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The synthesis of graphene oxide functionalized with dithiocarbamate group and its prominent performance on adsorption of lead ions

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ABSTRACT

A novel adsorbent, dithiocarbamate group functionalized graphene oxide (DTC-GO), was prepared to promote the adsorption efficiency for Pb(II) ions in aqueous solution. To get insight of the structure and property of DTC-GO, the technologies of Fourier Transform Infrared (FT-IR) Spectroscopy, Scanning Electron Microscopy (SEM), Thermal gravimetric analysis (TGA) and Raman spectra were used. All characteristic results verified the successful introduction of dithiocarbamate group on graphene oxide. The effects of contact time, solution pH, initial metal ions concentration and temperature on the adsorption of Pb(II) with DTC-GO were studied systematically. The adsorption models of isotherms and kinetics were employed to investigate the adsorption mechanism. Based on experimental data, Langmuir isotherm and pseudo-second-order kinetic models showed a better correspondence to the adsorption process. Furthermore, the maximum uptake of DTC-GO obtained from Langmuir isotherm reached to 132.01 mg/g. The values of ΔG^{θ} and ΔH^{θ} calculated from the experimental data indicated that the nature of the interaction between Pb (II) and DTC-GO was not only feasible and spontaneous but also exothermic in all cases.

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1. Introduction

The appearances of carbon materials have greatly pushed forward the development of our human society and brought much convenience in our daily life. As a member of carbon materials, graphene, a one-atom-thick 2D layer of sp^2-bonded carbon [1], has become a focus for its unique structure and excellent properties [2]. Its extraordinary physical and chemical properties [3, 4], such as the mechanical strength, electrical conductivity, thermal stability and large specific surface areas, motivate the potential applications of graphene in various fields, especially in adsorption of toxic contaminants from environments [5]. However, considering that graphene has poor dispersion in solvent, many researchers have devoted a great deal of effort to improve its performance. Graphene oxide (GO), as an oxidized form of graphene, possesses abundant functional groups on its surface, such as hydroxyl and carboxyl groups [6-8]. It is the reason why graphene oxide has the superiority to be a promising adsorbent and a superb precursor for the preparation of graphene composites.

As we all know, heavy metals such as lead, mercury, copper, zinc and cadmium have posed a great threat to us due to their adverse effect on human health and ecological systems. Being different from other pollutants, poisonous heavy metal ions are much easier to accumulate in human organisms and more difficult to be removed, which will make mortal damages to the tissues of our bodies [9]. In response to the problem of heavy metal pollution, various treatments, such as chemical precipitation [10], membrane separation [11], ion-exchange [12] and adsorption [13, 14], have been put into practice to remove heavy metals from aqueous solution. Among the conventional treatments, adsorption would be most suitably applied in removal of heavy metals [15] due to its eminent features of high effectiveness, simplicity, flexibility and low cost.

Of note, it is reported that the GO modified with suitable functional groups, especially the functional group containing sulphur, can better meet the desire to have outstanding adsorption ability and high efficiency for heavy metal ions [16]. This is because sulphur has a better affinity towards heavy metals through chelation in comparison with other functional groups [17, 18]. Based on the theory of hard and soft acids and bases (HSAB), dithiocarbamate, a soft base, could be used as selective adsorption material for removal of heavy metal ions. Additionally, the easier preparation and higher stability of dithiocarbamate modified GO make it more superior to other sulfur-bearing groups [19]. However, up till now, the dithiocarbamate group functionalized graphene oxide (DTC-GO) as the adsorbent to remove heavy metal ion has never been reported.

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The main purposes of this study are to recognize the excellent adsorption capacity and unique properties of DTC-GO. To satisfy these attempts, the technologies of FT-IR spectroscopy, TGA, SEM and Raman are utilized to obtain relative characteristics results. Furthermore, batch experiments are investigated to assess the performance and effectiveness of DTC-GO on removal of Pb(II) ions from aqueous solution. What is more, the adsorption models of isotherms and kinetics were used to investigate the mechanisms. And compared with other adsorbents reported in literatures, superior performances and advantages of DTC-GO on adsorption of Pb(II) ions are reflected.

2. Experiments

2.1. Materials and reagents

All the reagents used in this experiment were of analytical grade and used without further purification. Graphite (purity > 99.95%) were purchased from Shenzhen Nanotech Port Co., Ltd. The main reagents were lead nitrate, sodium ethoxide and carbon disulfide, which were obtained from Sinopharm Chemical Reagent Co., Ltd.

2.2. Preparation of GO and e-GO

The graphene oxide was synthesized according to a modified Hummers' method. Briefly, natural flake graphite was oxidized under the presence of mixed acid (concentrated H_2SO_4 and H_3PO_4) and $KMnO_4$. Before the reaction, 72 mL of concentrated H_2SO_4 and 8 mL of concentrated H_3PO_4 was well mixed in a beaker. Successively, the mixed acid was slowly added into a 150 mL round bottom flask containing 3 g $KMnO_4$ and 0.6 g flake graphite. The mixture in the flask was stirred to guarantee a good dispersion and allowed to react at 50 °C for 12 h. After the completion of the reaction, the product was poured into a beaker containing ice. After it cooled to room temperature, H_2O_2 (30%) was added dropwise into the mixture until no bubble was generated any more. Subsequently, the treatment of purification was realized by successively using abundant HCl solution (1 moL/L) to remove the residual metallic ions and copious distilled water to remove the acid. Finally, the GO obtained was dried under freeze-drying for several days.

