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Using graphene and its derivatives to remove copper ions from mine water

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Abstract:

China's mining industry plays a significant role in the country's economy but also poses environmental challenges, including pollution from heavy metals like copper. Traditional methods for removing copper ions from mine water have limitations in terms of effectiveness and cost-efficiency. This study explores the potential use of graphene and its derivatives as an alternative solution for adsorbing copper ions. Graphene oxide, in particular, shows promise due to its high surface area, chemical stability, and ease of production. The research findings demonstrate that graphene oxide has a high adsorption capacity for copper ions and can effectively remove them from mine water. This environmentally friendly approach offers a viable solution for mitigating copper pollution in China's mining industry while contributing to sustainable mining practices and enhancing water quality management. By advancing these technologies and exploring low-cost manufacturing methods for carbon nanomaterials, this research addresses industrial pollution challenges not only in China but also globally.

Keywords: graphene; copper ions; mine water.

1. Introduction

China is one of the major mining countries in the world. According to the national geological environment mapping survey of mines, there are more than 110,000 non-hydrocarbon mines in China, with a total area of about 1.04×10^5 km^2 and 187 types of mines, and the total amount of minerals extracted annually is estimated to be more than 1.36×10^{10} tons. Classified by the mining category, there are more than 16,500 energy mines such as coal, more than 10,900 metal mines, and more than 83,700 non-metallic mines such as building materials and chemical raw materials [1]. It could be seen that mine industry is an essential component of China's national economy, which plays an important role in economic development and social stabilization.

However, while mine industry greatly contributed to the development of China, it also caused contamination to the environment of many areas and cities in China, such as Mongolia, Shaanxi, Northwest China, and Northeast China. For example, reduced state sulfide in sulfide deposits and coal seams are exposed to an oxidizing environment during mining, with oxidation, decomposition, and dissolving in mine water, ultimately forming acidic mine water. This kind of water always has a low value of pH and high mineralization, which makes the acidic water highly corrosive to mining equipment and confines the growth of plants because of the increased toxicity. Additionally, during the process of mining, heavy metals like Cu, Zn, Pb, and Hg may enter mine water as mining and transportation, thus being harmful to organisms. As for all of the pollution caused by heavy metals, copper is a vital source. This article will mainly focus on the treatments of copper pollution since rather than extremely effecting on one side like Hg and Pb, which mostly impact on biological health, it could cause contamination in several aspects. Not only could Cu cause harmful biochemical effects, toxicity, and hazards in flora, fauna, and human beings, but also influence the toxic level of water and soil due to the increased copper ion concentration. The processing of copper-bearing minerals in Uganda has led to the accumulation of rock waste and residues near rivers, causing heavy metals to contaminate the waterways. This pollution is a result of the erosion causing the leaching of heavy metals with acid streams and transporting solid particles. Subsequent investigations have revealed higher concentrations of these toxic metals in the soil, tap water, and even the nails of local residents [2].

There are already conventional methods able to solve the problem of excess copper ions to a certain extent. Precipitation is widely used in removing copper action from wastewater by reacting with lime to form its metal hydroxide nowadays. However, this way is limited by the concentration of the metal ion and pH of the solution [3]. Another technology is ion exchange. The ion exchange technique has already been used to eliminate copper ions and other heavy metals in mine water successfully, which is economical for the recovery and recycling of wastewater in electroplating operations. However, the ion exchange process is considered to be expensive since it needs the recharge of resin and the disposal of a substantial volume of spent and the contaminant regenerant solution [3]. Obviously, each of these approaches has its flaws. The authors found that these problems could be solved to a certain extent by nanotechnologies.

This article will focus on the application of nanotechnology to ameliorate copper pollution of mine water in China. After searching for references, the authors found a potential method to solve this problem, which is through Carbon Nanomaterials, and talked about their conceptions, reaction mechanisms, and advantages.

