

Progress in Research on the Application of Graphene-Based Composite Aerogels in Wastewater Treatment

Yunzhe Wang

Wood Science and Engineering, Zhejiang A&F University, 311300, China

Wang18969060008@outlook.com

ABSTRACT

This paper reviews recent progress in research on graphene-based composite aerogels for wastewater treatment, with a focus on their preparation methods, structural characteristics, and performance in various wastewater treatment applications. Studies indicate that graphene-based composite aerogels possess excellent adsorption capacity, catalytic activity, and good regenerability, demonstrating significant potential in wastewater treatment. However, challenges such as the cost of graphene-based materials and structural stability in practical applications remain. This paper analyzes these issues and explores the future prospects for the application of graphene-based composite aerogels in environmental engineering.

KEYWORDS

Graphene-Based Composite Aerogels, Wastewater Treatment, Adsorption Performance, Catalytic Degradation, Structural Optimization.

1. INTRODUCTION

As industrialization and urbanization continue to advance, the issue of wastewater pollution has become increasingly severe, making the effective treatment of wastewater a critical topic in global environmental management. Traditional wastewater treatment technologies, such as physical, chemical, and biological methods, have proven effective to some extent but generally suffer from high energy consumption and the risk of secondary pollution, rendering them inadequate for meeting modern environmental protection demands. Against this backdrop, the development of advanced materials has become key to driving innovation in wastewater treatment technologies, with graphene-based aerogels (GBAs) showing significant potential due to their exceptional physicochemical properties.

GBAs, as three-dimensional (3D) porous materials, not only possess the high specific surface area and high porosity typical of traditional aerogels but also inherit the excellent electrical conductivity, chemical stability, and mechanical strength of graphene. These unique structural and performance characteristics enable GBAs to exhibit outstanding efficiency in adsorbing toxic pollutants such as heavy metal ions, organic dyes, and antibiotics, and they also facilitate good regeneration and recyclability in catalytic degradation and adsorption-separation processes.

Building on the foundation of graphene preparation, this paper reviews recent research progress on the application of GBAs in wastewater treatment, particularly their use in the removal of heavy metal ions and organic pollutants. Additionally, the structural advantages of GBAs in wastewater treatment applications are discussed, and future research directions are explored, with the aim of providing a

scientific basis for the development of more efficient and environmentally friendly wastewater treatment materials.

2. OVERVIEW OF GRAPHENE-RELATED TOPICS

2.1. Graphene

Graphene is a single-layer, two-dimensional crystal composed of carbon atoms arranged in a hexagonal honeycomb lattice through sp^2 hybridized orbitals [1]. This structure endows graphene with exceptional mechanical strength, electrical conductivity, and thermal conductivity, making it a subject of extensive research interest worldwide, particularly in fields such as biomedicine, energy storage, catalysis, and environmental remediation. It has become one of the key research hotspots in materials science and engineering technology. As research on its properties deepens and preparation techniques advance, the application areas of graphene are expected to further expand [2]. Currently, graphene is primarily produced through methods such as mechanical exfoliation, chemical vapor deposition (CVD), and the oxidation-reduction process [3]. Mechanical exfoliation is suitable for laboratory research and small-scale production of high-quality graphene; CVD is ideal for large-scale production of high-quality and large-area graphene; while the oxidation-reduction method is suited for large-scale, low-cost production, though it may not meet the required quality standards. Therefore, the choice of graphene preparation method typically depends on specific application requirements and cost considerations. The potential for large-scale production of graphene could further drive its application in wastewater treatment and other environmental remediation areas.

2.2. Graphene Aerogels

Graphene aerogel (GA) is a novel nanomaterial with a three-dimensional network structure formed by the assembly of two-dimensional graphene sheets. This structure imparts GA with excellent stability, extremely low density, very high specific surface area and porosity, as well as outstanding mechanical and electrical properties. GAs are primarily classified into graphene oxide-based aerogels and reduced graphene oxide-based aerogels [4]. GAs can be regenerated through simple physical or chemical methods, such as washing or thermal treatment, allowing the adsorbent material to be reused and reducing long-term operational costs. GA itself has good biocompatibility and environmental stability, ensuring that no secondary pollution is generated during the wastewater treatment process, which aligns with the trend toward green and sustainable development [5].

2.2.1. Preparation Methods

GA is typically prepared by first oxidizing graphite into graphene oxide (GO) using oxidants such as sodium nitrate in concentrated sulfuric acid. Subsequently, GO is reduced to reduced graphene oxide (rGO) in aqueous solution using chemical reducing agents such as sodium borohydride, ascorbic acid, or ethylenediamine. During this process, the oxygen-containing functional groups in GO are removed through reduction, gradually restoring the sp^2 regions, which enhances the electrical conductivity [6]. The rGO sheets are then cross-linked through hydrogen bonding, π - π stacking, and atomic coordination, forming a hydrogel with a rich porous structure [7]. The hydrogel is then subjected to drying processes, such as freeze-drying, supercritical drying, or ambient pressure drying [8], to remove the water content, resulting in a lightweight, high specific surface area, and porous material with good electrical conductivity and mechanical properties known as GA.

