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# Efficient Removal of Aqueous Copper (II) Ions Using EDTA-Modified Graphene Oxide: An Adsorption Study

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**Abstract**. Graphene oxide has drawn attention globally as it emerged as a promising adsorbent material with enhanced adsorption of environmental pollutants due to its eco-friendly attributes, high surface area, and cost-effectiveness for mass production. This economical solution is a promising and potentially transformative approach to heavy metal removal, contributing to a cleaner and more sustainable future. In this study, unmodified and modified graphene oxide were examined for the removal of copper (II) ions in an aqueous solution. Modified Hummer's method was utilized to synthesize the graphene oxide. The synthesized graphene oxide was then modified with N-trimethoxysilylpropylethylenediaminetriaceticacid (EDTA-silane), resulting in EDTA-modified graphene oxide (EGO). Batch adsorption tests were done for both adsorbents in order to determine the effects of various factors, such as pH, adsorbent dosage, and contact time. Additionally, in order to describe the adsorption behavior of the adsorption system, it was further fitted to isotherm and kinetic adsorption models. Results of adsorption study showed optimum adsorption for copper (II) ions was achieved at pH = 7, contact time = 45 min, and adsorbent dosage of 5 mg and 4 mg of unmodified graphene oxide (GO) and modified graphene oxide (EGO), respectively. The fundamental mechanism of both adsorbents was best explained by Langmuir isotherm model and the pseudo-second-order model, indicating that the adsorption system followed chemisorption. The adsorption capacity and maximum removal of copper (II) ions was 672.22 mg/g and 78.41% for GO, and 729.11 mg/g and 89.94% for EGO. The latter suggested that graphene oxide treated with EDTA-silane (EGO) has the higher capacity to adsorb copper (II) ions.

## Introduction

Water is necessary and important to human existence. A growing environmental concern on a global scale is water pollution caused by the indiscriminate disposal of metal ions and organic contaminants. Wastewater on various industries, including mining, batteries, metallurgical and chemical manufacturing, contains at least one harmful metal ion. Heavy metal contamination, such as nickel, cadmium, chromium, copper, mercury, lead, and arsenic, has negatively impacted water quality as a result of the demands of urbanization and industrialization [1]. Copper heavy metals are the third most commonly used industrial metal. Due to its increasing accumulation in organisms, this heavy metal is regarded as an eco-toxicological hazard [2]. Metal cleaning smelting, cardboard processing, paints, pigments, mining, fertilizers, electroplating baths, petroleum refining rinses for brass, wood pulp, printed circuit board production, and etching all produce significant quantities of copper metal ions in industrial wastewater [3]. According to studies, drinking water with 30 g of copper ions is fatal, and 1.3 mg/L of copper ions might result in diarrhea, stomach pains, and nausea, especially in infants [4]. According to the WHO and EPA standard reports, copper ions are extremely toxic even at low concentrations. The maximum allowable discharge of polluted copper ions in surface and well water for industry is 1 mg/L, while the maximum allowable copper ion concentration values for drinking water are 0.2 and 1.2 mg/L, respectively [5].

Chemical oxidation or reduction [6], ion exchange, electrochemical treatment, flotation membranes, desalination, chemical precipitation, membrane filtration, extraction, and adsorption have all been developed to remove Cu(II) ions from aqueous solutions. Adsorption is also used to remove heavy metals from wastewater. When applied to the treatment of wastewater, the majority of these techniques have some drawbacks and limitations. Desalination and electrochemical treatments, on the other hand, require relatively high operating costs, and precipitation is inefficient because it produces large quantities of sludge that require careful management [7]. Adsorption is the most common method because of its simplicity, adaptability, resistance to toxic substances, and high efficiency in large-scale applications. The main drawback of the adsorption method is the high cost of effective adsorbents, which makes wastewater treatment more expensive [8]. As a result, removing heavy metals from wastewater requires finding adsorbents that are both effective and cost-effective. Poor adsorption sites, low selectivity, and poor regeneration limit the practical applications of traditional adsorbents like activated carbon, clay, chitosan, magnetic sorbents, resins, silica, zeolites, metal oxides, and alginate in real processes. Thus, it would be beneficial to chemically modify conventional adsorbents to improve their performance by introducing particular functional groups [9].

Graphene oxide (GO) has attracted more attention as an effective adsorbent of dyes and heavy metal ions among the new carbon-based adsorbents due to its good dispersion in water, biocompatibility, and relatively simple and inexpensive preparation methods [10]. Improved hydrophilicity and enhanced interfacial interaction with adsorbates (metal ions and ionic dyes) are the outcomes of the oxygen-containing functional groups in GO, such as carboxyl groups at the edges and hydroxyl and epoxy groups on the basic plane. Metal complexes can be formed by donating a single pair of electrons from these functional groups to the empty orbitals of transition metal ions. According to the theory of hard and soft acids and bases (HSAB), these groups cannot interact strongly with heavy metals like Cu(II), but they can offer a unique opportunity to chemically modify GO. Therefore, the removal efficiency of GO-based materials can be significantly improved by functionalizing GO with molecules that contain strong chelating groups like nitrogen and thiol [11]. Additionally, the large specific surface area of GO offers an abundance of attachment sites for the functionalization of other substances, including ethylenediaminetetraacetic acid (EDTA). As a result, there may be more surface functional groups, which might improve the adsorption of heavy metals. EDTA is an effective chelating agent that, due to its two amine and four carboxylate groups, which can form stable complexes with metal ions [12]. EDTA has several uses, including as a dyeing auxiliary, stabilizer, softener, and in coordination titration [13]. In prior studies, EDTA chelation with divalent metals has been observed, in which one carboxyl group is freely accessible and one water molecule is coordinated to the metal center. Consequently, EDTA is a promising choice for the adsorption of heavy metals and can be functionalized with other materials such as GO. EDTA groups can be simply immobilized on hydroxyl groups of GO by silanization reaction with N-(trimethoxysilylpropyl)ethylenediaminetriaceticacid (EDTA-silane). Several nanomaterials, functionalized with EDTA, have been described and they demonstrated substantial adsorption tendencies towards divalent heavy metals such as Co, Hg, and Cu in aqueous solution [14].

