Removal Of Heavy Metals From Waste Water By Nanoparticles

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Abstract

Heavy metals in wastewater can cause serious environmental problems and could harm to human body. Therefore, heavy metals needs be removing from the wastewater. Coagulation base methods are popular used nowadays with proved effects. New methods such as the application of nanomaterials have brought more possibilities to increase the removal effects for certain heavy metals.

Among these nanomaterials, graphene oxide has gained a lot of interest because of its large surface area and unique structure. Moreover, graphene oxide is a environmentally friendly material. But most of the reported studies did not use real wastewater samples but simulate ones prepared in labs. Therefore, the removal effects needs to be experimentally evidenced by using real wastewater samples.

In this project, I have studied the removal effects of pristine and modified graphene oxide using wastewater collected at the wastewater treatment plant in Rajkot (Nyari wastewater treatment plant). Moreover, I have also studied the heavy metal removal effects of combined coagulation method and graphene oxide. Results has shown that graphine oxide has similar removal effects to the coagulation method, indicate the enormous potential of graphine oxide in wastewater treatment!

Keywords: Wastewater, Heavy metals, Graphene oxide, Removal efficiency

Introduction

Metal heavy are the elements metallic that has densities high above 3.5g/cm³ [1]. Another definitions of metal heavy can be made based on the numbers atomic (>20), or weight atomic. The most recognition definition is based on density. Lot heavy metals are poison or toxic [2] that can result in environmental issues or harms to the body human. The common metals heavy in sewage are [3]: quicksilver (Hg), copious (Cu), nick (Ni), leader (Pb), chrome (Cr), cad (Cd), zink (Zn), and iron-man (Fe). The metals heavy can be release to air, water, and soil during diverse processes like burning, shipping, and trash [4].

In the last ten years, the utilization raising of gadgets like telephones mobile and personal gadgets has caused metals heavy high-level in sewage, including Pb, Cd, Cu, and Fe. In lots countries, rules has been made to lessen the release of metals heavy to the environment.

Environmental impact of heavy metals:
Removing heavy metals from wastewater are crucial task in wastewater treatment, especially in...
development countries. The reason is because of the environmental impacts on plants, aquatic life, and ecology. Many heavy metals are even toxic for the human body because they can accumulate in body and cause serious health issues.

Genuinely, heavy metals may exist in soil, water, and air, depend on their chemical and physical state. The heavy metals in soil will be taken by the plant and then enter food chains that will have an impact on the ecosystem. The heavy metals in water have impacts on almost all organisms. The heavy metals in air will mainly have impacts on human and animals' health since it can be inhaled or cause skin issues.

Nanoparticles for removing heavy metals from wastewater is relatively recent development in water treatment field. By late 2000s and early 2010s, the application of nanoparticles for water treatment became more widespread. Researchers start conducting laboratory-scale experiments to demonstrate effectiveness of various nanoparticles as adsorbents for heavy metals. Iron-based nanoparticles, especially zero-valent iron nanoparticles, gained attention for their exceptional adsorption capabilities. As the field growth continued, scientists also starting to address problems linked with nanobit-based water treatment, like reusing and recovery of nanobits and maybe environmental issues concerning nanobits release and toxicity.

The research in the realm of nanobit-based heavy metal elimination from wastewater is in progress. Several investigations have shown the possibility of these technologies on a lab scale, but efforts are ongoing to increase and commercialize these solutions for broader applications in water treatment and environmental rehabilitation.

**Aim of Review:**

Despite the enormous potential of nanomaterials for use in eliminating heavy metals in wastewater, there are numerous studies that need to be conducted before it's practical in actual cases. For instance, most studies use fabricated wastewater samples made in labs that are much less complex than real wastewater.

The actual wastewater contains numerous organic matters that could potentially clog the nanomaterials and decrease the effectiveness of heavy metals removal. Research on real wastewater from treatment plants is in high demand. The aim of this project is to investigate how graphene oxide functions in eliminating heavy metals in real-life scenarios.

**New methods for removing heavy metals**

Recently, nanotechnology has been used to remove heavy metal ions in wastewater [6]. The most commonly used methods are adsorption and membrane separation [7]. Various nanomaterials [8] have been developed to efficiently remove heavy metals, including carbon-based nanomaterials [9], metal oxides [10], zero-valent nanoparticles, and nanocomposites.

Among carbon-based nanomaterials [9], carbon nanotube-based and graphene-based nanomaterials are the most frequently studied. The advantages of carbon-based materials are their large surface area, synergistic removal of both organic and inorganic materials, and ease of chemical and physical modification.

