Research Article

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Preparation of graphene oxide/chitosan complex and its adsorption properties for heavy metal ions

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Abstract: Graphene oxide hydrosol was added dropwise to the surface of chitosan (CS) to successfully obtain graphene oxide/chitosan composite (GC). The composite material was characterized by scanning electron microscopy and X-ray diffraction. The prepared adsorbent was used to simulate the static adsorption of copper, lead, and cadmium ions from 100 mL of 50 mg/L simulated wastewater samples. When the pH of the simulated wastewater is 6, initial dosage is 70 mg, adsorption time is 90 min, and temperature is 20°C; the adsorption capacities for copper, lead, and cadmium are 60.7, 48.7, and 32.3 mg/g, respectively. The adsorption and desorption cycle experiments show that the adsorption capacity of GC for copper ions can reach 86% of the initial adsorption capacity after ten cycles. The adsorption of lead ions on the composite conforms to the Freundlich adsorption isotherm model.

Keywords: adsorption, heavy metal ion, graphene oxide, chitosan

1 Introduction

In recent years, toxic heavy metal ions have widely been introduced into the aquatic environment due to the dumping of e-waste, the burning of fossil fuels, municipal waste treatment, mining and smelting, the application of chemical fertilizers and pesticides, and sewage [1]. Lead

poisoning is generally chronic, causing some changes in bones, leading to red blood cell disorders and therefore anemia and cancer. Cadmium enters the aquatic ecosystem through erosion of soil and bedrock, precipitation of atmospheric pollutants from industrial units, wastewater from polluted areas, and sludge and fertilizers used in agriculture. Most importantly, they easily accumulate in living organisms and cause a variety of diseases and death. Because these ions have high mobility and spread rapidly over large areas, removing them from the environment is one of the challenges facing science today [2–6]. At present, industrial methods for treating heavy metal wastewater mainly include chemical treatment methods such as chemical precipitation method [7] and electrochemical method [8–10], physical treatment methods such as ion exchange method [11,12] and adsorption method [13], and biological treatment methods such as plant treatment [14–16] and microbial treatment [17,18]. Among them, the adsorption method is considered to be an effective and economical method, and the design and operation of the adsorption process are also flexible, and some composite adsorbents are low in cost, and the treatment effect is observable [19,20].

Graphene oxide (GO) is one of the most widely studied adsorption materials in the past decade. It offers the advantages of large specific surface area, fast adsorption speed, and low preparation cost. Its structure contains a large number of oxygen-containing functional groups (epoxy, hydroxyl, carboxyl, etc.) that can react with heavy metal ions to form metal ion chelate compounds. Its unique structure with larger voids effectively shortens the diffusion path of heavy metal ions and thus has excellent ion trapping capabilities [21–25]. Chitosan (CS) is a chitin from seafood processing waste and is manufactured by the deacetylation of chitin. It is an environmentally friendly biopolysaccharide with an annual output of more than 10 billion tons. It has good biodegradability, biofunctionality, biocompatibility, and good safety. Its molecule contains a large number of amino groups and hydroxyl groups,

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which can provide dynamic adsorption sites and can coordinate with heavy metal ions, so it can be used as a high-performance composite adsorbent for various heavy metal ions [26–28].

So far, some published reports on graphene oxide/chitosan composites (GC) for wastewater adsorption treatment show that GC and GO composites have high stability and good mechanical properties [29–33]. It has excellent adsorption effect on toxic heavy metals such as Cu^{2+} , Pb^{2+} , and Cd^{2+} . At present, most studies are restricted to the study of the adsorption performance of a heavy metal ion, and there are relatively few reports on the treatment of multiple heavy metal ions in wastewater. In this study, GO and CS were added together to prepare composite adsorption material GC. The adsorption mechanism was investigated by means of scanning electron microscopy (SEM), X-ray diffraction (XRD), and other characterization methods. The adsorption characteristics of GC for copper, lead, and cadmium and the adsorption isotherm model of the adsorption process were discussed. It can be seen that GC material reduces GO agglomeration, increases specific surface area, and effectively increases active adsorption sites, resulting in the material having good adsorption performance. When the contaminated water contains copper, lead and cadmium ions at the same time, the use of this material allows the adsorption process to proceed better.

