

Preparation of Graphene Oxide/Polyaniline Composite Adsorbent and Its Adsorption Performance for Chromium (VI)

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Abstract

The adsorption properties of composite materials for heavy metal chromium were studied. [Method] The improved Hummer method was used to prepare graphene oxide, and the polyaniline-graphene oxide composite was prepared by dynamic interface polymerization process, the adsorption performance of heavy metal chromium ions in simulated environment was studied. Polyaniline-graphene oxide can significantly improve the adsorption capacity and adsorption efficiency of chromium ions. When the amount of polyaniline-graphene oxide is 1g/L, the solution pH is 7, and the adsorption time is 180min, the adsorption rate can reach 98.%. [Conclusion] Polyaniline-graphene oxide can be used as an adsorbent for heavy metals in sewage.

Keywords

Adsorption; composite material; Graphene oxide; Polyaniline.

1. INTRODUCTION

In the process of steel smelting, metal electrolytic production, electroplating, etc., in order to reduce the corrosion rate of metal surfaces, chromate passivation is usually used in chemical, pharmaceutical, printing and dyeing, and leather processing industries use chromate as a raw material. These industrial processes produce large amounts of chromium-containing wastewater. Chromium exists in the form of Cr (VI) and Cr (III) in water. Among them, Cr (VI) is 300 times more toxic than Cr (III)^[1]Cr (VI) has effects on human skin, mucous membranes and digestive system. Great irritant and corrosive effects, carcinogenic and mutation-inducing effects^[2] Cr (VI) has been listed as a priority control pollutant by the US Environmental Protection Agency and the Chinese Ministry of Environmental Protection. The direct discharge of Cr (VI) -containing wastewater will have a serious impact on the ecological environment and human health. Therefore, the efficient treatment of Cr (VI) -containing wastewater has become one of the current research hotspots. At present, the removal of Cr (VI) mainly uses ion exchange method, electrolytic method, chemical precipitation method, biofilm method and adsorption method [3]. Among them, the adsorption method has the characteristics of low cost, simple operation, and easy recovery, and has been widely used in environmental treatment. Commonly used adsorbents in recent years include activated carbon, natural organic adsorbents (corn straw, peanut skin, etc.), natural inorganic adsorbents (zeolite, clay, etc.), synthetic adsorbents (polyamine type anion exchange fibers, etc.), etc, but these adsorbents have certain restrictions on the agents. Therefore, the development of new and effective Cr (VI) adsorbents is a problem to be solved.

Among all kinds of adsorbents, polyaniline is a high molecular polyamine conductive polymer, which has become a widely used electrode material because of its advantages such as large

specific surface area, unique doping mechanism, and excellent electrochemical performance. At the same time, polyaniline molecules contain a large number of amine and imine functional groups, which have good complexation for heavy metal ions. Polyaniline has the advantages of good acid doping and alkali dedoping characteristics, redox reversible characteristics, and good environmental stability. It has been applied in environmental pollution treatment [11]. However, in the application process, polyaniline factors such as tight packing and low specific surface area make its adsorption efficiency low. In high-concentration Cr (VI) -containing wastewater, the adsorption performance of polyaniline is greatly reduced, which is limited in the wastewater treatment process. Graphene is a two-dimensional planar material with a large specific surface area and is widely used in the field of wastewater treatment. Graphene-based adsorbents show good performance in the adsorption of heavy metal ions, dyes, etc[4]. Compounding with polyaniline can increase its stacking area and specific surface area, thereby increasing its adsorption performance and capacity.

2. EXPERIMENTAL PART

2.1. Experimental Materials and Instruments

Graphite powder (99.95%), Aladdin reagent; aniline, ammonium persulfate, potassium dichromate, potassium permanganate, sodium nitrate, concentrated sulfuric acid, concentrated hydrochloric acid, hydrogen peroxide, and anhydrous ethanol are all analytical grade; all water is ultra-pure water. The main test instruments are ATY124 electronic balance, Tensor27 Fourier infrared spectrometer; VIS-7220 UV-visible spectrophotometer; PHS-3C precision pH meter; DF-101S heat-collecting constant temperature heating magnetic stirrer; SHA- Type B thermostatic water bath oscillator

Potassium dichromate needs to be dried at 120 ° C for 3 hours before use. Other reagents need not be treated before use.

