Attached β-cyclodextrin/γ-(2,3-epoxypropoxy) propyl trimethoxysilane to graphene oxide and its application in copper removal
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Abstract
The environmental applications of graphene oxide and β-cyclodextrin (β-CD) have attracted great attention since their first discovery. Novel nanocomposites were successfully prepared by using an esterification reaction between β-cyclodextrin/γ-(2,3-epoxypropoxy) propyl trimethoxysilane grafted graphene oxide (β-CD/GPTMS/GO). The β-CD/GPTMS/GO nanocomposites were used to remove the Cu$^{2+}$ from aqueous solutions. The characteristics of β-CD/GPTMS/GO were detected by scanning electron microscopy (SEM), Fourier transform infrared, X-ray diffraction (XRD), thermogravimetric analysis (TG) and energy dispersive X-ray (EDX). The dispersibility of graphene oxide was excellent due to the addition of β-CD. The adsorption isotherms data obtained at the optimum pH 7 were fitted by Langmuir isotherm model. The excellent adsorption properties of β-CD/GPTMS/GO for Cu$^{2+}$ ions could be attributed to the apolar cavity structure of β-CD, the high surface area and abundant functional groups on the surface of GO. The adsorption patterns of β-CD/GPTMS/GO were electrostatic attraction, formation of host-guest inclusion complexes and the ion exchange adsorption. The efficient adsorption of β-CD/GPTMS/GO for Cu$^{2+}$ ions suggested that these novel nanocomposites may be ideal candidates for removing other cation pollutants from waste water.

Key words | β-cyclodextrin, adsorption, copper ions, graphene oxide, removing

Introduction
With the development and progress of human society, the rapid growth of population, agricultural and industrial activities have caused more and more serious impact on the environment (Chen et al. 2016; Zeng et al. 2016). Heavy metal pollution has caused continuous deterioration to our water resources (Zhang et al. 2015). And industrial activities such as mining operations, electronics, electroplating, metal processing, textile, and battery manufacturing are considered as the major sources of Cu$^{2+}$ contamination (Adhoum et al. 2004); furthermore, Cu$^{2+}$ has been included in the agency for toxic substances and disease registry as a toxic, persistent and bio-accumulative substance (Teodoro et al. 2016). Therefore, increasing attention has been paid to the removal of Cu$^{2+}$ from aqueous solutions. And the usual processes of separating metal ions from aqueous solutions are ion-exchange (Akhila Maheswari & Subramanian 2004), coprecipitation (Soylak et al. 2005; Soylak & Tuzen 2008), extraction (Ma et al. 2015), membrane filtration (Ihara et al. 2008), electrolysis (Feng et al. 2007) and adsorption (Boyaci et al. 2010). The adsorption seems to be the more effective method for water decontamination applications due to its low cost, simple operation, no or little use of organic solvents, and high efficiency for separating the metal pollution from aqueous solutions (Ahmaruzzaman 2008).

In recent years, the study of carbon materials has been promoted to a high position for its unusual physico-chemical properties and possible application in various fields. Graphene is one of the carbon materials, which has a two-dimensional single atomic layer of sp2 bonded carbon, becoming a ‘rising star’ among all other carbon materials in various research fields due to its unique physicochemical properties (Rao et al. 2010; Devadas et al. 2012). Graphene can be widely used in adsorption for its large specific surface area. Li et al. (2012) reported that reduced graphene oxide (rGO) adsorbs Sb through reaction between graphene...
oxide (GO) with hydrazine hydrate, the adsorption isotherm accords with Langmuir mode and the maximum adsorption capacity was 7.463 mg/g. Compared with rGO, the hydrophilic property of GO is more favorable and GO easily forms a complex with metal ion because of the presence of oxygen-containing functional groups on the GO sheet. Sitko et al. (2013) studied the adsorption of GO for divalent metal and showed aggregation and precipitation of GO in a strong acidic environment; the reason is that the negatively charged functional groups of GO were neutralized by heavy metal cations in water. In this work, GO was fabricated by a series of inexpensive ingredients, which reduces experimental cost.

The structure of β-cyclodextrin (β-CD) is toroidal, and the truncated cone contains an apolar cavity, primary hydroxyl groups and the secondary hydroxyl groups lying on the outside and inside, respectively. Then some metals can combine with the functional groups of the β-CD outside. Some researchers had proved that carboxymethyl-β-CD has the ability to combine with heavy metals such as cadmium, nickel, strontium and mercury through the interactions between the metal ions and carboxyl functional groups (Wang & Brusseau 1995; Brusseau et al. 1997). Recently, Li et al. showed that α-, β- and γ-cyclodextrin/poly (acrylonitrile) composite nano fibers possessed good performance at applications in Cu²⁺ adsorption (Li et al. 2014).