2 Experiment

2.1 Materials

Graphite powder (analytical grade), CS (Shanghai LanJi Biological Company), 30% H_2O_2 , NaNO_3 , H_2SO_4 , HCl , NaOH , and K_2MnO_4 are analytical purification reagents.

2.2 Preparation of composite adsorbent

According to the Hummers method, the graphite oxide solids were prepared in three stages of low temperature, medium temperature, and high temperature, ground into powder, and dried for use [34]. The prepared graphite oxide powder accurately weighing 0.25 g was added to 250 mL of distilled water, and after ultrasonic dispersion for 300 min at 300 W, 1.0 mg/mL of GO hydrosol was obtained.

The prepared 1.0 mg/mL of the GO hydrosol was added dropwise to 0.5 g of CS, and the mixture was adjusted to a paste and fully wetted and dried. The above dropping process was repeated ten times, the coating thickness of GO on CS was increased, and drying was carried out to obtain a dark brown GC adsorbent which was ground, weighed, and dried.

2.3 Characterization

The structural characterization of all samples was performed using SEM EVO MA 25/LS25 tungsten wire scanning electron microscope for morphology analysis. XRD (LabXRD-6100 type) was carried out under the conditions of a Cu target as a radiation source, a test voltage and current of 40 kV and 40 mA, respectively, and a scan rate of $5^\circ/\text{min}$.

2.4 Static adsorption experiment

A certain concentration of Cu^{2+} , Pb^{2+} , and Cd^{2+} standard mixture was prepared as simulated wastewater sample, and the Cu^{2+} , Pb^{2+} , and Cd^{2+} concentrations were determined to be 50 mg/L. At a certain temperature, separate standard volume mixtures of different volumes were placed in a 250 mL shake flask, pH of the standard mixture was adjusted with HCl solution and NaOH solution, and then quantitative GC was added as a composite adsorbent and shaken with a constant temperature oscillator. At different times, after centrifugation, the supernatant in the mixture was taken to measure the concentration of lead, cadmium, and copper ions, and the adsorption capacity of the composite adsorbent was calculated.

In this experiment, the general calculation formula for the adsorption capacity of the composite adsorbent for the metal ion solution is as follows:

$$q_e = \frac{(c_0 - c_e)}{W} \times V \quad (1)$$

where q_e is the adsorption capacity after adsorption equilibrium (mg/g), c_0 is the ion concentration of simulated wastewater sample before adsorption (mg/L), c_e is the ion concentration of simulated wastewater sample after adsorption (mg/L), W is the dosage of the composite adsorbent (g), and V is the volume of simulated wastewater samples (L).

Scheme 1: Experimental ideas and experimental conditions of this study.

In this experiment, the calculation formula for the adsorption rate of metal ions in simulated wastewater samples by composite materials as adsorbents is as follows:

$$R (\%) = \frac{c_0 - c_e}{c_0} \times 100\% \quad (2)$$

where R is the adsorption rate (%).

2.5 Adsorption isotherm fitting experiment

The adsorption isotherm of lead ions is taken as an example. Initial concentrations of 50 mL Pb²⁺ solution are 20, 50, 60, 80, and 100 mg/L, respectively. The pH of the solution was adjusted to 6, and 50 mg of GC adsorbent was added, and the reaction was carried out for 90 min at ambient temperature. After the reaction,

the mixture was separated, the concentration of lead ions in supernatant is measured, and the adsorption capacity of the composite adsorbent was calculated. The obtained data are fitted by Langmuir and Freundlich adsorption isotherm models [35–37].

2.6 Adsorption–desorption cycle experiment

In order to further research the adsorption and reuse performance of the prepared GC materials, adsorption–desorption cycle experiments were performed taking adsorption of copper ions as an example. In a 250-mL shake flask, 100 mL of 50 mg/L copper ion solution was taken, the pH of the solution was adjusted to 6, and 70 mg of the adsorbent was added to the solution. The mixture was centrifuged at ambient temperature, rotated at 150 rpm and shaken for 90 min, and the supernatant was measured. The concentration of copper ions was calculated, and the adsorption capacity and adsorption rate were calculated. Then, the adsorbed saturated GC material was washed with distilled water and placed in a clean shaking flask, to which an HCl solution of pH 1 was added. The mixture was shaken under the above-mentioned shaking conditions, and the fully desorbed GC material was washed and dried. To determine the reusability of the GC material, the adsorption experiments were repeated ten times according to the above procedure. The adsorption capacity and the adsorption rate of the composite material for Cu^{2+} were obtained.

