Application of Graphene in Wastewater Treatment of Explosive Production

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Abstract. The composition of explosive wastewater is complex and contains a large number of toxic and explosive hazardous chemicals, which makes the treatment process of explosive wastewater quite cumbersome and dangerous. Typical components in explosives wastewater are listed and classified in this paper. Usually, carbon materials are used to treat explosive wastewater. For example, activated carbon has a high specific surface area, so it has a good adsorption effect on organic pollutants. In addition, activated carbon can also be modified to have the ability to degrade organic pollutants, such as TNT and nitrobenzene. Graphene is a new type of carbon material, which not only has the advantages of large specific surface area, but also has excellent chemical stability. Due to its excellent chemical stability, graphene will not be significantly oxidized during the treatment of explosives wastewater. It makes graphene and its composites a very promising new material for explosive wastewater treating.

Keywords: graphene, explosives waste water, adsorption performance, degradation performance

1 Introduction

Explosive/energetic materials play a vital role in defense, industry and other fields, but at the same time, the large amount of wastewater generated in their production process has also become an urgent environmental problem. The importance of explosive/energetic material wastewater treatment is self-evident. These effluents usually contain high chemical oxygen demand (COD), strong acidity, high salinity and contain special hazardous substances, such as energetic materials such as TNAZ, DNTF, BuNENA, etc. And TNT (TNT), Dienti (DNT), RDX (RDX), Oktogin (HMX), nitroglycerin (NG), nitrocotton (NC) and other highly toxic substances. If discharged directly without effective treatment, it will cause serious damage to the ecological environment such as soil and water, and threaten the health of human beings and other organisms.

The traditional methods for the treatment of wastewater containing energetic materials mainly include extraction, reverse osmosis, electrodialysis, iron-carbon microelectrolysis, physical and chemical methods, membrane separation combined with biological methods, etc. However, these approaches have many limitations. For ex-

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ample, physical methods such as extraction have the disadvantage of high secondary pollution; The electrolysis method has the disadvantages of high energy consumption and difficult scale. The wastewater from the synthesis of energetic materials with high acidity and nitrate content is highly corrosive to reverse osmosis, electrodialysis and other membranes. The strong oxidizing nitrogen oxides produced by nitric acid under the action of current and the waste liquid of mixed nitrate and sulfur acid greatly reduce the service life of the membranes and increase the treatment cost. Moreover, the effect of high salt on membrane blocking is obvious, which greatly increases the operation and maintenance cost of membrane separation method and hinders its industrial application.

As a new material with great application potential, graphene has brought new hope for the treatment of explosive/energetic material wastewater. Graphene has a large specific surface area and rich pore structure, the adsorption of pollutants mainly depends on its own oxygen-containing functional groups and aryl groups. In terms of hydrophilic and hydrophobic properties, the adsorption of pollutants by graphene materials can be divided into hydrophilic adsorption and hydrophobic adsorption. In terms of physical and chemical properties, the adsorption of pollutants by graphene materials can be divided into physical adsorption and chemical adsorption. Physical adsorption is mainly based on intermolecular forces, including electrostatic action, π-π stacking, hydrophobic action, hydrogen bond and van der Waals force. Chemisorption is based on chemical bonding, for example, the complexation of oxygen atoms on graphene oxide with metal ions will promote adsorption.

Studies have shown that graphene and its composites can adsorb heavy metal ions, dyes, antibiotics, pesticides, crude oil[1], etc. In the treatment of explosive/energetic material wastewater, graphene can remove a variety of harmful substances in wastewater through adsorption, which has the advantages of high efficiency, environmental protection and low cost [2]. In addition, graphene can also be combined with metal fillers and/or metal oxide fillers for micro-electrolysis reactions, further improving the efficiency of wastewater treatment. Graphene has a high application prospect in the treatment of explosive/energetic material wastewater, which is worthy of further study.