In this study, graphite powder was used to synthesize graphene oxide. The graphene oxide was then modified using EDTA-silane. The general aim of this study was to determine the adsorption efficiency of EDTA-modified graphene oxide for the removal of Copper (II) ions from aqueous solutions. Specifically, it aimed to: (1) synthesize graphene oxide (GO) from graphite powder; (2) modify graphene oxide using EDTA-silane; (3) determine optimum parameters, such as pH, adsorbent dosage, and contact time required in the removal of Cu(II) ions in aqueous solution using GO and EGO as adsorbents; (4) determine the adsorption capacity and % removal of Cu (II) ions using GO and EGO as adsorbents at optimum conditions; and (5) describe the adsorption behavior of GO and EGO using adsorption studies, in particular isotherms and kinetics for the removal of Cu(II) ions using UV/Vis spectrophotometry analysis after various adsorption experiments.

## Methodology

**Synthesis of Graphene Oxide (GO).** Graphene Oxide was synthesized according to the modified Hummer's method as described by Paulchamy et al. (2015) [15]. The analytical-grade reagents used in this experiment were sourced from manufacturers located abroad and supplied by a distributor based in the Philippines. A mass of 4 g of graphite powder and 4 g sodium nitrate were mixed in 180 mL of 98% sulfuric acid kept under ice bath to maintain the temperature at 0-5°C with continuous stirring. The mixture was stirred for 4 hours at this temperature and 24 g of potassium permanganate was added to the suspension very slowly. The rate of addition was carefully controlled to keep the reaction temperature lower than 15°C. The mixture was diluted with very slow addition of 368 mL deionized water and kept under stirring for 2 hours. The ice bath was then removed, and the mixture was stirred at 35°C for 2 hours. The above mixture was kept in a reflux system at 98°C for 10-15 minutes. After 10 minutes, the temperature was changed to 30°C which gives brown colored solution. After another 10 minutes, the temperature was changed to 25°C, and maintained for 2 hours. The solution finally was then treated with 30% of 40 mL hydrogen peroxide. Deionized water (200 mL) was placed in two separate beakers and an equal amount of 300 mL of solution prepared was added to each beaker and stirred for 1 hour. It was kept for 3-4 hours without stirring, to allow the particles to settle. The resulting mixture was washed repeatedly by centrifugation at 4000 rpm for 8 minutes with 10% hydrochloric acid and then with deionized water several times until it formed a gel-like substance (pH-neutral). After centrifugation, the gel-like substance was oven-dried at 40°C for 24 hours. Graphene oxide was then stored at room temperature for further adsorption experiments.

**Surface Modification of Graphene Oxide.** Graphene Oxide was modified with EDTA-silane following the procedure conducted by Jeon and Kim, (2022) [16]. For reaction of GO with EDTA, 1 g of GO was dispersed in 50 mL deionized water and 400 mL of EDTA-silane (5.0 wt%) was added to this suspension. Then this mixture was stirred for 12 h at 75°C. Finally, the product was purified with repeated washing with deionized water. The produced solution was dehydrated in an oven for 13 h at 65 °C. The final product was called EGO and was used for adsorption studies.

**Characterization of the Adsorbents.** The samples were delivered to the Central Mindanao University in Maramag, Bukidnon, Philippines and was examined using Fourier Transform Infrared Spectrometer (Shimadzu IR Affinity-1S) for FTIR analysis with a transmission accessory to assess the potential role of the functional groups on the surface of both the GO and EGO in Cu(II) adsorption.

**Adsorption Experiments for Cu(II) Adsorption.** To produce the 100 ppm stock Cu(II) solution, 0.268 g of copper(II) chloride dihydrate ($CuCl_2{\bullet}2H_2O$) was dissolved in 1000 mL of deionized water. In the batch experiments, both GO and EGO adsorbents were introduced to the copper (II) ion solution under optimal conditions. The effect of pH (3-7), adsorbent dosage (2-6 mg), and contact time (15-75 min) were some of these parameters. Every experiment was conducted with a known initial concentration of 25 mg/L in a 25 mL Cu(II) ion solution. Either NaOH or $H_2SO_4$ were added to the mixture to modify the pH. The initial concentration and contact time were varied from 5 mg/L to 45 mg/L and from 15 min to 75 min, respectively, for the isotherm and kinetic investigations.

**Analytical Methods.** After all the batch adsorption experiments, the UV-Vis Spectrophotometer (Biobase BK-D560 Double Beam Scanning UV/VIS Spectrophotometer) was used to examine the remaining Cu(II) in the filtrates added with concentrated 25% v/v Ammonia ($NH_3$) solution to form a colored- complex that adsorbed at the wavelength $\lambda = 615$ nm. The concentration of retained Cu(II) ions in the adsorbent phase was used to calculate the adsorption capacity. The Cu(II) ions adsorption capacity ($q_e$) and removal efficiency (%) were calculated according to the following equations:

$$q_e = \frac{(C_o - C_e)\,V}{m}\ . \tag{1}$$

$$\%\ \text{Removal} = \frac{(C_o - C_e)}{C_o}\ \text{x}\ 100\ . \tag{2}$$

where $C_o$ and $C_e$ are the initial and equilibrium concentrations (mg/L) of Cu(II) ions respectively, V is the volume of the metal ion solution in (L) and m is the amount of the adsorbent used in grams (g).

To ascertain the effectiveness and identify significant differences between the factors applied to the adsorbent, the kinetics and equilibrium adsorption of the GO and EGO was calculated.

