Research Progress on the Adsorption of Antibiotics in Aqueous Solutions Using Graphene-Based Materials

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Abstract: Antibiotic pollution in aquatic environments has become a global ecological issue. Long-term exposure can induce the emergence of drug-resistant bacteria and genes, threatening the stability of ecosystems and human health. Due to its simplicity, high efficiency, and low cost, adsorption is one of the primary technologies for removing antibiotics from aquatic environments. Graphene-based materials, with their ultra-large specific surface area, abundant surface functional groups, and excellent physicochemical properties, hold great potential for antibiotic adsorption.This paper reviews the structural characteristics of typical graphene-based materials, including graphene, graphene oxide, and doped/modified graphene. It systematically summarizes their adsorption performance and behavior toward common antibiotics-such as tetracyclines, quinolones, and sulfonamides-in aquatic environments. The study analyzes the key influencing factors during the adsorption process, the underlying adsorption mechanisms, and the patterns by which modification strategies regulate adsorption performance.It summarizes the current challenges faced by graphene-based materials in practical applications for antibiotic adsorption in water bodies and predicts future development directions, with the aim of providing a reference for the modification and optimization of graphene-based adsorbents as well as their engineering applications in the treatment of antibiotic pollution in aquatic environments.

Keywords: Graphene-Based Materials; Aquatic Environment; Antibiotics; Adsorption Performance; Adsorption Mechanism; Material Modification

1. Introduction

Due to the widespread use of antibiotics in medicine, livestock farming, aquaculture, and other sectors, large quantities of antibiotics that have not been fully metabolized enter natural aquatic environments via domestic sewage, aquaculture wastewater, and pharmaceutical wastewater, making them typical emerging micropollutants [1]. Although antibiotic concentrations in aquatic environments are low (in the ng/L to μg/L range), these substances exhibit persistence, bioaccumulation, and biological activity. Long-term exposure can induce antibiotic resistance in aquatic microorganisms, and the spread of drug-resistant bacteria and genes further exacerbates public health risks. Moreover, the presence of antibiotics can have toxic effects on the growth and reproduction of aquatic organisms, disrupting the balance of aquatic ecosystems [2]. Consequently, the development of efficient, economical, and environmentally friendly technologies for removing antibiotics from aquatic environments has become a research focus in the field of environmental engineering.

Currently, the main antibiotic removal technologies for aquatic environments include adsorption, photocatalytic degradation, advanced oxidation, and biodegradation [3]. Due to its advantages-such as not requiring complex reaction conditions, producing no secondary pollution, and allowing for the recovery and regeneration of adsorbents-the adsorption method has become the preferred technology for antibiotic removal in actual water bodies, with the core focus being the development of high-performance adsorbent materials [4]. Graphene is a two-dimensional honeycomb-structured nanomaterial composed of sp^2-hybridized carbon atoms. It possesses an extremely large specific surface area (theoretically up to 2,630 m^2/g), excellent mechanical properties, and chemical stability. Functional groups such as hydroxyl, carboxyl, and amino groups can be introduced onto its surface through oxidation, doping, or compositing, significantly enhancing its adsorption capacity for pollutants [5]. Due to their unique structure and excellent properties, graphene-based materials-including native graphene, graphene oxide (GO), reduced graphene oxide (rGO), and various modified graphene composites-have attracted significant interest from researchers in the field of antibiotic adsorption in aquatic environments, and related studies have yielded numerous results.

This paper begins with the structural characteristics of graphene-based materials to systematically summarize the current state of research on the adsorption of various types of antibiotics by graphene-based materials. It analyzes the influencing factors and mechanisms of action during the adsorption process, investigates the effectiveness of material modification in improving adsorption performance, identifies some existing issues in current research, and predicts the future development of graphene-based adsorbents. This provides a theoretical basis and technical reference for the engineering application of graphene-based adsorbents in the treatment of antibiotic pollution in aquatic environments.