Table 1 A summary of various substances that have been studied for the removal of heavy metals from wastewater. The advantages and disadvantages of these materials are also listed.

<table>
<thead>
<tr>
<th>Category</th>
<th>Materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-based nanomaterials</td>
<td>Carbon nanotube-based</td>
<td>Large surface area</td>
<td>Difficult to suspend uniformly</td>
</tr>
<tr>
<td></td>
<td>Graphene-based</td>
<td>Synergistic removing effect</td>
<td></td>
</tr>
<tr>
<td>Metal oxides</td>
<td>Iron oxides (Goethite, hematite, maghemite, magnetite)</td>
<td>High removal capacity Selectivity</td>
<td>Aggregation of the nanomaterials</td>
</tr>
<tr>
<td></td>
<td>ZnO, MgO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zero-valent metal nanomaterials</td>
<td>TiO₂, MnO, Al₂O₃</td>
<td>High reducing capacity</td>
<td>Easy to be oxidized (iron)</td>
</tr>
<tr>
<td>-------------------------------</td>
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<tr>
<td>Nanocomposites</td>
<td>Inorganic-supported nanocomposites</td>
<td>Organic-supported nanocomposites</td>
<td>Combine the advantages of different nanomaterials</td>
</tr>
</tbody>
</table>

**Comparison of Traditional Methods and Methods Using Nanoparticles**

**Efficiency:**
Nanoparticle-based methods often provide higher removal efficiencies due to their large surface area, tunable surface chemistry, and selectivity.

**Selectivity:**
Some nanoparticles can be designed to be highly selective for certain heavy metals, reducing the risk of essential trace metals being removed.

**Reusability:**
Nanoparticles can be recycled and reused, making them cost-effective in the long term compared to some traditional methods.

**Environmental Impact:**
Many nanoparticle-based methods produce less secondary waste compared to traditional methods such as chemical precipitation.

**Operational complexity:**
Nanoparticle-based methods can be more complex to implement and require considerations for nanoparticle recovery and disposal.

**Cost:**
Although the cost of nanoparticles has decreased over time, they can still be more expensive than certain conventional treatments.

Nanoparticle-based methods have several advantages, including high efficiency, selectivity, and reduced environmental impact. However, its application depends on the specific heavy metals present, cost constraints, and operational feasibility in a particular wastewater treatment scenario.

Combining nanoparticle-based methods with traditional or other emerging technologies may provide the most effective and cost-effective solution for removing heavy metals from wastewater.

**Using graphene oxide to remove heavy metals**

Graphene oxide has attracted great attention in heavy metal removal due to its unique properties such as large surface area, layered structure, chemical activity, and mechanical properties [12, 13]. Both pure graphene oxide and modified graphene oxide have been used in studies investigating their potential to remove various heavy metals.

Pure graphene oxide can be used for heavy metal removal because it contains a large amount of epoxide (C-O-C), hydroxyl (-OH), and carboxyl groups (-COOH), which are suitable as heavy metal adsorbents [14].

The reported data show that pure graphene oxide has different maximum adsorption capacities for different heavy metals B. 1119 mg/g for Pb, 530 mg/g for Cd, and 246 mg/g for Zn. These differences are due to the different interactions between heavy metal ions and functional groups on graphene oxide. However, since this value was obtained from different studies, it could not be quantitatively compared because the study conditions were different and the structure of graphene oxide was also different.

Note that graphene oxide does not have a defined structure as the size, molecular weight, and content of epoxide (C-O-C), hydroxyl (-OH), and carboxyl (-COOH) groups vary from study to study.

Surface modification of pristine graphene oxide has been reported to enhance the processing capacity of some heavy metals.
Furthermore, through surface modification, graphene oxide can be made to have a selective removal effect on specific heavy metals. For example, graphene oxide modified with -NH2 groups can have five times the removal power of the original graphene oxide [15].

**Methodology**

**Synthesis of Graphene Oxide:**

Laboratory-prepared graphene oxide was synthesized using a modified Hummer method [16]. Briefly, 1.0 g of graphite was added to 70 mL of 98% sulfuric acid while stirring in an ice bath. Then, 9.0 g of KMnO4 was carefully added to the suspension. The temperature of the reaction suspension should not exceed 30 °C. The reaction was then maintained at 40° C, for 30 minutes using a water bath. Then 150 ml of water was added to the suspension and the water bath was then heated to 95°C and maintained for 15 minutes. The solution was then diluted with 500 mL of water and 15 ml of H2O2 (30%) was carefully added. At this point the suspension turned dark brown. After the reaction was completed, the graphene oxide was collected by vacuum filtration and rinsed with 500 mL of 1:10 aqueous HCl. The collected sample were then dried in an oven at 60 °C overnight.