The adsorption isotherm model of graphene oxides towards Cu(II) ions was examined by plotting data fit to two isotherm models namely Langmuir isotherm model and Freundlich isotherm model. The monolayer type of adsorption is basically described by the Langmuir model. The availability of interpretable parameters is the key to its advantages. However, because it is structured, its application is restricted to monolayer adsorption. Adsorption Isotherms will be represented by the expression described by Dąbrowski (2001) [17] as shown:

$$\frac{1}{q_e} = \frac{1}{K_L q_{max}} \cdot \frac{1}{C_e} + \frac{1}{q_{max}}\ . \tag{3}$$

where $K_L$ represent the Langmuir equilibrium adsorption constant (L/mg) and $q_{max}$ is the Langmuir maximum adsorption capacity (mg/g). These two parameters of the Langmuir isotherm can be calculated using the slope and the intercept of the plot $1/q_e$ vs $1/C_e$ from the equation.

Similar to the Langmuir model, the Freundlich model is also an empirical equation. It is used to estimate the adsorption intensity of the sorbent towards the adsorbate that can be used for multilayer adsorption on heterogeneous sites. It assumes that the adsorption heat distribution and affinities toward the heterogeneous surface are non-uniform. The linear form of the Freundlich equation can be expressed in the following equation as described by Boparai et al. (2011) [18]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e\ . \tag{4}$$

where 1/n is described as the adsorption intensity and $K_F$ is Freundlich adsorption constant related to adsorption capacity (L/mg). Moreover, the slope and intercept of the plot log $q_e$ vs log $C_e$ from the equation can also be used to calculate both of these parameters.

Moreover, the following equations were used to calculate pseudo first-order and pseudo second-order, respectively, using the experiment data on the effect of contact time:

$$\ln(q_e - q_o) = -k_1 t + \ln q_e\ . \tag{5}$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad . \tag{6}$$

## Results and Discussion

**Adsorbent Structural Characterization**. To provide a substantial approximation to the nature of the synthesized graphene oxide, both the unmodified and modified graphene oxide underwent a Fourier Transform–Infrared Spectroscopy (FTIR). The spectra of the adsorbents were measured in the range of 400–4000 $cm^{-1}$. The distinctive absorptions of GO (highlighted in yellow) and EGO (highlighted in orange), as well as the raw graphite (highlighted in blue) were depicted in Fig. 1, while Table 1 provides a summary of the significant peaks alongside their corresponding functional groups.

Table 1. Characterization of GO and EGO using FTIR Analysis.

| Adsorbent | Band Positions ($cm^{-1}$) | Assigned Functional Group |
|---|---|---|
| **GO** | 3380-3390 | O-H stretching |
| | 1790-1800 | C=O stretching |
| | 1610-1625 | C=C stretching |
| | 1050-1080 | C-O stretching |
| **EGO** | 3400-3500 | O-H stretching |
| | 1700-1730 | C=O stretching |
| | 1605-1615 | C=C stretching |
| | 1125-1250 | C-N stretching |
| | 900-925 | Si-O stretching |

Figure 1 shows the spectra of the raw graphite, and both modified and unmodified graphene oxide, wherein there is a noticeably higher % transmittance for the modified graphene oxide compared to the unmodified graphene oxide – which could be representative of the unmodified graphene oxide and its hygroscopic nature [19].

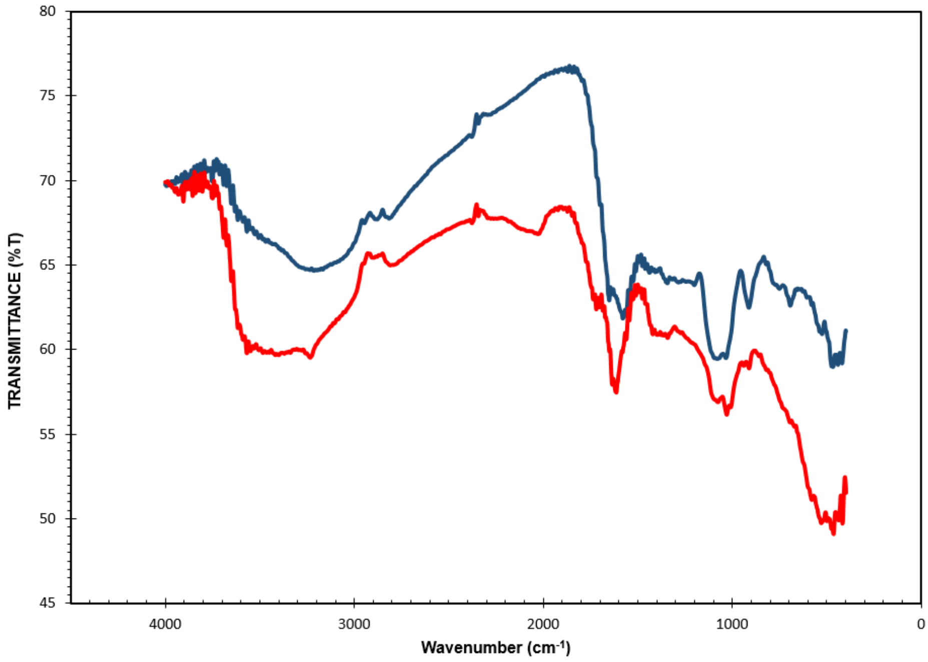


**Fig. 1**. Infrared spectra of unmodified and modified synthesized graphene oxide (Orange, EGO; Yellow, GO; Blue, Graphite)

The absence of any significant peak in the graphite FTIR spectrum suggests that bulk graphite is chemically inert [20]. However, different functional groups were visible in the FTIR spectra of the modified and unmodified graphene oxide. Furthermore, the graph shows a broad peak of hydroxyl group (-OH) at 3384 $cm^{-1}$ where it fell between the range of 3380-3390 $cm^{-1}$, indicating the presence of absorbed water molecules on the surface of GO. Therefore, it shows that this GO sample has strong hydrophilicity. The absorption peak at 1805 $cm^{-1}$ represents the carbonyl group (C=O) where it fell between the range of 1790-1800 $cm^{-1}$ that relates to carboxylic acid and its existence is at the edge of GO. The absorption peak of C=C vibration at 1614 $cm^{-1}$ from the $sp^2$ bonds of the aromatic rings of GO, as well as from possible scissoring mode of the water present in the samples represents the graphitic domain where the range is between 1610-1625 $cm^{-1}$. It indicates the exfoliation happened where oxygen had been introduced during oxidation process thus contributes to the hydrophilic nature of GO sample [21]. Finally, the peak absorption at 1075 $cm^{-1}$ corresponds to the presence of epoxy group (C-O-C), which lies between the range of 1050-1080 $cm^{-1}$ [22].