2. Structural Characteristics of Typical Graphene-Based Adsorption Materials

This category of materials refers to various substances modified through physical or chemical methods using graphene as a scaffold. They primarily include native graphene, graphene oxide, reduced graphene oxide, as well as doped and composite-modified graphene. The adsorption performance of graphene-based materials toward antibiotics is directly determined by their structural differences[6]. Raman spectroscopy is a key method for characterizing the number of layers and stacking configurations of graphene-based materials, and can effectively identify the structural differences of different materials such as graphene, graphene oxide, and reduced graphene oxide[7].

2.1 Raw Graphene

Raw graphene consists of a single layer of sp^2-hybridized carbon atoms arranged in a tight lattice, forming a perfect two-dimensional honeycomb crystal structure. Its extremely large specific surface area provides a vast number of active sites for the adsorption of antibiotic molecules. The π-π conjugated system on its surface can interact with antibiotic molecules containing aromatic ring structures through π-π stacking, which serves as the primary structural basis for adsorption [7]. However, native graphene has strong interatomic bonding between carbon atoms, lacks distinct surface functional groups, and exhibits poor hydrophilicity. It tends to agglomerate in aqueous solutions, significantly reducing its effective specific surface area. Furthermore, it has poor adsorption capacity for polar antibiotics and cannot be used directly [8].

2.2 Graphene Oxide (GO)

Graphene oxide is a derivative of pristine graphene obtained through oxidation with strong acids. Its surface and edges are substituted by a large number of oxygen-containing functional groups, primarily including hydroxyl (-OH), epoxy (-C-O-C-), and carboxyl (-COOH) groups [9]. The introduction of oxygen-containing functional groups significantly enhances the hydrophilicity of GO, allowing it to disperse well in aqueous solutions and preventing agglomeration; polar functional groups such as carboxyl and hydroxyl groups can form hydrogen bonds and electrostatic interactions with antibiotic molecules, markedly improving the adsorption capacity for polar antibiotics [10]. Since the oxidation process introduces defects and wrinkles into GO, its specific surface area and the number of active adsorption sites are increased. However, the oxidation process partially disrupts the sp^2 hybridized structure of GO, weakening the π-π conjugated system and thereby reducing the π-π stacking interactions with antibiotics containing aromatic rings [5].

2.3 Reduced Graphene Oxide (rGO)

Reduced graphene oxide is a product obtained by removing some oxygen-containing functional groups from GO through methods such as chemical reduction or thermal reduction. During its preparation, part of the sp^2 hybridized structure is restored, and the π-π conjugated system is strengthened, but a certain amount of oxygen-containing functional groups is still retained. rGO possesses the π-π conjugation characteristics of pristine graphene as well as the surface functional group advantages of GO. It can adsorb aromatic antibiotics via π-π stacking interactions and polar antibiotics via hydrogen bonding and electrostatic interactions. Furthermore, its hydrophobicity is higher than that of GO, making it easier to separate and recover in water, thereby addressing the issue of GO's poor recoverability[10]. The degree of reduction of rGO influences its structural properties: a higher degree of reduction results in a more complete sp^2 hybridized structure and stronger π-π interactions, but also leads to a lower content of oxygen-containing functional groups and weaker electrostatic and hydrogen bonding interactions.

2.4 Modified Graphene-Based Materials

To further enhance the adsorption performance of graphene-based materials, researchers have employed structural modifications such as doping with heteroatoms (e.g., nitrogen, sulfur, and phosphorus) and composites with metal oxides, carbon materials, and polymers. Heteroatom doping introduces electronic defects into the graphene framework, altering the charge distribution and thereby enhancing electrostatic interactions and π-π stacking interactions with antibiotic molecules [11]; in nitrogen-doped graphene, pyridine nitrogen and pyrrole nitrogen sites can form coordinate bonds with antibiotic molecules, significantly increasing the adsorption capacity.Composite modification leverages the advantages of different materials; for example, composites of graphene with metal oxides such as TiO_2 and Fe_3O_4 not only increase the material's specific surface area but also enhance adsorption capacity through the complexation of metal ions with antibiotic molecules. Furthermore, the magnetic properties of Fe_3O_4 provide the material with magnetic separation capabilities, facilitating the recovery of the adsorbent [12]; Composites of graphene with macromolecular polymers such as chitosan can further enrich surface functional groups, improving the material's hydrophilicity and biocompatibility.

