Application of Graphene Technology in the Removal of Heavy Metal Ions in Wastewater

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Abstract. Nowadays, heavy metal pollution has become a serious problem. Toxic heavy metal ions can result in extreme damage to the environment and human society. Under that situation, methods that can remove the heavy metal ions in water have been required. Graphene technology can be widely applied to the removal of heavy metal ions. This article will explain the preparation of graphene oxide and reduced graphene oxide and the efficiency and influence factors of the method applied in water treatment. The method can remove many kinds of mainly occurring toxic heavy metal ions with very high efficiency. Also, large-scale production of graphene oxide can be achieved. The removal of heavy metal ions in water by graphene technology can be a practical method in the water treatment field.

Keywords: Wastewater, graphene, metal ions s.

1. Introduction

Water pollution by heavy metal ions pollutants has become the most severe issue in the world. Wasted water can be released by many industries like chemical manufacturing, electronic devices manufacturing, fertilizer industry, and so on. Some of the extremely toxic ions like Pb^{2+}, Cd^{2+} and Hg^{2+} contained inside the wasted water which had caused numerous disasters like the Minamata disease, Toyama iati itai disease, and mercury poisoning in wheat grains in Iraq. We are currently living in the "pollutant removal era," in which wastewater treatment has evolved from a voluntary and optional practice to a multi-stage process that is essential for significantly raising the standard of drinking water and water released into the environment. Then, graphene-based removal technology has various benefits, including being highly efficient, affordable, and simple to operate. It is also regenerative and adaptable for large-scale wastewater treatment operations. These factors can all contribute to the application of the graphene material absorption-based method and increase the efficiency of water treatment. Graphene oxide-based materials can produce several ways to absorb heavy metal ions such as eelectrostatic interaction, π-π stack, hydrophobic interaction, and complexation. Because of these properties, the graphene-based material can have a much higher efficiency of absorption than the traditional materials [1].

In this article, the preparation and application of graphene in the removal of heavy metal ions in wastewater will be introduced.

2. Graphene Oxide(GO) and Reduced Graphene Oxide (R-GO)

Compared to the normal nanographene, there are more oxygen-containing functional groups on the surface of the graphene oxide, such as hydroxyl group, carboxyl group, and carbonyl group. In that case, many specific features can be added to the normal nanographene. The structure of the graphene oxide is shown in Fig.1. The reduced graphene oxide can be formed by removing those oxygen-containing functional groups (hydroxyl group, carboxyl group, and epoxy group) from the graphene oxide [1]. Various forms of nanocomposite materials can be created by combining graphene oxide and reduced graphene oxide with metal, metal oxide nanoparticles, biomolecules, semiconducting nanoparticles, and polymers. The sheet of graphene oxide experiences several changes during reduction, including an insulator, semiconductor, and semimetal transition. The restoration of sp2 hybridized carbon atoms is the key cause. The oxygen and defect sites in reduced graphene oxide are what allow for simple chemical bonds with various substances. In that situation, graphene oxide and reduced graphene oxide can be the efficient material that can be used to remove the heavy metal ions inside the water.

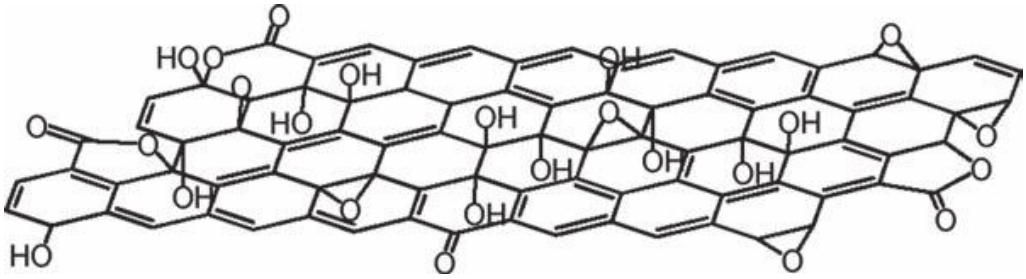

Figure 1. The structure of GO [2].

2.1. Preparation of Graphene Oxide and Its Derivative

The methods of producing graphene oxide can be divided into two ways including the ttop-down exfoliation method and the bottom-up growth method. Today, people mainly use REDOX stripping method to prepare graphene oxide and reduced graphene oxide [2]. The basic idea is to introduce oxygen-containing functional groups (such as hydroxyl, keto group, ether bond, etc.) between the graphite layers to weaken the van der Waals force between them, destroy the conjugated structure of graphite by using a strong acidic medium, and then obtain graphene oxide. The process of obtaining reduced graphene oxide involves separating and adding reducing agents through ultrasonic reduction, as well as other methods such as thermal reductive, microwave reduction, electrochemical reduction, and other methods. The mechanism is shown in Fig. 2. This method can make sure that the cost of producing graphene oxide is low and mass production can be achieved, thus removing heavy metal ions from water resources can be widely applied.