After the surface functionalization, the O-H stretching, C=O stretching, and C=C stretching peaks at 3464, 1720, and 1610 $cm^{-1}$, respectively, were not significantly affected, but C-O stretching peaks were diminished with appearance of new peaks at 1128 and 910 $cm^{-1}$ from C-N and Si-O stretching due to functionalization with the amine and alkoxysilyl groups in EDTA- silane, respectively [23]. These changes indicated that EDTA-silane was successfully immobilized onto the surface of GO through the reaction between hydroxyl groups of GO and N-(trimethoxysilyl) group of EDTA-silane.

**Batch Adsorption Studies**. To profile the adsorption capabilities of both the GO and EGO, three parameters, namely: (1) pH, (2) adsorbent dosage, and (3) contact time, served as experimental parameters for the batch adsorption experiments. The correlation between pH, adsorbent dosage, and contact time is crucial in understanding the efficiency of adsorption processes. Optimal pH enhances adsorption efficiency based on surface charge interactions. Higher adsorbent dosages can improve removal rates until saturation is reached. Sufficient contact time is necessary to achieve equilibrium, with optimal times depending on the other two factors. Other variables such as temperature (298 K), initial concentration (25 ppm), volume (25 mL), and the rate of mechanical stirring (300 rpm) are consistent unless otherwise stated.

**Effect of pH.** The effect of pH on the adsorption of Cu(II) ions using GO and EGO is shown in Fig. 2.

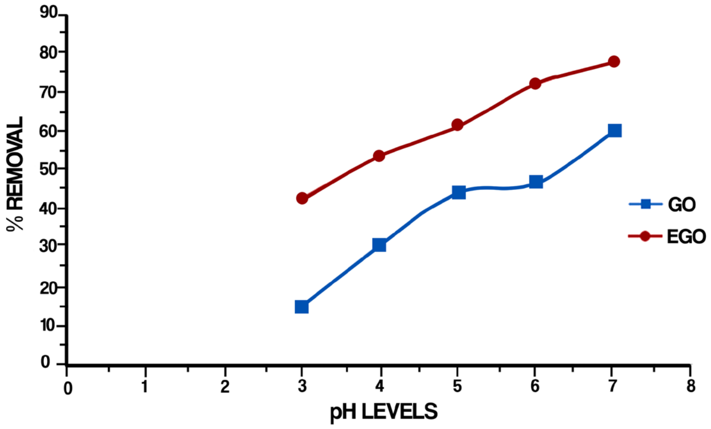


**Fig. 2.** Effect of pH towards adsorption of Cu(II) ions by GO and EGO

The pH value of the solution is one of the most significant factors that control the adsorption of heavy metal ions to solid particles, which could have an impact on the surface potential characteristics of adsorbent and the relative distribution of metal ion species, particularly the protonation-deprotonation reactions at various pH levels. In this study, pH was varied at a range of 3 to 7. The results demonstrated that the percentage removal of GO-based materials for Cu(II) is pH responsive in which when pH was raised to 7, the percentage of Cu(II) removed by GO and EGO also increased steadily, reaching a maximum value of 60.00% and 77.78%, respectively. Furthermore, the adsorption capacity of GO and EGO was 152.03 mg/g and 197.06, respectively. Graphene oxide (GO) effectively removes pH from solutions through various mechanisms. Its high surface area and functional groups, such as hydroxyl, carboxyl, and epoxy, attract and hold onto ions and molecules. GO's ion exchange processes lower pH, while its surface charge changes with the pH, attracting negatively charged species. GO can also participate in chemical reactions with pollutants, such as oxidizing agents or redox reactions, leading to the removal of specific contaminants. GO's ability to induce flocculation and aggregate at higher concentrations further aids in solution treatment. At low pH values, the high concentrations of $H^+$ and $H_3O^+$ in solution would compete with heavy metal ions to attach to the available binding sites of GO and EGO which reduced the adsorption of metal ions at low pH. On the other hand, at high pH levels, the oxygen-containing functional groups on the surfaces of GO and EGO were readily protonated. Metal ion binding can be facilitated by adding more sites and ligands. The enhancement of electrostatic interaction between positively charged metal ions and negatively charged GO and EGO surfaces is a contributing factor to an increase in adsorption capacity seen with increasing solution pH [24]. Moreover, a study by White et al. (2018) stated that precipitation of copper as $Cu(OH)_2$ is more likely to be dominant than Cu(II) ions as pH>7. Proving this claim, an additional adsorption at pH=8 was conducted, and a formation of precipitate was observed having a removal rate of 33.33% and an adsorption capacity of 92.03 mg/g for GO, and 47.93% and an adsorption capacity of 134.10 mg/g for EGO. The observed decrease in adsorption after pH 7 can be attributed to the formation of soluble hydroxyl complexes. After pH 7, there are comparatively tiny quantities of three species: $Cu(OH)^+$, $Cu(OH)_2$, and $Cu^{2+}$, which have a major impact on metal adsorption [25].