3. Factors Influencing and Mechanisms of Action of Antibiotic Adsorption by Graphene-Based Materials

3.1 Major Influencing Factors

The adsorption process of antibiotics in aquatic environments by graphene-based materials is influenced by various factors, primarily solution pH, temperature, ionic strength, initial antibiotic concentration, and coexisting pollutants. Among these, solution pH and ionic strength have the greatest impact on adsorption performance [13]. To visually illustrate the patterns of action and effects of these core influencing factors, they have been summarized in Table 1, clearly presenting the specific mechanisms of action and variations in effectiveness of different factors on the adsorption of antibiotics by graphene-based materials.

Table 1. Core Influencing Factors and Mechanisms of Antibiotic Adsorption by Graphene-Based Materials

Influencing Factor	**Mechanism of Action**	**Patterns of Changes in Adsorption Performance**
Solution pH	Altering the charge state of antibiotic molecules and the surface charge distribution of graphene-based materials to regulate electrostatic interactions	Taking tetracycline as an example: When pH < 7, negatively charged GO attracts positively charged or amphiphilic tetracycline via electrostatic forces, resulting in good adsorption; when pH > 7, tetracycline becomes negatively charged and repels GO via electrostatic forces, leading to reduced adsorption performance
Ion Strength	Low concentrations trigger a "salt-out effect," while high concentrations cause "competitive adsorption"; divalent cations exhibit stronger competitive adsorption than monovalent cations	Low concentrations of inorganic ions: antibiotic solubility decreases, and adsorption capacity increases; high concentrations of inorganic ions: compete with antibiotics for active sites, reducing adsorption capacity; the inhibitory effect of Ca^{2+}/Mg^{2+} is significantly stronger than that of Na^+/K^+
Temperature	Most adsorption is exothermic physical adsorption; some modified materials exhibit chemical adsorption	When physical adsorption dominates: As temperature increases, the adsorption equilibrium shifts toward desorption, and adsorption capacity decreases; when chemical adsorption dominates: As temperature increases, adsorption reactions are promoted, and adsorption capacity increases slightly
Co-existing	Macromolecular organic	Humic acids, proteins, and other substances reduce

contaminants	compounds compete for adsorption sites; heavy metal ions form complexes with antibiotics or coordinate with functional groups on the adsorbent	the utilization of adsorption sites; heavy metal ions indirectly alter adsorption efficiency through complexation/coordination, resulting in an overall decrease in adsorption performance

The solution pH not only alters the charge state of antibiotic molecules but also affects the charge distribution on the surface of graphene-based materials, thereby modulating the adsorption process through electrostatic interactions [13]. Tetracycline molecules are positively charged at pH < 3, amphoteric at pH = 3–7, and negatively charged at pH > 7;In aqueous solutions, GO carries a negative charge due to the dissociation of surface carboxyl groups. At pH < 7, electrostatic attraction exists between GO and positively charged or amphoteric tetracycline molecules, resulting in good adsorption; at pH > 7, electrostatic repulsion reduces adsorption performance [10].

Ion strength: In aqueous environments, inorganic ions such as Na^+, Ca^{2+}, Cl^-, and SO_4^{2-} are present. Changes in ion strength can lead to the “salting-out effect” or “competitive adsorption.”Low concentrations of inorganic ions can reduce the solubility of antibiotic molecules in water through salting-out, making them more readily adsorbed onto the adsorbent surface. High concentrations of inorganic ions compete with antibiotic molecules for active sites on the adsorbent surface, resulting in reduced adsorption capacity. Research findings indicate that divalent cations such as Ca^{2+} and Mg^{2+} exhibit stronger adsorption competition than monovalent cations such as Na^+ and K^+ [13].