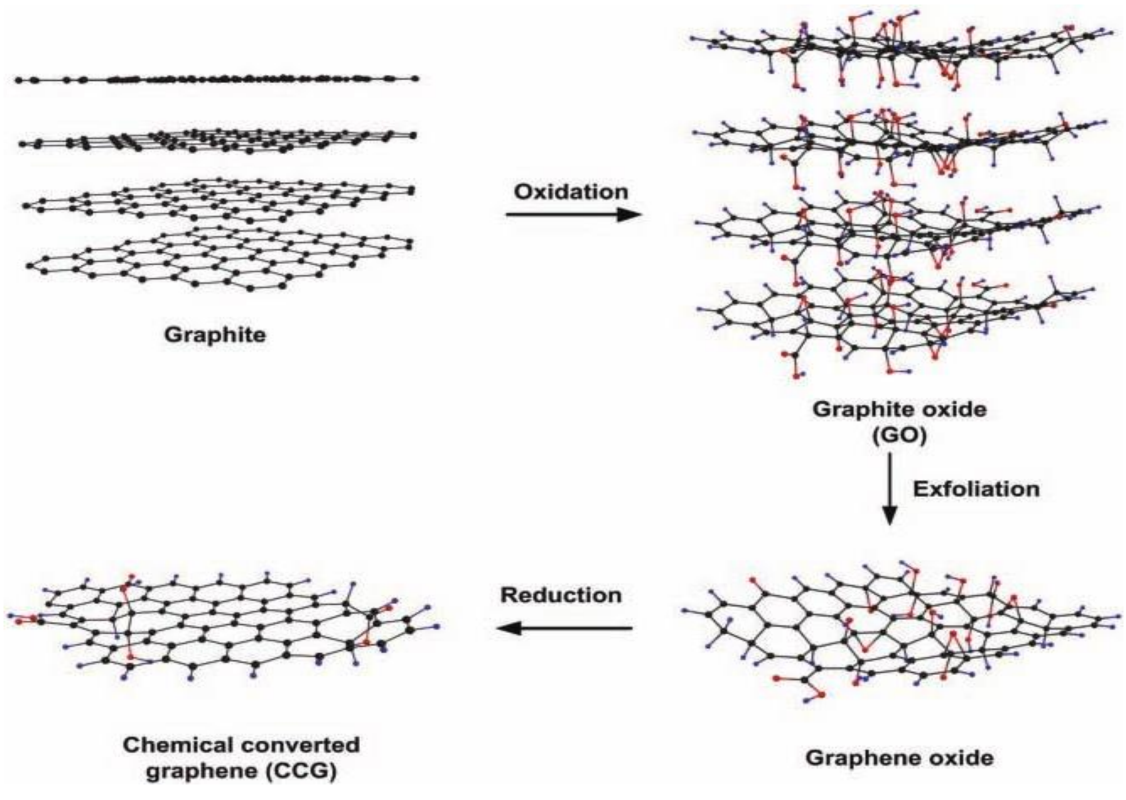

Figure 2. The basic mechanism of REDOX stripping method [2].

2.1.1. Hummers method

Among the REDOX stripping methods, the Hummers method is one of the most commonly used methods to produce graphene oxide materials because of timeline of the preparation process is relatively suitable and safe. The method achieves the goal [3]. By oxidizing potassium permanganate with graphite powder in strong sulfuric acid, graphite flakes that are brown and have carboxylic acid groups at the edges and phenolic hydroxyl groups and epoxy groups on the plane are produced. By ultrasonic or vigorous stirring at high shear, this graphite sheet layer can be peeled into graphene oxide, resulting in a stable single-layer graphene oxide suspension in water that is light brown yellow. The conjugated network's great functional efficiency explains why the graphene oxide sheet acts as an insulator. Partial reduction treatment can be used to create graphene sheets with chemical modifications. The process of producing graphene oxide by using the Hummers method is shown in Fig. 3 [4]. This oxidation-strip-reduction procedure can successfully make insoluble graphite powder processable in water, providing a way to produce reduced graphene oxide, although the resulting graphene product or reduced graphene oxide both have more flaws that make it less conductive than the original graphene.

