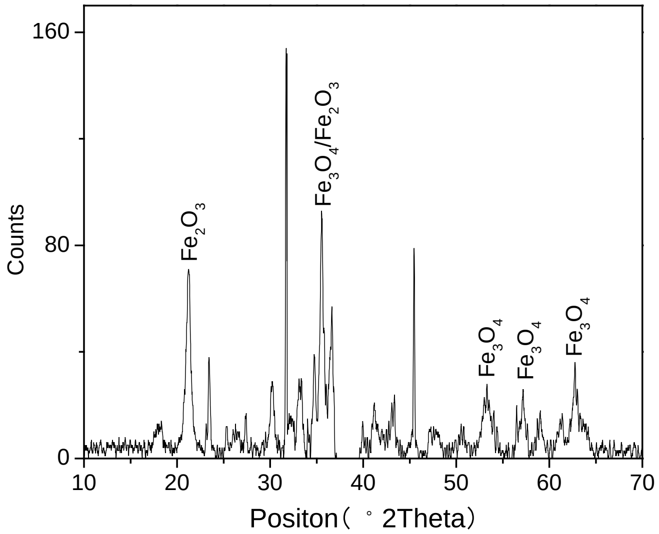

Fig.1 X-ray diffraction pattern of magnetic GQDs.

3. 2 FT-IR analysis

Infrared spectra of magnetic GQDs (Fig.2) shows the broad and bands in the region of 3400cm^{-1} are assigned to O-H stretching [12], those at 2889cm^{-1} , 2821cm^{-1} and 1334cm^{-1} to C-H stretching [13] and band appears at 1622cm^{-1} is attributed to the C=O bond of carboxylic acids [14]. The peak observed at 1040cm^{-1} is due to Fe-OH structural vibration. The peak at 624cm^{-1} and 558cm^{-1} is attributed to the Fe-O bond vibration of ɤFe_2O_3 and Fe_3O_4 [15,16]. It shows that the prepared magnetic GQDs has abundant functional groups and the formation of magnetic iron oxide.

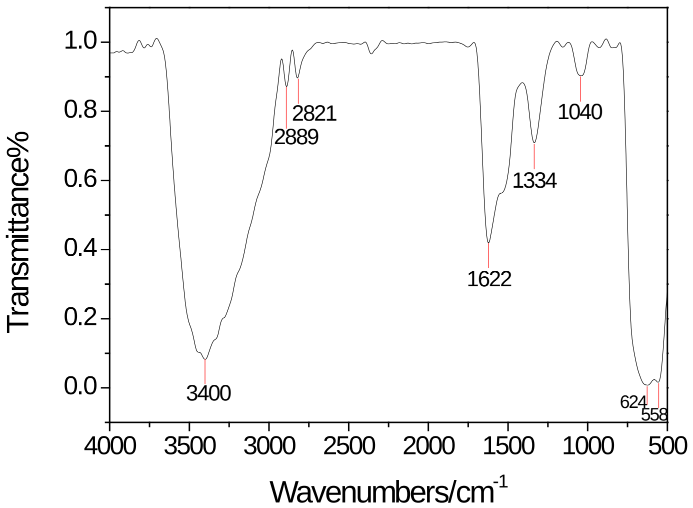

Fig.2 Infrared spectra of magnetic GQDs.

3.3 XPS analysis

In order to further study the composition of magnetic GQDs, XPS analysis of the composites was carried out. As shown in Fig.3, when the surface of the iron oxide nanoparticles is coated with GQDs, the contents of C and O are 22.75% and 60.28%. Indicated that GQDs have been successfully loaded onto the surface of iron oxide nanoparticles.

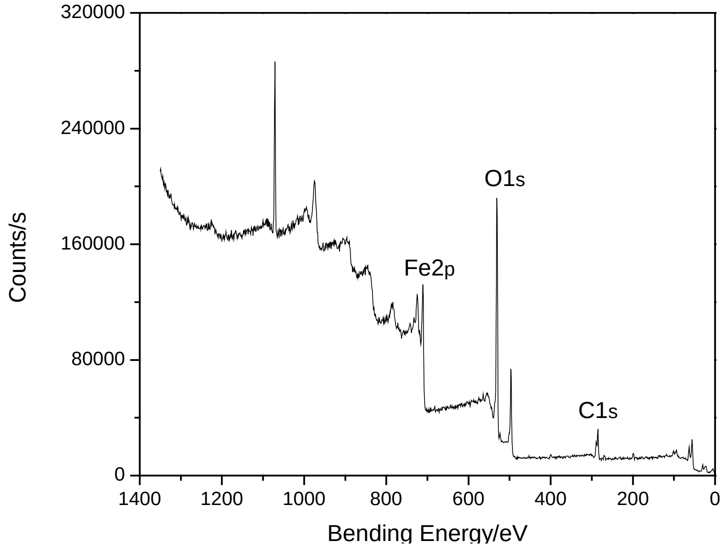

Fig.3 XPS spectra of magnetic GQDs.

3.4 Magnetic measurements

Hysteresis loops were used to characterize the magnetic properties of the material. As can be observed in Fig.4, the sample hysteresis loop about the origin of the center symmetry, indicating that it did not hysteresis, remanence and coercivity are 0, the sample was superparamagnetic.When the applied magnetic field strength increased from 0 to 111.9Oe, the composite rapidly magnetized with a magnetization of 7.9emu / g. The specific saturation magnetization value was measured to be 20.2 emu/g. This indicated that the experimentally prepared composite material is highly magnetic. The experiment found that the use of magnets can be quickly separated composite materials and solutions as shown in Fig.5.