**Effect of Adsorbent Dosage.** Adsorbent dosage is an important consideration for the removal of heavy metal ions. The ability to remove substances from a solution can be influenced by varying the amount of adsorbent, which can impact its overall effectiveness. In this study, the adsorbent dosage was varied from 2 mg to 6 mg. Fig. 3 shows the effect of adsorbent dosage for both GO and EGO on the Cu(II) removal having a substantial and noticeable rise in the adsorption of Cu(II) at 5 mg with 74.60% and an adsorption capacity of 89.11 mg/g for GO and 4 mg with 80.95% and an adsorption capacity of 117.74 mg/g for EGO. One could reasonably expect that a higher dosage of adsorbent would result in more exchangeable sites being available for the metal ions. However, after 5 and 4 mg for GO and EGO, respectively, a decrease in the removal percentage was observed. These results can be explained from the perspective of the adsorbent as well as the adsorbate. (1) The absorbent perspective. Adsorption percent increases, when more adsorbates are adsorbed at increasing adsorbent dosages. However, as the dosage of the adsorbent increases, less free adsorbates remain, resulting in a decrease in the amount of adsorption. (2) The absorbent perspective. Increasing the dosage of adsorbent results in an increase in adsorption sites, which in turn adsorbs more free adsorbates and raises the adsorption percent. Adsorbents, however, have the potential to aggregate at large dosages, which would reduce the amount of adsorption [26]. Furthermore, the unmodified GO required a significantly higher adsorbent dosage (5 mg) compared to EGO (4 mg) for optimal copper removal can be due to the EDTA modification of EGO and its pore structure. Introducing nitrogen-containing functional groups and chelating agents onto the graphene oxide surface provides additional binding sites for copper ions, potentially increasing the adsorption capacity at lower dosages. Modifications can also alter the pore structure of graphene oxide. This might increase the accessibility of internal pores, leading to higher copper uptake at lower dosages [27].

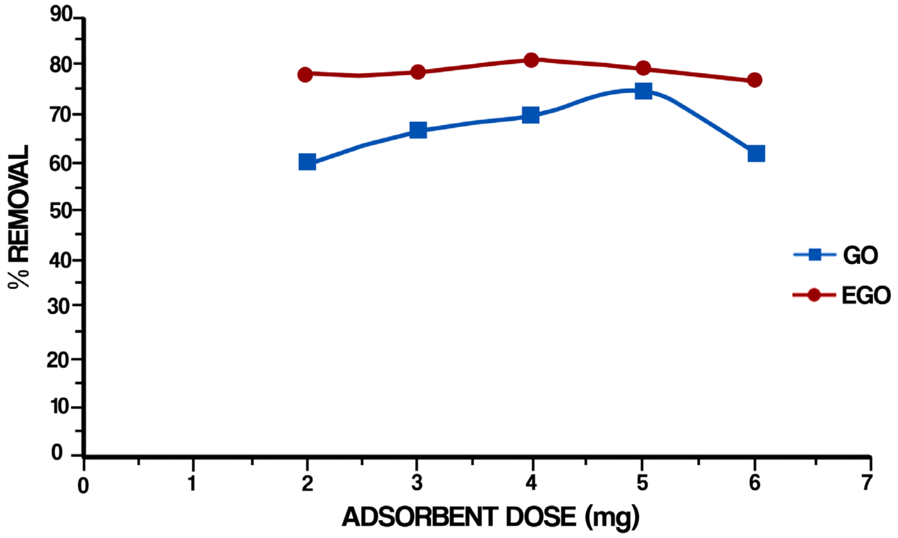


**Fig. 3.** Effect of adsorbent dosage towards adsorption of Cu(II) ions by GO and EGO.

**Effect of Contact Time.** Contact time is one of the critical adsorption parameters as it influences the mass transfer rate of substances. The suitable contact time of each adsorbent depends on the equilibrium point. For majority of metal ions, the removal efficiency initially increases dramatically and then increases slowly until the contact time is extended to reach equilibrium [24]. Regardless of the other experimental parameters, the duration of contact time in an adsorption system has a substantial impact on the adsorption kinetics. For the purposes of this investigation, the adsorption contact time was varied at 15, 30, 45, 60, and 75 minutes. Fig. 4 shows that the contact time for both GO and EGO affect the removal of Cu(II) ions, with a significant and discernible increase in Cu(II) adsorption occurring at 45 minutes is 78.41% with an adsorption capacity of 91.17 mg/g for GO, and 89.94% with an adsorption capacity of 135.6 mg/g for EGO. It is clear from the graphical representation that as the contact duration increases from 15 to 45 minutes, the percentage of copper ions removed increases. The initial increase in efficiency could be related to the availability of bindings sites on adsorbent. There is an abundance of adsorption sites available in the initial phase of the adsorption process, which makes it easier for Cu(II) ions to attach to these sites [28]. Because there is less rivalry among the adsorbate molecules for binding sites on the adsorbent surface, this availability promotes a higher rate of adsorption. However, beyond a certain point, an increase in contact time may not result in any further adsorption, indicating that the adsorption process has reached equilibrium. Eventually, all the sites get filled, and no further adsorption can occur, reaching a saturation point [25].