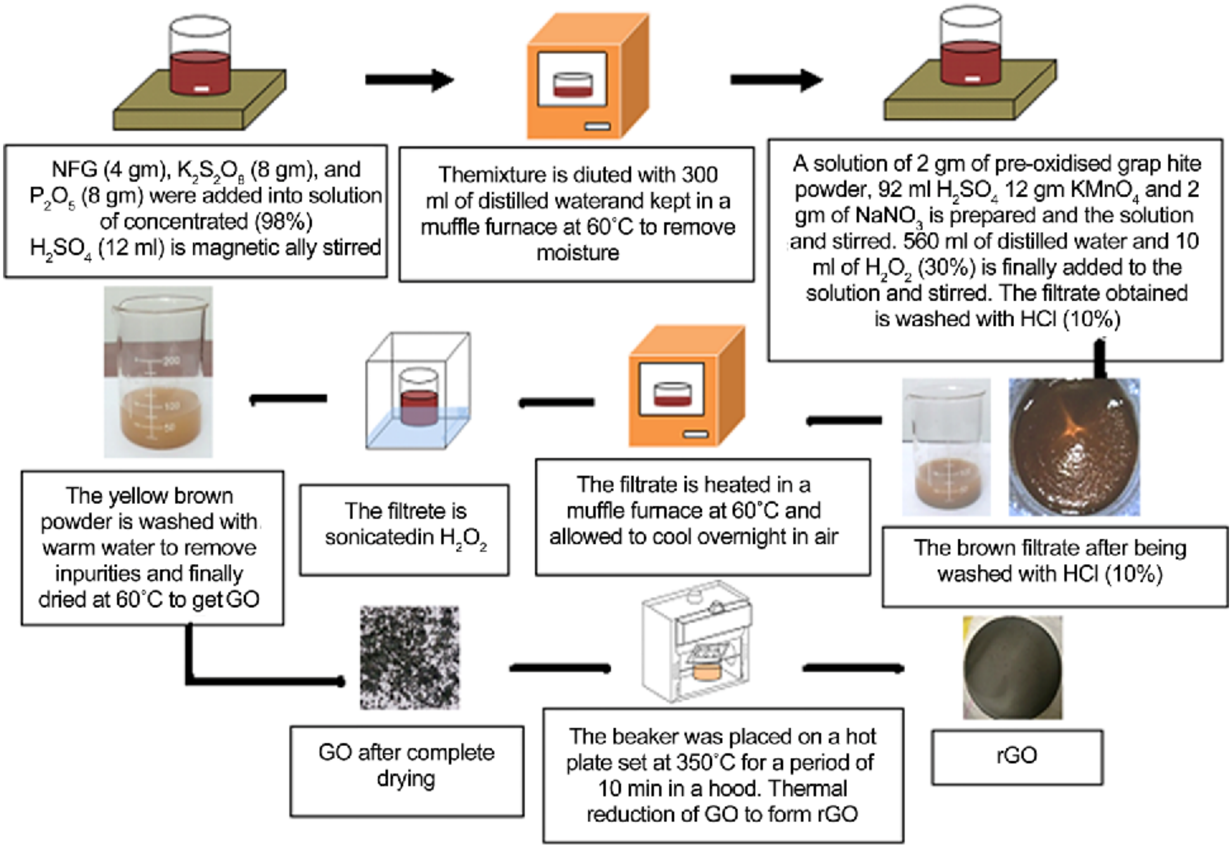

Figure 3. The process of a kind of modified Hummers method [4].

2.1.2. Chemical vapor deposition (CVD) method

There are still many practical methods to prepare graphene oxide materials instead of REDOX stripping method. For example, the chemical vapor deposition method is the most possible method that can prepare graphene in both massive areas and high quality in recent times. CVD means [1, 2] using carbon sources such as methane and ethanol (carbon-containing precursors) to decompose and release carbon atoms in high-temperature conditions, and then grow graphene by annealing deposition on a substrate (mostly metal substrate). By using metal with low soluble carbon content like copper and platinum as the substrate, the carbon atoms are directly attached to the metal surface to form a large monolayer of graphene. However, a disadvantage of this method is the excessive cost. The substrate must made of some noble metal, otherwise, the efficiency will decline.