The experimental ideas and experimental conditions of this study are presented in Scheme 1.

3 Results and discussion

3.1 Material characterization results and analysis

As can be seen from Figure 1a, GO after sonication exists in the form of a single-layer sheet structure, and wrinkles are formed on the surface due to folding and curling between the graphite sheets. In Figure 1b it can be clearly seen that the inside of the sheet-like structure is more evenly dispersed with some irregular particles. Analysis shows that CS is uniformly loaded into the interior of GO, and CS does not undergo significant agglomeration. GO loaded with CS has a large load dispersibility, which increases the specific surface area

Figure 1: Scanning electron micrographs of (a) GO and (b) GC.

of GC, thereby increasing the reaction rate of the reactive functional groups on the composite with the copper, lead, and cadmium ions in the simulated wastewater sample, which is beneficial to improving the adsorption performance of the material.

It can be seen from Figure 2 that GC exhibits a characteristic peak of GO at $2\theta = 10.8^\circ$ and a weak characteristic peak of CS at $2\theta = 20.3^\circ$. From the comparison of the diffraction angles of the two materials, it is obvious that the diffraction angle of GC is smaller than that of CS, which indicates that the GC is more crystalline compared to CS, thereby improving the adsorption performance of GC.

3.2 BET aperture analysis

As can be seen from Table 1, the GC material has an average pore diameter of 10.28 nm. It can be seen that the surface of the composite material has a relatively uniform mesoporous structure. Therefore, in the adsorption process, some physical adsorption effects are

Figure 2: XRD patterns of CS and GC.

Table 1: BET aperture analysis results

Report item	Result value
Single point total pore adsorption	10.28 nm
average pore diameter	

inevitable, and the column filling rate in the adsorption process will increase with the increase in the lead, cadmium, and copper ion concentration. This greatly helps in improving the physical adsorption performance of the composite adsorbent.

3.3 Static adsorption of simulated wastewater samples by GCs

3.3.1 Effect of pH on the adsorption performance of GC in simulated wastewater samples

The pH of quantitatively mixed standard simulated wastewater samples was 1, 2, 3, 4, 5, and 6, respectively, so that the adsorption equilibrium was fully achieved, and adsorption capacity was calculated. Figure 3 shows the effect of pH on the adsorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} on GC in simulated wastewater samples.

The pH of the simulated wastewater affects the active adsorption sites on the molecular structure of the composite and the presence of metal ions in the wastewater. As shown in Figure 3, when the pH is less than 2, the adsorption capacity of the GC complex for copper, lead, and cadmium ions is relatively low, but as the pH value increases, the adsorption capacity also increases. When the pH is less than 3, the adsorption capacity of the composite adsorbent for lead is higher than that for copper and cadmium, which indicates that

Figure 3: Effect of pH on the adsorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} by GC.

the active adsorption sites on the GC are more likely to bind to lead ions at a lower pH of the solution. During the process of improving pH from 1 to 6, there was no sediment in the simulated wastewater. The copper, lead, and cadmium ions in water samples only chelated with the complex, indicating that there was no further loss of copper, lead, and cadmium ions. Among the different pH values selected by the experiment, the optimal adsorption pH for the copper, lead, and cadmium ions in the simulated wastewater samples was 6.

3.3.2 Effect of dosage on the adsorption performance of GC in simulated wastewater samples

GC of 10, 30, 50, 70, 90 mg were added to the quantitatively mixed standard simulated wastewater samples as adsorbents. The adsorption capacity was calculated after the adsorption was completed. The effect of dosage on the adsorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} on GC in simulated wastewater is shown in Figure 4.

