Preparation of cyclodextrin-modified graphene oxide and its adsorption properties for Pb (II)

Lingcong Li, Bing Chen, Ziwen Su, Jinmei Wu, Zhenxing Pan, Zhiping Fu*

School of Chemistry & Environment Engineering, Shaoguan University, Shaoguan city, Guangdong Province, 512005, China

*Corresponding author’s e-mail: 461285396@qq.com

Abstract. In this paper, the improved Hummers method was used to prepare graphene oxide (GO) and modified by cyclodextrin to prepare cyclodextrin-modified graphene oxide (CDGO) composites. The composites were characterized by Fourier transform infrared spectroscopy (FTIR) and X-ray powder diffraction (XRD). The adsorption properties of GO and CDGO for Pb\(^{2+}\) were measured by atomic absorption spectrophotometer. The results showed that the number of functional groups of the modified material and the adsorption sites increased. The adsorption capacities of GO and CDGO for lead were respectively 86.47 mg/g and 165.52 mg/g, which were consistent with the quasi-secondary kinetic model and Langmuir isotherm adsorption model. CDGO showed better adsorption capacity.

1. Introduction
Heavy metal pollution is one of the most harmful water pollution problems [1]. Heavy metals are highly toxic and metabolize very slowly in the environment, which is easy to be bio-enriched and will eventually magnify the harm [2]. The content of Pb (II) in drinking water should not exceed 0.05 mg/L [3], and long-term exposure to Pb (II) for adults may lead to hypertension, tooth and kidney damage [4].

There are various treatment methods for heavy metals in water, including chemical precipitation, adsorption, electrolysis, ion exchange and biological treatment. In industrial production, adsorption is highly competitive and is the most commonly used method to treat metal pollution [5]. Graphene oxide (GO) exhibits excellent adsorption properties in heavy metal ion adsorption [6-8]. GO has a large number of oxygen-containing functional groups on its surface, which can introduce a variety of chemicals with specific properties on the GO surface, such as macromolecules, inorganic nanomaterials and bio-molecules, so as to achieve the purpose of modification and obtain functional GO composites that can be applied in various fields.

Cyclodextrins (CD) is a natural circular oligosaccharide formed by starch under the action of cyclodextrin glucosyltransferase [9-12]. Cyclodextrin was grafted onto the surface of GO as a carrier material to prepare the cyclodextrin-graphene oxide (CDGO) composite material. The composite material has good mechanical properties and large specific surface area, which increased the envelope site of cyclodextrin molecule. CDGO has the characteristics of large adsorption capacity, easy separation and good adsorption effect. It can be used in the separation and enrichment of heavy metals in wastewater and the treatment of organic wastewater. It provides a simple and feasible method for environmental pollution treatment and waste recycling.
2. Experiment

2.1. Chemicals
Flake graphite of 325 meshes from Qingdao Jinrilai Graphite Co., Ltd was used to prepare GO. β-cyclodextrin, potassium permanganate, nitric acid, barium potassium tartrate, lead nitrate and pyridine were purchased from Da Mao Chemical Reagent Factory. 98% concentrated sulfuric acid and 37% hydrochloric acid were purchased from Kaixin Chemical Reagent Co., Ltd. All the reagents were reagent grade and used without further purification.

2.2. Preparation of GO
Firstly, dried graphite powder (2 g) was slowly added to a flask containing concentrated H₂SO₄ (60 mL) under agitation. After stirring at 7 °C for 10 min, KMnO₄ (12 g) was added gradually, and the flask was kept under low temperature condition for 2 h. Then, the temperature of the water bath was raised to 39 °C and the reaction was continued for 3 h. After that, deionized water (180 mL) was added, and the temperature of the water bath was raised to 80 °C for 20 minutes under stirring. An appropriate amount of 30 % H₂O₂ was add to the reactor and the color of the solution was changed to brilliant yellow. Then deionized water (2000 mL) was added to the mixture. After left to stand and clearly stratifying, the supernatant of the solution was poured out. The GO was then obtained by centrifugation and washing with 5% hydrochloric acid and deionized water to PH=7. Finally, the as-prepared GO was vacuum dried at 60 °C and grounded to powder for use.