Modification of graphene oxide

(3-Aminopropyl) triethoxysilane (APTES) was used to modify graphene oxide. Briefly, 1 mL of APTES was added to 10 mL of 5 mg/mL graphene oxide suspension and stirred for 10 min. The modified graphene oxide was then collected by vacuum filtration and rinsed with water.

After these processes, the collected samples were redispersed in 10 ml of water in the laboratory of VVP Engineering College. The figure shows the reaction between APTES and graphene oxide [17].

**Figure.** schematic representation of two commonly described reaction routes for the functionalization of GO with APTES: ring opening of the epoxide group by the APTES amine (a); OH reacts with the ethoxysilane group of APTES (b). This figure is taken from reference [17].

**FTIR of graphene oxide**

FTIR (Fourier transform infrared spectroscopy) was performed on a Nicolet 6700 spectrometer. The wavenumber range is 400 to 4000 cm-1.

**Treatment**

The collected wastewater samples were first filtered to remove large solid wastes. Different amounts of graphene oxide (produced, purchased, and modified in the laboratory) were then added to yield concentrations of 0.6, 1.2, 2.4, 4.8, and 9.6 mg/L, respectively. The mixture was then shaken to suspend and held for 24 hours. The suspension was then filtered by vacuum filtration to remove graphene oxide. Two or three replicates of each sample were prepared for analysis.

Samples were kept for 10, 25, and 60 min before the filtration for the study of treatment time, the mixtures.

**Synergistic effects of graphene oxide and poly aluminum chloride (PAX-15)**

To investigate the synergistic effect, both PAX-15 and graphene oxide were added to wastewater samples. The concentrations of PAX-15 are 16 mg/L and 11.2 mg/L.
The concentrations of graphene oxide are 4.8 mg/L and 9.6 mg/L. The mixture of wastewater, PAX-15 and graphene oxide was stirred for 25 minutes and then vacuum filtered.

**Analysis**

The wastewater samples after treatment were sent to environmental audit lab, at VVP Engineering College, Rajkot which is a certified lab.

**Results**

**Removal effects of lab-made graphene oxide**

Five different concentrations were used to study the removal effect of laboratory-produced graphene oxide. However, some samples are contaminated. It is not clear when or where the samples became contaminated.

The figure shows the removal efficiency of lab-made graphene oxide for various heavy metals. This indicates that graphene oxide has the highest Cr removal efficiency, which can reach 72.2%. Note that the Cr concentration after treatment was below the detection limit of the device, so the actual removal effect was higher than 72.2. The second highest removal efficiency is for Zn, and 59.4% of Zn in wastewater can be removed by graphene oxide.

Removal efficiency of laboratory-produced graphene oxide (GO) against various heavy metals at different concentrations.

Graphene oxide at 4.8 mg/L seems to be the most effective in removing Zn, but at a higher concentration of 9.6 mg/L, agglomeration of graphene oxide occurs, which may reduce its effectiveness.

For Cd, the highest removal efficiency was 52.9%. Similar to Zn, the highest efficiency was observed at a graphene oxide concentration of 4.8 mg/L. For Pb, Cu, and Ni, the removal efficiency of laboratory-produced graphene oxide was not very good, with an efficiency of less than 30%.

**Removal effects of purchased graphene oxide**

After discovering impurities in samples treated with laboratory-made graphene oxide, they decided to use the purchased graphene oxide for further research.

The purchased graphene oxide is subjected to an additional purification process that removes more metal residues from the graphene oxide product.

Additionally, the optimal concentration for removing heavy metals is generally 4.8 mg/L, so we narrowed the concentration range to 2.4 to 9.6 mg/L.

Although the removal efficiency of modified graphene oxide was not superior to that of purchased graphene oxide, it seems that the concentration of modified graphene oxide with the highest removal effect was shifted to a lower concentration. For Cr, Pb, and Cd, the highest removal efficiency was found to be 2.4 mg/L. These results suggest that this modification could lead to a reduction in the usage of graphene oxide in wastewater treatment.

The figure shows the removal efficiency of purchased graphene oxide for various metals. This number does not include Ni. Since the concentration of Ni is always higher than in untreated wastewater, it is likely that the purchased graphene oxide contains Ni.
Unlike the laboratory-produced graphene oxide, the purchased graphene oxide has a high removal effect on Pb, reaching 78.6% at a graphene oxide concentration of 4.8 mg/L.