2. The introduction of graphene its derivatives

2.1 Graphene

Graphene is a carbon nanomaterial composed of tightly packed sp2-bonded carbon atoms arranged in a honeycomb lattice crystal in two-dimensional layers, each layer one atom thick. With a sheet thickness of 0.34 nm, graphene is currently one of the strongest and thinnest nanomaterials available [5, 6]. Due to its low water solubility, graphene is constrained in certain fields. In addition, a few drawbacks of the single-component graphene material include poor electrochemical activity, facile agglomeration, and challenging manufacturing, which significantly restrict the use of graphene [6]. Preparing graphene derivatives is a useful strategy to get around these restrictions and broaden the uses of graphene. For instance, applying strong oxides to graphite will result in the addition of carboxyl, hydroxyl, and epoxy groups to the basal plan of graphene oxide via means of graphite layers [7]. It is a strong contender for the adsorption of both organic and inorganic wastewater from water due to its high surface to weight ratio and chemical stability [4]. In recent years, people have widely used carbon nanomaterials such as graphene and its derivatives as adsorbents owing to their extraordinary surface properties, easy modification, large specific surface area, controlled structural varieties, high chemical stability, porosity, low density, ease of regeneration, and reusability. In addition, Strong acidity and abundant functional groups characterize graphene oxide, which exhibits good adsorption for cationic and basic chemicals through electrostatic and hydrogen bonding interactions.

2.2 Graphene oxide

The chemical structures of graphene and its derivatives can be seen in fig.1. Graphene oxide is more advantageous than graphene due to its ease of processing, large-scale production, and cheap cost of manufacture [6]. Recently, several adsorbents such as graphene oxide (GO), reduced graphene oxide (rGO), GO sponges, chemically functionalized GO, and GO nanocomposites have demonstrated efficacy in eliminating pollutants from industrial, residential, and agricultural wastewaters [4].

The function of graphene and its derivatives in the dynamic adsorption of heavy metal ions has been documented

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in a number of investigations. Electrostatic interactions control physisorption, the primary mode of adsorption to graphene and its derivatives. Because the surface of graphene oxide has negatively charged oxygen functions, GO is better suited for the adsorption of positively charged aqueous pollutants [4]. In addition, GO is a soft material with a wide aspect ratio that can be easily bent by outside forces on its morphology and structure. When metal ion adsorption is present and the pH of the solution is changed, GO could be seen to aggregate. According to Chowdhury et al., GO aggregation adheres to the DLVO theory and Schulze-Hardy rule, which states that aggregation is mostly dependent on cation type and ionic strength but very weakly dependent on pH in the range of 4–10 [4]. It was also discovered that interactions between faces and edges are the means by which GO aggregation takes place. It is shown that heavy metal cations Ag (I), Cu (II), Cd (II), Pb (II) and Cr (III) might destabilize GO more efficiently than regular cations like K (I), Na (I), Ca (II), and Mg (II) via surface adsorption during the heavy metal removal process employing GO. Through pcation interactions, heavy metal ions may be able to easily overcome electric double-layer (EDL) suppression, anchor to the graphene oxide (GO) surface, and disrupt the surface potential. This will ultimately cause the structural transformation of 2D GO into 1D tube-like, 2D multi-overlapped sheets, and 3D sphere-like structures [4]. Kinetic observation showed that the thickness of the hydration shell and the electronegativity of the metal can control the morphological change of GO after metal adsorption [4]. Generally, Langmuir adsorption isotherms are followed by graphene and graphene-based nanocomposites, showing monolayer formation of the contaminant onto the graphene nanocomposite surface. Oxygen functionalities, such as –OH, –COO–, –C–O–C–, and –COOH, are present on the surface of GO and rGO in varying amounts, and they can form bonds with pollutants in water. The two main interactions between the dye (adsorbate) and GO (adsorbent) are electrostatic interactions between the electron-rich graphene oxide and cationic dyes, and p–p interactions between the p electron cloud of the GO rings and aromatic rings of the dye [4]. Excellent adsorption characteristics of intrinsic GO/rGO for the removal of metal ions have been demonstrated in numerous investigations [4]. Wu et al. showed that Cu(II) adsorption onto GO nanosheets adhered to the Freundlich model; complexation, ion-exchange, and electrostatic interactions are thought to be responsible for the adsorption mechanism. Toxic metal ions are mostly adsorbed onto GO nanosheets by chemisorption, which is also followed by the development of metal complexes with oxygen functions on the GO surface. Thus, it is feasible for people to use graphene and GO to adsorb copper ions in mine water.