Temperature: The adsorption process of antibiotics by graphene-based materials is predominantly exothermic physical adsorption. An increase in temperature shifts the adsorption equilibrium toward desorption, resulting in a decrease in adsorption capacity. However, for some modified versions of graphene-based materials, due to the presence of chemical adsorption, an increase in temperature promotes the adsorption reaction, leading to a slight increase in adsorption capacity.

Coexisting contaminants refer to substances such as humic acid, proteins, other organic pollutants, and heavy metal ions present in actual water bodies. Large-molecule organic compounds like humic acid compete with antibiotic molecules for adsorption sites, while heavy metal ions form complexes with antibiotic molecules or undergo coordination with functional groups on the adsorbent surface, thereby affecting adsorption performance [14].

3.2 Major Adsorption Mechanisms

The adsorption of antibiotics in aquatic environments by graphene-based materials results from the combined action of multiple mechanisms. Based on the types of interactions between antibiotic molecules and the material surface, the primary adsorption mechanisms can be categorized as follows.

π-π stacking. This is the core mechanism by which graphene-based materials adsorb antibiotics containing aromatic ring structures. The sp^2-hybridized carbon atoms in graphene-based materials form a large π-conjugated system. Aromatic ring structures in antibiotic molecules, such as benzene, quinoline, and naphthalene rings, can undergo π-π stacking with this conjugated system, causing the antibiotic molecules to be adsorbed onto the material surface.The higher the degree of sp^2 hybridization in the material, the more complete the π-π conjugated system, the stronger the π-π stacking interaction, and the better the adsorption performance for antibiotics containing aromatic rings [9].

Hydrogen bonding. Polar functional groups on the surface of graphene-based materials (GO, rGO, and composite-modified graphene), such as hydroxyl, carboxyl, and amino groups, can form intermolecular hydrogen bonds with polar groups in antibiotic molecules, such as amino, hydroxyl, and carbonyl groups. This is the primary mechanism for the adsorption of polar antibiotics.The strength of hydrogen bonding depends on the types and concentrations of surface functional groups; the higher the content of oxygen-containing functional groups and amino groups, the more pronounced the hydrogen bonding and the greater the adsorption capacity.

Electrostatic interactions. The dissociation of functional groups or the doping of heteroatoms on the surface of such materials imparts a certain charge, leading to electrostatic attraction or repulsion with charged antibiotic molecules in the aqueous solution, which in turn affects the adsorption efficiency.Carboxyl groups on the

GO surface dissociate into negatively charged -COO⁻ ions in aqueous solution, which can form electrostatic attractions with positively charged tetracycline and ciprofloxacin molecules; nitrogen-doped graphene, due to the higher electronegativity of nitrogen atoms compared to carbon atoms, carries a positive charge on its surface, enabling electrostatic attraction with negatively charged sulfonamide antibiotic molecules [13].

Coordination bonding/complexation. In materials of this type-whether doped with heteroatoms (nitrogen, sulfur, phosphorus) or composed of metal oxides-the heteroatom sites or metal ions on the surface can form coordination bonds with amino, carboxyl, or hydroxyl groups in antibiotic molecules, or engage in complexation with the antibiotic molecules, thereby enhancing adsorption capacity. In nitrogen-doped graphene, the pyridine nitrogen can form coordinate bonds with oxygen and nitrogen atoms in tetracycline molecules, while Fe^{3+} in Fe_3O_4 /graphene composites can form complexes with ciprofloxacin molecules [15].

After being modified to form a porous structure (mesoporous or microporous), channel-adsorption materials can utilize the filling of pores to adsorb antibiotic molecules into the interior of the channels, thereby increasing the adsorption capacity. The larger the specific surface area of the material and the more complex the pore structure, the stronger the channel adsorption effect [9].

Some studies indicate that hydrophobic interactions and van der Waals forces also contribute to the adsorption process. Different materials of this type play varying roles in the adsorption of different types of antibiotics, and the adsorption process is accomplished through the combined action of various mechanisms [10].