2.2. Preparation of Graphene Oxide (GO)

Add a certain amount of concentrated H_2SO_4 to a three-necked flask, add 2g of graphite powder under ice bath (0 ~ 4 ° C), and add 6g $KMnO_4$ slowly and several times after vigorous stirring. After the $KMnO_4$ and graphite powder are evenly mixed, add 1g $NaNO_3$. Stirring was continued for 1 h in an ice water bath to obtain a dark green mixed solution. Then, the reaction temperature was raised to 40 ° C, and the reaction was continued to be stirred for 3 hours. After the reaction was completed. The mixed solution changed from dark green to a viscous red-brown solution, then the temperature was raised to 80 ° C., 80 mL of distilled water was slowly added, and the mixture was thoroughly stirred to obtain a dark golden yellow solution. After the solution was cooled to room temperature, 15 mL of H_2O_2 was added dropwise. The reaction solution was filtered with bright yellow, washed with 1M HCl and distilled water several times, centrifuged to neutrality, freeze-dried and ground to obtain graphite oxide.

2.3. Preparation of Graphene Oxide Polyaniline (GO-PANI) Composite Adsorbent

0.15g of graphene oxide was dispersed in 100mL of water by ultrasound. After 1h, 11.41g of ammonium persulfate was weighed into the dispersion, and then ultrasonicated for 0.5h to completely dissolve it, and 4.5mL of concentrated hydrochloric acid was added to the dispersion. Take 4.557mL of aniline in 10mL of CCl_4 in a fume hood, pour the dispersion into the CCl_4 mixture, add a stir bar, and stir in a magnetic stirring device for 24h. The obtained black-green solution was suction-filtered and washed with anhydrous ethanol and distilled water several times until the filtrate was clear and the absorbance was measured as 0. The obtained filtrate was dried in a vacuum oven at 60 ° C. for 24 h, and the block solid was taken out and ground to a uniform fine powder, which was set aside for use.

2.4. Analysis Method

The Cr⁶⁺ concentration in the aqueous solution was measured by diphenylcarbazide spectrophotometry.

2.5. Test Method

(1) Chromium standard stock solution.

Weigh 0.2830 g of potassium dichromate, transfer it into a 1000 mL volumetric flask using a distilled aqueous solution, dilute it to the mark with water, and shake well.

(2) Chrome standard use fluid.

Pipette 5.00mL of chromium standard solution into a 500mL volumetric flask, dilute to the mark with distilled water, and shake well.

(3) Configuration of developer.

0.2 g of dibenzylcarbazide is dissolved in 50 ml of acetone. After dibenzylcarbazide is completely dissolved, it is transferred to a 100 ml volumetric flask, diluted with water to the mark, and shaken.

(4) Drawing of standard curve.

Take 7 50mL colorimetric tubes, add 0, 0.5, 1, 2, 4, 7, and 10mL of chromium standard use solution in sequence, dilute with water to the mark, add (1 + 1) sulfuric acid and phosphoric acid 0.5mL, shake, add 2mL developer, shake well. At 5min standstill at a wavelength of 540nm, the absorbance was measured with a 3cm cuvette and a standard curve was drawn.