After that, 0.4 g GO, 1.3 g 1-(3-Dimethylaminopropyl)−3-ethylcarbodiimide hydrochloride (abbreviated as EDC) and 0.5 g 4-dimethylaminopyridine (abbreviated as DMAP) were transferred into a 100 mL round bottomed flask which contained 40 mL ethylenediamine (abbreviated as EDA) solution. Then, the mixture was allowed to magnetically stir at 40 °C for 24 h. After the reaction, the products were separated using a 0.45 μm PTFE and washed with excess acetone and deionized water. At last, the obtained material (abbreviated as e-GO) was dried under freeze-drying.

2.3. Preparation of DTC-GO composite

Grafting of sulfur groups on e-GO was synthesized as follows: 400 mg of e-GO and 48 mL of sodium ethoxide solution were added into a 150 mL round bottomed flask, which was stirred at room temperature for 3 h. The synthesis of the adsorbent was completed after the addition of 5.6 mL carbon disulphide and heated to 50°C for 24 h under magnetic stirring. In the next step, the product was filtered through a 0.45 μm PTFE membrane and purified by copious deionized water and acetone in order to remove the residuals. The dithiocarbamate group functionalized graphene oxide (abbreviated as DTC-GO) was dried under freeze–dried.

2.4. Characterization methods

The structures of materials were investigated by FT-IR spectroscopy using a Nicolet 6700 FT-IR spectrometer in the range of 400–4000 cm^{-1}. The morphology of DTC-GO was characterized by a scanning electron microscopy (SEM, MIRA3 TESCAN). Thermogravimetric analysis (TGA) was carried out by using a SDT Q600 V8.0 Build 95 thermal analyzer in argon with a heating rate of 10 °C/min from room temperature to 800 °C. Raman spectra were determined by a Renishaw Raman spectrometer with a 514 nm laser at a power of 4.7 mW.

2.5. Batch adsorption experiment for removal of Pb(II)

The adsorption behavior of DTC-GO for Pb (II) ion was evaluated on the experimental parameters such as initial metal ions concentration, pH, contact time and temperature. Before the batch experiments, a stock solution of Pb(II) were prepared by dissolving a certain amount of $Pb(NO_3)_2$ in distilled water and then diluted to the desired initial concentration. The desired pH was adjusted by using aqueous solution of 0.1 mol/L HCl and 0.1 mol/L NaOH. In order to avoid the formation of metal hydroxides, the effect of pH on adsorption was investigated in the range of 2.0−5.8. The effect of pH on adsorption was conducted in a series of 50 mL conical flasks, which contained 5 mg of adsorbent and 20 mL of 50 mg/L Pb(II) ion solution with different initial pH. Afterwards, the flasks were placed in a thermostatic water-bath shaker for a certain time at 25 °C. When the adsorption reached to equilibration, the adsorbent was separated by filtration and the concentrations of the initial and residual Pb(II) ion were measured by atomic absorption spectrophotometric. The adsorption capacity of adsorbent for Pb(II) was calculated according to the following equation [20]:

$$q_e = \frac{c_0 - c_e}{m} \times V, \tag{1}$$

where c_o and c_e (mg/L) stand for the original and equilibrium concentration of Pb(II), respectively; q_e is the equilibrium adsorption capacity of metal ions (mg/g), V is the volume of the solution (L), and m is the mass of the absorbent (g).

In the kinetic experiments, the performance of the adsorbent on Pb (II) aqueous solution was subjected to the interaction time between metal ions and adsorbent. The kinetic adsorption was conducted as following: 5 mg of DTC-GO and 20 mL of 50 mg/L Pb(II) solution were added into the flasks. Then the suspensions were shaken at 25 °C in a certain speed with the contact time ranging from 5 to 120 min. In addition, the pH value of Pb (II) solution was selected at 5.3. Meanwhile, all samples were taken out at predetermined time intervals to obtain the kinetic adsorption data and the concentration of the remaining metal ion solution was monitored by atomic absorption spectrophotometer.

In order to evaluate the adsorption capacity of the DTC-GO, the equilibrium adsorption experiments was carried out by placing 5 mg of DTC-GO into flasks containing 20 mL of metal ions in different initial concentrations (from 20 to 100 mg/L) with the value of pH at 5.3. Afterwards, all flaks were put in three thermostatic water-bath shaker, where the temperature was maintained at 25°C, 35°C, 45°C, separately. After that, the following operations were done as mentioned above.

3. Results and discussion

3.1. Characterization of GO composites

To confirm the presence of functional groups on the surface of graphene oxide composites, the FT-IR was utilized in this study. As expected, the typical peaks could be shown in Fig. 1. In the

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