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Research progress on the adsorption of pollutants in water by oxidized graphene

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Abstract:

As a novel nanomaterial, oxidized graphene has attracted attention due to its unique physical properties and abundant oxygen-containing functional groups. This paper analyzes the structure of oxidized graphene, and around its structure and properties, explains the main adsorption mechanisms of oxidized graphene for metal ions and organic matter in water. It discusses and summarizes the main factors that affect the adsorption capacity of oxidized graphene, and looks forward to its application prospects and future research directions in the field of water treatment.

Keywords: graphene oxide, Adsorption Mechanism, Metal Ions, Organic Matter

1 Introduction

In recent years, pollution caused by industrial wastewater discharge poses a serious threat to the safety of freshwater resources. As humans at the top of the food chain, being exposed to large amounts of toxic and harmful substances present in wastewater, these substances can be transmitted to humans through the food chain. Therefore, the treatment of wastewater is of great importance to humans.

Pollutants in water can be classified based on their physical properties into suspended matter, colloidal matter, and dissolved matter. Pollutants such as suspended matter and colloids can be removed through processes like coagulation, sedimentation, filtration, and disinfection. However, it is difficult to remove dissolved pollutants using traditional methods, posing a key technical challenge for ensuring drinking water safety, advanced wastewater treatment, and resource utilization. Furthermore, global water scarcity is also a serious issue. In the face of the challenge of water shortage, in addition to the rational and sufficient utilization of existing water resources, treated wastewater and seawater can also be transformed into usable water resources after appropriate treatment. [1]

Carbon-based adsorption materials (such as activated carbon, fullerenes, etc.) have strong adsorption capabilities and are widely used in wastewater treatment, including tertiary treatment of urban sewage, heavy metal wastewater treatment, and organic industrial wastewater treatment. In recent years, graphene has emerged as a new type of two-dimensional nanomaterial, with a large specific surface area and good chemical stability. Scholars both domestically and abroad have paid extensive attention to and conducted research on oxidized graphene as a potential excellent adsorbent. [2–4]

Oxidized graphene, as a derivative of graphene, has excellent adsorption advantages due to its two-dimensional single-atom structure. Compared to traditional adsorbents, the complex porous structure of oxidized graphene and its composite materials gives it a higher adsorption rate, enabling rapid adsorption of various pollutants. Moreover, relative to other materials, oxidized graphene is more biocompatible and has a smaller impact on aquatic ecosystems. Its biodegradability also makes its application in aquatic environments more sustainable. The application of these advantages in the field of water treatment can enhance the sustainable management of water resources, improve water quality, and help address human health issues. Research and development in oxidized graphene materials will have a significant impact on the field of water treatment, playing an important role in modern economic development and people's daily lives.

2 The structure of oxidized graphene

Oxidized graphene is obtained by chemically introducing oxygen functional groups (such as hydroxyl and carboxyl groups) onto graphene. [5]

This results in oxidized graphene having a larger interlayer spacing and a different electronic structure compared to graphene itself. Its basic unit consists of carbon atoms arranged in a honeycomb-shaped planar structure in sp^2 hybridization form, but in oxidized graphene, this surface structure is modified by oxygen atoms and functional groups such as hydroxyl groups, leading to a transition of the hybridization of some carbon atoms from sp^2 to sp^3[6]. The changes not only increase the material's surface area but also introduce new chemical and physical properties. The high specific surface area of oxidized graphene provides more active sites, increasing the chances of contact with pollutants, thereby enhancing removal efficiency[7] fast adsorption kinetics, excellent regeneration towards heavy metal ions based on the perfect integration of surface adsorption and in-depth bulk uptake.\n \n , \n \n Novel three-dimensional (3D. Increased its hydrophilicity, enabling better dispersion in water. However, due to a lack of accurate detection methods, it is difficult to confirm the nature and distribution of oxygen functional groups on oxidized graphene. This limitation greatly restricts the application of oxidized graphene[8]optical, mechanical, and chemical properties. Pristine graphene is desirable for applications that require a high electrical conductivity, while many other applications require modified or functionalized forms such as graphene oxide due to its good dispersibility in various solvents. Surface functional modification of graphene and graphene oxide is of crucial importance for their broad applications. Functionalization of graphene enables this material to be processed by solvent assisted techniques, such as layer-by-layer assembly, filtration. It also prevents the agglomeration of single layer graphene and maintains the inherent properties. Structurally modifying graphene and graphene oxide through chemical functionalization reveals the numerous possibilities for tuning its structure. Several chemical and physical functionalization methods have been explored to improve the stabilization and modification of graphene. This review focuses on the surface functional modification of graphene and graphene oxide. The preparation method, basic structure and properties of graphene and graphene oxide were briefly described firstly. On the one hand, in the light of bonding characteristic, the surface functionalization of graphene and graphene oxide is divided into non-covalent binding modification, covalent binding modification and elemental doping. On the other hand, non-covalent functionalization contains four categories: π-π stacking, hydrogen bonding, ionic bonding effect and electrostatic interaction. Meanwhile, covalently functionalization includes four categories: carbon skeleton modification, hydroxy modification, carboxy modification and epoxy group modification due to the reactive functional groups. Doping functionalization consists of N, B, P and other different elements. According to the classification of surface structure characteristics, selected typical case has described the functional modification process in detail. The properties and application prospects of the modified products are also summarized. Finally, current challenges and future research directions are also presented in terms of surface functional modification for graphene and graphene oxide.","container-title":"Acta Chimica Sinica","DOI":"10.6023/A16070360","ISSN":"0567-7351","issue":"10","journalAbbreviation":"Acta Chim. Sinica","language":"zh","page":"789","source":"DOI.org (Crossref. Currently, it is widely acknowledged that the distribution of functional groups in oxidized graphene follows the Lerf-Klinowski model.