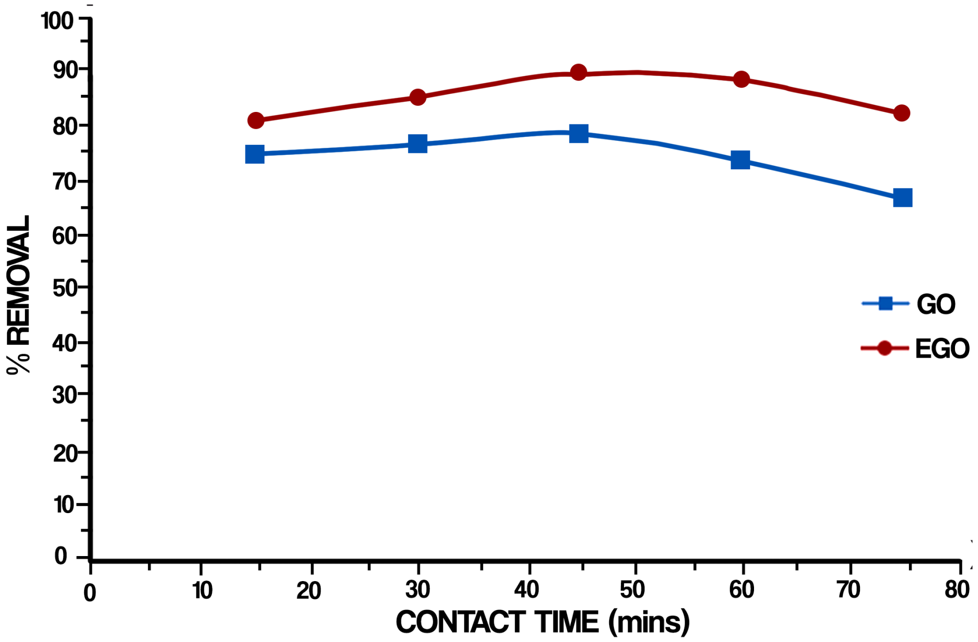


**Fig. 4**. Effect of Contact Time towards Adsorption of Cu (II) by GO and EGO.

**Comparative Analysis of Adsorbents.** The data from the adsorption experiments involving different pH levels, varying adsorbent dosages, and different durations of contact time were subjected to the following tests: Two-way Analysis of Variance (ANOVA) and t-tests at a significance level of 0.05 to investigate further into the collected data concerning the adsorption characteristics of both GO and EGO. These experiments sought to compare the adsorption characteristics of both GO and EGO. The information obtained from the experiment measuring adsorption performance provided slopes depicting the rate of Cu(II) ions removal under different conditions, allowing for comparative analysis. Slopes showing the rate of removal of Cu(II) ions under various conditions were acquired from the experiment evaluating adsorption performance, enabling a comparative analysis. Table 2 and Table 3 present the results of the Two-way ANOVA and t-test analysis conducted on both GO and EGO under three different parameters (pH, adsorbent dosage, and contact time).

**Table 2.** Two-way Analysis of Variance (ANOVA) for GO vs EGO over % Removal of Cu(II) ions

| Conditions of GO vs EGO | F value | F critical |
|---|---|---|
| Varying pH | 5 | 2.87 |
| Varying Adsorbent dosage | 5.71 | |
| Varying Contact Time | 4.20 | |

**Table 3.** t-Test analysis for GO vs EGO over % Removal of Cu(II) ions.

| Conditions of GO vs EGO | P value | P critical |
|---|---|---|
| Varying pH | $3.21 \times 10^{-4}$ | 0.05 |
| Varying Adsorbent dosage | $7.96 \times 10^{-7}$ | |
| Varying Contact Time | $1.64 \times 10^{-7}$ | |

Table 2 shows the result of the two-way ANOVA analysis, where the percentage removal of Cu(II) ions for both types of adsorbent at varying pH, adsorbent dosage, and contact time are statistically significant. It shows that the calculated F-values were larger than the F-critical value, indicating that the types of adsorbents and the varying parameters used affect the percentage removal of Cu(II) ions in the solution and their means differ significantly from each other. Meanwhile, results in Table 3 describes that in all conditions, EGO have a significant difference (p value < p crit) in terms of percent removal towards Cu(II) ions. The positive p values also show that there is a positive significant difference, suggesting that the modification improved the efficiency of Cu removal from the solution by adsorption. Furthermore, it provides more evidence in favor of the notion that adding functional groups from EDTA-silane may improve the ability of graphene oxide to adsorb heavy metal ions like Cu(II) from aqueous solutions.

**Adsorption Isotherm and Kinetics.** The adsorption behavior of GO and EGO concerning Cu(II) ions were graphically analyzed and fitted to both Langmuir and Freundlich isotherms. The purpose of this analysis was to ascertain if a multilayer adsorption mechanism or chemisorption monolayer adsorption was employed in the interaction between the adsorbate (Cu(II) ions) and the adsorbent (GO and EGO). When adsorbate molecules form a single layer on the adsorbent surface, the Langmuir model usually implies monolayer adsorption; in contrast, the Freundlich model predicts a multilayer adsorption phenomenon, in which adsorbate molecules create multiple layers or display heterogeneous adsorption behavior [29]. To determine which model best captures the adsorption behavior in this particular system, these different models are compared.

The graphs illustrating the linearized data for Langmuir (Fig. 5a and 5b) and Freundlich (Fig. 5c and 5d) isotherms, indicate that for both GO and EGO, the $R^2$ value associated with Langmuir isotherm model, 0.9780 and 0.9314, respectively are higher than the Freundlich isotherm model, 0.9599 and 0.8782 as shown in Tables 4 and 5. Based on these findings, the Langmuir isotherm model, which describes how the adsorbate forms a monolayer at maximum coverage in certain active sites on the adsorbent surface, best describes the adsorption systems of both GO and EGO. When a binding site is occupied by sorbate, it is assumed that no more adsorption will occur there for a monolayer coverage to exist. As a result, there is a one-to-one ratio between the adsorbate and the adsorbent, and it is unlikely that the adsorbate will stack [30].

**Table 4.** Langmuir Parameters of GO and EGO towards the Adsorption of Cu(II) ions.

| Adsorbent | Langmuir Parameters | | | |
|---|---|---|---|---|
| | $q_{max}$ (mg/g) | $K_L$ (L/mg) | $R_L$ | $R_2$ |
| GO | 672.22 | 0.01626 | 0.7110 | 0.9780 |
| EGO | 729.11 | 0.03370 | 0.5427 | 0.9314 |

**Table 5.** Freundlich Parameters of GO and EGO towards the Adsorption of Cu(II) ions.

| Adsorbent | Freundlich Parameters | | |
|---|---|---|---|
| | $K_F$ | 1/n | $R_2$ |
| GO | 10.5977 | 0.9681 | 0.9599 |
| EGO | 30.3506 | 0.6686 | 0.8782 |

Furthermore, the results of this study were used to determine the maximum monolayer saturation capacity of two materials, GO and EGO. Based on theoretical calculations, it was found to be 672.22 mg/g for GO and 729.11 mg/g for EGO which indicates that EGO has a significantly greater capacity than GO for molecules to be adsorbed in a single layer on its surface, suggesting that EGO may have a stronger potential for adsorption. Furthermore, the equilibrium factor (RL) of Langmuir isotherm displays a positive value (GO: 0.7110, EGO: 0.5427). The type of isotherm is indicated by the value of RL, which can be either irreversible (RL =0), favorable (0<RL <1), linear (RL =1), or unfavorable (RL >1).

