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# Evaluating the Viability of Graphene Oxide for the Removal of Ni(II) Ions From Waste Water

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# Evaluating the Viability of Graphene Oxide for the Removal of Ni(II) Ions From Waste Water

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by

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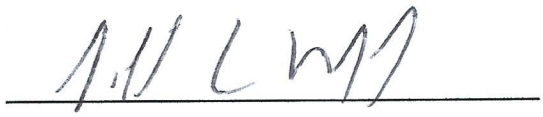

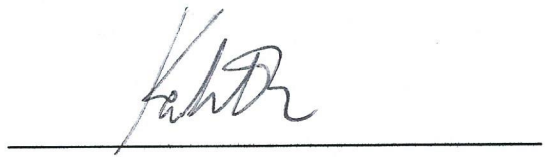

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# Abstract

When levels of heavy metal ions such as nickel (Ni), copper (Cu), lead (Pb), Zinc (Zn), and Cobalt (Co) exceed the tolerance values for industrial wastewater, it can devastate the environment as well as the health of the individuals consuming the water. Heavy metal ions are not biodegradable and will accumulate in organic matter.(1) This accumulation leads to toxic levels in the blood and hence damage to nerve tissue, kidneys, the liver, and other vital organs. (2) Effective removal processes of these heavy metals from water must be developed. This study explores a method to adsorb nickel from water with graphene-based materials. Adsorption is used because it is cost effective and relatively simple. Concentration and pH dependent batch tests were performed to measure the nickel adsorption onto graphene oxide that had been prepared via the Hummer's method. Our results show graphene oxide uptake values reached up to 365.9 mg of Ni(II) per gram of GO. The results also demonstrate that there was a strong impact from pH on graphene oxide uptake of Ni(II).

# Introduction

The toxic, non-biodegradable nature of heavy metals alongside their propensity to accumulate in organic matter has pushed the topic of heavy metal pollution into the spotlight in recent decades. Nickel is present in many organisms naturally; however at elevated levels it can become toxic for several organisms including humans.(2) Over the past several decades, the interest in developing techniques for removing nickel from wastewater has grown. This interest is partially spurred because of an increase in the

industrial and commercial significance. Since nickel waste is produced by several growing industries, including metallurgy, battery production, electroplating, it is important that nickel uptake methods are advance.(1)

Nickel waste enters the water supply and is then ingested by humans or the animals that humans consume.(2) Human exposures to large amounts of nickel from the environment can lead to several devastating health conditions. These conditions include skin allergies, lung fibrosis, cancer of the respiratory tract and iatrogenic nickel poisoning. Nickel has the ability to replace other 2+ charged ion metals found in enzymes and proteins inside the body; this alters the function and activity of the enzyme and is most likely the cause of its toxicity. Interest in the nickel concentration of waste water spurred after techniques to measure it were discovered such as electrothermal atomic absorption spectrometry.(2)

Many methods can be utilized for removing heavy metals from water. These include adsorption, chemical precipitation, ion exchange, filtration, membrane separation, and reverse osmosis.(3) Precipitation is one of the most common because it is very simple and cheap, but it produces large amounts of toxic sludge that is difficult to dispose(3). Ion exchange provides an effective method for replacement of unwanted ions. However it uses resins that can be must be replaced over time. Finding a material with a high affinity for adsorbing nickel, or any other heavy metal, would provide another relatively cheap method for nickel removal however, the best system for removing the most nickel at the lowest cost would probably be a combination of these

methods. One potential material that could be used for adsorbing nickel from water is graphene oxide.

The chemical composition of graphene is oxide is a hexagonal carbon ring backbone with various oxide functional groups attached. Hydroxide and epoxide groups are attached to the top and bottom of the graphene oxide, while carboxylic groups are attached to the sides or ends of the graphene oxide sheet. The graphene oxide created in this research, has been prepared via a modified Hummer's Method. There are several characteristics that make graphene oxide ideal for Ni(II) uptake. The affinity of the carboxylic acid group for nickel is well known.(4) This group is very polar and contains a partial negative charge that is very attracted to positively charged ions such as nickel. Graphene oxide is also known to have a very high surface area per unit mass ratio. The theoretical specific area is 2620 $m^2/g$.(5) This gives promise to the nickel uptake efficiency of the material. Graphene oxide is fairly cheap to produce, and does not require sophisticated equipment to make. Its chemical makeup is mostly carbon which is an abundant element so there is no concern for scarcity. In our method of producing graphene oxide we used graphite as the principle ingredient, oxidized it with potassium permanganate, and washed the product around fifteen times to create a pure product.

