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Graphene Oxide-Based Electrodes with Constant Magnetic Field-Assisted Electrodeposition System to Raising the Efficient of Cu^{2+} Removal

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ABSTRACT

In this work higher Cu^{2+} removal efficiency was achieved by graphene oxide GO-based electrode with the constant magnetic field (CMF)-assisted electrodeposition system. The GO was initially synthesized by the electrochemical exfoliation method in the electrolyte containing custom-made surfactant. The as-prepared GO solution was then spray coated on the pre-heated stainless steel-cathode before annealed at 400°C for 1 hour. GO-based electrode with CMF-assisted electrodeposition system was successful removed 89.1% of Cu^{2+} from aqueous solutions as compared to the electrode without GO of only 75.5% of Cu^{2+} removal within a fixed 3 hours' time. The efficient of Cu^{2+} removal by GO-based electrode was believed due to the high specific surface area of GO that increases the accommodation of the active species (Cu^{2+}) at the electrode surfaces. In the meantime, it was found that the presence of CMF of 23 Gauss parallel to cathode surfaces enhances the convection and mass transport of Cu^{2+} charged species to the electrode as compared to the absence of the CMF on an electrodeposition system. This phenomenon was due to the Magneto-Hydrodynamics (MHD) effect of CMF which is based on the Lorentz force that increases the Cu^{2+} deposition efficiency by reducing the diffusion layer thus increasing the ions transfer into the electrical double layer. The electrodes before and after Cu^{2+} deposition was examined by electron microscopy, energy dispersive x-ray, and Raman spectroscopy, and the concentration of remaining Cu^{2+} in the solution was analyzed using atomic absorption spectroscopy. From the analysis done shows that the GO-based electrode with CMF-assisted electrodeposition system pave a new and pragmatic route for efficient removal of heavy metal ions.

1. INTRODUCTION

Nowadays, the rapidly growth of many industries has encouraged the high production of heavy metals which are introduced in many pollutants in the air, water, and soil. The introduction of heavy metals in water pollution gives a more serious impact on the body system. Heavy metals like copper ion (Cu^{2+}) are the most common heavy metal ion found in wastewater due to their highly utilized in different applications [1]. Therefore, the increasing amounts of Cu ion metal discharge in the natural freshwater cause many health problems including hemolysis, liver, chronic disease kidney and influenza syndrome when it was directly consumed by human being [2].

This unhealthy environment gained many public interests in recent years. Therefore, an array of methods to eliminate heavy metal especially Cu (II) ion from water have been proposed. Among the entire methods including precipitation, ion exchange, membrane, electrolysis, oxidation and adsorption, the electrolysis such as electrodeposition approach implemented in aqueous solution was the effective method [3]. Many advantages such as inexpensive, energy efficiency it is having lower temperature; it could be used on a range of contaminants such as gases and liquids in small quantities or large and sufficiently stable and efficient electrode materials for electrochemical water purification [4]. However, due to the drawback of high cost and complexity technologies, the highly efficient, green and economical method was paid an attention. Among these established methods, the electrodeposition method through electrochemical process offers ease, rapid and efficient method as an absorbent method to remove the heavy metals from the water especially Cu where this metal is easy to remove [5].

Graphene oxide (GO), a derivative of graphene, has attracted significant attention due to its unique properties such as high surface area, excellent mechanical strength, and tunable surface chemistry. These properties make GO an ideal candidate for various applications, including environmental remediation, particularly in the removal of heavy metals from water [6].

In recent, GO from graphene-based materials possesses great potential and efficient absorbers in treating heavy metal ions in the purification process of water [7]. The GO sheets were highly loaded with the oxygen-containing functional groups such as hydroxyl, carboxyl, carbonyl and epoxy [8]. These oxygen groups can directly react with the heavy metal ions in order to form metal ion complex thus promising in removal of heavy metals [9, 10].

The use of GO in heavy metal removal has been extensively studied. The GO's oxygen-containing functional groups, such as hydroxyl, epoxide, and carboxyl groups, facilitate the adsorption of heavy metal ions through various mechanisms including electrostatic interactions, ion exchange, and surface complexation [11]. Also, modifications of GO, such as the introduction of additional functional groups or the formation of composites with other materials, have been explored to enhance its adsorption capacity and selectivity towards specific heavy metals [12].

