

Adsorption of heavy metals in water by chitosan-graphene oxide composites

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Abstract:

Heavy metal pollution poses a serious threat to the ecological environment and human health. The adsorption method has become a mainstream research direction due to its high efficiency and simplicity. The CS-GO material formed by the composite of chitosan and graphene oxide overcomes the defects of single materials through a synergistic effect, significantly improving the adsorption stability and capacity. This paper focuses on CS-GO composites and proposes that static batch experiments can be used to study their adsorption performance, combined with kinetic, isotherm models and X-ray photoelectron spectroscopy to explore the action mechanism. Studies have shown that its adsorption involves multiple mechanisms such as electrostatic interaction, surface complexation, pore filling and ion exchange, and it has a high adsorption capacity for heavy metals such as Pb^{2+} , Cd^{2+} and Cu^{2+} , with the synergistic effect enhancing selectivity and stability. This composite material shows application value in fields such as industrial wastewater treatment and drinking water purification, but it faces challenges such as high cost of large-scale preparation, poor adaptability to actual wastewater and insufficient long-term stability. Future research should focus on low-cost preparation, pilot-scale verification and the development of long-term regeneration technologies to promote its transformation from laboratory research to engineering applications.

Keywords: Chitosan-graphene oxide composite (CS-GO composite); Heavy metal adsorption; Synergistic effect; Wastewater treatment; Adsorption mechanism

1. Introduction

Heavy metal pollution has become a global environmental problem. Industrial and agricultural wastewater discharges lead to excessive concentrations of

lead, cadmium, mercury, and other heavy metal ions in water bodies, posing a serious threat to ecosystems and human health. The toxic nature of heavy metal ions is to interfere with the structure and function of biomolecules, which can bind to the active centre of

enzymes (e.g., sulfhydryl - SH) and inhibit enzyme catalysis; displace essential metal ions from biomolecules, e.g., the inhibition of δ -aminolevulinic acid dehydrogenase (ALAD) by Pb^{2+} leads to impairment of haemoglobin synthesis and causes anaemia^[1]; induce Reactive oxygen species (ROS) are produced in excess, leading to lipid peroxidation and DNA breaks, resulting in apoptosis or cancer^[2]. Traditional treatment methods, such as chemical precipitation and ion exchange, have defects such as high cost and secondary pollution^[3-5], while adsorption has attracted much attention and become a research hotspot because of its easy operation and high efficiency.

2. Properties and applications of chitosan and graphene oxide

Chitosan is a natural cationic polysaccharide produced by deacetylation of chitin, which is biocompatible, degradable and non-toxic. Its molecular chain is rich in amino and hydroxyl groups, which endows it with excellent chelating ability and adsorption properties^[6]. In the field of environmental remediation, chitosan can effectively capture heavy metal ions through electrostatic interactions and ligand bonding, e.g., the adsorption capacity of Cu^{2+} can reach 205 mg/g, but it has the drawbacks of solubility and poor mechanical properties^[7].

Graphene oxide is a derivative of graphene, the surface contains a large number of oxygen-containing functional groups, including epoxy, carboxyl and hydroxyl, etc., the specific surface area is as high as 2630m²/g, the mechanical strength is very large, and the Young's modulus can be up to 1TPa comparable to that of diamond, and in composite materials, graphene oxide can significantly enhance the mechanical strength and thermal stability, and its layered structure and sp² hybridised carbon skeleton can provide a rich active site for the adsorption of heavy metals ([7]). Its layered structure and sp² hybridised carbon skeleton also provide abundant active sites for heavy metal adsorption^[8]. However, the composites are still prone to agglomeration and difficult to be recycled^[9].

The synergistic effect of the composites is mainly reflected in three aspects: the amino group of chitosan and the carboxyl group of graphene oxide are cross-linked through amide bonding, the carboxyl peak of GO (1720 cm⁻¹) is weakened, and the amino group peak of CS (1650 cm⁻¹) and the carboxyl peak of GO merge into a new peak near 1600 cm⁻¹, which is attributed to the C=O stretching of the amide bond. C=O stretching vibration of the amide bond^[10]; the two-dimensional structure of graphene oxide prevented the agglomeration of chitosan molecular chains, and scanning electron microscopy showed an increase in porosity^[11]; the surface zeta potential test showed that the

positive charge density of the composites was increased by a factor of 2 compared with that of pure chitosan at pH 5^[12]. After composite, chitosan molecular chains can be entangled or adsorbed on the surface of GO lamellae or even inserted into GO interlayers through the above interactions, which not only solves the problem of GO agglomeration, but also makes use of the lamellar structure of GO as a "reinforcing skeleton" to significantly enhance the mechanical strength (e.g., tensile strength, modulus of elasticity) and structural stability (e.g., resistance to swelling); at the same time, the hydrophilicity and biocompatibility of chitosan can improve the interfacial compatibility of GO, expanding its application in aqueous or biological systems, thus showing that this composite material has a great potential for the application of adsorption of water to heavy metals.

In this paper, we focus on the adsorption property study, mechanism of action and practical application of chitosan-graphene oxide (CS-GO) composites in the treatment of heavy metals in wastewater, to sort out the progress of the study and point out the future direction, and to provide a reference for the research in this field.