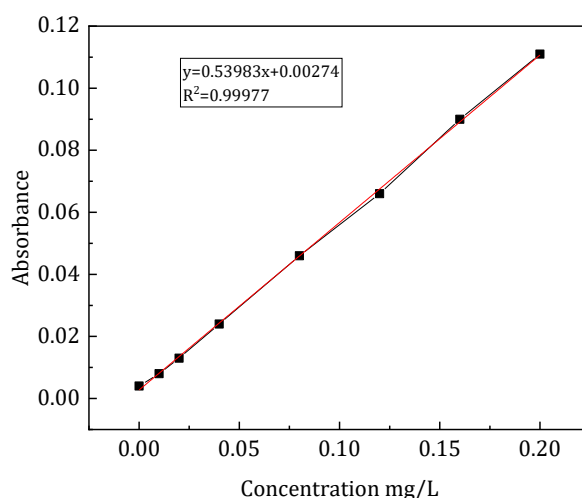


Fig 1. The standard curve line of Cr(VI)

(5) Adsorption test.

Add a certain concentration of chromium ion solution to the Erlenmeyer flask, and then accurately weigh a certain amount of polybenzylamine-graphene oxide composite adsorbent, adjust the pH, and react in a constant temperature water bath shaker. After a certain time, remove the solution. After centrifugation, measure the absorbance of the chromium solution, and calculate the adsorption rate according to formula (1):

$$V_s = [(C_1 - C_2) / C_1] \times 100\% \quad (1)$$

In formula (1),

V_s is the adsorption rate;

C_1 is the concentration of the solution before adding the adsorbent;

C_2 is the concentration of the solution after adding the adsorbent.

2.6. Conditional Optimization

Effect of adsorption time on the adsorption performance of chromium ions. Take three 50mL solutions from the stock solution and add them to a 100mL Erlenmeyer flask. Add 0.1g of composite adsorbent and shake them in a constant temperature shaker. The adsorption time is 30, 60, 90, 120, 150, 180, 210, 240, 270, 300, 330min. After centrifugation in a centrifuge (1000r / min, 4min), take the supernatant and measure the chromium ion concentration. And calculate the adsorption rate. It can be seen from Figure 2 that in the initial stage of adsorption, with the increase of the adsorption time, the adsorption rate of the composite adsorbent for the chromium ion solution gradually increased, and the adsorption amount increased slowly after 180 min, and the adsorption rate basically reached the adsorption equilibrium. The time is easy to control, and the adsorption time is 180 minutes in subsequent tests.

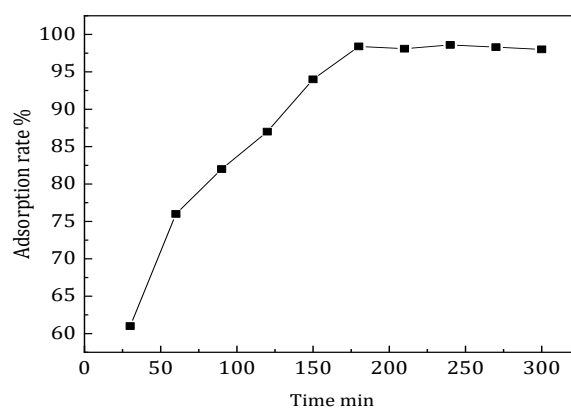


Fig 2. Relationship between adsorption time and adsorption rate

Effect of the amount of composite adsorbent on the adsorption performance of chromium ions. Pipette 7 50mL chromium ion solutions from the stock solution into a 100mL Erlenmeyer flask, add 0.020, 0.050, 0.080, 0.100, 0.120, 0.150, 0.200g of adsorbent, and shake the reaction at room temperature for 180min. After centrifugation in a centrifuge (10000r/min, 4min), the supernatant was taken and the absorbance of the residual chromium ion solution was measured. It can be seen from Figure 2 that the adsorption rate increases with the increase in the amount of adsorbent used. When the amount of adsorbent is increased to 0.100g, the adsorption rate does not increase significantly, indicating that the amount of adsorbent used at this time has basically saturation. In order to save costs and maximize adsorption efficiency, the amount of adsorbent used is determined to be 0.100g.