4. Adsorption Performance of Graphene-Based Materials for Antibiotics in Aquatic Environments

There are numerous types of antibiotics in aquatic environments. Based on their chemical structures, they are classified into tetracyclines, quinolones, sulfonamides, and β-lactams, among others. Among these, tetracyclines, quinolones, and sulfonamides have become the primary focus of adsorption studies on graphene-based materials due to their high usage rates and detection frequencies.Researchers both domestically and internationally have conducted extensive experimental studies on the adsorption performance of various types of tgraphene-based materials toward single or mixed antibiotics. The results indicate that graphene-based materials exhibit good adsorption capacity for various antibiotics, and that adsorption performance is significantly influenced by factors such as material type, antibiotic type, and initial concentration.

4.1 Adsorption of Tetracycline Antibiotics

Tetracycline antibiotics (tetracycline, oxytetracycline, and chlortetracycline) are broad-spectrum antibiotics containing polycyclic aromatic rings and multiple polar functional groups. They are frequently detected in aquatic environments and are a key focus of adsorption studies on graphene-based materials. Peng Bo prepared modified graphene oxide materials and investigated their adsorption performance for tetracycline in aqueous solutions [8]. The results indicated that the maximum adsorption capacity of this material for tetracycline was 268.8 mg/g (Under the experimental conditions of pH = 6, initial concentration of 200 mg/L, temperature of 25°C, dosage of 0.5 g/L, and equilibrium time of 180 min),which is significantly higher than that of traditional adsorbents such as activated carbon, and it maintained good adsorption performance over a wide pH range. The Ag-graphene-TiO_2 composite material prepared by Zou Ze prepared an Ag-graphene-TiO_2 composite material that achieved an oxytetracycline adsorption capacity of 196.1 mg/g(Under experimental conditions of pH = 5, initial concentration 100 mg/L, temperature 25°C, and dosage 0.8 g/L) ,with an adsorption equilibrium time of only 60 minutes, demonstrating rapid and highly efficient adsorption [7]. Graphene-based materials exhibit excellent adsorption of tetracycline antibiotics, primarily due to π-π stacking, hydrogen bonding, and electrostatic interactions between the material and the antibiotic molecules:The benzene and naphthalene rings in the tetracycline molecule form π-π stacking with the sp^2 hybridized structure of this material, while polar functional groups such as amino and hydroxyl groups form hydrogen bonds with oxygen-containing functional groups on the material’s surface. Additionally, the charge distribution on the material’s surface interacts electrostatically with the charged nature of the tetracycline molecule.

Due to their combination of polycyclic aromatic rings and multiple polar functional groups, tetracycline antibiotics are highly efficient adsorbates for graphene-based materials. The common adsorption mechanism for graphene-based materials involves the synergistic interaction of π-π stacking, hydrogen bonding, and electrostatic forces;Modified graphene-based materials exhibit adsorption capacities for tetracycline antibiotics that are significantly higher than those of traditional adsorbents. Furthermore, some composite materials demonstrate rapid adsorption capabilities and maintain good adsorption performance across a wide pH range. The synergistic optimization of material structure and functional groups is key to enhancing the adsorption performance of graphene-based materials.

4.2 Adsorption of Quinolone Antibiotics

Quinolone antibiotics (ciprofloxacin, levofloxacin, norfloxacin, etc.) possess a quinoline ring structure and contain polar groups such as amino and carboxyl groups in their molecules, making them another typical class of antibiotic pollutants in aquatic environments. Wang Xiaoying prepared biomass-derived graphene materials exhibited a maximum adsorption capacity of 189.4 mg/g(Under the experimental conditions of pH = 6, initial concentration of 100 mg/L, temperature of 25°C, dosage of 1.0 g/L, and equilibrium time of 120 min) for ciprofloxacin; in actual water samples, the removal rate of ciprofloxacin could still reach over 85%, demonstrating excellent practical application potential [14]. Wu Nan found that the adsorption capacity of N-rGO for levofloxacin was 212.7 mg/g(Under experimental conditions of pH = 7, initial concentration 200 mg/L, temperature 25°C, dosage 0.5 g/L, and equilibrium time 240 min), significantly higher than that of pristine graphene or GO . This is primarily due to changes in the charge distribution of the material following nitrogen doping, which markedly increases the electrostatic interactions with levofloxacin molecules, and the formation of coordinate bonds between the pyridine nitrogen sites and the antibiotic molecules[17].The adsorption of quinolone antibiotics by such materials is primarily mediated by π-π stacking, electrostatic interactions, and coordinate bonding, and their adsorption performance is significantly influenced by the degree of material hybridization, the content of surface functional groups, and the type of heteroatom doping.

