Effect of the oxygen-containing functional group of graphene oxide on the aqueous cadmium ions removal

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ABSTRACT

The adsorption process of graphene oxide (GO) with oxygen-containing functional groups towards cadmium ions was investigated. GO synthesized from graphite by using the modified Hummers method was characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), Fourier transform infrared spectrometer (FT-IR) and X-ray photoelectron spectroscopy (XPS). The oxygen-containing groups on the surfaces of GO played an important role in Cd(II) ion adsorption onto GO. The results of batch experiments indicated that maximal adsorption, which was found to be 23.9 mg/g, could be achieved over the broad pH range of 6.0–7.0. Adsorption isotherms were better fitted by Freundlich model than by Langmuir model and kinetic studies suggested that adsorption was controlled by chemical adsorption. According to FT-IR and XPS analyses of before and after Cd(II) adsorption on GO, electrostatic attraction and cation exchange between Cd(II) and O-containing functional groups on GO were the dominant mechanisms responsible for Cd(II) sorption.

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1. Introduction

Heavy metal pollution is a common environmental problem that will destroy the living surrounding. Numerous metals such as mercury, lead, cadmium, etc. are known to be highly toxic. Cadmium like other heavy metals can be introduced into surface waters in amounts significant to human health by industrial effluents [1].

Graphene, a planar monolayer of carbon atoms, possesses large surface area, excellent electrical, thermal and mechanical properties and becomes the hotspot in multidisciplinary field [2–4]. It can be prepared from graphite, a low-cost material. In the family of graphene derivatives, graphene oxide (GO) is a single sheet form graphite and has the ideal 2D structure with a monolayer of carbon atoms packed into a honeycomb crystal plane [5]. And the specific surface area of GO is up to $2620 \, m^2/g$ [6]. Graphene oxide, produced by the oxidation of graphite, contains a range of reactive oxygen functional groups, e.g. epoxides, hydroxyl, carbonyl, and carboxyl groups [7].

Recent reports show that oxygen groups on GO play a major role in metal ions sorption, especially the multivalent metal ions [8–10]. Few-layered GO nanosheets were used to remove Cd(II) ions from aqueous solutions [11]. Cd(II) sorption was considered to mainly take place at oxygen-containing functional groups. The maximum sorption capacity of Cd(II) on GO nanosheets at pH 6.0 ± 0.1 and $T = 303 \, K$ reached up to 106.3 mg/g. Yang et al. reported a huge Cu(II) adsorption capacity of GO via an aggregation process caused by the oxygen groups binding to Cu(II) [12]. GO has an adsorption capacity for Cu(II) approximately 10 times of active carbon. However, the chemical nature of the interaction between the oxygen-containing functional groups on GO and the heavy metals is not yet understood well.

The present work aims to analyze the role of the oxygen-containing functional groups on GO in the adsorption of Cd(II). Batch experiments were performed to evaluate the effect of the contact time and the initial pH value on the Cd(II) sorption by the carbons. The Cd(II) adsorbed GO was also investigated by FT-IR and XPS to further study the Cd(II) adsorption mechanisms.

2. Materials and methods

2.1. Materials

All of the chemical reagents used in this study were of analytical grade. A Cd(II) stock solution of 1000 mg/l was prepared

by dissolving 1000 mg cadmium powder in a nitric acid solution. Experimental solutions of the desired concentration were obtained by the appropriate dilution of the stock solution.

2.2. Preparation of graphene oxide

GO was prepared by using the modified Hummers method from the natural graphite using concentrated H_2SO_4 and $KMnO_4$ to oxidize the graphite layer. Briefly, 1.0 g of $NaNO_3$ was dissolved in 50 ml of H_2SO_4, then 1.0 g of graphite was added slowly with stirring in an ice–water bath and kept 30 min after dissolved completely, and 18.0 g of $KMnO_4$ was slowly added over about 30 min. Then 50 ml deionized water was added over about 1 h with stirring at $T = 309 \pm 1$ K, and the mixture was further stirred for 2 h at 309 ± 1 K. Then the solution was heated in water bath at 368 K for 30 min. After that, 180 ml deionized water was added to the mixture, and 20 ml of H_2O_2 (30 wt%) was added in the suspension slowly. The desired products were rinsed with HCl (10% v/v) and ultrapure water. The centrifugation and ultrasonication were recycled for several times until the pH reached a constant value. The desired products were dried at 333 K for 24 h, and thus the graphene oxide was derived.

2.3. Characterization methods

Surface topography and the microcomposition analysis were conducted on a HITACHI-S4800 scanning electron microscope equipped with an Oxford X-ray energy dispersive spectroscopy (EDS) system. The AFM images were obtained with a XE-100. Diluted GO was coated onto exfoliated mica to dry in ambient atmosphere for AFM measurement. The infrared transmittance spectra in the range between 400 and 4000 cm^{-1} were collected using a Nexus 670 spectrometer in KBr pellet state. The spectrum of pure KBr pellets prepared under identical conditions as for the sample pellets was subtracted to avoid the influence of water absorbed by the KBr powder. The XPS spectra were obtained using an ESCALAB 250Xi Physical Electronics spectrometer. The photoelectron spectra were analyzed with a hemispherical mirror assuring an energy resolution of approximately 0.5 eV. Five hours after placing the samples in situ at 10^{-7} Pa vacuum, their surface was clean enough for measurements. The binding energy in the range of −10 to 1350 eV and the core-level characteristic peaks for C 1s and O 1s were measured. The background was subtracted using Shirley's approximation. The concentrations of the Cd(II) ions in batch experiments were determined using an AFS-230E atomic fluorescence spectrometer.