The GO have been used in many applications due to it exhalent properties such as high electrical conductivity [13], large surface area and thermal properties [14]. The using GO as an adsorbent agent to removal heavy metals has already been reviewed by several authors [15]. Recently study have been used GO with ethylenediaminetetraacetic acid (EDTA) as nanocomposite were applied to the removal of heavy metals, such as Pb^{2+}, Cu^{2+} [16]. Moreover, Dithiocarbonate-graphene oxide was used to capture Cu^{2+} and Cd^{2+} then remove them from aqueous solutions [17]. Another study was used GO/cellulose to adsorb metal ions (Cu^{2+}) from water, they found efficiency of removal Cu ions increases with an increase in the GO/cellulose ratio [18].

Electrodeposition, a sophisticated electrochemical technique, has emerged as a pivotal tool in the domain of water treatment, specifically for the mitigation of heavy metal pollution. This method exploits the principle of electrolysis to facilitate the deposition of metal ions onto electrode surfaces, thereby extracting them from the aqueous medium. The process is characterized by its operational simplicity, high removal efficiency, and the potential for metal recovery, which aligns with the contemporary environmental mandate for sustainable and resource-efficient technologies [19].

The efficacy of electrodeposition in heavy metal removal is contingent upon various factors, including the electrode material, electrical parameters, and the chemistry of the electrolyte solution [20]. Recent advancements in electrode design, such as the development of nanostructured electrodes and the incorporation of conductive polymers, have significantly enhanced the performance and applicability of electrodeposition systems [21, 22]. These innovations have not only improved the removal rates of heavy metals but also expanded the technique's capability to address complex mixtures of pollutants. Furthermore, the synergistic integration of electrodeposition with other water treatment technologies, such as membrane separation and advanced oxidation processes, has given rise to hybrid systems that offer comprehensive solutions for water purification [23]. These integrated approaches are particularly promising for treating industrial effluents that contain a variety of contaminants at varying concentrations.

As the global water crisis intensifies and the need for effective heavy metal removal becomes more pressing, electrodeposition stands out as a technology with considerable potential. Its ability to be scaled and automated, coupled with its environmental compatibility, positions electrodeposition as a key strategy for safeguarding water quality and promoting circular economy principles in the treatment of heavy metal-laden wastewaters [24].

Some studies point to the importance of a static magnetic field (CMF) to influence the orientation and behavior of graphene oxide, leading to improved electrolytic properties and new applications. The importance of using constant magnetic fields lies in modifying the properties of graphene oxide-based materials, especially in the context of electrode applications. The use of constant magnetic fields also improves the electrolytic properties of graphene oxide-based electrodes, leading to increased electrochemical surface area and reactivity [25].

This study focuses on a novel electrodeposition approach using a GO-coated cathode and a constant magnetic field (CMF) assisted electrodeposition system. The integration of CMF is aimed at enhancing the efficiency of Cu^{2+} removal from water, leveraging the unique properties of GO and the magnetic field's influence on electrodeposition dynamics. By exploring this innovative combination, the research aims to contribute to the development of simpler, greener, and more efficient methods for heavy metal ion removal from contaminated water sources. This introduction thus sets the stage for examining the effectiveness of GO-coated electrodes under the influence of CMF in improving the removal efficiency of Cu^{2+} ions. The used of high porosity GO-coated cathode with the presence of external magnetic field assisted electrodeposition system were believed to increase the concentration of removal Cu^{2+} from water.

2. METHODOLOGY

2.1 Synthesis of graphene oxide (GO)

Graphene oxide (GO) was initially synthesized using electrochemical exfoliation method in an electrolyte solution containing triple-chain TC14 surfactant of 0.1 M concentration. Figure 1 shows the schematic diagram of the GO synthesis process using two graphite rods (Goodfellow, 99.5% purity with a diameter and length of 10 and 150 mm) were partially immersed in the prepared TC14 electrolyte solution and connected to 7 V potential for 24 hours. The experimental setup was done at room temperature. The details of the GO production process were reported in previous work [26].