The quinoline ring structure and polar groups of quinolone antibiotics enable a common adsorption mechanism involving π-π stacking, electrostatic interactions, and coordinate bonding with graphene-based materials. Among these, heteroatom doping can significantly enhance electrostatic and coordinate bonding interactions, substantially increasing adsorption capacity;Modified materials such as biomass-derived graphene-based materials and nitrogen-doped reduced graphene oxide not only exhibit high adsorption capacities for quinolone antibiotics but also demonstrate excellent removal efficiency in actual water systems, indicating strong potential for practical application. The degree of material hybridization and the type of heteroatom doping are the key factors in regulating the adsorption performance of graphene-based materials.

4.3 Adsorption of Sulfonamide Antibiotics

Sulfonamide antibiotics (such as sulfadiazine, sulfamethoxazole, and sulfadimethoxine) contain benzene rings and sulfonamide groups (-SO_2NH-) in their molecular structures. They are highly polar and have high solubility in water, making them difficult to remove using traditional adsorbents [1,2]. Due to their abundant surface functional groups, graphene-based materials exhibit good adsorption capacity for sulfonamide antibiotics. The graphene/chitosan composite adsorbent prepared by Wang Leichao achieved an adsorption capacity of 156.3 mg/g (Under the experimental conditions of pH = 5, initial concentration of 100 mg/L, temperature of 25°C, dosage of 1.0 g/L, and equilibrium time of 150 min)for sulfadiazine . The addition of chitosan enriched the surface of the material with amino and hydroxyl groups, forming numerous hydrogen bonds with the sulfonamide pyrimidine molecules. Meanwhile, the π-π conjugated system of graphene formed π-π stacking interactions with the benzene rings of sulfonamide pyrimidine, collectively enhancing the adsorption performance[13].Studies indicate that the adsorption of sulfonamide antibiotics by this type of material is primarily achieved through hydrogen bonding and π-π stacking interactions, as sulfonamide antibiotics have weak charge distribution, and electrostatic interactions contribute little to adsorption.

Due to their high polarity and water solubility, sulfonamide antibiotics pose a challenge for traditional adsorbents. The common mechanism for their adsorption by graphene-based materials involves the synergistic action of hydrogen bonding and π-π stacking, with electrostatic interactions contributing to a lesser extent; By combining with macromolecular polymers such as chitosan, the surface polar functional groups of graphene-based materials can be enriched, strengthening hydrogen bonding and thereby achieving efficient adsorption of sulfonamide antibiotics, providing an effective material option for the removal of highly polar, highly soluble antibiotics.

4.4 Adsorption of Other Types of Antibiotics

In addition to the three antibiotics mentioned above, researchers have also conducted studies on the adsorption of β-lactam and macrolide antibiotics by this graphene-based materials. Yi Wenwen prepared graphene-based nanocomposites exhibited an adsorption capacity of 128.2 mg/g(Under the experimental conditions of pH = 6, initial concentration of 80 mg/L, temperature of 25°C, dosage of 0.8 g/L, and equilibrium time of 180 min) for amoxicillin (a β-lactam antibiotic), with the adsorption mechanism primarily involving hydrogen bonding and electrostatic interactions; Guan Bingbing found that graphene/TiO_2 composites achieved an erythromycin (macrolide) removal rate of over 90%, with π-π stacking and surface complexation serving as the primary adsorption driving forces[9][15]. Graphene-based materials exhibit good adsorption performance for various types of antibiotics, with particularly effective adsorption for antibiotics containing aromatic ring structures and a high number of polar functional groups. Their maximum adsorption capacity is also significantly higher than that of traditional adsorbents such as activated carbon and zeolites, demonstrating distinct material advantages.