2 Theoretical Basis of Graphene Wastewater Treatment

2.1 Characteristics and Advantages of Graphene

As a new type of nanomaterial, graphene has shown unique characteristics and advantages in wastewater treatment, such as high specific surface area and good adsorption properties.

2.1.1 High Specific Surface Area.

Graphene has an extremely high specific surface area, which gives it a huge advantage in adsorbing pollutants in wastewater treatment. For example, the polyaniline-modified graphene oxide (PANI/GO) composite material synthesized by Shao et al. using in-situ polymerization technology has a maximum adsorption capacity of 1960 mg/g for U(VI) at pH=5.0 and 610 mg/g at pH=3.5, two orders of magnitude higher than traditional adsorbents and nanomaterials. This is due to the high specific surface area of graphene, which can provide more adsorption sites, thus greatly improving the adsorption capacity of pollutants.

Graphene/carbon nanotube composites can be used in electrochemical sensors for the detection of acetaminophen (APAP), and show excellent selectivity and stability due to the high surface area and multi-mode pore structure of graphene/carbon nanotube composites, which can provide a large sensing area and an efficient transport channel. In wastewater treatment, graphene with a high specific surface area can quickly adsorb a large number of pollutants, such as heavy metal ions, organic dyes, etc., effectively reducing the concentration of pollutants in wastewater.

2.1.2 Excellent Adsorption Properties.

The principle of graphene adsorption of pollutants in explosive/energetic material wastewater mainly includes physical adsorption and chemical adsorption. Physical adsorption is mainly based on intermolecular force, including electrostatic action, hydrophobic action and van der Waals force. For example, graphene can be divided into hydrophilic and hydrophobic adsorption for pollutants. The oxygen-containing functional group of graphene oxide is mainly "hydrophilic", which is easy to combine with hydrophilic substances, and easy to combine with metal sulfides, metal atoms, oxides and other forms to form graphene oxide intercalation composite materials, which can effectively adsorb and remove a variety of toxic and harmful pollutants in water. Aryl alkyl is mainly a "hydrophobic group" that tends to bind hydrophobic substances and effectively adsorb oil pollutants.

Chemisorption is the adsorption based on chemical properties, such as the adsorption function caused by the complexation of oxygen atoms and metal ions of graphene oxide. In the treatment of explosive/energetic material wastewater, graphene can effectively remove various harmful substances in the wastewater, such as heavy metal ions and energetic material molecules, through these adsorption mechanisms. At the same time, the good adsorbability of graphene is also related to its unique two-dimensional structure, which enables graphene to fully contact with pollutants and improve adsorption efficiency.

In summary, the high specific surface area and good adsorption of graphene make it have great advantages in the treatment of explosive/energetic material wastewater, and provide a new idea and method for solving the problem of wastewater treatment.

2.2 Types and Functions of Graphene Composites

Graphene composites play an important role in wastewater treatment, and different types of composites have their own unique applications and effects.

2.2.1 Graphene-nanocomposites.

Graphene-nanocomposites show significant advantages in wastewater treatment. For example, Cheng et al. prepared graphene oxide (GO) by Hummers method, then functionalized GO, and finally prepared reduced graphene oxide /Ag nanoparticle complex using TETA as reducing agent by hydrothermal method. The detection limits of the compound for trace concentrations of Cu^{2+}, Cd^{2+} and Hg^{2+} are 10~15M, 10~21M and 10~29M, respectively, which can be used in the sensor for the detection of trace heavy metal ions. The magnetic graphene oxide nanocomposites (MGO) prepared by Lingamdinne et al. have excellent magnetic properties, high specific surface area and high chemical stability, and have been widely used to remove heavy metals, radionuclides and organic dyes from water-based environments. Jabeen et al. prepared zero-valent iron nanoparticle graphene composite (G-nZVI) by reducing graphene oxide and ferric chloride with sodium boride under argon atmosphere. Through adsorption experiment, it was found that G-nZVI composite with a load of 6 wt% GO had the highest adsorption capacity for Pb (II).