Then both GO and β-CD are used to remove the heavy metals from aqueous solutions due to the specific characteristics. There are certain grafting processes using L-ascorbic acid as the reducing agent in GO and β-CD (Xu et al. 2010; Lu et al. 2015; Ye et al. 2015; Liu et al. 2014). In this work, a novel grafted material based on β-cyclodextrin with γ-(2,3-epoxypropoxy) propyl trimethoxysilane (GPTMS) functionalized GO was developed as shown in Figures 1 and 2. And GO was combined with β-CD through GPTMS. Eventually, β-CD/GPTMS/GO was synthesized successfully. And the adsorption behavior of the β-CD/GPTMS/GO sorbent was observed by considering Cu²⁺ as target metal and the mechanisms of surface interactions were investigated through atomic absorption spectrometry analyses. Most importantly, β-CD/GPTMS/GO exhibits a very good adsorption for Cu²⁺ and provides a good application prospect in Cu²⁺ removal.

**EXPERIMENT**

Reagents

Study materials are as follows: natural graphite powder (provided by Chengdu Organic Chemistry limited company of Chinese Academy of Sciences), GPTMS, acetone, acetic acid, N,N-dimethylformamide, sodium hydroxide, acetic acid, diphenylcarbazide (DPCI), and 4-azidophenylpropionamide (4-APP). The average molecular weight of β-CD was 1,134.98. Concentrated sulfuric acid (H₂SO₄, 98%), phosphoric acid (H₃PO₄), potassium permanganate (KMnO₄), sodium nitrate (NaNO₃), copper sulfate pentahydrate (CuSO₄·5H₂O), hydrogen peroxide aqueous solution (H₂O₂, 30%), anhydrous ethanol (analytical reagent grade), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were obtained from Chengdu Kelong Chemical Reagent Factory.

**Synthesis of β-CD-grafted GO hybrid material**

The GO was synthesized by modified Hummers method (Chen et al. 2013) from natural graphite powder. The functionalized β-CD was obtained by this method (He et al. 2014). The synthetic route and synthesis mechanism are shown in Figure 1(a) and 1(b). β-CD/GPTMS (2.0 g) was dissolved in 30 mL deionized water, and the pH of the solution was adjusted to 4–6 with acetic acid solution, and stirred for 1 h to obtain the product of hydrolysis. GO (0.5 g) was added to the solution and dispersed by ultrasonic cleaners.
for 30 min; then, the suspension was refluxed at 85 °C for 10 h. The resulting solution was rinsed repeatedly with a large amount of deionized water to remove the unreacted β-CD/GPTMS and then filtered to give rise to the β-CD/GPTMS/GO supramolecular hybrid material. The schematic reaction of β-CD/GPTMS and GO is illustrated in Figure 2.

Characterization

Fourier transform infrared (FT-IR) spectra of GPTMS, β-CD, β-CD/GPTMS and β-CD/GPTMS/GO were recorded on an FT-IR spectrometer (WQF-520, Beijing) to characterize their structures. X-ray diffraction (XRD) analysis was measured using a Pert Pro diffractometer (The Netherlands) with Copper Ka radiation source; the scanning rate was 2°/min, and scanning range was about 5–70°. Thermo gravimetric analyzer (TGA) was recorded on a TGA/SDTA851 (METTLER, Switzerland) in the range of 50–800 °C. The morphologies, structure and energy dispersive X-ray (EDX) analysis of GO, β-CD, β-CD/GPTMS and β-CD/GPTMS/GO were examined by scanning electron microscopy (SEM, JSM-7500F).

Adsorption studies

To study the influence of parameters such as the contact time, pH, contact temperature and ion initial concentration for the removal of Cu²⁺, the batch experiments were conducted as follows: A specified amount (5 mg) of β-CD/GPTMS/GO adsorbent was added to 50 mL of a solution containing a specified concentration of the Cu²⁺ at room temperature, and the mixture was stirred for 220 min to allow the mixture to equilibrate. The effect of pH on the adsorption of Cu²⁺ was studied over the range of 2–12 and the solution pH was changed by adding 0.1 M HCl and 0.1 M NaOH solution. The effect of the adsorption was conducted at five different temperatures (303, 308, 313, 318 and 323 K) (Huang et al. 2016; Kalinke et al. 2016) with the same contact time, same solution pH and same concentration. The Cu²⁺ concentrations that were tested ranged from 5 to 200 mg/L⁻¹. The adsorption capacity (Wang et al. 2014a) was calculated using the following mass balance equation (Kampilanonwat & Supaphol 2014):

\[
Q_e = \frac{C_0 - C_e}{W} \times V
\]

where \( Q_e \) (mg/g) is the equilibrium adsorption capacity per gram dry weight of the adsorbent; \( C_e \) (mg/L) is the equilibrium Cu²⁺ concentration and \( C_0 \) (mg/L) is the Cu²⁺ initial concentration; \( V \) (L) is the volume of Cu²⁺ solution and \( W \) (g) is the dry weight of the adsorbent.