# Methods

1) Graphene Oxide Preparation:

The Graphene Oxide was prepared using a modified Hummer's method. Graphite powder (0.2-0.8g) and $NaNO_3$ (0.2-0.8g of 98+%) were mixed in 23mL of conc. 12M $H_2SO_4$ solution under stirring in an ice bath for 15 minutes. Then 4 grams of potassium permanganate were added very gradually under stirring at 400 rpm. This suspension was stirred for 30 more minutes on ice. This solution was transferred into an ice bath at 20°C for 90 minutes. The solution was placed in the water bath at 40 degrees Celsius and stirred for 90 more minutes. Exactly 50 mL of water was then added to the solution at a rate of 12 mL per minute followed by 6 mL of hydrogen peroxide at a rate of 3 mL per minute. Then 100 mL of DI water was added to the solution. The solution was then washed once at 4000 rpm for 3 min with 5% HCl in DI water, once with 50/50 water/acetone, and finally multiple times with regular DI water. This washing was done through centrifugation, removal of the supernatant, and addition of more wash solution. This was repeated at least 14 more times with DI water at 35-45 degrees Celsius. Then the graphene oxide was place on a watch glass and allowed to dry for 24 hours in an oven at 55 degrees Celsius. Once dried, the graphene oxide was exfoliated via sonication for two hours to prepare a suspension of 2.6 mg/ml of graphene oxide.

2) Absorption testing:

Adsorption testing was done using U-0080D Hitachi Photodiode Array Bio-spectrophotometer. An initial absorbance spectrum was done for the Ni(II) batch

solution to create a standard curve. Using the spectrum generated, the maximum nickel absorption peak was found to be located at 391nm. All subsequent absorbance measurements were done at this wavelength. For each batch test, samples were prepared, shaken for 24 hours, and then analyzed using spectrometry. Mass adsorbed was calculated by finding the change in concentration using spectrometry and multiplying by the volume of the mixture. This was normalized by dividing out the mass of the graphene oxide.

The first batch test was the pH dependent testing. This was done first to because it gave insight to the appropriate pH for the largest amount of nickel removal from graphene oxide. The pH test was completed by preparing samples of graphene oxide and Ni(II) at pH 2-7. These samples were prepared by taking 18 ml of 1mg/ml Ni(II) and adding that to 5 ml of 2.6 mg/mL of GO. Immediately after the pH was then altered by adding diluted NaOH or HCL and the batch testing was performed and analyzed.

The second test, the concentration test, was completed to find the optimal concentration of nickel and graphene oxide. Samples were prepared by adding 1 ml of 2.6 mg/mL graphene oxide to 18 mL of nickel solutions of varying concentrations. All concentration tests were performed at the optimal pH of 6 to insure the largest amount of nickel was being adsorbed. The Ni(ii) concentrations of the samples ranged from 150 mg/L to 650 mg/L. The resulting adsorbed mass was plotted against the equilibrium concentration of Ni(II).

3) Characterization of GO and GO polymer:

The *FEI Nova Nanolab 200 Duo-Beam Workstation* was used to take high resolution SEM images with a 15 kV electron beam. Afterwards, FTIR was used to evaluate the presence of functional groups on the GO.

# Results

1) Characterization

The SEM image in Figure 1 shows a rippled surface as we would expect from a thin layered carbon backbone with many oxygen groups. The FTIR shows that the expected carbon bonds are present C=O , C=C and C-OH as shown in Figure 2.

2) pH testing

The impact of pH can cause a large difference when performing adsorption testing. Therefore it was imperative to study the impact of pH on Ni(II) uptake. Our results shown in Figure 3 demonstrate that the uptake of nickel by graphene oxide increased significantly as pH increased from pH 2 to pH 6. The results also indicate that the uptake of nickel is the lowest at around pH 2 and slightly decreases again after pH 6-7. The total uptake at pH 2 was 14% of the total uptake at pH 6.