3. APPLICATIONS OF GRAPHENE-BASED COMPOSITE AEROGELS IN WASTEWATER TREATMENT

3.1. Organic Dyes and Solvents

Organic solvents and dyes in wastewater, often originating from industries such as textiles, printing, and pharmaceuticals, typically possess complex chemical structures, volatility, and toxicity, posing potential threats to environmental health.

The combination of graphene with biomass materials can produce composite aerogels that are environmentally friendly, cost-effective, and possess excellent adsorption properties. Qi et al. [9] developed a graphene oxide-chitosan aerogel (GO/CS) with high porosity and good mechanical properties by combining GO with chitosan (CS) through hydrogel formation followed by freeze-drying. In this composite, GO provides a large specific surface area and abundant oxygen-containing functional groups, while Gong [10] pointed out that CS improves the porosity and mechanical strength of the aerogel, thus enhancing its adsorption efficiency and stability. Due to the good biocompatibility and degradability of GO/CS, it has become a promising bio-adsorbent in water treatment. GO/CS has shown excellent performance in adsorbing cationic dyes like methylene blue and anionic dyes like methyl orange, with actual adsorption effects influenced by factors such as the amount of adsorbent, solution pH, temperature, and ionic strength [11-13]. Increasing the GO content significantly enhances the adsorption performance for methylene blue, while increasing the CS content is crucial for the removal of methyl orange. NaOH and HCl can be used as desorption agents to regenerate GO/CS after adsorption of methylene blue and methyl orange, with Wang [14] confirming that the regenerated GO/CS retains at least 70% of its original adsorption capacity, indicating good regeneration performance and reusability.

Wang [15] innovatively synthesized copper oxalate composite graphene aerogel (GA-SC) by combining graphene with copper oxalate (CuC_2O_4). During the preparation of GA-SC, the introduction of CuC_2O_4 nanoparticles enhanced the electrostatic cross-linking between GO layers, preventing the stacking of graphene sheets and significantly improving the material's mechanical stability and hydrophilicity. Additionally, the doping of specific Cu ions significantly increased the catalytic efficiency of the GA [16].

3.2. Antibiotic Substances

Ke [17] prepared a three-dimensional network-structured WP/GO porous aerogel with excellent adsorption performance for ciprofloxacin (CIP) in wastewater using GO and waste printing paper (WP) as raw materials and polyvinyl alcohol (PVA) as a crosslinking agent through a simple mixing and freeze-drying method. The adsorption process is a spontaneous endothermic reaction, and higher temperatures favor the adsorption of CIP by the aerogel material. Compared to WP alone, the chemical cross-linking between WP, GO, and PVA forms a tight network structure, improving the thermal stability of the WP/GO aerogel. The study found that when the WP: GO mass ratio was 1:3, the maximum adsorption capacity for CIP reached 158 mg/g, indicating that the WP/GO1:3 aerogel has high efficiency and a fast adsorption rate for CIP. Wang et al. [18-19] also successfully prepared a nano-magnetic composite graphene aerogel ($\text{Fe}_3\text{O}_4@\text{rGO}$) using a one-pot method and applied it to the environmental adsorption of common veterinary antibiotics such as chlortetracycline (CTC), tetracycline (TTC), and oxytetracycline (OTC). This composite material exhibited excellent adsorption performance, reaching adsorption equilibrium for these antibiotics in wastewater within a very short time. Moreover, the adsorption capacity remained stable over a wide pH range (4–8). Compared to pure Fe_3O_4 and rGO, this composite material significantly enhanced adsorption capacity, particularly for CTC and TTC. Ma [20] synthesized GA/CTNs composites, which demonstrated significant adsorption and removal effects on four common sulfonamide antibiotics

(sulfadiazine, sulfisoxazole, sulfamethoxazole, and sulfadimethoxine). The adsorption process was spontaneous and endothermic, with higher temperatures favoring the adsorption process.