The highest removal efficiency of up to 72.2% was found for Cr. This is comparable to the value for laboratory-produced graphene oxide. However, at a high concentration of 9.6 mg/L, the removal efficiency of purchased graphene oxide to Cr decreased. Such a phenomenon has not been observed in laboratory-produced graphene oxide.

The cadmium removal efficiency was stable at 57.1% at the tested graphene oxide concentration. For Cu, purchased graphene oxide had higher removal efficiency than laboratory-produced graphene oxide, and the highest removal efficiency of up to 52.1% was found at a purchased graphene oxide concentration of 4.8 mg/L.

For Zn, we found that the removal efficiency increased as the concentration of purchased graphene oxide increased. However, the effectiveness of Zn removal is not as good as that of graphene oxide produced in the laboratory.

**Removal effects of modified graphene oxide**

According to reports, modified graphene oxide can enhance the removal effect of some heavy metals. In this project, we modified purchased graphene oxide with APTES and added -NH2 groups to the graphene oxide.

**Figure** shows the removal efficiency of modified graphene oxide. In contrast to the purchased graphene oxide, the modified graphene oxide had the highest Cr removal efficiency, which was 72.2% at a modified graphene oxide concentration of 2.4 mg/L.

In the case of Pb, the removal efficiency was actually lower than that of purchased graphene oxide.

For Cd, there was no difference in removal efficiency between modified graphene oxide and purchased graphene oxide, and the removal efficiency remained stable at the investigated graphene oxide concentrations.

Although the removal efficiency of modified graphene oxide is not better than that of purchased graphene oxide, it is thought that the concentration of modified graphene oxide, which has the highest removal effect, has shifted to a lower concentration.

For Cr, Pb, and Cd, the highest removal efficiency was found to be 2.4 mg/L. These results suggest that this modification could lead to a reduction in the usage of graphene oxide in wastewater treatment.

**Treatment time**

We investigated how treatment time affects the removal efficiency of heavy metals from wastewater.

The results showed that for Cd, a treatment time of 10 min was sufficient to remove most metal ions, and the Cd concentration after treatment was below the detection limit of the instrument.

For Pb, the removal efficiency can reach 70% after 10 min treatment, which is a very nice result comparing to the 80% removal efficiency using PAX-15 for a treatment time of 25 min.

For Cr, the removal efficiency after 10 min of treatment was 68.2%, while it was 77.3% for the PAX-15 treated sample. For Ni, the removal efficiency was 20.6% after 10 min of treatment. This time the sample appears to be contaminated with zinc. Therefore, no results were displayed.
Discussion

Removal efficiency:

Due to their different chemical structures, the removal efficiency of laboratory-produced graphene oxide and purchased graphene oxide differs for each heavy metal. The difference in the chemical structures of these two graphene oxides is the content of oxygen-containing groups such as -OH (hydrogen groups), -COOH (carboxylate groups), and C-O-C (epoxide groups). These three groups have different affinities for different heavy metals. Therefore, laboratory-produced graphene oxide and purchased graphene oxide have different removal efficiencies.

The figure shows a comparison of the removal efficiency of laboratory-produced graphene oxide and purchased graphene oxide.

Lab-grown graphene oxide can remove more Zn than purchased graphene oxide. In general, purchased graphene oxide has better removal efficiency than laboratory-produced graphene oxide.

We found that the maximum removal efficiency of modified graphene oxide was not much better compared to purchase graphene oxide. For Cu, the removal efficiency is only slightly higher. It can be seen that the maximum removal efficiency was achieved at a concentration of 2.4 mg/L for the modified graphene oxide, while it was 4.8 mg/L for the purchased graphene oxide.

The removal effect of graphene oxide on various heavy metals was classified according to efficiency. Figure 10 compares laboratory-produced and purchased graphene oxide with PAX-15 used in a wastewater treatment plant.
From the figure, it can be seen that the purchased graphene oxide and PAX-15 have the same order: Pb > Zn > Cd > Cu > Ni (PAX-15 samples only). However, graphene oxide prepared in the laboratory has the order Cr > Zn > Cd > Pb > Cu > Ni, with different sites for Cr and Pb. The reason for the difference may be the different content of -OH, -COOH, and C=O groups.

The purchased graphene oxide has a high content of -OH groups, so it has a similar effect to PAX-15, which is dominated by -OH groups. Graphene oxide produced in the laboratory was found to have a higher content of -COOH groups. Therefore, the order is different from the purchased graphene oxide and PAX-15. Although Figure 10 shows the maximum removal efficiency, the maximum values for different metals are not obtained from the same graphene oxide concentration. For example, the highest efficiency for Cr in purchased graphene oxide was at a concentration of 2.4 mg/L, while for Zn it was 9.6 mg/L.