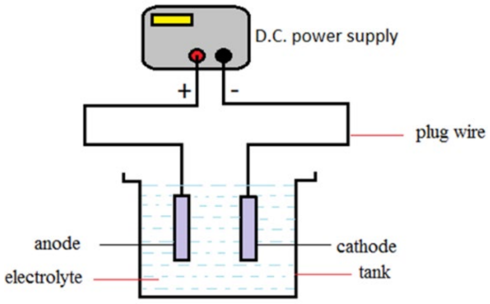


Figure 1. The schematic diagram of electrochemical exfoliation method to produce GO

2.2 Preparation of graphene oxide–based electrodes

Stainless steel plates of 48 height × 28 width × 0.5 thickness mm^3 dimension (Figures 2 (a)-(c)) were used as working electrodes for the removal of Cu^{2+} heavy metal ions via CMF-assisted electrodeposition system. The electrodes were ultrasonically cleaned by using acetone, methanol, and DI water for 10 minutes respectively and blow-dried with compressed argon gas before pre-heating on a hot plate at 120℃ for 10 minutes. The GO solution was then spray coated on the one side of pre-heated steel cathode at 10 cm spraying distance of the sprayer nozzle and the cathode. The cathode was then annealed at 400℃ for 1 hour in argon ambient as shown in Figure 2 (d).

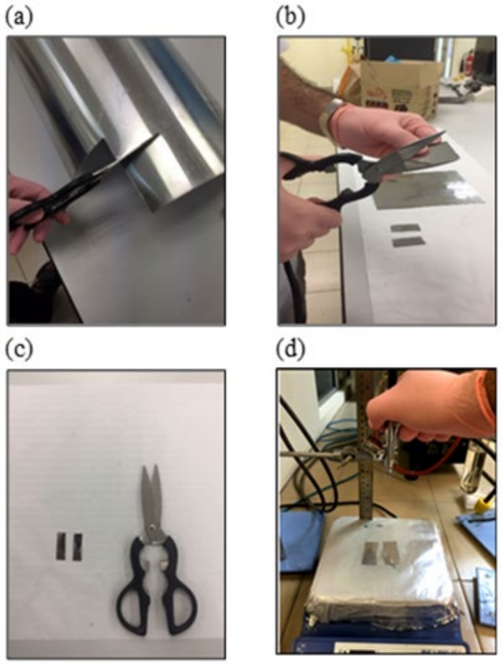


Figure 2. (a)-(c) Preparation of stainless-steel plate with the dimension of 48 height × 28 width × 0.5 thickness mm^3; (d) The spray deposition technique for the preparation of GO-based electrodes

2.3 Preparation of constant magnetic field-assisted electrodeposition system

The magnetic coil used in this study was custom-manufactured in our laboratory to provide a consistent magnetic field for investigating its influence on the electrodeposition process. The magnetic field (B) of 23 G for effective electrodeposition of heavy metal ion was generated by 120 loops of copper solenoid (Figures 3 (a)-(c)) with an applied current of 1.2 Amp. Magnetic field applied was perpendicular to the electric field, E and parallel to the surface of the cathode as presented in Figures 3 (c)-(e) in order to create Lorentz force, FB for MHD assisted electrodeposition system. The spacing between steel cathode and anode was fixed at 10 mm with an applied voltage of 2V and the current supplied was 0.003A in electrodeposition system with the presence and absence of CMF. The experiments were carried out using GO-coated cathode in comparison to cathode without GO that was performed in both presence and absence of CMF for 1, 2 and 3 hours. The samples were label as (1) GO coated cathode with CMF; (2) GO-coated cathode; (3) cathode with CMF and (4) cathode.

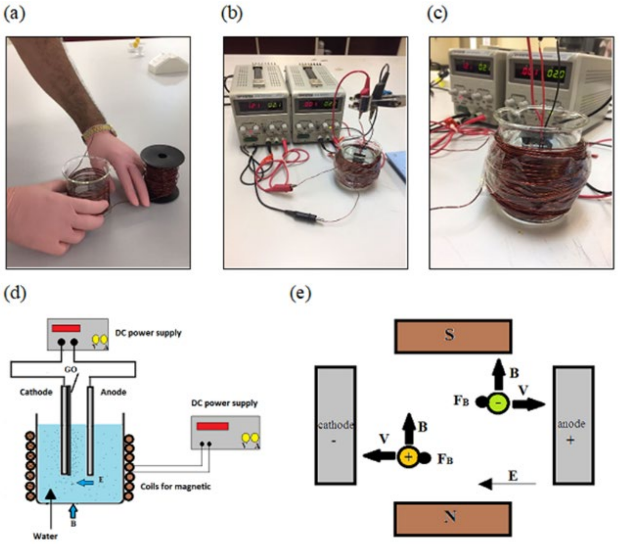


Figure 3. (a) The making of 120 loops of copper wire for generating 23 G magnetic field; (b)-(c) The electrodeposition system with GO-based electrode and CMF applied; (d) The schematic diagram of GO-based electrode with CMF-assisted electrodeposition system assembly for heavy metal ion removal; (e) The diagram of FB resulted from CMF in the process of electrodeposition of a paramagnetic of Cu^{2+} and negative ions in the setting of B⊥E where E is electric field and V is the velocity of ions

2.4 Preparation of the stock solution

Among the various heavy metals, copper ions (Cu^{2+}) are often used as a model contaminant due to their widespread presence in industrial effluents and their potential toxicity to aquatic life and human health [27].