3) Initial Concentration Test

Because of the tendency of increased concentrations to drive equilibriums, it is important to look at the impact of changing the initial concentration on the Ni(II) uptake. The results in Figure 4 showed that the Ni(II) uptake increased as the initial concentration of nickel increased from 150 mg/L to 450mg/L and stayed relatively steady in the range of 450 mg/L to 650 mg/L. The nickel uptake maxed out at 365.9 mg of Ni(II) per gram of graphene oxide.

# Analysis

These results validate that graphene oxide has great potential in the field of carbon based adsorption materials. The maximum uptake value in this study was 365.9 mg of Ni(II) per gram of graphene oxide. This value was much better than many similar materials like oxidized carbon nanotubes or commercial grade activated carbons which have values in the range of 10-40 mg/g.(6) While graphene oxide is still rarely seen in use for adsorption today, it shows a lot of promise for the removal of heavy metal Ions in concentrated environments. Similar studies have confirmed that it also has a great uptake values for Cadmium(II) and Cobalt(II). (5)

The extremely high uptake of the Ni(II) is most likely due to an interaction between the electron dense oxygen molecules and the electron deficient metal ions. To further improve this phenomenon, future work should focus on improving the extent to which the graphene oxide is oxygenated. One possible cause for lower oxygenation was our use of centrifugation in the cleaning process. While centrifugation separated most of the fluids from the graphene oxide, some of the more hydrophilic graphene oxide molecules most likely remained suspended in the supernatant. This supernatant was later discarded and the graphene oxide was wasted. The more oxygenate molecules were most likely the most hydrophilic and thus those graphene oxide molecules that were discarded were likely the most adsorbent. Further chemical processing also shows promise in increasing the number of carboxylic groups on the graphene oxide, and thus increasing the oxygenation and potential adsorption of nickel by graphene oxide.

The pH results show that the adsorption of Ni(II) ions could be reversed by pH manipulation. This means that there is a clear way to recover the nickel ions. This reduces the amount of toxic waste that is produced from the Nickel removal process and allows for reuse of graphene oxide.

Although there are health concerns related to graphene oxide pollution, by modifying the production methods, these concerns can be mitigated. One of the primary safety concerns is the presence of impurities in graphene oxide, which could be fixed by a more refined process. (7) Another suggested improvement on the graphene oxide materials is to make the graphene oxide sheets smaller than the size of a macrophage. This size decrease would allow many organisms to dispose of any graphene oxide that found its way into their bodies. (7)