The RL values for EGO (0.5427) and GO (0.7110) are both significantly below 1 when analyzed in which according to the Langmuir isotherm model, suggests that the adsorption behavior for both materials is favorable. An efficient and desirable adsorption process is indicated by a favorable RL value (0<RL<1). Lower RL values (EGO) in this situation imply greater favorability of the adsorption process.

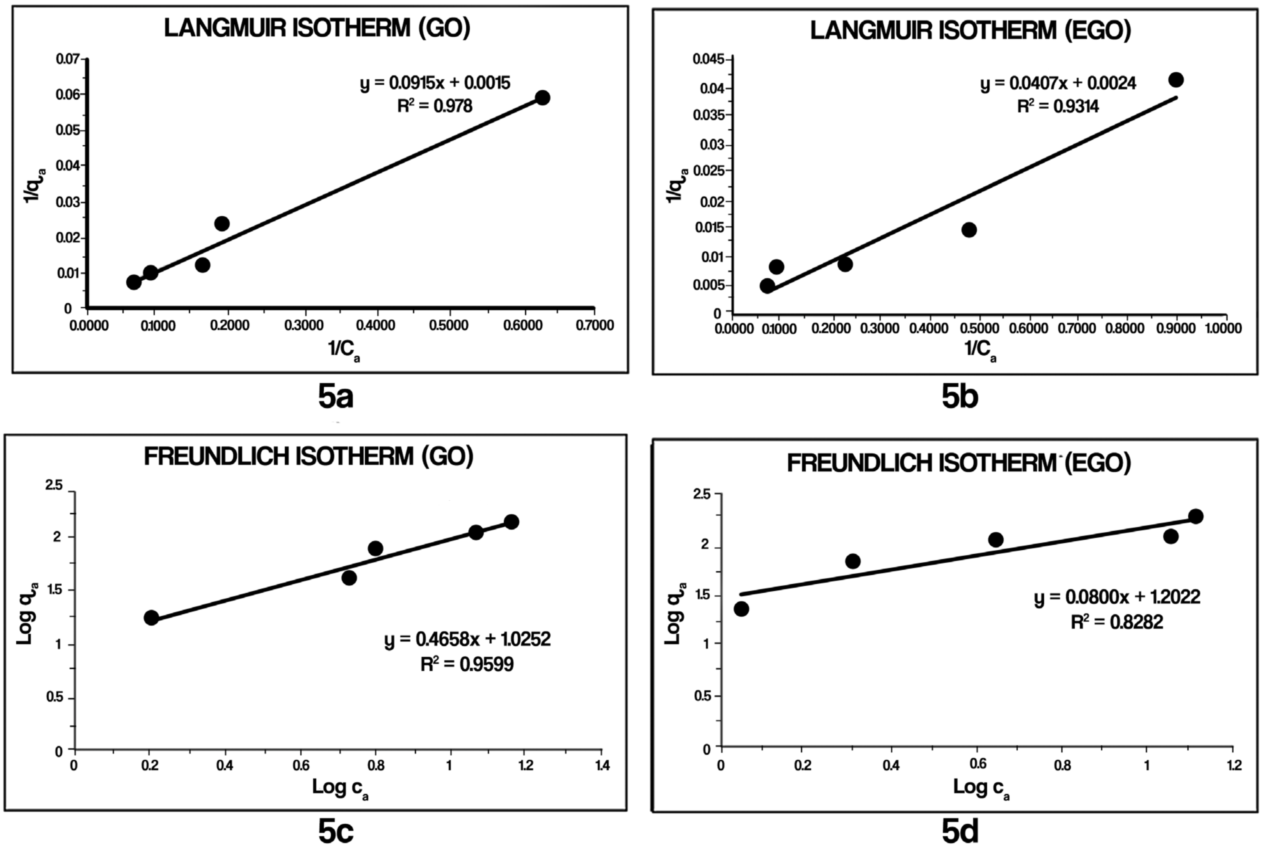
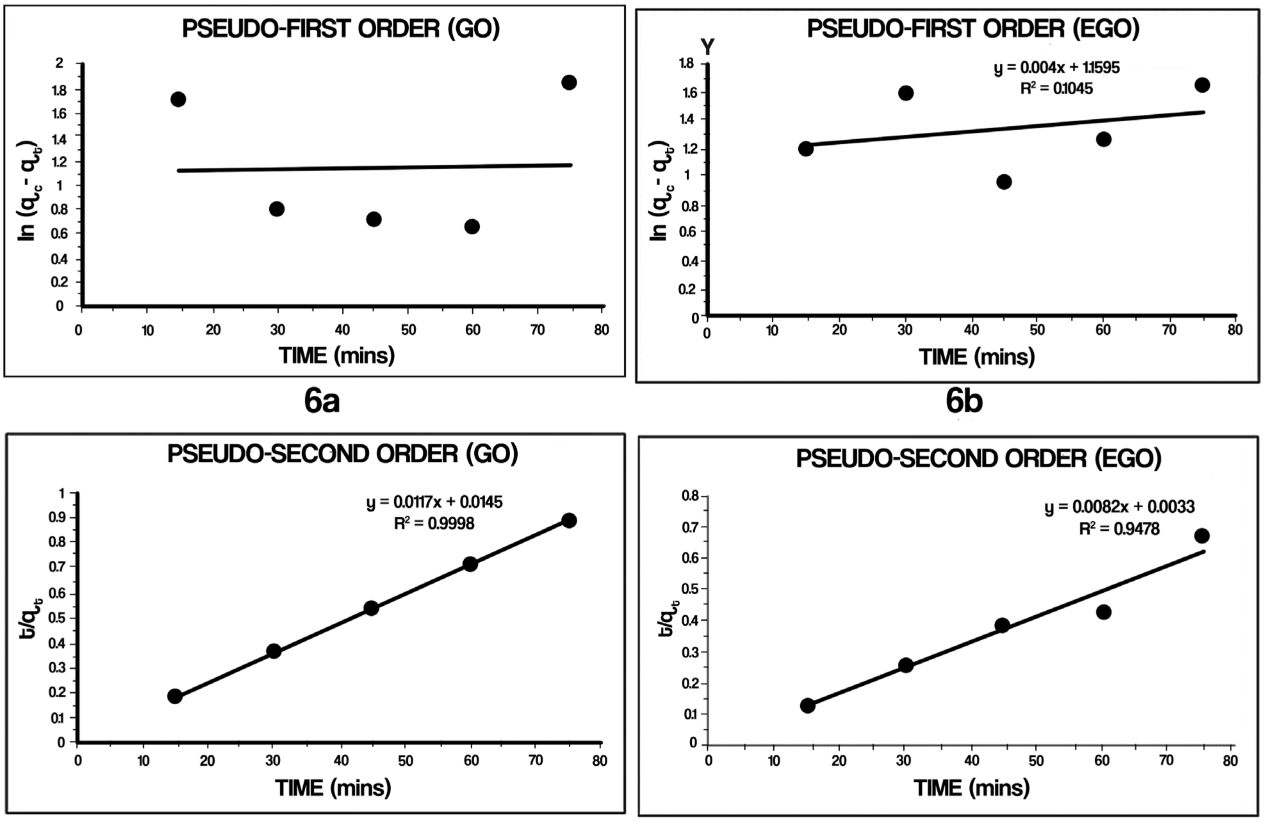