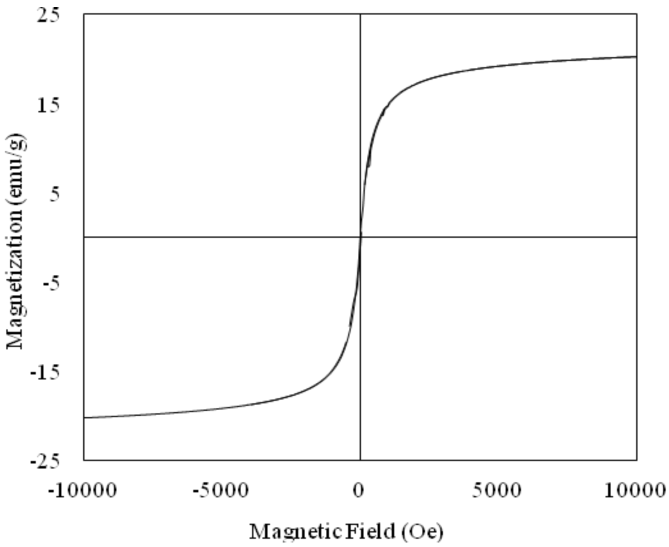

Fig.4 Magnetization curve of magnetic GQDs.

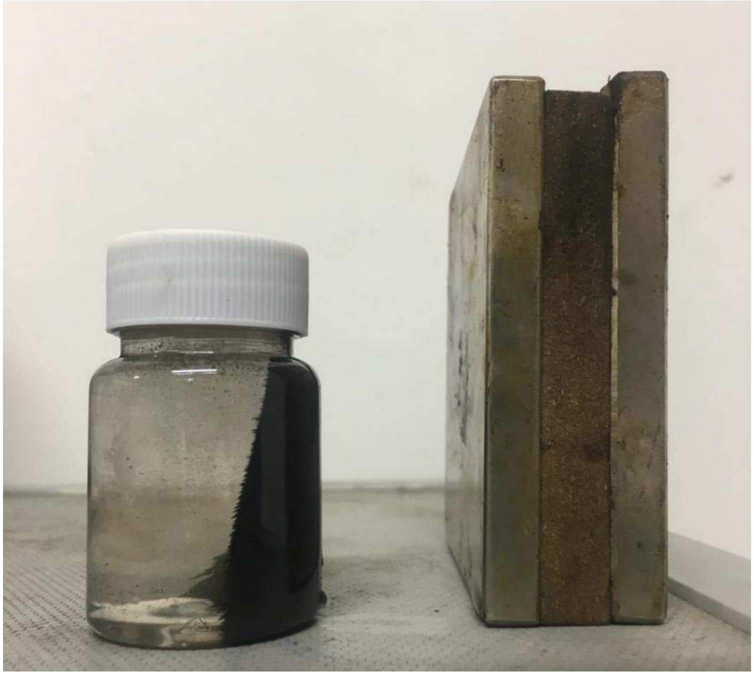

Fig.5 Particles attracted by magnet.

3.5 Adsorption study

We used magnetic GQDs as adsorbent for crystal violet dye adsorption experiments. Adsorption of different adsorbent dosage was shown in Fig.6. With the increase of the amount of magnetic GQDs, the adsorption rate of crystal violet is gradually increased. When the amount of magnetic GQDs was 10 g/L, the removal rate of was more than 90%. And the maximum adsorption capacity was 20mg/g when the adsorbent dosage was 2g/L.

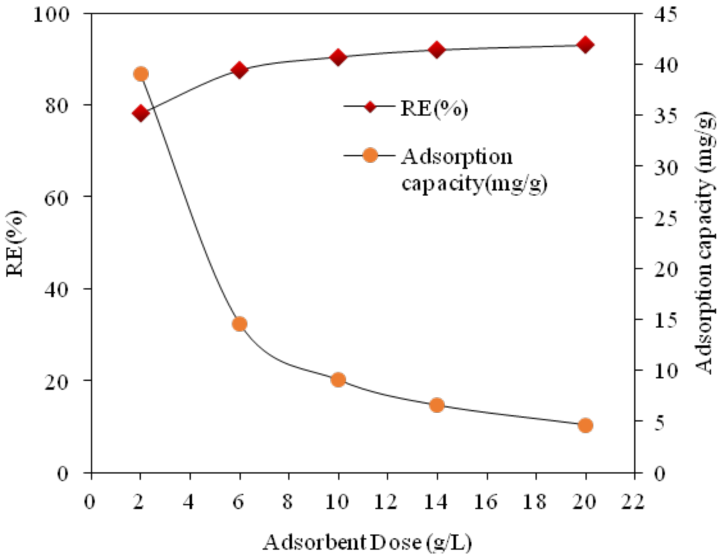

Fig.6 The effect of magnetic GQDs dosage on adsorption efficiency(Remaval efficiency, left axis. Adsorption capacity, right axis)

4. Conclusion

In this study, green tea extract was used to precipitate GQDs on the surface of iron oxide nanoparticles, and successfully prepared and characterized magnetic GQDs. Experimentally prepared magnetic GQDs can be quickly separated from the solution by applying a magnetic field and has high removal efficiency for crystal violet dye. It provides a convenient way for collecting and reusing graphene materials.

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