Graphene-based materials also exhibit good adsorption performance for other antibiotics, such as β-lactams and macrolides. The adsorption mechanisms vary depending on the structural characteristics of the antibiotics: hydrogen bonding and electrostatic interactions are the primary mechanisms for β-lactams, while π-π stacking and surface complexation dominate the adsorption of macrolides; graphene-based materials exhibit superior adsorption performance for antibiotics rich in aromatic rings and polar functional groups, with adsorption capacities far exceeding those of traditional adsorbents. They demonstrate the advantages of broad-spectrum, highly efficient adsorption materials, offering the potential for the synergistic removal of multiple antibiotics in aquatic environments.

5. Modification and Optimization Strategies for Graphene-Based Materials

5.1 Existing Issues and Directions for Modification and Optimization

Research on graphene-based materials for antibiotic adsorption in aquatic environments has achieved certain results; however, the translation of laboratory findings into practical engineering applications still faces numerous challenges. These issues can be briefly summarized as follows: high preparation costs; cumbersome small-scale laboratory preparation methods, high raw material costs, and low yields, making large-scale industrial production difficult ; poor recovery and regeneration performance, with some materials (such as GO) being difficult to separate after adsorption, and the adsorption capacity of magnetically modified materials decreasing significantly after multiple regenerations; weak resistance to interference in actual water bodies, where inorganic ions and coexisting pollutants in complex water systems compete for adsorption sites, resulting in poor selectivity for mixed antibiotic adsorption;Biological safety and environmental risks remain unclear; due to their nanoscale nature, the migration and transformation patterns of graphene-based materials in water are poorly understood, and their toxic effects on aquatic organisms have not yet been fully elucidated; research on adsorption mechanisms is insufficient, with a lack of precise characterization at the molecular level, making it impossible to provide theoretical guidance for targeted modification [18].

To address these issues, researchers have developed various modification and optimization strategies, including oxidation modification, reduction modification, heteroatom doping, and composite modification. Through targeted structural regulation, these strategies resolve issues related to material hydrophilicity, agglomeration, adsorption performance, and recoverability, thereby enhancing the adsorption performance of graphene-based materials and strengthening their practical application potential. The effects and characteristics of various modification strategies are summarized in Table 1, which outlines the modification methods, core mechanisms, advantages, and limitations of the four primary modification strategies for graphene-based materials. Among these, composite modification stands out as the strategy with the greatest potential for future engineering applications due to its ability to simultaneously enhance adsorption performance and confer multifunctionality.

5.2 Roles and Application Potential of Various Modification Strategies

Oxidation and reduction modifications are fundamental modification methods for graphene-based materials, primarily used to adjust hydrophilicity/hydrophobicity and the degree of π-π conjugation. They can specifically address issues such as the poor hydrophilicity of native graphene, its tendency to agglomerate, or the weak π-π stacking in GO; however, these two methods have conflicting effects on performance regulation and must be selected appropriately based on the target antibiotic type [10].

Heteratom doping modification, on the other hand, can significantly enhance adsorption capacity and selectivity by altering the material’s electronic configuration, making it a key approach for developing high-performance adsorbents. By introducing active sites through the doping of heteroatoms such as nitrogen, sulfur, and phosphorus,enhancing electrostatic and coordinate bonding interactions. This approach is particularly effective for improving the adsorption performance of quinolone and tetracycline antibiotics; however, due to the difficulty in controlling modification conditions and doping levels, breakthroughs are still needed for large-scale application [19].