The advantage of graphene-nanocomposites is that, on the one hand, the introduction of nanoparticles increases the specific surface area of the composite material and provides more adsorption sites, thereby improving the adsorption capacity of pollutants. On the other hand, the special properties of nanoparticles (such as magnetic properties) can make the composite easier to separate and recycle after treating wastewater, improving the reusability of the material.

2.2.2 Graphene-polymer Composites.

Graphene-polymer composites also play an important role in wastewater treatment. Graphene polymer composite material has excellent electrical conductivity, mechanical properties, energy storage and other properties, which can realize the detection and treatment of sewage. In 2006, Ruoff et al reported graphene/polystyrene composites. Subsequently, the related research of graphene/polymer composite materials has made rapid development, and then become a research hotspot.

Shao et al. synthesized polyaniline-modified graphene oxide (PANI/GO) composite material by in-situ polymerization technology, and applied it to pre-concentrate U(VI) in aqueous solution. The maximum adsorption capacity of PANI/GO composite for U(VI) reached 1960 mg/g at pH 5.0 and 610 mg/g at pH 3.5, which was two orders of magnitude higher than that of traditional adsorbents and nanomaterials. PANI/GO composites have ideal tolerance to high concentration salt and good recycling performance. Therefore, PANI/GO composite has a good application prospect in extracting U(VI) from nuclear fuel aqueous solution and removing environmental pollution.

The graphene/polyamide composite prepared by Saleh et al. has good adsorption performance, high regeneration efficiency, and high adsorption capacity (158.2mg /g) for Sb(III) in aqueous solution, so it can be used as a new adsorbent for Sb(III) removal. Hu et al. prepared graphene oxide/polypyrrole (GO/PPY) composite material, which has a very high adsorption capacity for phenol and aniline, and can be regenerated by the desorption of phenol and aniline by ethanol, and the adsorption capacity is not significantly reduced, so it can be recycled.

Zheng et al. used urushiol to react and polymerize with graphene oxide (GO) sheets to form 3D graphene polyurushiol (3D-PU-G) connected by a polymer skeleton. Compared with traditional 3D-G, 3D-PU-G composites have significantly improved hydrophobicity, adsorption capacity, mechanical strength and recyclability, which is very suitable for water purification. For example, 3D-PU-G has high stability and strength above 20 kPa, and the adsorption capacity of various organic solvents and oils in water is also increased by 1.62 to 1.97 times compared with 3D-G. After running more than 100 cycles, the 3D-PU-G composite still showed highly stable strength and adsorption capacity, while the 3D-G composite could only run 3 cycles.

The characteristics of graphene-polymer composites are that the introduction of polymers can improve the dispersion of graphene and prevent the agglomeration of graphene, thereby improving the adsorption performance of the composite. At the same time, the function of the polymer can give the composite material specific adsorption properties, so that it can be targeted to remove different types of pollutants in the wastewater. In addition, some graphene-polymer composites also have good recycling properties, reducing the cost of wastewater treatment.

3 Types of Explosive and its Waste Water Components

3.1 Types of Common Explosive/Energetic Materials

As an important energetic material, explosive has been widely used in national defense, industry and other fields. Typical military energetic materials are: TNT (2,4, 6-trinitrotoluene, code TNT), Dinitrotoluene (dinitrotoluene, code DNT), picric acid (2,4, 6-trinitrophenylphenol, code PA), 1,3, 3-trinitroazacyclobutane (TNAZ),3, 4-dinitrofurazan oxyfurozan (DNTF) and other nitro compounds, RDX (cyclotrimethyltrinitramine, code RDX), Octozin (cyclotetramethylenetetranitramine, code HMX), hexanitrohexazazane (code CL-20), Tetracil (2,4, 6-trinitrobenzenitrine, code TE), nitroguanidine (nitroimine urea, code TE), In addition, civilian explosive products also include mononitrotoluene, m-dinitrotoluene, nitroxylene, nitrobenzene, aniline, dianiline, o-toluidine, ammonium ladder explosive and so on.