3.3. Heavy Metal Ions

In the study of GA (graphene aerogels) for the adsorption of heavy metal ions, Li et al. [21] enhanced GO adsorbents by combining them with molybdenum disulfide (MoS₂) to create a graphene oxide-MoS₂ composite aerogel (GMAs). This material proved effective in the adsorption of heavy metal ions. Yu [22] developed a magnetic graphene aerogel material—Fe₃O₄/rGO—by combining Fe₃O₄ nanoparticles with GO at a 1:2 ratio and adding ethylenediamine as a control agent during synthesis. Fe₃O₄/rGO exhibited excellent adsorption performance for heavy metal ions, with the process being endothermic and spontaneous. The adsorption efficiency was influenced by factors such as pH and adsorption time [23]. Under conditions of 25°C and a pH of 6, the adsorption capacities of Fe₃O₄/rGO for Cu(II), Pb(II), and Cd(II) were 314.5, 58.48, and 56.12 mg/g, respectively, showing the strongest adsorption for Cu(II), followed by Pb(II) and Cd(II). Additionally, since Fe₃O₄ is a magnetic nanomaterial, its successful incorporation onto the GO aerogel surface enables quick and easy separation via an external magnetic field, enhancing the efficiency of Fe₃O₄/rGO in separation and recycling. Studies have confirmed that this material can achieve rapid magnetic separation within 40 seconds while maintaining high selectivity and excellent cyclic adsorption performance [24-27].

Zhao et al. [28] utilized a solution blending method and freeze-drying technique to prepare sodium alginate/graphene oxide (SA/GO) composite aerogels, using sodium alginate (SA) and graphene oxide (GO) as raw materials and selecting calcium carbonate and glucono delta-lactone as crosslinking agents. This composite aerogel demonstrated superior adsorption performance for Cu(II), with mechanical properties significantly enhanced as GO content increased. When the GO mass fraction reached 3%, the SA/GO composite aerogel exhibited a 35.9% improvement in Cu(II) adsorption compared to pure SA aerogel. Additionally, by blending SA with GO and amino-terminated hyperbranched polymers (HBP-NH₂), a novel SA/GO/HBP-NH₂ composite aerogel was prepared. When the SA concentration was 2 wt%, and the GO and HBP-NH₂ contents were 3 wt% and 4 wt% of SA, respectively, the SA/GO/HBP-NH₂ composite aerogel showed optimal adsorption performance for Cu(II), Pb(II), Co(II), and Cd(II) ions. When the GO content reached 7%, the dry and wet mechanical properties of the GO/SA composite material improved by 42.5% and 212%, respectively, compared to the SA matrix. These findings indicate that the incorporation of GO significantly enhances both the adsorption performance and mechanical strength of SA aerogels [29-30].

3.4. Radioactive Nuclides

Radioactive isotopes, such as uranium, pose significant challenges due to their radioactivity and associated chemical toxicity, complicating their treatment. The stability and persistence of these isotopes in the environment result in long-term impacts, with their radioactivity having profound negative effects on human health and ecosystems.

Tang et al. [31] developed CNTs/GO aerogels using GO and carbon nanotubes (CNTs) as raw materials through a freeze-drying method. These aerogels possess a large specific surface area and abundant oxygen-containing functional groups, providing advantages for the adsorption and removal of radioactive uranium(VI). The oxygen-containing functional groups on the GO surface offer key active sites for the adsorption of uranium(VI) [32]. Research by Wang [33] indicated that the adsorption performance of uranium(VI) is influenced by various factors. At lower pH values, uranium(VI) mainly undergoes weak physical adsorption or outer-sphere surface complexation with GO. As the pH increases, deprotonation of surface functional groups leads to the formation of strong chemical adsorption or inner-sphere surface complexes, enhancing the adsorption performance. The CNTs/GO aerogel shows consistent behavior in this regard, with its adsorption efficiency effectively

optimized by adjusting the pH. Additionally, the porous structure of the CNTs/GO aerogel plays a crucial role in influencing its adsorption performance. Zhao et al. [34] found that when the mass ratio of CNTs to GO was 3:7, the resulting aerogel had the largest and most uniform pores, facilitating the entry and fixation of uranium(VI) molecules, significantly improving adsorption capacity.

4. CONCLUSION

GBA, as a novel three-dimensional porous material, have demonstrated significant potential in wastewater treatment. Their exceptional adsorption capabilities, catalytic activity, and renewability have led to considerable progress in the removal of organic pollutants, heavy metal ions, and radioactive nuclides. However, despite extensive research on their application in the catalytic degradation of organic pollutants, studies on their effectiveness in treating other types of contaminants, such as inorganic pollutants and specific industrial chemicals, remain relatively scarce, limiting the broader application of GBA.

Currently, the structural stability and regenerative capacity of GBA still require further improvement. Although existing preparation techniques can produce aerogels with good adsorption and catalytic properties, their mechanical strength and cyclic stability during long-term use need enhancement. Moreover, the catalytic efficiency of GBA in treating pollutants under high flow rates and high concentrations needs further optimization, particularly in improving stability and catalytic performance under high flow conditions.

Future research should focus on the following areas:

- (1) Expanding the application of GBA in the catalytic degradation of other types of pollutants and developing more targeted composite materials.
- (2) Optimizing the internal pore structure and surface properties to enhance material stability and catalytic performance under high flow rates and high concentrations.
- (3) Reducing production costs while ensuring material performance to promote the practical application of GBA in environmental engineering.

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