\[
Q_e = \frac{C_0 - C_t}{W} \times V
\]

where \( Q_e \) (mg/g) is the amount of adsorbed Cu²⁺ per gram dry weight of the adsorbent at any time; \( C_t \) (mg/L) is the Cu²⁺ concentration at the time (t) and \( C_0 \) (mg/L) is the Cu²⁺ initial concentration; \( V \) (L) is the volume of Cu²⁺ solution and \( W \) (g) is the dry weight of the adsorbent.

Adsorption isotherms and dimensionless constant separation factor

In this work, Langmuir and Freundlich isotherms are used to describe the equilibrium adsorption between the liquid and solid phases. The most important parameter of model designs for the adsorption experiment had been successfully applied to describe the adsorption process.

The Langmuir isotherm can be expressed as Equation (1)

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}},
\]

and the Freundlich isotherm can be expressed as Equation (2)

\[
\ln q_e = \ln K_F + \left( \frac{1}{n} \right) \ln C_e,
\]

where the \( q_{max} \) is the maximum adsorption capacity, \( Ce \) is the adsorption concentration of Cu²⁺, \( K_L \) is the Langmuir adsorption constant (L mg⁻¹), and \( K_F \) and \( n \) are the Freundlich constant related to the adsorption capacity and the adsorption intensity, respectively.

In addition, the essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor \( (R_L) \) given by the following equation:

\[
R_L = \frac{1}{1 + K_L C_0}
\]

where \( K_L \) (L mg⁻¹) is the Langmuir constant and \( C_0 \) (mg L⁻¹) is the initial concentration in the liquid phase. The value of \( R_L \) indicates the shape of the isotherm to be either unfavorable \( (R_L > 1) \), linear \( (R_L = 1) \), favorable \( (0 < R_L < 1) \) or irreversible \( (R_L = 0) \) (Ai et al. 2011).
RESULTS AND DISCUSSION

Characterizations of materials

Figure 3 shows the FT-IR curve of GPTMS, β-CD, β-CD/GPTMS and β-CD/GPTMS/GO, respectively. From the FT-IR curve of β-CD/GPTMS, 753 cm⁻¹ is the weak absorption peak and 1,085 cm⁻¹ is the stretching vibration of Si-O-Si. 2,939 cm⁻¹ and 2,871 cm⁻¹ are attributed to the characteristic peaks of -CH₃ and -CH₂ of the GPTMS. This result certificated that the β-CD powders were modified by GPTMS successfully. The abundant oxygen-containing functional groups exist on the surface of GO (Wang et al. 2014b), such as O-H, –COOH group and C-O-C group. From the FT-IR spectrum of β-CD/GPTMS/GO could be seen the characteristic peaks of β-CD/GPTMS and GO. All the peaks indicated that β-CD/GPTMS/GO had been successfully synthesized.

As is displayed in Figure 4(a), β-CD showed high intensity diffraction peaks with main diffractions at 6.26°, 9.21°, 12.65°, 17.19° and 21.13° (2θ). On the other hand, as shown in Figure 4(a), β-CD/GPTMS also presented a larger amorphous phase except for some characteristic peaks of β-CD. This could certify that β-CD was modified by GPTMS successfully. If the β-CD was mixed with GPTMS by a simply physical method, then the XRD diffraction patterns would only render the diffraction peaks of β-CD, whereas the results of β-CD/GPTMS showed that part of the β-CD diffraction peak (2θ = 6.26°, 12.65°, 17.19°) and other diffraction peaks disappeared. The analysis of XRD could reveal that β-CD had reacted with GPTMS and a new compound had been formed (He et al. 2014); this result was consistent with FT-IR.

Figure 4(b) illustrates the XRD patterns of GO and β-CD/GPTMS/GO samples. As shown in Figure 4(b), the GO has an intense crystalline peak (Park et al. 2015) at 9.98° (001) and 42.35° (100), corresponding to d-spacing of 0.886 nm. The interlayer spacing of GO sheets can be attributed to its oxygenated functional groups introduced by the modified Hummers method. The characteristic peak of GO changed to a wide peak by reacting with β-CD/GPTMS, so a new bond had been formed. The characteristic peak of GO and β-CD also can be detected as shown in Figure 4(b), indicating that the emergence of β-CD characteristic peak and the change of the peak intensity fully demonstrated the success of β-CD modified GO.