3 Adsorption performance research method

The adsorption performance was tested by static batch experimental method: 50 mg of composites were weighed and reacted with 50 mL of heavy metal ion solutions of different concentrations (Pb^{2+} , Cd^{2+} , Cu^{2+}) in a thermostatic oscillator, respectively, controlling the system pH (2-7), temperature (25-45 °C) and contact time (5-360 min). An inductively coupled plasma emission spectrometer (ICP-OES, PerkinElmer Optima 8300) was used to determine the concentration of residual metal ions in the solution, and the instrumental detection limit was 0.01 mg/L. The adsorption capacity was determined according to the formula :

$$q_e = (C_0 - C_e) V / m \quad (1)$$

Where: q_e - equilibrium adsorption capacity (mg/g)

C_0 - initial concentration of metal ions (mg/L)

C_e - initial and equilibrium concentrations of metal ions (mg/L), the

V - volume of the solution (L)

m - mass of adsorbent (g).

The kinetic studies were performed by fitting the experimental data with quasi-primary and quasi-secondary kinetic models; Langmuir and Freundlich models were applied for isotherm analyses. The chemical state changes of the elements on the surface of the material before and after adsorption were analysed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha), and the

mechanism of the adsorption sites was investigated by density-functional theory (DFT) calculations. The repeatability of the method was verified by five parallel tests with the relative standard deviation < 5%, which indicates the good reliability of the method.

4 Adsorption properties of CS-GO composites

4.1 Physicochemical basis of adsorption process

The adsorption of heavy metal ions on the surface of CS-GO composites involves multiple physicochemical mechanisms, and the core driving forces and characteristics are as follows:

(1) Electrostatic interactions: protonated amino groups ($-\text{NH}_3^+$) on the surface of the composites bind to negatively charged heavy metal ions (e.g., Cd^{2+} , Pb^{2+}) via Coulombic forces, with a significant effect of pH. It has been shown that the amino group protonates the most at $\text{pH}=5-6$, with an adsorption capacity of 120-180 mg/g for divalent metal ions^[13-14].

(2) Surface complexation: the carboxyl ($-\text{COOH}$) and hydroxyl ($-\text{OH}$) groups at the edges of graphene oxide formed stable five-membered cyclic chelates with Cu^{2+} , etc., and the binding constants, $\log K$, were 4.8-5.2; XPS analyses showed that the orbital binding energies of the $\text{Cu}2p_{3/2}$ orbitals were shifted by 0.8-1.2 eV after the adsorption, which confirms that the Cu-O ligand bonds were formed^([15-16]),15-16).

(3) Pore filling effect: It was found to contribute about 15-30% of the adsorption capacity, and the adsorption experiments on Hg^{2+} showed that the internal diffusion rate increased by 3-5 times for pore sizes > 2 nm^[13]; DFT calculations confirmed that the expansion of graphene lamellae spacing to 0.8 nm reduced the As (III) diffusion energy barrier^[15].

(4) Ion exchange mechanism: alkaline conditions ($\text{pH}>7$) dominate, and a 1:1 molar ratio exchange of Na^+/K^+ with Cr (VI) in the composite material, as shown by the EXAFS spectrum, results in the formation of a stable $[\text{CrO}_4]^{2-}$ tetrahedral structure (Cr-O coordination number 4)^[16].

(5) Thermodynamic and kinetic characterisation of the adsorption process: the isotherms are consistent with the Langmuir-Freundlich mixed model, with a maximum monolayer adsorption (q_m) of 292 mg/g of Pb^{2+} , and a coefficient of heterogeneity of $n=0.87$; the kinetic data fit the quasi-secondary model optimally, and the chemisorption rate constant $k_2=3.6\times10^{-3}$ g/(mg·min); thermodynamic parameters $\Delta G^\circ=-28.5$ kJ/mol (ΔG° - standard Gibbs free energy change, kJ/mol), $\Delta H^\circ=-15.2$ kJ/mol (ΔH° -- stan-

dard enthalpy change, kJ/mol), confirming that adsorption is a spontaneous exothermic process.

4.2 Synergistic effect of chitosan and graphene oxide

The synergistic interaction between CS and GO significantly enhances the adsorption performance, and the core mechanism is reflected in three levels:

(1) Synergistic coordination of functional groups: the amino and hydroxyl groups of chitosan combine with the carboxyl and epoxy groups of GO through hydrogen bonding network to jointly provide coordination sites^[15].

(2) Structural optimisation to enhance active site exposure: molecular dynamics simulations show that GO lamellae form a three-dimensional porous structure, which provides a dispersive scaffold for chitosan, resulting in an increased exposure rate of the active site^[15].

(3) Strong interfacial interactions enhance stability: TEM observations revealed that heavy metal ions are preferentially enriched at the CS-GO interface, and the interfacial metal concentration is higher than that in the single-component region^[17].

(4) Synergistic interactions also enhance selectivity: in competitive adsorption experiments, the selectivity coefficient of the composites for $\text{Cd}^{2+}/\text{Zn}^{2+}$ was increased, which was attributed to the π - π stacking of GO to enhance the stereoselectivity of chitosan^[14].