2.3. Preparation of cyclodextrin graphene oxide (CDGO)
The β-cyclodextrin was immobilized in an alkaline medium by using epichlorohydrin as a crosslinking agent, and a water-insoluble cyclodextrin-modified graphene oxide CDGO was synthesized.

2.4. Adsorption experiment on Pb (II)
The absorbance of a series of standard solutions was measured by an atomic absorption spectrophotometer to obtain a Pb²⁺ standard curve. The condition wavelength was 283.3nm, and the current of the hollow cathode lamp was 3 mA. The optimal input of lead ions, adsorption kinetics and isothermal adsorption experiments were investigated using flame atom.

3. Results and discussion

3.1. Structure Characterization
Figure 2. Infrared spectrum of natural graphite, GO, β-CD and CDGO.

Figure 3. XRD pattern of natural graphite, GO and CDGO.

It can be seen from Figure 2 that in the infrared spectrum of β-CD, the strong peaks at 3389 cm\(^{-1}\) and 1032 cm\(^{-1}\) were respectively attributed to the associated hydroxyl group and the stretching vibration peak of the hydroxyl group. Compared with CDGO infrared spectra, in addition to maintaining the overall structure of β-CD, the corresponding peak at 1732 cm\(^{-1}\) was the C=O stretching vibration in the carbonyl group or carboxyl group in the layered structure of GO. It was indicated that the addition of β-CD affects the chemical structure of the composite material. CDGO possesses active oxygen-containing functional groups such as carbonyl, carboxyl, hydroxyl and epoxy groups, which was beneficial to the adsorption of heavy metal ions.

It is seen from the XRD patterns in Figure 3 that graphite has a strong diffraction peak at 2θ = 26.48°, which is a characteristic peak of graphite. It shows that the spatial structure of the crystallites of graphite is very regular and the degree of crystallization is high. Compared with graphite, GO showed a slightly broad characteristic diffraction peak with a very high intensity near 2θ=10.46°, while the peak at 2θ=26.46° almost disappeared. This is because in the oxidation process, the graphite is sufficiently oxidized, the original crystal shape is destroyed, and a large amount of oxygen-containing groups are inserted into the molecule to form an interlayer compound, and a new crystal structure is formed. CDGO showed the characteristic peak of GO at 2θ=10.04°, indicating that the modification did not significantly change the layer spacing. Meanwhile, CDGO showed 2θ=26.46° diffraction peak, suggesting that the reaction between β-CD and GO resulted in the change of complex structure.

3.2. Adsorption of Pb (II) by GO and CDGO

3.2.1. Standard curve of Pb (II)
The linear equation of Pb\(^{2+}\) standard curve was A=0.0118C+0.0085, residual the sum of squares was R\(^2\) = 0.9975.

3.2.2. Optimal inputs of GO and CDGO to Pb (II) adsorption
The influence of GO input on the removal of Pb\(^{2+}\) was shown in Figure 4. With the increase of GO and CDGO input, the adsorption sites of Pb\(^{2+}\) supplied per unit volume will be more, which strengthens the probability of Pb\(^{2+}\) contacting and combining with active sites, leading to the rapid increase of removal rate. When the mass of adsorbent increased to a certain amount, the adsorption rate of Pb\(^{2+}\) in the solution no longer changed significantly. The possible reason is that too much adsorbent will trigger aggregation, so that the effective surface area and the effective adsorption sites of the adsorbent are correspondingly reduced. When the input of CDGO was 0.03g, the removal rate of Pb\(^{2+}\) was about 95%, close to the peak value. So the optimum CDGO dosage is between 0.03 and 0.04 g.
The Figure 5 shown that the GO and CDGO to reach adsorption equilibrium in a short period of time. When the oscillation time is within 10 minutes, the removal rate of Pb$^{2+}$ by the adsorbent is very fast. This was because in the initial stage of adsorption, there was a large amount of active site for chelating heavy metal ions on the adsorbent. And the concentration of lead ions was relatively large at this time, so that the adsorption capacity of the adsorbent on Pb$^{2+}$ was particularly strong. However, the adsorption capacity tended to be stable after 20 min. The possible reason was that on the one hand, with the progress of adsorption, the active sites on the adsorbent decrease, and the concentration of Pb$^{2+}$ decreases, leading to a decrease in the probability of their chelation; on the other hand, as the adsorption proceeds, the proton H$^+$ on the reactive functional groups (amino, hydroxyl, carboxyl, etc.) on the adsorbent was released into the solution, resulted in a decrease in the pH of the water sample and a weakened electronegativity of the solution, which hindered the adsorbent's adsorption of Pb$^{2+}$ and extended the adsorption time to reach equilibrium. At 120 min, the adsorption capacity of GO on Pb$^{2+}$ was 70.17mg/g, and CDGO on Pb$^{2+}$ was 120.84 mg/g.