2.4. Batch experiments

2.4.1. Determination of point of the zero charge (pHpzc)

For the determination of pHpzc, a defined amount (10 mg) of adsorbent was suspended in 10 ml of a 0.1 M $NaNO_3$ solution, used as an inert/background electrolyte in a 50 ml stopper conical flask. The initial pH of the solution was adjusted to 3.0 using 0.01 M HNO_3 or 0.01 M NaOH. The suspension was allowed to equilibrate for 4 h at 200 rpm in a shaker bath at room temperature (293 ± 1 K). After completion of the equilibration time, the mixture was filtered, and the final pH value of the filtrate was measured. This set of experiments was performed at a pH interval of 1.0.

2.4.2. Adsorption experiments

The batch adsorption experiments were performed with 10 mg of GO and 10 ml of aqueous Cd(II) solutions with desired concentrations and in appropriate pH. The initial pH was adjusted by the addition of 0.01 M HCl or 0.01 M NaOH to the desired pH values. Then the suspensions were shaken in an oscillator at 200 rpm for
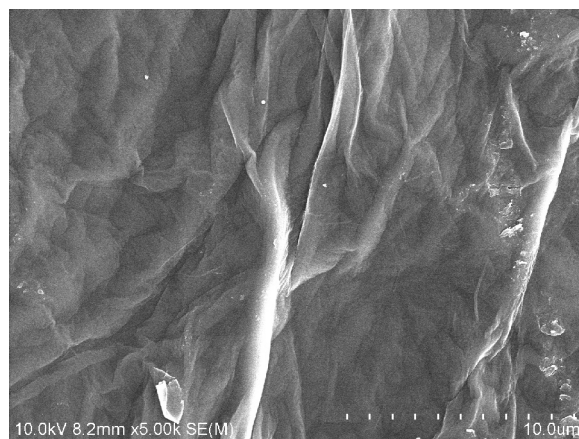

Fig. 1. SEM micrograph of the GO.

4 h to achieve adsorption equilibration. After equilibrium, the residual aqueous Cd(II) concentrations in solutions were determined by atomic fluorescence spectroscopy. The uptake amount of Cd(II) at equilibrium (Q_e, mg/g) was calculated by the equation:

$$Q_e = \frac{(C_0 - C_e)V}{W}$$

where C_0 and C_e are the initial and equilibrium concentration of Cd(II) (mg/l), respectively; V is the solution volume (L); and W is the mass of adsorbent used (g).

3. Results and discussion

3.1. Characterization of GO

Fig. 1 shows the SEM image of the GO. It was obvious that the structure of GO was layered with some crumples and partially transparent. Elemental analysis of GO by SEM/EDS revealed the presence of 57.3 at% of C and 42.7 at% of O as the basic elements. This result indicated that a considerable amount of oxygen-containing functional groups present on the surface of GO.

According to AFM image (Fig. 2), the thickness of GO nanosheets was approximately 1.9 nm corresponding to two layers. Because the thickness of monolayer GO nanosheet was reported as approximately 0.8–1.0 nm [13]. After the Cd(II) adsorption, many apophyses could be observed. The result should be caused by the adsorbed Cd(II) and demonstrated that Cd(II) was adsorbed onto the surface of GO.

In the FT-IR spectrum (Fig. 3), the absorption bands at 1620 cm^{-1} (C=C) [6] and 1363 cm^{-1} (C—OH) [14] could be both seen before and after Cd(II) adsorption. The absorption band at 1730 cm^{-1} on the GO surfaces attributed to the C=O stretching modes of carboxyl groups became shifted and weaker after Cd(II) adsorption suggesting some carboxyl groups on the GO consumed by sorption [15].

XPS was employed to identify the coordination types between Cd(II) and these functional groups. The XPS spectra of C 1s and O 1s were presented in Fig. 4a and b. The C 1s spectra of the GO indicated a considerable degree of oxidation with different functional groups: (C-I) C—C at 284.79 eV, (C-II) C—O (phenolic, alcohol and ether) at 286.77 eV and (C-III) O=C—O (carboxyl and ester) at 288.38 eV [16]. The O 1s spectra of the GO were composed of two types of peaks with differentiated binding-energy values corresponding to (O-I) C—OH or C—O—C at 532.60 eV and (O-II) C=O at 531.14 eV [17].

After the Cd(II) adsorption, the binding energy of O-I and O-II on the surfaces of GO shifted from 532.60 and 531.14 eV to 532.94 and 531.42 eV, respectively, indicating that the O atom was an electron donor when the interaction takes place [18]. Additionally, some