5 Practical Application Challenges and Directions for Improvement

5.1 Current applications in water treatment

CS-GO composites have demonstrated significant application value in the field of water treatment, and their performance advantages are mainly reflected in the following levels:

(1) Industrial wastewater treatment: The composites showed excellent adsorption performance on wastewater containing heavy metals such as Pb^{2+} , Cd^{2+} , Cu^{2+} and other heavy metals^[18], and the adsorption capacity was significantly higher than that of traditional activated carbon, with the maximum adsorption capacity of 368.38 mg/g (As(III))^{([19]),} and the adsorption capacity of kinetics reached 368.38 mg/g (As(III))^{([19]),} and the adsorption capacity of kinetics reached 368.38 mg/g (As(III))^{([19]),} and the adsorption capacity was significantly higher than that of traditional activated carbon.^[19], and the adsorption kinetics conformed to the quasi-secondary model (Langmuir isotherm). The adsorption equilibrium could even be reached within 5 min after modification by phosphonation (GO-CS-P), and the maximum adsorption capacity for Eu-

(III) was 106.14 mg/g, which was superior to that of most of the traditional adsorbent materials^[20].

(2) Drinking water purification: The surface-modified CS-GO materials showed high selectivity for low concentrations of heavy metals (<1 mg/L), for example, the carboxylation modification can significantly improve the adsorption capacity of As (III), and the actual pilot test data showed that it can reduce the arsenic content of drinking water to below the WHO limit^[(19), The]. The continuous operation of the composite material-filled columns still maintained high initial adsorption efficiency, which verified its long-term stability. efficiency in continuous operation, which verifies its long-term stability.

(3) Adaptability to complex water bodies: In high salinity wastewater (NaCl concentration >5%), the adsorption capacity of the cross-linked CS-GO materials for Cd²⁺ decreased significantly lower than that of pure chitosan, which showed a stronger anti-interference ability^[21]. Amino-functionalized materials can remove heavy metals and dyes simultaneously, achieving efficient removal of Cu²⁺ and methyl orange through synergistic effects^[22].

(4) Scale-up bottlenecks: Material moulding and processing is a key challenge for industrial applications. Preparation as porous microspheres or aerogels can improve hydraulic performance, such as composite microspheres in expanded bed reactors with significantly lower pressure drop and longer backwash cycles^[23]. Economic analysis shows that the cost of tonnes of water treatment is competitive with ion exchange resin, but the mechanical strength still needs to be further improved by modification.

(5) Regeneration and recycling performance

The regeneration and recycling performance of the composite material is very important in order to be put into practical application, which can reflect the life cycle of the material, and then determine the cost and other key factors of practical application, which directly affects its economy.

By means of polyethyleneimine modification or glutaraldehyde cross-linking, the recycling stability of the material can be significantly improved, for example, the modified material can still maintain a high removal rate after several cycles. Membrane immobilisation technology can keep material loss to a low level, but needs to be weighed against the sacrifice of adsorption capacity, and life cycle assessment shows that when the number of cycles exceeds a certain threshold, the total treatment cost can be lower than that of activated carbon.

(6) Mechanical strength, chitosan dissolves readily in acidic environments (pH<3) and the material is easily broken in dynamic water flow, resulting in a significant decay in adsorption capacity over operating time. These

problems can be countered by material modification and process optimisation. Glutaraldehyde cross-linking significantly improves the stability of the material under acidic conditions, and techniques such as glycidyl methacrylate grafting can enhance mechanical strength.

Overall, the main factors limiting the practical application of CS-GO materials are the high cost of scale-up preparation, the complexity of the actual wastewater matrix and the lack of long-term stability of the composite materials. Future research should focus on the functional modification of composites to enhance the selectivity, the use of composite magnetic nanoparticles or biochar to reduce the cost, and the design of continuous flow adsorption columns based on the complexity of the actual water quality in order to adapt to the actual wastewater treatment process.

6. Conclusion and Outlook

Because of the synergistic effect of chitosan and graphene oxide, the CS-GO composites are better than single materials in adsorption capacity, stability and biocompatibility, and are highly efficient heavy metal adsorbents, and their adsorption performance is regulated by the preparation method, pH, temperature and other environmental factors, and the core mechanisms include electrostatic interactions, surface complexation, pore filling, and ion exchange, which synergistically enhance the selectivity and stability of the materials for adsorption of heavy metals in water. The synergistic effect significantly improves the selectivity and stability of water and metal adsorption.

Future research is suggested to focus on three aspects: first, it should aim to continue to develop low-cost scale-up preparation processes to reduce the cost of graphene oxide raw materials; second, practical complex wastewater treatment pilot tests should be carried out to verify the long-term operational performance of the material under multi-component interference, thereby obtaining materials effective in practical applications; third, the research and development of long-term regeneration technology, combined with intelligent design (e.g., responsive adsorbent materials), is crucial to improve recycling efficiency and promote the transformation from laboratory research to engineering application. Additionally, expanding the application of these materials in other fields, such as soil remediation, can further explore their environmental governance value.

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