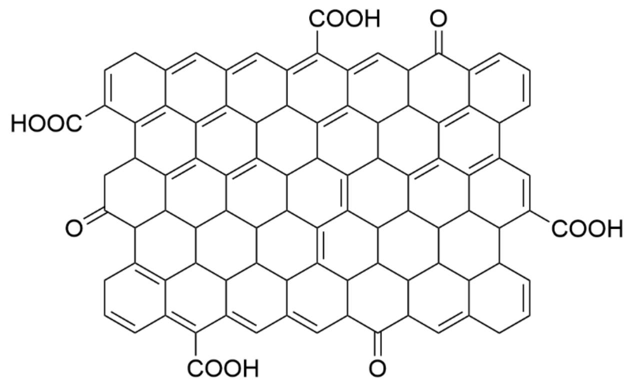

Figure 1 schematic diagram of the GO structure(based on the lerf-klinowski model) [9]

These advantages make oxidized graphene have a broad application prospect in water environments, effectively addressing issues such as water pollution and water resource management, promoting the protection and sustainable utilization of water environments.

3 The adsorption mechanism of oxidized graphene on pollutants in water and the influencing factors

In terms of water treatment applications, studies have shown that oxidized graphene oxide (GO) and its composite materials exhibit excellent adsorption performance in the treatment of heavy metals and organic dye wastewater. In particular, for heavy metal ions such as copper, hexavalent chromium, mercury ions, and organic dyes such as methylene blue, methyl orange, GO and its composite materials demonstrate high adsorption capacity[10]. These studies demonstrate the potential application prospects of oxidized graphene in the field of water treatment, where it can be used as an efficient adsorbent for wastewater treatment and environmental protection.

3.1 Metal ions

3.1.1 The adsorption mechanism of metal ions by oxidized graphene

Oxidized graphene effectively adsorbs metal ions in water through various mechanisms, including electrostatic attraction, chelation, and ion exchange[11].The adsorption mechanism mainly involves two methods: physical adsorption and chemical adsorption. Physical adsorption is mainly achieved through van der Waals forces. Due to the large specific surface area and abundant adsorption sites of oxidized graphene, it can facilitate the physical adsorption of metal ions. Chemical adsorption is achieved through the formation of covalent or ionic bonds. The functional groups on the surface of oxidized graphene undergo coordination reactions with the metal ions in water, forming stable compounds to remove the metal ions. Ion exchange is mainly the result of the exchange reaction between the surface functional groups of oxidized graphene and the metal ions in the solution. Generally, the H^+ on the surface functional groups of oxidized graphene exchanges with the metal ions, thereby immobilizing the metal ions on the surface of oxidized graphene. Therefore, oxidized graphene demonstrates good metal ion adsorption performance and can serve as an effective adsorbent for water purification and wastewater treatment.

3.1.2 The main influencing factors of oxidized graphene adsorption of metal ions

The adsorption capacity of oxidized graphene for metal ions is influenced by factors such as pH, ionic strength, temperature, the quantity of oxygen-containing functional groups, and the presence of other coexisting ions[12]. The adsorption capacity of GO decreases with the increasing degree of oxidation. As the temperature rises, the adsorption rate of metal ions by oxidized graphene also increases; as the temperature decreases, the adsorption rate decreases. If the pH value decreases, the adsorption rate of metal ions by oxidized graphene will also decrease significantly. Therefore, to improve the adsorption rate, it is necessary to control these factors that have a significant impact on the adsorption efficiency.

3.2 Organic Matter

3.2.1 Adsorption Mechanism of Graphene Oxide for Organic Matter

The adsorption mechanism of oxidized graphene for organic compounds in water mainly includes physical adsorption and chemical adsorption. Physical adsorption is primarily due to the layered structure and high specific surface area of oxidized graphene, providing ample adsorption sites for organic molecules. This adsorption is mainly attributed to van der Waals forces or π-π stacking interactions between the surface of oxidized graphene and organic molecules. Chemical adsorption is because the functional groups on the surface of oxidized graphene can interact with the functional groups in organic compounds (carboxyl, phenolic hydroxyl, etc.) through hydrogen bonding or electrostatic interaction, forming stable chemical bonds[13].