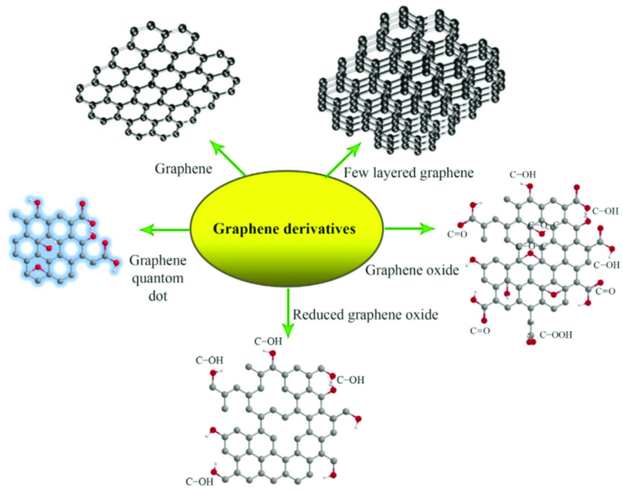

Fig 1. The chemical structures of graphene and its derivatives [8]

3. Synthesized methods of graphene and Graphene oxide

3.1 Graphene

Using the scotch tape method, Novoselov et al. obtained graphene in 2004 and were awarded the Noble Prize in 2010. Currently, there are two ways to prepare graphene: top-down and bottom-up. Chemical synthesis, liquid-phase exfoliation, and scotch tape exfoliation are examples of top-down techniques. Molecular beam epitaxy and CVD form the majority of bottom-up techniques.

3.2 Graphene oxide

Numerous accounts exist regarding the synthesis of Graphene oxide (GO), and the resulting products' structures vary slightly. Richard Offeman and Williams Hummers Jr. presented one of the oldest approaches in 1958. This was the overall procedure. First, concentrated sulfuric acid and oxidizers like sodium nitrate were combined with graphite [7]. Then, potassium permanganate was added while maintaining a strict temperature control, and at the very end of the procedure, reducing and reaction-stopping chemicals such as hydrogen peroxide were added [7]. A high yield of powdered product and colloidal suspension is produced by this approach [7]. Subsequently, several research teams refined the preparation process even more by concentrating on three key variables: temperature, time, and precursor ratio [7]. Marcano et al., for instance, synthesized GO using the Tours approach and produced high-quality GO by eliminating sodium nitrate from the final product and adding phosphoric acid as a crucial precursor [7]. This method's exceptional product quality and ease of use make it superior to earlier approaches [7]. However, there are still two issues with different iterations of the Hummers method: It was obvious that there would be a high oxidant and intercalating agent consumption, and most synthesis methods take a long time to complete, all of which add up to expensive costs and limited scalability in real-world applications [9]. In recent years, a new improvement of $NaNO_3$-free Hummers methods was proposed. A team decreased the quantity of concentrated sulfuric acid and partially substituted K_2FeO_4 for $KMnO_4$. It demonstrates that GO can be effectively synthesized in a shorter amount of time and with a relatively low ratio of auxiliary agents to graphite [9].

4. The advantage of graphene and its derivatives

4.1 Adsorption mechanism of graphene oxide and its effect

Since graphene oxide (GO) is an oxidized version of graphene with oxygen-containing groups present, it has hydrophilic characteristics. It makes graphene oxide nanosheets possible to effectively generate metal complexes by electron pair sharing in order to absorb metal ions [10].

A team conducted an experiment and the following equation was utilized to determine the efficiency of Cu(II) removal by GO.

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

where *R (%)* represents the Cu(II) removal efficiency, *C0* (mg/L) and *Ce* (mg/L) represent the concentration of Cu(II) before adsorption and after 30 minutes, respectively [9]. Experiments showed that the R of GO was 68.2%, which shown noticeably great efficiency of removing the Cu(II) [9].