2.2. Absorption Based Mechanism

Nowadays, heavy metal pollution is a serious environmental problem. Cleaning the water resources and removing the toxic heavy metal elements by using an absorption based method is suitable for application in a large scale application. Also, this method is cost-effective, re-usability and high efficiency [5]. Graphene oxide and its derivative like reduced graphene oxide have a large surface area, an abundant amount of oxygen-containing functional groups and good mechanical strength. These properties make graphene-based material have been acknowledged as a kind of efficient and ideal material that can be applied in the field of decontamination of wastewater containing toxic heavy metal ions. It can interact with metal ions by electrostatic interaction and ion exchange, and the oxygen atom on the surface has a lone pair of electrons, which can be complexed with metal ions by sharing electron pairs so that the metal ions in the water body are adsorbed on it [5]. Previous studies have shown that the adsorption capacity of graphene oxide for metal ions is significantly better than that of the traditional adsorption material activated carbon, and also better than the reported adsorption materials like carbon nanotubes (CNT). While the adsorption force is derived from electrostatic attraction, complexation, and cation bonding, the adsorption of heavy metal ions by graphene oxide is primarily dependent on the type and number of oxygen-containing functional groups on its surface as well as the - conjugated structure on the substrate surface. Under acidic conditions, the degree of GO ionization and the quantity of negative charge on the GO surface initially rise as pH increases. The primary mechanism for heavy metal adsorption on graphene oxide is electrostatic interaction. The hydroxyl group on the surface of graphene oxide can form coordination bonds with metal ions to produce complexes as the pH is gradually raised, and complexation and metal ion exchange start to take over as the primary mechanisms of GO interaction with heavy metals.

3. Application

3.1. Removal of Metal Ions

Graphene oxide-based materials can remove various types of heavy metal ions from water effectively. For example, Pb^{2+}, Ag^{+}, Cu^{2+}, Fe^{3+}, etc. Those are the most common heavy metal ions that cause pollution. Here are some examples of heavy metal ions that the graphene oxide absorption method can remove.

3.1.1. Pb^{2+}

Lead is one of the most commonly occurring pollutants, young children and women are particularly vulnerable to lead. Much research indicates that graphene oxide, reduced graphene oxide, and their derivative can absorb and remove Pb^{2+} from polluted water effectively [5]. A pH of 5-7 is ideal for removing Pb^{2+}. Excellent Pb^{2+} binding abilities have been demonstrated by graphene and GO sheets [6]. Sitko et al. used GO sheets to significantly reduce Pb^{2+} (1119 mg/g). Additionally, they noticed how the GO dispersivity in water changed following adsorption. The tendency of GO to aggregate and precipitate after becoming complex with a metal ion is a crucial stage in the process of removing the complexed adsorbent. Peng et al. also reported that GO sheets have a high adsorption capacity of 766 mg/g. Under the normal situation, the concentration of Pb^{2+} inside the polluted water cannot reach a very high level. According to the data from research, the ratio between Pb^{2+} that has been absorbed and graphene oxide or its derivative in mass is nearly 1:1. In that case, graphene oxide and its derivative can clean up Pb^{2+} inside water resources with little amount due to the low concentration of Pb^{2+}.

3.1.2. Cu^{2+}

Although copper pollution has been rarely reported, especially for water resources, copper finds extensive applications in microelectronics and can pollute the environment. To solve this problem, the graphene oxide-based nanocomposite materials absorption method can be applied. Among the derivatives of graphene oxide, The most frequently used adsorbents being investigated for Cu ion removal are magnetic graphene oxide sheets and amino-modified GO substrates (GO-NH2) [7]. For the elimination of various metal ions, Huang et al. employed graphene oxide with an amino-functional

(GO-NH2) [8]. Cu^{2+} had an absorption capability of 26.25 mg/g, it was discovered. Magnetic GO with an amino modification has been shown to have the greatest documented copper absorption (578 mg/g). When the magnetic GO sheets (mGO) were functionalized with amino groups, copper uptake was seen to virtually double (319 mg/g for mGO to 578 mg/g for amino-mGO) in all pH settings.

3.1.3. Cd^{2+}

Cadmium is one of the most toxic heavy metal elements. The pollution of soil and river caused by cadmium have resulted in the serious Toyama itai itai disease. Compared to the traditional absorption-based method, the graphene oxide-based absorption method is more effective [9]. Park et al. created reduced graphene oxide nanosheets conjugated with magnetic iron oxide or silver (R-GO/Fe_3O_4, rGO/Ag, R-GO/Fe_3O_4/Ag), and they assessed the nano composites' ability to adsorb Cd^{2+}. The composites' Cd^{2+} adsorption capacities were as follows: R-GO (433.2 mg/g), R-GO/Fe_3O_4/Ag (386.7 mg/g), R-GO/Ag (372.8 mg/g), and R-GO/Fe_3O_4 (292.7 mg/g). Although the adsorption capacity was reduced as a result of the functional transformation, it was still higher than that of the majority of other absorbents used to remove Cd^{2+}.