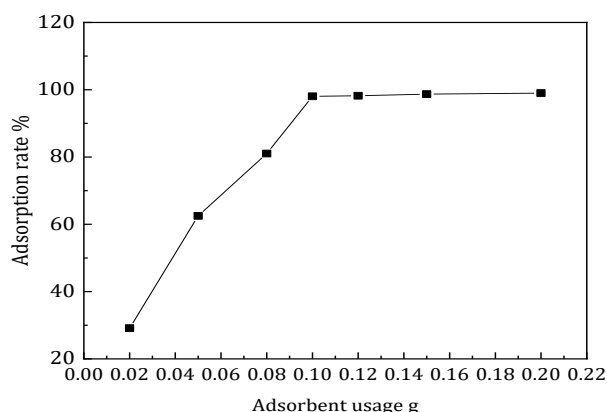


Fig 3. Relationship between dosage of PANI-GO oxide composites and adsorption rate

Effect of solution pH on chromium ion adsorption performance. Take 6 parts of 50mL of chromium solution in a beaker and adjust the pH of the solution to 3, 4, 7, 9, 11, 13. Accurately weigh 6 portions of the 0.1 composite adsorbent and add them to 6 conical flasks, and shake them in a constant temperature shaker for 180min. After the adsorption was completed, the supernatant was taken after centrifugation (10000 r/min, 4min) in a centrifuge, the residual chromium ion concentration was measured, and the adsorption rate was calculated. It can be seen from Fig. 4 that the adsorption rate of polyaniline-graphene oxide for chromium ions is high in peracid and neutral environments, and the adsorption rate is reduced in weak alkaline environments. The optimal pH should be in strong acid environments. However, since the strong acid environment requires higher actual operating conditions, the optimal pH is determined to be 7.

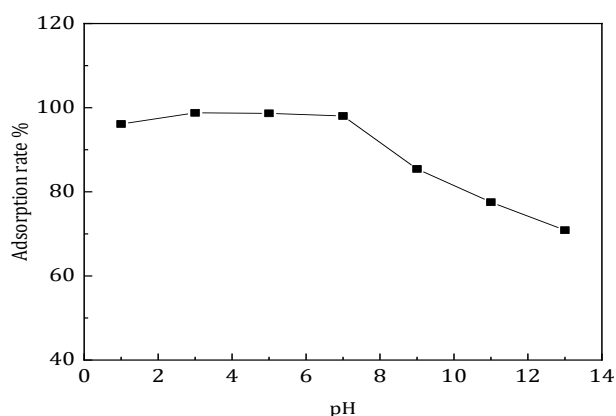


Fig 4. Relationship between pH and adsorption rate

3. RESULTS AND DISCUSSION

3.1. Adsorption Kinetics

The relationship between the adsorption amount of graphene oxide polyaniline composite adsorbent Cr^{6+} and the adsorption time is shown in FIG. 2. It can be seen from FIG. 2 that the adsorption amount of graphene oxide polyaniline composite adsorbent for Cr^{6+} all increases with time, and the adsorption amount basically stabilizes after 180 minutes, and the adsorption equilibrium is reached. Because the graphene oxide polyaniline composite adsorbent is doped with amine groups, the amine group is reducing, and Cr^{6+} can be reduced to a low-priced Cr^{3+} .

The amine is oxidized into imine groups, which has good properties for heavy metal ions Networking.

3.2. Effect of Dosage on Adsorption

The results of graphene oxide polyaniline composite adsorbent adsorption on Cr^{6+} under different dosage conditions are shown in Figure 3. It can be seen from FIG. 3 that as the dosage is increased, the adsorption rate of the graphene oxide polyaniline composite adsorbent Cr^{6+} gradually increases. This is because the specific surface area and active adsorption sites provided by the graphene oxide polyaniline composite adsorbent increase with the increase of the dosage, and the adsorption rate also increases.