Figure 5 provides the TGA curves. As for β-CD, the first stage of a sharp decrease in weight upon heating occurs with increasing temperature to 110 °C, which can be attributed to the hydrophilicity derived from hydrophilic groups on the outside wall. The β-CD presents a manifest weight loss around 300 °C, which is due to the decomposition of β-CD.
(corresponding to a weight loss of 68.00 wt. %). There is not a marked weight loss in the TG curves of β-CD/GPTMS because of no hydrophilic groups, and the weight loss is 59.75 wt. %. The TGA curve of GO exhibited three obvious steps of mass loss as in literature (Botas et al. 2013); the weight loss before 100 °C is caused by the release of trapped water in these materials. The weight loss of GO starts from 1,100 °C to 300 °C (corresponding to a weight loss of about 24.83 wt. %). The functionalization of GO affords a much higher heat resistance to β-CD/GPTMS/GO (as compared with GO). The content of the β-CD/GPTMS/GO can be calculated as 45.47 wt. % based on the weight-loss stage assigned to the thermal decomposition of the grafted β-CD/GPTMS. It is likely that there are intermolecular interactions between β-CD and GO such as intermolecular hydrogen bonding interactions. Thus, β-CD grafted on GO surfaces could enhance the heat resistance of GO.

The as-prepared powder of GO had typical crumpled wave-like sheets, which was the intrinsic nature of graphene, as observed by SEM (Figure 6(a)). Its crumpled sheets seemed to be unfolded to some extent, due to the existence of many oxygen-containing groups on the surface of GO. The β-CD was structured block, and some cracks existed on the surface of β-CD (Figure 6(b)). The surface of β-CD was covered by a ‘wedding dress’ (Figure 6(c)), thus indicating that modification of β-CD was successful with GPTMS and a new compound had been formed; this also was consistent with FT-IR, XRD and TG. As shown in Figure 6(d), the structure of GO was not broken; the β-CD/GPTMS material was loaded on the surface of GO and was marked by black circles in Figure 6(d).

**Adsorption experiment studies**

**Effect of contact time**

The contact time of Cu^{2+} solution is an important parameter of the adsorption process, as shown in Figure 7. The
adsorption capacity increased dramatically with time at 0–50 min, while the amount of Cu$^{2+}$ ions adsorbed by β-CD/GPTMS/GO had little change and all showed high adsorption efficiency after 60 min. The high adsorption efficiency could be due to the nonporous nature of GO and the abundant surface functional groups on the nano-material. There is another reason for the high adsorption efficiency of β-CD/GPTMS/GO: that the cavity structure of β-CD could load Cu$^{2+}$ and some functional groups on the surface of β-CD, meaning that the β-CD could enhance the adsorption efficiency of the GO. The result indicated that β-CD/GPTMS/GO had an excellent adsorption of Cu$^{2+}$ and reached equilibrium at 60 min.

**Effect of pH**

Figure 8 shows the effect of pH on the adsorption of Cu$^{2+}$ ions. The surface charge of β-CD/GPTMS/GO was affected by the initial solution pH because of the oxygen-containing groups it contains (Deng et al. 2013; Wang et al. 2013). Adsorption experiments were conducted using pH range 2.0–12.0, to observe optimal pH and achieve the maximum adsorption capacity for Cu$^{2+}$. As shown in Figure 10, the adsorption capacity of Cu$^{2+}$ ions increases with the increasing of solution pH. This might be due to less negligible competitors, such as H$^+$. However, with the further increasing of pH from 8 to 12, the adsorption capacity of Cu$^{2+}$ became more and more high. This could be attributed to the formation of Cu(OH)$_2$. The adsorption of heavy metal was discussed only in the form of ions in this research; therefore, a pH of 7 was selected for further studies, to maintain a near neutral pH value in the Cu$^{2+}$ solution.