3.2 Composition of Explosive/Energetic Material Wastewater

There are many kinds of common explosive/energetic materials, and different explosive/energetic materials have different production processes. In the synthesis process of energetic materials, various intermediate products and by-products will be produced, which may enter the wastewater and increase the difficulty of wastewater treatment. Wastewater may be produced in all aspects of the production process, and the components in the wastewater are greatly different. The main pollution components in typical explosive wastewater are shown in Table 1.

Table 1. Main pollution components in typical explosive wastewater[3]

Name of explosive	Major polluting component
TNT	TNT, DNT, trinitrobenzoic acid, dinitrocresol, trinitrobenzene, dinitrophenol, tetranitromethane, unknown substance
RDX	Ulotropine, RDX, HMX, RDX oxide, nitric acid, unknown substance
HMX	Ulotropine, nitric acid, formaldehyde, methylamine, dimethylamine, dimethylnitrosamine, copper, acetic acid, ammonium nitrate
NC	Oxalic acid, malic acid, formic acid, glycolic acid, butyric acid, malonic acid, tartaric acid, trihydroxyglutaric acid, dihydroxybutyric acid, hydroxypyruvate, saccharic acid, hydroxymalonic acid, cyanide, nitrate, nitrite
NG	Nitroglycerin, dinitrate glycerin, nitrate, sulfate, sodium salt
NGu	Ammonium nitrate, nitroguanidine, guanidine nitrate
Smokeless powder	Anthracite granules, nitrocellulose, nitroglycerin, solvent (ethanol, ether, ethyl acetate, acetone, etc.), stabilizer (diphenylurea and its derivatives, diphenylamine and its derivatives), plasticizer (o-phthalate, dinitrotoluene, etc.), lead salt

Classification of the components of explosive/energetic material wastewater mainly includes the following aspects: (1) Organic components, including energetic material molecules and organic solvents, such as TNT, RDX, HMX, toluene, ethanol, methanol, acetonitrile, dimethyl sulfoxide and so on, toluene, ethanol, methanol, acetonitrile, dimethyl sulfoxide and so on. (2) Inorganic substance, including strong acids and inorganic salts, such as nitric acid, sulfuric acid, sodium chloride, ammonium nitrate, ammonium perchlorate, etc. Wastewater with high acidity is highly corrosive to treatment equipment and pipes, and also affects subsequent biological treatment processes. Wastewater with high salinity will block treatment methods such as membrane separation, reduce treatment efficiency and increase treatment costs. (3) Heavy metal ion, including arsenic, chromium, lead, copper, cobalt, selenium, etc. The existence of heavy metal ions will not only cause serious pollution to the ecological environment, but also cause great harm to human health.

There are many kinds of common explosive/energetic materials, and the components of the production wastewater are complex, containing high chemical oxygen demand (COD), strong acidity, high salinity and special dangerous substances, such as energetic materials such as TNAZ, DNTF, BuNENA, etc. And TNT (TNT), Dienti (DNT), RDX (RDX), Oktogin (HMX), nitroglycerin (NG), nitrocotton (NC) and other highly toxic substances. If the waste water is discharged directly without effective treatment, it will pose a serious threat to the ecological environment and human health.