![Figure 4. The effect of GO dosage on the removal of Pb$^{2+}$.](image1)

![Figure 5. Effect of time on the adsorption of Pb$^{2+}$.](image2)

It could be seen from Figure 6 and 7 that the correlation coefficient R$^2$ of GO and CDGO aligned with the secondary kinetic model was 0.999, while the R$^2$ of the quasi-primary kinetic model was 0.731, 0.692 and 0.486, respectively. The adsorption of Pb$^{2+}$ by GO and CDGO was more consistent with the quasi-secondary kinetic model, that was, the control of chemical adsorption rate. The theoretical equilibrium adsorption capacities q$^e$ of GO and CDGO were 70.42 mg/g and 120.77 mg/g, respectively, which were substantially equal to the actual equilibrium adsorption capacities of 69.58 mg/g and 120.25 mg/g.

![Figure 6. Pseudo-first-order adsorption kinetics.](image3)

![Figure 7. Pseudo-second-order adsorption kinetics.](image4)
3.2.3. Isothermal adsorption curves and Thermodynamic analysis of Pb (II) by GO and CDGO

The isotherm adsorption curves of GO and CDGO for Pb\(^{2+}\) were shown in Figure 8. The maximum saturated adsorption capacities of GO and CDGO for Pb\(^{2+}\) were 86.47 mg/g and 165.52 mg/g, respectively. As the concentration of Pb\(^{2+}\) increases, the mass transfer driving force between the adsorbent and Pb\(^{2+}\) also increases, so the easier it was for Pb\(^{2+}\) to enter the active site on the surface of the adsorbent. However, since the adsorption sites on the surface were limited and the concentration of Pb\(^{2+}\) was over high, the hydrolysis of Pb\(^{2+}\) occurs easily in water, and the removal rate of Pb\(^{2+}\) would decrease. GO and β-CD were linked together by epichlorohydrin, which not only retained the adsorption site of GO, but also introduced the outer hydrophilic -OH of β-CD, and had chelation effect on high-priced metal ions and facilitated the adsorption of lead ions.

![Figure 8. Isothermal adsorption curves of GO and CDGO on Pb\(^{2+}\).](image)

![Figure 9. Langmuir isotherm adsorption model of Pb\(^{2+}\) by GO and CDGO.](image)

Figure 9 were the Langmuir isotherm adsorption model for Pb\(^{2+}\), respectively. The correlation coefficients R\(^2\) of the Langmuir isotherm adsorption model for GO and CDGO were 0.9976 and 0.9288. From the correlation coefficient R\(^2\), it could be concluded that the adsorption of GO and CDGO were more consistent with the Langmuir isotherm adsorption model.

4. Conclusions and prospects

In summary, GO with high oxidation degree was prepared by modified hummer method, and cyclodextrin-graphene oxide (CDGO) composite was prepared from GO, which has good adsorption effect and good anti-caking property. The results shows that the maximum adsorption capacity of CDGO for Pb\(^{2+}\) in aqueous solution is 165.52mg/g, which is about twice the maximum adsorption capacity of GO. The adsorption of GO and CDGO were more consistent with the quasi-secondary kinetic model and Langmuir isotherm adsorption model. CDGO has a short adsorption time for Pb\(^{2+}\) and a large adsorption capacity, which leads to good application prospects for CDGO in removing heavy metals from water.

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