Composite modification is currently the most widely studied modification method and holds the greatest potential for future engineering applications. By combining graphene with metal oxides, polymers, and other materials, not only can adsorption performance be improved, but the material can also be endowed with multifunctionality, such as magnetic separation and photocatalytic degradation. This achieves an integrated “adsorption-degradation-recovery” effect, significantly enhancing the material’s practical application value. Fe_3O_4 /graphene composites combine the high adsorption capacity of graphene with the magnetic properties of Fe_3O_4. After adsorption, they can be rapidly separated and recovered using an external magnetic field, resolving the challenge of material recovery ; Graphene/TiO_2 composites not only adsorb antibiotics but also regenerate the adsorbent for reuse by photocatalytically degrading the adsorbed antibiotics under light irradiation, effectively resolving issues related to material recovery, regeneration, and secondary pollution, thereby meeting the core requirements of practical engineering applications [8][13]. In addition, coupling graphene-based materials with photothermal catalysis, advanced oxidation, and other technologies can build an 'adsorption-degradation' integrated system, which has a significant effect on the deep removal of antibiotic pollutants [20].

6. Conclusion

Due to their extremely large specific surface area, abundant surface functional groups, excellent physicochemical properties, and diverse modification methods, graphene-based materials have become highly promising materials in the field of antibiotic adsorption in aquatic environments. They demonstrate broad-spectrum and highly efficient adsorption of common antibiotics such as tetracyclines, quinolones, and sulfonamides, far outperforming traditional adsorbents such as activated carbon and zeolites. The adsorption mechanisms of graphene-based materials exhibit differentiated synergistic effects depending on the structural characteristics of the antibiotics. π-π stacking is the core mechanism for adsorbing antibiotics containing aromatic rings, while hydrogen bonding and electrostatic interactions dominate the adsorption of polar antibiotics. Coordination bonding/complexation and pore adsorption provide additional room for enhancing the adsorption performance of modified materials;Solution pH and ionic strength are the key environmental factors influencing the adsorption process; adsorption efficiency can be modified by regulating electrostatic interactions and competition for adsorption sites.

Addressing existing challenges in the preparation, application, and mechanistic studies of graphene-based materials, future research and development should focus on the following directions: Developing low-cost, large-scale green preparation processes using biomass such as straw, wood chips, and chitosan as raw materials; establishing continuous industrial-scale production technologies to reduce costs and increase yields, thereby laying the foundation for large-scale applications [2][13]; Continuously improving modification strategies, with a focus on developing composite modification techniques; integrating technologies such as magnetic separation and membrane separation to enhance the separation and recovery rates of adsorbents; and developing mild and efficient regeneration methods, such as low-temperature desorption and photocatalytic regeneration, to improve the material's recyclability [3][7][19] ; Conducting adsorption application studies in actual water bodies to investigate the interference mechanisms of co-existing pollutants, preparing graphene-based materials with high resistance to interference and high selectivity, and simulating engineering scenarios through dynamic adsorption experiments such as fixed-bed adsorption columns to provide technical parameters for engineering applications [1][20] ; Conduct systematic biosafety and environmental risk assessments to clarify the migration, transformation, and degradation patterns of materials in aquatic environments, evaluate their toxicity to aquatic organisms and microorganisms, and develop environmentally friendly graphene-based materials to mitigate environmental risks [8][10]; Utilize advanced techniques such as XPS, FTIR, AFM, and molecular dynamics simulations to deeply investigate adsorption mechanisms at the molecular level, identify adsorption sites and configurations, and achieve targeted modification and optimization of materials [5][6][9]; Develop multifunctional graphene-based materials that integrate adsorption, photocatalysis, and advanced oxidation technologies to achieve integrated adsorption, degradation, and recovery. Coupling these with membrane separation and advanced oxidation technologies will establish novel water treatment processes capable of achieving deep removal of antibiotics from aquatic environments, thereby providing innovative technical solutions for the practical management of antibiotic pollution in water bodies.

As research continues to advance, the preparation and modification technologies for graphene-based materials will be continuously refined, and their engineering applications in the treatment of antibiotic pollution in aquatic environments will gradually be realized, providing robust technical support for ecological and environmental protection as well as public health safety.

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