**Fig. 5.** Adsorption isotherm of Cu(II) ions. (a) Langmuir adsorption isotherm using GO; (b) Langmuir adsorption isotherm using EGO; (c) Freundlich adsorption isotherm using GO; and (d) Freundlich adsorption isotherm using EGO.

To ascertain the characteristics of adsorption (either physisorption or chemisorption) of GO and EGO towards the removal of Cu(II) ions, this study examined both the pseudo-first-order kinetics by Rudzinski and Plazinski (2006) [31] and the pseudo-second-order kinetics developed by Ho and McKay (1999) [32]. Since the longest adsorption exposure of the experiment was obtained during this effect of contact time, data from it was employed (Table 6). These data were graphed and analyzed by applying linearized forms of both the pseudo-first-order (Fig. 6a and 6b) and pseudo-second-order equations (Fig. 6c and 6d).

**Table 6.** Comparison of Adsorption Kinetics of Both GO and EGO.

| | Pseudo-First Order | | | Pseudo-Second Order | | |
|---|---|---|---|---|---|---|
| | q1 (mg/g) | K1 | R² | q2 (mg/g) | K2 | R² |
| GO | 3.0607 | $1.02 \times 10^{-5}$ | 0.001 | 85.71 | 0.0094 | 0.9998 |
| EGO | 3.1884 | $5.29 \times 10^{-5}$ | 0.1045 | 121.59 | 0.0206 | 0.9478 |



6a 6b

6c 6d

**Fig. 6**. Adsorption kinetics of Cu(II) ions. (a) Pseudo-First order kinetics using GO; (b) Pseudo-First order kinetics using EGO; (c) Pseudo-Second order kinetics using GO; and (d) Pseudo-Second order kinetics using EGO.

As observed from the data in the Figures, the $R^2$ values that came from the pseudo-second-order model (0.9998 for GO and 0.9478 for EGO) were significantly higher than the $R^2$ values that came from the pseudo-first-order model. Based on the assumption that chemical sorption or chemisorption is the rate-limiting step, the pseudo-second-order model, which predicts behavior across the entire adsorption range, provides a better explanation for the adsorption kinetics of GO and EGO towards Cu(II) ions. With these results, it is further proven that the GO-Cu(II) and EGO-Cu(II) sorption systems follow chemisorption where chemical interaction occurs between the adsorbate and the functional group present works as binding sites of the surface of the adsorbent [33].

The pseudo-second-order kinetic model has become among the most popular ways to fit rate data for adsorption of metal ions, dyes, and other compounds from aqueous solution [34]. In addition, Wang and colleagues (2013) [35] investigated various parameters, such as pH, adsorbent dosage, contact time, temperature, and coexisting ions, on the adsorption performance of graphene oxide

(GO) for the removal of heavy metals in batch reactions. The findings demonstrated how well the adsorption process fit the pseudo-second-order kinetic model and the Langmuir isotherm, demonstrating the effectiveness of GO as an adsorbent.

## Conclusions

The removal of Cu(II) ions from aqueous solutions was investigated by the use of graphene oxide. The removal efficiency of both GO and EGO in response to copper(II) ions was found to be strongly influenced by variations in pH, adsorbent dosage, and contact time. The removal efficiency of these two adsorbents was found to be limited by achieving a state of equilibrium and the saturation of binding sites. Since the adsorption process of both GO and EGO favors a Langmuir isotherm and a pseudo-second-order model, the removal of Cu(II) ions was best described by chemisorption, thus the formation of an adsorbate monolayer takes place in specific active sites on the surface of GO and EGO. However, following further investigations may be conducted to enhance the current results of the study, to wit: (1) additional parameters be tested, such as agitation speed, ionic strength, point of charge, and temperature in batch adsorption experiments to properly determine the optimal working conditions of the unmodified and modified GO; (2) enhancing the yields of the adsorbents through the use of efficient equipment and standard procedures is also strongly advised for practicability of synthesis; (3) in-depth study of the reusability of EGO should be further explored to confirm the longevity of EGO as an adsorbent. An essential component of assessing the adsorption performance of the material is the number of cycles at which the adsorbent may continue to function. different desorbing or regenerating solvents, like acids, bases, and chloride salts, can be used in these studies looking into the reusability of adsorbent; (4) the potential and versatility of EGO as an adsorbent for various pollutants can also be assessed by removing additional heavy metal ions and organic and/or inorganic compounds; and (5) it is also advised that more replicates be carried out and that more values of pH, contact time, and adsorbent dosage ranges be investigated, to further extrapolate the results and produce effective and reliable estimates to the trend of adsorption. Nevertheless, this study presents a Cu (II) removal by a simple and cost-effective adsorbent. Therefore, for effective copper uptake, chemically produced EGO may be a preferable option than unmodified GO.

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