3.1.4. Hg^{2+}

Mercury is also extremely toxic. Just like cadmium, Mercury pollution also caused many serious disasters. The most famous one is the Minamata disease. Nowadays, the graphene-based absorbent technology has been applied to the removal of Hg^{2+} [7]. Yap et al. have tried to use polyamine functionalized rGO made by hydrothermal/chemical reduction to remove Hg^{2+} from rivers and seawater. The produced polyamine/rGO adsorbent had a Hg^{2+} uptake of over 85% compared to the reported 16% for commercial activated carbon.In a multimetallic solution containing Hg^{2+}, Pb^{2+}, Co^{2+}, Cd^{2+}, and Cu^{2+}, the adsorbent also demonstrated strong selectivity toward Hg^{2+} (>70%). The adsorbent's Hg^{2+} absorption efficiency in a real water system was 74% for river water and 56.5% for seawater. The decrease in mercury absorption in seawater was attributed to the existence of mercury as chloro-complexes ($HgCl_2$ and $HgCl_3$) caused by the presence of a considerable amount of chloride ions. With this technology, people can avoid a disaster like the Minamata disease happening again.

3.2. Factors Affecting the Removal of Metal Ions Using Graphene

Several factors can influence the absorptive capacity of graphene oxide, like pH value, ionic strength, number and type of oxygen-containing functional groups that graphene oxide has, and natural organic matter.

3.2.1. pH value

There are two aspects that the pH value can affect the speed and amount of absorption to the heavy metal ions by using graphene oxide-based materials [10]. First off, the pH level has an impact on the graphene oxide surface's charged characteristics. The isoelectric point affects the adsorption characteristics of graphene oxide in the aqueous phase. The surface of graphene oxide has a negative charge due to the presence of carboxyl and hydroxyl groups. If the isoelectric point is lower than the pH value of the solution, the capacity of positive heavy metal ions in the solution to adsorb is strong. On the contrary, if the pH value of the solution is lower than the isoelectric point, the GO surface is positively charged, and the adsorption effect is weakened accordingly. In addition, the pH value also affects the charged properties of the adsorbed material. At different pH, metal ions will form different compounds, and the electrical properties of this compound will also affect the adsorption of GO to metal ions. In general, GO's adsorption of heavy metal ions is suitable for acidic conditions, but if the pH is too small, it may destroy the structure of GO, or H^+ in the water body will produce competitive adsorption with heavy metal ions, resulting in a decrease in adsorption capacity.

3.2.2. Ionic strength

Here are three ways that ionic strength can affect the absorption. The ionic strength will affect the electrostatic interaction between GO and adsorbent [10]. Electrostatic action is the main mechanism of GO adsorption of heavy metals at low pH. When the ionic strength in the solution increases, the electrostatic interaction between the adsorbent and the adsorbent will be weakened accordingly. The second one is ion competitive absorption [10]. The electrolyte ions added to the solution will have competitive adsorption with the adsorbent ions of the solution itself, thus inhibiting the adsorption of heavy metals. The adsorption capacity decreased with the increase in ionic strength. The third one is producing salt out or salt solubilization effect with absorbent [10]. When the electrolyte is added to the solution, the ion will compete with the adsorbent ion of the solution itself for the solvent molecule, and the solvent molecule will move to the strong electrolyte square, causing the hydration and solubility of the weak electrolyte square to decline, so that it is more inclined to be adsorbed.

3.2.3. NOM

Natural organic matter(NOM) including humus, polysaccharide, amino acid, etc. Organic matter usually contains many functional groups that can influence the absorbing process of graphene oxide [10]. On the one hand, the presence of NOM will considerably increase the stability of GO because it will produce spatial energy repulsion, which will expose more adsorption sites and increase the capacity of heavy metal ions to bind to them. On the other side, NOM molecules will be adsorbed by GO via hydrogen bonding, Lewis acid-base interaction, or interaction, taking up its surface functional groups and limiting its capacity to bind heavy metals, among other things. The graphene-based method needs to be used in a wild environment like streams, rivers, and oceans which contain large amounts of natural organic matter. Thus the influences caused by NOM are hard to avoid.

4. Summary

Toxic heavy metal ions released into the water environment will cause extreme damage to human health and ruin the ecosystem. How to remove them from the aquatic environment or decrease the influence caused by the heavy metal ions has become a challenging issue nowadays. Graphene oxide and reduced graphene oxide have large surface area, large amounts and variety of functional groups, and good mobility charge carriers. These properties make graphene-based materials very practical and efficient materials in removing heavy metal ions by using an absorption-based method. Also, because of its efficiency, reusability, and adaptability, the method has been considered and proven as a successful way to remove heavy metal ions from water. In that case, the application of the graphene-based absorption method should be largely used in the water treatment field to face the water pollution challenge successfully.

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