4.2 The Environmental effect of carbon nanomaterials

The most widely used technique for eliminating dangerous inorganic contaminants from wastewater is adsorption [4]. Adsorption is a quick, affordable, safe for the environment, and simple technique. The adsorbent can be reused multiple times without losing its effectiveness [4]. Because of properties their size and shape dependent properties, environmentally benign nature, abundance, and ease of handling, carbon-based nanomaterials are becoming more and more popular in the scientific community as nanoadsorbents for water treatment [4]. Carbon-based nanoadsorbents should have high specific areas, environmentally benign synthesis methods, minimal energy requirements, and quick adsorption kinetics for effective adsorption [4].When compared to bulk materials, the nano-range materials have a much higher surface to volume ratio, which makes them unique and greatly increases their potential for surface applications.

5. Further trends and suggestion

For carbon nanomaterials (CNMs) -based water purification technologies to advance, production costs must be lowered and the environmental effects of CNMs must be carefully examined. The expense of producing CNMs on a big scale is high. Commercialization of nanomaterials depends on further study and advancements in CNM synthesis. But with better synthetic techniques, such using inexpensive, environmentally benign precursors, increasing manufacturing, and streamlining the supply chain, fabrication prices will go down. It is yet unknown how to produce G and GO on a large scale. It is definitely necessary to conduct more research into the low-cost manufacture of CNMs for use in environmental applications.

6.Conclusion

Addressing copper pollution in China's mining industry is crucial for environmental sustainability and public health. This article highlights the significant contributions of the mining sector to the economy while simultaneously exposing the severe environmental impacts, particularly from heavy metals like copper. Traditional methods for copper removal from wastewater, such as precipitation and ion exchange, have notable limitations that hinder their effectiveness and cost-efficiency. In contrast, the use of nanotechnology, specifically graphene and its derivatives, presents a promising alternative for effectively adsorbing copper ions, thus mitigating the pollution problem. The high adsorption capacity and environmental compatibility of graphene oxide make it a viable solution for water treatment applications. This research underscores the importance of innovating cost-effective and environmentally friendly methods for producing carbon nanomaterials, paving the way for their practical application in addressing industrial pollution and enhancing water quality. Ultimately, advancing these technologies can significantly contribute to the sustainable management of mining-related environmental challenges in China and beyond.

References

[1] Li Jianzhong, Zhang Jinde. Discussion on the work of mine geo-environmental investigation of China. Hydrogeology &

ISSN 2959-6157

Engineering Geology, 2018, 45(4) :169-172.
[2] Shrivastava, A. K. (2009). A review on copper pollution and its removal from water bodies by pollution control technologies. Indian Journal of Environmental Protection, 29(6) : 552-560.
[3] Izydorczyk, G., Mikula, K., Skrzypczak, D., et al. Potential environmental pollution from copper metallurgy and methods of management. Environmental Research, 2021, 197 : 111050.
[4] Gusain, R., Kumar, N., & Ray, S. S. Recent advances in carbon nanomaterial-based adsorbents for water purification. Coordination Chemistry Reviews, 2020, 405 : 213111.
[5] Mbayachi, V. B., Ndayiragije, E., Sammani, T., et al. Graphene synthesis, characterization and its applications: A review. Results in Chemistry, 2021, 3 :100163.
[6] Yu, W., Sisi, L., Haiyan, Y., et al. Progress in the functional modification of graphene/graphene oxide: A review. RSC advances, 2020, 10(26) : 15328-15345.
[7] Razaq, A., Bibi, F., Zheng, X., et al. Review on graphene-, graphene oxide-, reduced graphene oxide-based flexible composites: From fabrication to applications. Materials, 2020, 15(3) : 1012.
[8] Oprea, M., Voicu, S. I. Cellulose composites with graphene for tissue engineering applications. Materials, 2020, 13(23) : 5347.
[9] Yu, H., Zhang, B., Bulin, C., et al. High-efficient synthesis of graphene oxide based on improved hummers method. Scientific reports, 2016, 6(1) : 1-7.
[10] Jiang, S., Do, H., Yusuf, A., et al. Camellia oleifera shell–reduced graphene oxide for adsorption of copper (II). Materials Chemistry and Physics, 2024, 314 : 128818.