As can be seen from Figure 4, the adsorption capacity of GC for copper, lead, and cadmium ions generally increases with increasing dosage. When the dosage is less than 70 mg, the adsorption capacity of the composite for copper and lead increases linearly, but when the dosage is more than 70 mg, the adsorption capacity for copper and cadmium remains basically unchanged; when the dosage is more than 50 mg, the adsorption capacity for cadmium does not increase significantly. In order to ensure that the GC has high adsorption capacity for copper, lead, and cadmium ions and reduces cost, the optimum amount of GC is 70 mg.

Figure 4: Effect of dosage on the adsorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} by GC.

With the increase in the dosage, the active adsorption sites the GC complex provides increase, the binding probability of the copper-lead-cadmium ions to the functional sites increases, and the adsorption capacity increases rapidly. When the dosage continues to increase, the concentration of copper, lead, and cadmium ions in the simulated wastewater sample decreases as the adsorption process progresses, resulting in a decrease in the binding rate. An excessive addition of the composite causes it to agglomerate in the water sample, and the specific surface area is reduced. Hence, it becomes difficult to increase the adsorption capacity.

3.3.3 Effect of adsorption time on the adsorption performance of GC in simulated wastewater samples

One hundred milliliters of 50 mg/L simulated wastewater sample were taken, the pH of the sample was adjusted to 6, and 70 mg of the prepared composite material was added as adsorbent. The mixture was oscillated 5, 10, 20, 40, 70 min, respectively, at ambient temperature and 150 rpm. After centrifugal separation at 90 and 120 min, the concentrations of Cu^{2+} , Pb^{2+} , and Cd^{2+} in the supernatant were measured. The adsorption capacity of the composite material was calculated based on the changes in ion concentration before and after adsorption for different adsorption times, and the results are shown in Figure 5.

It is known from Figure 5 that in the initial adsorption stage of 0–20 min, the concentration of copper, lead, and cadmium ions is relatively large, and

Figure 5: Effect of adsorption time on the adsorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} by GC.

a large number of active sites on the adsorbent can chelate copper, lead, and cadmium ions. Therefore, the adsorbent is under a particularly strong adsorption capacity for copper, lead, and cadmium ions. However, after 20 min, the adsorption capacity increased slowly with the increase in adsorption time. After 90 min, the adsorption equilibrium was attained, and the adsorption capacity did not increase significantly. This is because the active sites on the adsorbent are reduced and the concentration of copper, lead, and cadmium ions in the water sample is lowered, resulting in a reduced possibility of chelation. In addition, the proton H^+ in the reactive functional groups in the GC complex amino group is released into the solution. In the middle, the pH of the water sample is reduced, and the electronegativity of the solution is weakened, which hinders the adsorption of copper, lead, and cadmium ions by the adsorbent and increases the adsorption time to reach equilibrium. Therefore, optimal adsorption time for GC to adsorb copper, lead, and cadmium is 90 min.

3.3.4 Effect of adsorption temperature on the adsorption performance of GC in simulated wastewater samples

GC were used to simulate the adsorption process of wastewater samples at temperatures of 20, 30, 40, 50, and 60°C. The adsorption capacity of the composites was calculated after the adsorption was completed. The experimental results are presented in Figure 6. Analysis shows that the adsorption capacity of the adsorbent for

Figure 6: Effect of adsorption temperature on the adsorption of Cu^{2+} , Pb^{2+} , and Cd^{2+} by GC.

lead, cadmium, and copper ions increases with the increase in the adsorption temperature, but the effect is not noticeable. Considering consumption reduction in experiments and industrial production, the adsorption experiments can be performed at ambient temperature.

3.4 Data analysis of adsorption isotherm fitting experiment

The effect of initial concentration of lead ions in the solution on the adsorption capacity of GC adsorbent is shown in Figure 7.

Figure 7: Effect of initial concentration of lead ion solution on the adsorption performance of GC adsorbent.

It can be seen from Figure 7 that when the initial concentration of lead ions is 20 mg/L or less, since the concentration of lead ions is relatively low, the effective active sites on GC adsorbent at this stage are not fully utilized. When the concentration changes from 20 to 100 mg/L, the utilization rate of the effective active sites on the GC adsorbent gradually increased and the adsorption capacity of the composite adsorbent for lead ions also gradually increased [38,39].