**Effect of temperature on adsorption capacity of adsorbent**

The adsorption temperature is another important role in the adsorption process (Konicki et al. 2012). In order to study the effect of temperature, five different temperatures (298 K, 303 K, 308 K, 313 K and 318 K) were designed for the experiment at pH 7.0 for 60 min. As shown in Figure 9, the adsorption capacity of Cu$^{2+}$ increased from 42.956 mg/g to 44.795 mg/g with the temperature increasing from 298 K to 318 K, which could be attributed to the moveability of β-CD/GPTMS/GO increasing with the increase of temperature, so that the adsorption capacity of Cu$^{2+}$ ions was related to the contact degree with those active groups on the surface of β-CD/GPTMS/GO. However, the adsorption capacity of Cu$^{2+}$ at 308 K and 313 K is slightly less than at 303 K, due to the moveability of β-CD/GPTMS/GO being
accelerated so that some adsorptive Cu\textsuperscript{2+} was separated from the surface of β-CD/GPTMS/GO. The maximum adsorption of β-CD/GPTMS/GO was 44.795 mg/g at 318 K.

### Adsorption isotherms

The adsorption isotherm is shown in Figure 10. The two models were fitted to the adsorption of Cu\textsuperscript{2+} by the β-CD/GPTMS/GO, and the interrelated parameters are shown in Table 1. The R\textsuperscript{2} value of Langmuir was higher than for Freundlich, indicating that Langmuir isotherms fitted the experimental data better than Freundlich isotherms, and the maximum adsorption capacity of Cu\textsuperscript{2+} is 352.7105 mg·g\textsuperscript{-1}. Furthermore, it is considered to be a favorable adsorption process when the R\textsubscript{L} value is within the range 0–1. And the R\textsubscript{L} value in this work is from 0.02857 to 0.85471, indicating that the adsorption of Cu\textsuperscript{2+} onto β-CD/GPTMS/GO is advantageous, and the n value of Freundlich model is >2, which supports the favorable adsorption of Cu\textsuperscript{2+} by β-CD/GPTMS/GO. The above results suggest that the Langmuir model is better fitted to the adsorption model of β-CD/GPTMS/GO to remove Cu\textsuperscript{2+} ions.

#### Removal mechanism

The adsorption performance of β-CD/GPTMS/GO is apparent from the adsorption experiment. There are three mechanisms by which Cu\textsuperscript{2+} can be removed from solution by β-CD/GPTMS/GO (Figure 11), and these are described below. (1) The hydroxyl and carboxyl groups on the surface of GO and β-CD result in the nanosheets having a negatively charged surface (Bradder et al. 2014). Cu\textsuperscript{2+} is cationic. Therefore, the adsorption of Cu\textsuperscript{2+} onto β-CD/GPTMS/GO may be attributed to electrostatic attraction. (2) The structure of β-CDs can enable them to bind Cu\textsuperscript{2+} into their cavities to form stable host-guest inclusion complexes. (3) GO as one of the carbon materials with high surface area and functional groups can remove Cu\textsuperscript{2+} from solution, which is attributed to ion exchange adsorption between GO and Cu\textsuperscript{2+} in the solution.

### Table 1 | Parameters for Langmuir and Freundlich isotherms model

<table>
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<tr>
<th>Ion</th>
<th>Adsorbent</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu\textsuperscript{2+}</td>
<td>β-CD/GPTMS/GO</td>
<td>352.7105</td>
<td>132.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1700</td>
<td>5.32</td>
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<td>0.9999</td>
<td>0.98706</td>
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#### Figure 10 | The adsorption isotherms of Cu\textsuperscript{2+} adsorbed by β-CD/GPTMS/GO at initial heavy metal ions concentration from 1 to 200 mg/L, adsorbent dose 5 mg, pH 7.0 and room temperature for 60 min. The data from the experiment have been fitted by Langmuir and Freundlich models.

#### Figure 11 | Proposed removal mechanism of Cu\textsuperscript{2+} by β-CD/GPTMS/GO nanocomposite.
CONCLUSIONS

β-CD/GPTMS was successfully modified and β-CD/GPTMS/GO was synthesized by a facile esterification reaction in solution using GO as a base. The β-CD was modified by GPTMS through the epoxy groups of GPTMS with the -OH of β-CD. The β-CD/GPTMS/GO was attached to GO nanosheets through the hydroxy of GPTMS silicon esterification reaction with the carboxyl of GO. It is a new way to connect β-CD with GO using GPTMS. The β-CD/GPTMS/GO showed remarkable adsorption performance under neutral condition (pH 7), which might provide the site for the adsorption and enhance the dispersion of GO due to the presence of β-CD and GPTMS on the GO. The β-CD/GPTMS/GO could remove Cu$^{2+}$ through electrostatic attraction, host-guest inclusion complexes and the ion exchange adsorption. The material had some advantages, including effective adsorption and being environment friendly. This study will provide a referential strategy to design function of GO, which is a very promising candidate for the application in the field of the cationic removal from aqueous solutions under moderate conditions.

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