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# Appendix

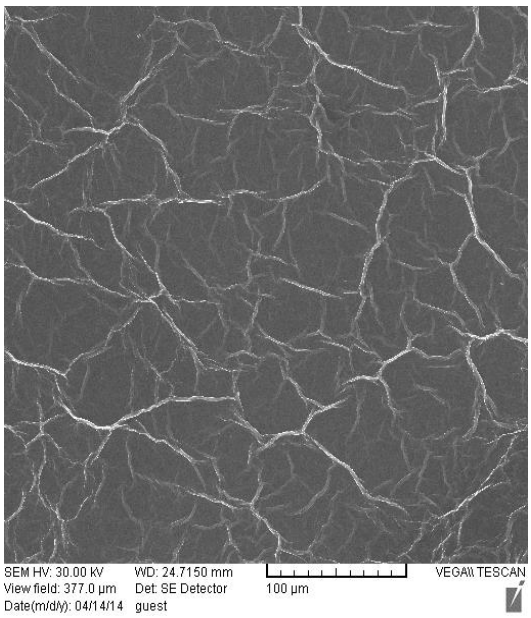


Figure 1: SEM of Graphene Oxide

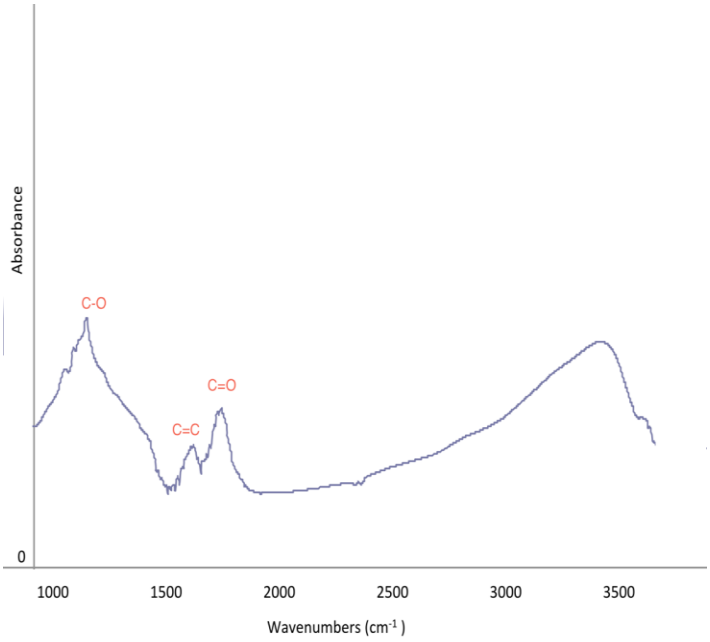


Figure 2: FTIR of Graphene Oxide

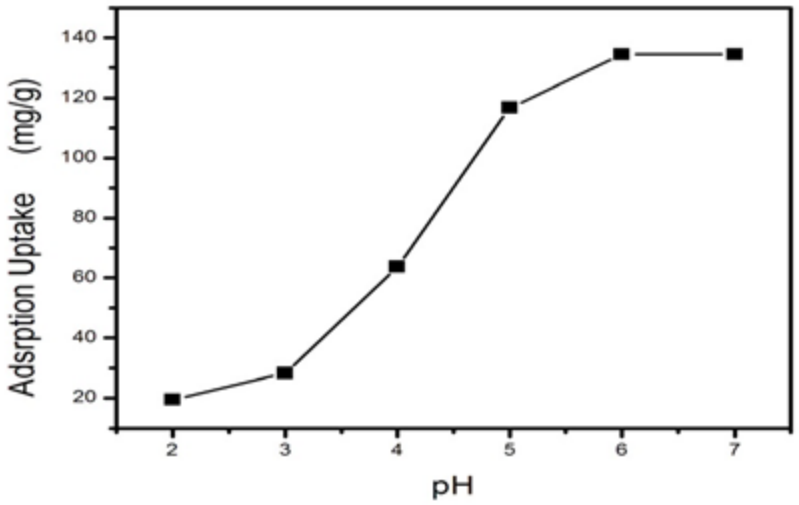


Figure 3: pH Impact on Adsorption of Ni(II) on GO

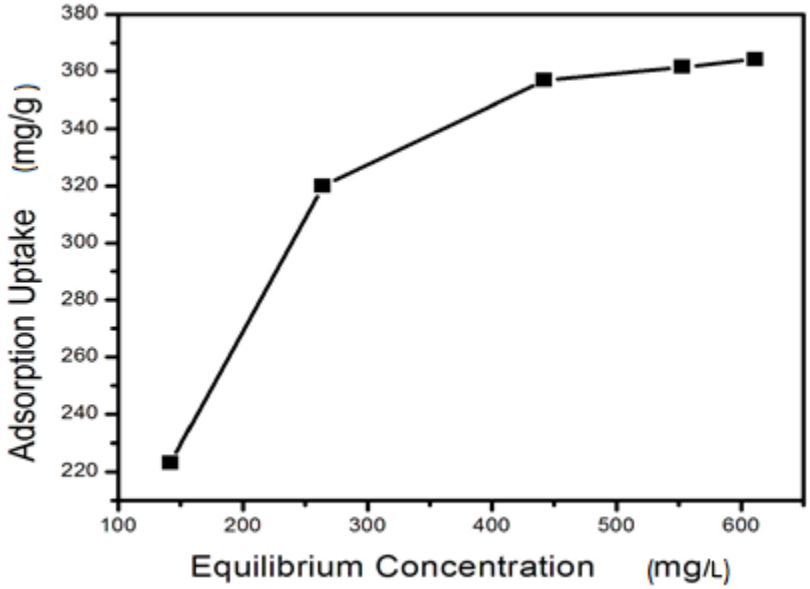


Figure 4: Effect of Initial Concentration of Ni(II) on adsorption by GO