In relation to the characteristics of organic compounds, there are several aspects to consider. First, π-π conjugation is significant, particularly for organic compounds containing aromatic rings. Oxidized graphene can exhibit strong π-π interactions with these compounds, which is beneficial for the adsorption of aromatic ring structure organic compounds. Additionally, electrostatic adsorption plays a role. Under specific pH conditions, the functional groups on the surface of oxidized graphene may carry positive or negative charges, and corresponding organic molecules (such as charged organic acids or bases) can be adsorbed through electrostatic attraction.

3.2.2 The main influencing factors of oxidized graphene adsorption of organic compounds

GO mainly adsorbs organic pollutants through interactions such as π-π interaction in the unoxidized regions and hydrogen bonding. The main influencing factors of graphene oxide (GO) adsorption of organic compounds include its unique structural characteristics, the types and quantities of surface functional groups, and the environmental conditions of the water. The adsorption capacity of GO mainly depends on its unoxidized aromatic regions; an increase in the degree of oxidation leads to a decrease in its adsorption capacity. The abundant oxygen-containing groups on the surface of GO provide sites for various interactions with organic compounds, such as electrostatic interactions, hydrogen bonding, Lewis acid-base interactions, etc. In addition, environmental factors such as pH value, ion intensity, temperature, etc., also affect the adsorption performance of GO for organic compounds. Therefore, adjusting these conditions and the characteristics of GO can optimize its adsorption capacity for organic compounds.

4 Research on the Application of Graphene Oxide in Water Treatment

4.1 Application Research in the Treatment of Heavy Metal Wastewater

Li et al[14]conducted a study on the adsorption performance of magnetic graphene oxide composite materials prepared by the composite of graphene oxide and iron powder for Cu^{2+}. The results showed that temperature had a low impact on the adsorption of magnetic graphene oxide. However, the adsorption time, initial concentration of Cu^{2+}, and pH value significantly influenced the adsorption effectiveness of graphene oxide.Bao et al[15] used the properties of β-CD and GO to composite the two, synthesizing β-CD/GO adsorption material, and tested its static adsorption performance for Co^{2+}. The results showed that the composite material β-CD/GO had a high adsorption capacity for Co^{2+}. When the pH value was 6, the adsorption time was 3 hours, and the initial mass-volume concentration reached 100 mg/L, the adsorption capacity could reach 150.28 mg/g.

4.2 Research on the Application in Organic Contaminated Wastewater

He et al[16] utilized graphene oxide, ferric chloride, ferrous chloride, and other raw materials to prepare magnetic two-dimensional nanomaterial, which was then used for the adsorption of organic dyes. The results indicated that the adsorption of methylene blue by magnetic graphene oxide gradually increased with the extension of time, and the adsorption equilibrium point appeared at around 4 hours. Moreover, after adsorbing the pollutants, magnetic graphene oxide could be separated using a magnetic field, and the adsorbent could be recycled by degrading the adsorbed substances for further use.Zhang et al[17] prepared carboxylated graphene oxide and then used amidation reaction to graft polyethyleneimine on its surface, obtaining carboxylated graphene oxide/polyethyleneimine materials, and studied its adsorption performance for methyl orange. The optimal adsorption conditions of GO-COOH-PEI for MO were found to be: pH of 5.0, initial mass concentration of MO at 150 mg/L, volume of 10 mL, amount of GO-COOH-PEI at 7 mg, adsorption temperature at 25°C, and adsorption time of 120 minutes. Under these conditions, GO-COOH-PEI achieved a removal rate of 99.29% for MO.

In summary, graphene oxide and its composite materials prepared by various methods, such as magnetic graphene oxide, chitosan/graphene oxide composite aerogels, have all demonstrated excellent adsorption performance. Graphene oxide and its composite materials have broad prospects for application in the field of water treatment. Future research needs to further explore the adsorption mechanisms and application effects of graphene oxide under complex pollution conditions to realize its practical engineering application value. Currently, there is relatively little research on the coexistence of multiple pollutants in actual wastewater, and further exploration of the application potential of graphene oxide composite materials in complex wastewater treatment is needed.

5 Conclusion and Prospects

This article reviews the effects and mechanisms of graphene oxide in the removal of metal ions and organic pollutants from water, as well as the research progress in its applications in the field of water treatment. The adsorption capacity of graphene oxide is influenced by various factors, such as pH, temperature, and the amount of oxygen-containing functional groups.

Although graphene oxide shows great potential in the field of water treatment, current research is mostly focused on the laboratory level. Further research is needed to investigate its performance and effectiveness in actual engineering applications. Future research should focus more on the adsorption performance under complex water conditions and on enhancing the stability and reusability of graphene oxide and its composite materials, in order to more effectively apply these materials in practical water treatment engineering.

With the deepening of research and technological advancements, the application of graphene oxide and its composite materials in the field of water treatment will become more widespread and efficient. Particularly in the treatment of water containing complex pollutants, optimizing the structure and functions of the materials can further enhance their adsorption efficiency and selectivity to adapt to different types and concentrations of pollutants in various water environments. In addition, developing new synthesis methods to reduce the preparation cost of materials is also an important direction for future research. Ultimately, achieving large-scale application of graphene oxide and its composite materials in the field of water treatment is of great significance for the protection of water resources and the environment.

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