3.3. Effect of pH on adsorption

The effect of pH value on the adsorption of Cr^{6+} by graphene oxide polyaniline composite adsorbent is shown in Figure 3. It can be seen from Figure 3 that the adsorption effect of graphene oxide polyaniline composite adsorbent on Cr^{6+} first increases and then decreases with the increase of pH value. When $\text{pH} = 3$, the reduced graphene oxide polyaniline composite adsorbent and graphite oxide The polyaniline composite adsorbent has the best removal effect on Cr^{6+} . This is because when the pH value is low, Cr (VI) mainly exists in a large amount in the form of HCrO_4^- , the concentration of H^+ in the solution is large, the surface of the adsorbent has a large positive charge, and interacts with HCrO_4^- through electrostatic interaction, while Cr (VI) Both H and H^+ are susceptible to the lone pair electrons of the amine group in the molecule of the reduced graphene oxide polyaniline composite adsorbent. When the acidity is stronger, the H^+ concentration becomes larger, and Cr (VI) and H^+ are more competitive. With the increase of pH value, the OH^- in the solution increases, the positive charge on the surface of the adsorbent decreases, Cr (VI) is mainly in the form of CrO_4^{2-} , OH^- and CrO_4^{2-} compete with each other, and the adsorption effect decreases.

3.4. Comparison of Polyaniline and Its Composite Adsorption Performance

In 50mL of a 50mg / L chromium ion solution, add 0.1g of polyaniline and polyaniline graphene oxide composite adsorbents, shake in a constant temperature shaker for 180min at room temperature, remove the reaction liquid, and centrifuge in a centrifuge (10000r / min, 4min), take the supernatant, measure the residual concentration of chromium ions, and calculate the adsorption rate. The test results show that under the same conditions, when polyaniline and its complexes were added to the chromium ion solution, the adsorption rate of polyaniline on chromium ions reached 73%, and after the polyaniline was compounded with graphene oxide, the adsorption effect was significantly improved and the adsorption The rate can reach 98%.

4. CONCLUSION

(1) In this test, polyaniline-graphene oxide was synthesized by in-situ polymerization, and the adsorption performance of chromium ions was investigated. The results show that the composite has good adsorption performance for chromium solution. When the amount of adsorbent is 0.1 g, the reaction time is 180 min, and the pH is 7, the adsorption rate of chromium ion solution is as high as 98%. Therefore, this test method provides a certain theoretical basis for the adsorption of chromium solution.

(2) Graphene oxide polyaniline composite adsorbent has better pore structure and distribution than polyaniline, has mesoporous and microporous structure, and has a large specific surface area, which is conducive to increasing the adsorption capacity.

(3) Adsorption experiments show that graphene oxide polyaniline composites have adsorption properties, which can be combined with its conductivity to further exert the synergistic effect of electrolysis-adsorption on the removal of pollutants in wastewater.

REFERENCES

- [1] Chromium and cancers of the gastrointestinal tract: A meta-analysis[J]. *Cancer Epidemiology*, Vol. 34(4), p. 388-399.
- [2] Khosravi R , Fazlzadehdavil M , Barikbin B , et al. Removal of hexavalent chromium from aqueous solution by granular and powdered Peganum Harmala[J]. *Applied Surface Science*, Vol. 292(2014), p. 670-677.
- [3] Kobya M. Removal of Cr (VI) from aqueous solutions by ad-sorption onto hazelnut shell activated carbon: kinetic and equilibrium studies[J]. *Bioresource Technology*, Vol. 91(2004), p. 317-321.
- [4] Neudeck A,Petr A,Dunsch L.The redox mechanism of polyaniline studied by simultaneous ESR–UV–vis spectroelectrochemistry[J]. *Synthetic Metals*,Vol. 107(1999),p. 0-158.
- [5] Li S,Lu X,Xue Y,et al. Fabrication of Polypyrrole/Graphene Oxide Composite Nanosheets and Their Applications for Cr(VI) Removal in Aqueous Solution[J]. *PLoS ONE*, Vol. 7(2012), p. 43-328.
- [6] Geim,A.K, Novoselov, K.S.The rise of graphene[J]. *Nature Materials*, Vol. 6(2013), p. 183-191.