4 The Application of Graphene in the Treatment of Explosive Wastewater

4.1 Adsorption

4.1.1 Adsorption of Heavy Metal Ions.

Graphene has excellent adsorption capacity for heavy metal ions in explosive/energetic material wastewater. For example, the treatment of heavy metal wastewater by graphene materials mainly uses its large specific surface area and excellent adsorption properties. According to relevant experimental data, in the treatment of explosive wastewater containing heavy metal ions such as arsenic, chromium, lead, copper, cobalt and selenium, graphene can quickly adsorb these ions and reduce the heavy metal content in the wastewater. Experiments have shown that the three-dimensional graphene macrobody prepared by chemical vapor deposition has a strong adsorption capacity for Pb^{2+}, and its adsorption capacity is 882 mg/g. Chai Jing et al. obtained graphene by reducing graphene oxide with acetyl acetone, and tested the adsorption performance of Pb^{2+}. The maximum adsorption capacity was 105.4mg /g. In addition, graphene-nanocomposites are also outstanding in adsorption of heavy metal ions. For example, the prepared magnetic graphene oxide nanocomposites (MGO) have excellent magnetic properties, high specific surface area, high chemical stability and other characteristics, and have been widely used to remove heavy metals from water-based environments.

4.1.2 Adsorption of Organic Pollutants.

Graphene also has a good adsorption effect on organic pollutants in explosive/energetic material wastewater. Severo et al.[4] used 3D graphene sponge material to adsorb p-nitrophenol and p-nitrophenol in wastewater, and the adsorption process reached equilibrium in less than 5 min. The maximum adsorption capacity of p-nitrophenol was 1842 mg/g and 879.6 mg/g at 30°C. Yang Jinbei et al.[5] prepared graphene by REDOX method and studied its adsorption behavior for 4-nitrophenol. The adsorption process of graphene for 4-nitrophenol is endothermic adsorption and can be spontaneous adsorption. Huang Q et al.[6] prepared the PAA-grafted GO membrane, and the retention rates of p-nitroaniline were 14.1% and 60.2% at pH=3 and 11.

4.2 Degradation

Graphene is not only excellent at adsorbing pollutants in explosive/energetic material wastewater, but also plays an important role in degrading these pollutants.

4.2.1 Zero-Valent Iron Reduction Method.

Chen Y T et al.[7] prepared rGO supported zero-valent iron (nZVI/rGO) using RGO as support material, which can treat the TNT content in wastewater to less than 0.1mg/L when the material dosage is 40 g/L and pH=6. Zhang C X et al.[8] used reduced graphene (APR) supported with gold nanoparticles as a two-dimensional template and successfully constructed a supercrosslinked polymer (APfR-HCP) with porous structure on the surface of graphene by solvent braided method. The specific surface area of APfR-HCP was up to 568 m2/g, which greatly improved the catalytic ability of 4-nitrophenol. Moreover, 4-nitrophenol can be reduced to 4-aminophenol within 4 min. Sun Y L[9] prepared nano zero-valent iron-magnetic graphene composite (nZVI@MG) and investigated its removal properties of total hexanitrohexazazine isobolustrane (CL-20) from wastewater. The experiments showed that nZVI@MG could completely degrade 50 mg/L CL-20 solution within 120 min. The degradation of commercial iron powder, nano-zero-valent iron (nZVI) and nano-zero-valent iron-graphene composites (nZVI@rGO) was only 27.9%, 53.2% and 57.7%, respectively.

4.2.2 photocatalysis.

Shen B et al.[10] prepared a composite nano-catalyst composed of Cu_2O and graphene oxide (rGO). The nanocomposites were characterized by X-ray diffraction, transmission electron microscopy and UV-VIS diffuse reflection absorption spectroscopy. The results show that Cu_2O particles can be fixed on the surface of rGO, and Cu_2O improves the optical properties of rGO, thus improving the utilization of visible light. Compared with Cu_2O under the same conditions, the photodegradation activity of Cu_2O/rGO composite on TNT red water is improved, and the COD removal rate is 45%, which is three times that of Cu_2O, which verifies the feasibility of photocatalytic treatment of TNT red water by Cu_2O/rGO composite. Zhang L F[11] successfully prepared reduced graphene oxide composites loaded with CeO_2 and Fe_2O_3 by hydrothermal method, and realized the treatment of nitroaromatic compounds wastewater under ultraviolet light. Sun X F et al.[12] constructed a non-toxic and environmentally friendly α-Fe_2O_3/RGO/mpg-C_3N_4 nanocomposite containing Z-type heterostructure photocatalyst, large specific surface area, visible light response, and the degradation rate of TNT can reach 99.57% under the condition of visible light 12 h. Feng H et al.[13] developed a batch preparation method of photocatalytic materials for the degradation of explosive wastewater. Zhou Feng et al. [14] prepared a series of GO/g-C_3N_4 aerogel materials for catalytic degradation of undimethylhydrazine (UDMH) wastewater. The results show that when the mass fraction of GO is 25%, the catalytic degradation of UDMH wastewater is the best and stable. After 5 cycles, the photocatalytic activity is only reduced by 7.15%.