**Selectivity:**

Selective removal of heavy metals from wastewater is of great importance when recycling metals. There is a strong need for methods with good selectivity. In this project, it was found that graphene oxide produced in the laboratory could selectively remove Cr at a graphene oxide concentration of 9.6 mg/L. However, high selectivity for Cr does not mean that other heavy metals are not removed. However, the removal efficiency decreases.

The following figure shows the removal efficiency of lab-made graphene oxide for various heavy metals. At a concentration of 9.6 mg/L, the removal of Cd, Ni, and Pb was strongly inhibited. In this way, Cr can be selectively removed from wastewater.

We found that purchased graphene oxide did not exhibit as much selectivity as laboratory-prepared graphene oxide. Particularly at a concentration of 9.6 mg/L, the metal separation efficiency is between 40% and 60%. At the purchased graphene oxide concentration of 2.4 mg/L, the removal efficiency was distributed over a wider range.

However, selectivity is difficult to detect. For modified graphene oxide, it was found that at a concentration of 2.4 mg/L, it could selectively remove Cr, Pb, and Cd. At this concentration, the removal effects of Cu and Zn were suppressed.

The reason for the difference in selectivity between purchased graphene oxide and laboratory-produced graphene oxide is due to structural differences. Figure 12 shows the FTIR spectra of two graphene oxides [18].

This figure shows that the C=O band is stronger in the purchased graphene oxide. However, the C=O groups in purchased graphene oxide are much weaker than those in lab-produced graphene oxide. The ratio of C=O and C=C bands is stronger in purchased graphene oxide than in laboratory-produced graphene oxide, indicating that purchased graphene oxide contains more -COOH groups. These structural differences result in different selectivity’s for the two graphene oxides.

**Treatment Time:**

The removal effect of graphene oxide appears to be very fast when added to wastewater samples. The removal efficiency after 10 minutes reaches 90% of the final effectiveness after 24 hours. However, in the future it would be interesting to reduce the treatment time to a few minutes and see the actual reaction kinetics. If successful, graphene oxide could be used to remove heavy metals from wastewater.

**Synergistic effect:**

Unfortunately, we could not detect a synergistic effect of the mixture of graphene oxide and PAX-15 after trying two different concentration ratios. However, better effects may be obtained by...
adapting the experimental procedure. Graphene oxide and PAX-15 were mixed at the same time.

However, the interaction of graphene oxide and PAX-15 produced aggregates, reducing the synergistic effect. If you add two reagents in sequence, for example, first you add graphene oxide at a low concentration, then after 10 minutes he adds PAX-15 (graphene oxide takes effect after 10 minutes, and the time (as it may be even shorter). In this case, you can expect better results.

Future Perspectives

The results of this project showed that graphene oxide can be used to remove heavy metals in wastewater with similar efficiency to the currently used PAX-15. Interestingly, graphene oxide showed some selectivity towards different metals at different concentrations.

Different modifications are expected to result in different selectivity’s. Therefore, further research is needed in the future to functionalize graphene oxide to increase its selectivity toward various metals.

Another thing not studied here is the removal of organic matter in wastewater by graphene oxide. This project focused solely on heavy metals. However, since organic matter and heavy metals coexist in wastewater, graphene oxide has the potential to remove organic matter. In the future, more studies should be conducted to investigate the effect of graphene oxide on the removal of organic matter.

Conclusion

This project investigated the removal effects of different graphene oxides on several heavy metals in wastewater. The results showed that different graphene oxides may have different effects. Laboratory-produced graphene oxide is the cheapest of the three graphene oxides, and its removal efficiency is very useful, especially for Zn. Also, graphene oxide created in the laboratory can have some selectivity towards Cr at high concentrations. Purchased graphene oxide has the best removal effect, but low selectivity for various metals. Modified graphene oxide has the same removal efficiency as purchased graphene oxide for various metals, but requires less material due to its lower concentration.

Compared to PAX-15, which is used in wastewater treatment plants, graphene oxide has a similar removal effect for the heavy metals studied in this project. However, the processing time with graphene oxide is shorter than that with PAX-15, at 10 minutes. In addition, the concentration of PAX-15 currently used is 52 mg/L, which is several times higher than that of graphene oxide (9.6 mg/L). From these perspectives, graphene oxide is superior to PAX-15. However, other factors such as mass production rate and cost must also be considered.

References

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