In order to further study GC, based on the above experimental data, Langmuir and Freundlich simulation equations were fitted to the process of adsorption of lead ions on GC, and kinetics of the adsorption of lead ions on the composite adsorbent was further studied. The results are shown in Figure 8.

According to Figure 8, the fitting correlation $RL = 0.95$ of the Langmuir model is lower than the fitting correlation $RF = 0.96$ of the Freundlich model. This indicates that the adsorption process is more consistent

Figure 8: (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm.

with the Freundlich model. Analysis of Figure 8 shows that the heterogeneity constant of the Freundlich model is more than 1, indicating that the ion concentration on the surface of the adsorbent is increased, the critical energy of adsorption is increased, and the attraction between metal ions is enhanced, which can further increase layer adsorption capacity.

Combined with the applicable characteristics of the Freundlich adsorption model, it is concluded that as the concentration of lead ions in the sample increases, the surface of the adsorbent becomes a heterogeneous surface, which in turn achieves multi-layer adsorption effect of the adsorbent and causes the surface of the adsorbent to strongly interact with lead ions; on the other hand, reason for improving adsorption capacity of adsorbent for lead ions is that lead ions are filled into the pores and cracks on the surface of the adsorbent, and efficiency of combining active sites on the surface of the adsorbent with lead ions increases.

Based on the above analysis, the Langmuir and Freundlich empirical models were compared to the results of fitting lead ions to GC. The composites are known to be suitable for medium- and high-concentration adsorption. In the case where the other conditions described above are unchanged, the concentration of simulated wastewater should be appropriately increased. In the process of adsorption of lead ions with respect to the lead ion concentration, the adsorption rate of lead ions remained basically stable, while the adsorption capacity showed a linearly increasing trend.

3.5 Adsorption analysis experiment results

The analytical results of adsorption of copper ions at different pH are illustrated in Figure 9. When the pH is 1, more than 82% of copper ions on GC material adsorbed with copper ions are desorbed. As pH increases, desorption rate decreases significantly. The reason for that is proton hydrogen ions in the solution compete with GC adsorbing copper ions for active sites. When pH is less, the copper ions bound on the GC material are easily replaced by proton hydrogen ions in the solution.

It can be seen from Figure 10 that after ten adsorption-desorption cycles, the copper adsorption capacity of the GC material can reach 86% or more of the initial adsorption capacity. It can be seen that GC materials can be reused to adsorb heavy metal ions.

Figure 9: Desorption rate of Cu^{2+} in hydrochloric acid solution at different pH.

Figure 10: Changes in adsorption capacity and adsorption rate of Cu^{2+} by adsorption and desorption of GC for ten times.

4 Conclusions

1. The characterization results of SEM, XRD, and the like show that the GC adsorbent has been successfully synthesized. The pore size analysis showed that the single point total pore adsorption average pore diameter was 10.28 nm, which is characteristic of a mesoporous material, and the adsorption process exhibited physical adsorption.
2. When the pH is 6, the initial dosage is 70 mg, and the adsorption reaction time is 90 min, at ambient temperature, after GC adsorption in simulated wastewater

samples, the maximum adsorption capacity for copper, lead, and cadmium can reach 60.7, 48.7, and 32.3 mg/g, respectively. The adsorption isotherm fitting experiment finds that the adsorption process of lead ions by GC is more consistent with the Freundlich model. The reutilization performance of GC was determined by adsorption analysis experiments. The experimental results have shown that hydrochloric acid is an effective solution for desorption. After using GC for ten adsorptions, the copper ion adsorption capacity can still reach 86% of the initial adsorption capacity, which shows that in addition to the advantages of low cost and high adsorption capacity, GC also have good cycle performance.

3. GC not only overcomes the disadvantages of graphene and CS, but also makes full use of the advantages of large adsorption capacity of graphene material and excellent chelation ability of CS, and realizes the complementary advantages of the two materials. The GC adsorbent obtained through a simple synthesis process can achieve better results, which provides another new idea to the industry for developing simple, economical, and rapid treatment of sewage containing lead, cadmium, and copper ions.

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