4.2.3 Persulfate Oxidation Process.

Ren L X[15] prepared a series of heterogeneous supported Co_3O_4/3D N-GN catalysts using nitrogen-doped three-dimensional graphene (3D N-GN) as the carrier and Co_3O_4 as the active component by a one-step hydrothermal method, and analyzed the internal mechanism of its catalytic activation of perbisulfate (PMS) to degrade nitrobenzene. When the dosage of Co_3O_4/3D N-GN catalyst was 3600 mg/L, the dosage of PMS was 2.0 g/L, and pH=6, the catalytic oxidation system had the best degradation effect on nitrobenzene, the removal rate of nitrobenzene was 84.23%, and the removal rate of COD_{Cr} was 80.27%.

4.2.4 Coupled Anaerobic Biotechnology Method.

Jing W et al.[16, 17] studied the enhancement of nitrobenzene degradation by anaerobic biotechnology coupled with graphene oxide (GO) and reduced graphene oxide (RGO). It is concluded that the coupled system has better pollutant removal performance and stability at high nitrobenzene concentration, low hydraulic residence time and high salinity. The quinone group on the surface of RGO is reduced, the conjugation property is partially restored, the conductivity is enhanced, and the reduction of nitrobenzene is promoted[18].

4.2.5 Electrocatalytic Reduction Method.

Tan C[19] prepared a self-supported needle-like rGO/CoP/CF electrode, which showed high electrochemical reduction activity and could remove 91.5% of 10 mg/L nitrophenol within 40 min under 20 mA conditions.

Graphene can promote the degradation of pollutants in wastewater by catalysis. The principle of catalytic degradation of pollutants mainly includes the following aspects: First, graphene has excellent electrical conductivity, which can accelerate electron transfer and promote the REDOX reaction. For example, in energetic material wastewater, graphene can be used as a catalyst carrier, combining with metals or metal oxides to form an efficient catalytic system. These catalysts are able to activate oxidants such as peroxonosulfates (PMS) and produce strong oxidizing free radicals such as sulfate free radicals ($SO_4^{-}\bullet$) which attack organic contaminants in wastewater and decompose them into harmless small molecules.

Secondly, the large surface area and abundant pore structure of graphene provide more active sites for the catalyst and enhance the catalytic activity. At the same time, the two-dimensional structure of graphene allows it to be in full contact with pollutants, improving catalytic efficiency. In addition, graphene can also interact with pollutants through π-π stacking and hydrogen bonding to further promote the catalytic degradation reaction.

5 Conclusion

The principle of graphene adsorption of pollutants in explosive/energetic material wastewater includes physical adsorption and chemical adsorption, and the two-dimensional structure enables it to fully contact with pollutants and improve adsorption efficiency. Some oxygen-containing functional groups on the surface of GO/RGO may provide the possibility for loading other functional materials. Loading functional materials can further improve the effect of graphene treatment of explosive/energetic material wastewater. In the future, we can continue to explore its combination with MOOF, new photocatalyst, quantum dots, etc., and its application in the treatment of explosive wastewater.

Graphene has great potential and application prospect in the treatment of explosive/energetic material wastewater. At present, the main constraint is the high price of graphene materials, and future research should continue to explore the combined application of graphene with other methods, as well as the optimization of process parameters, to provide a more effective solution to solve the problem of explosive/energetic material wastewater treatment.

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