Analytical-grade chloride salt solutions which was obtained from Merck was used to prepare the stock solution containing 1000 mg/L of Cu (II) heavy metal ions by dissolving 1.9844g copper II chloride ($CuCl_2$) in 1000 mL of deionized water. To obtain the required concentrations of 100 mg/L of Cu (II), metal chloride salts was diluted with deionized water. Approximately 250 ml of Cu^{2+} electrolyte at neutral pH was consumed during the electrodeposition process. The concentration of remaining Cu^{2+} in the solution was determined by atomic absorption spectroscopy (AAS; Buck Scientific, model 210 VGP) were conducted at variety of electrodes (GO-coated cathode with CMF; GO-coated cathode; cathode with CMF and cathode) and contact time of 1, 2 and 3 hrs. An atomic absorption standard calibration solution of 996 μg ml^{-1} nickel in 2% HNO_3 and a blank solution were used to calibrate the AAS. Samples were diluted to 1/100 of the original concentration to perform the AAS analyses. The instrument manual for the nickel lamp lists the following specifications: wavelength 232.0 nm, slit 0.2 nm, detection limit 0.02 mg L^{-1}, linear range 3 mg L^{-1} and flame type AA, lean/blue.

The removal percentage of heavy metal ions and equilibrium adsorption capacity were calculated based on the equations as follows:

$$\%\ \text{Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

$$q_e = \frac{(C_o - C_e)\,V}{m} \qquad (2)$$

where, C_o and C_e are the initial and equilibrium heavy metal ion concentration (mg/L), respectively; q_e is the equilibrium adsorption capacity (mg/g); V and m are the volume of the solution (L) and adsorbent dosage (g), respectively [28].

2.5 Sample characterizations and metal ion concentration measurements

The GO was thoroughly characterized using a combination of advanced techniques to assess its morphological, structural, optical, and chemical properties. Field Emission Scanning Electron Microscopy (FESEM) and Energy-Dispersive X-ray Spectroscopy (EDX) were used to study the surface morphology and elemental composition of the GO sheets. High-Resolution Transmission Electron Microscopy (HRTEM) offered detailed views of the atomic structure and layer stacking. Micro-Raman spectroscopy provided insights into the carbon lattice vibrations, indicating the level of disorder and defects. Fourier-Transform Infrared Spectroscopy (FTIR) identified the functional groups present, while X-ray Diffraction (XRD) determined the crystalline structure and interlayer spacing. Furthermore, Ultraviolet-Visible (UV-Vis) spectroscopy and FTIR were employed to evaluate the optical properties, revealing the absorption behavior and the influence of vibrational modes on light interactions. Collectively, these methods enabled a comprehensive evaluation of the GO's characteristics, which is essential for determining its potential in heavy metal removal and environmental remediation applications.

The characterizations in this work are divided into two main characterization which were (i) structural and (ii) metal ion concentration measurements. The structural of GO-coated electrode before and after the electrodeposition of Cu^{2+} in both the presence and absence of CMF during the experiment were characterized using FESEM, micro-Raman spectroscopy, x-ray and energy dispersive x-ray spectroscopy (EDS), HRTEM, FT-IR, XRD, UV-Vis spectroscopies, TGA analysis, and AFM. This is to investigate the physical changes, defect and functional groups of GO before and after deposition of heavy metal ions. The concentration of heavy metal ions remaining in the solution was analyzed using AAS for every one hour of electrodeposition and DC Gauss meters was used for the measurement of magnetic field applied to the system.

3. RESULTS

3.1 Graphene oxide characterization

Before directly proceed the GO as an electrode for the electrodeposition of Cu^{2+}, several initial characterizations were performed on the GO. Figures 4 (a)-(b) shows the FESEM and HRTEM images of the GO that were produced via electrochemical exfoliation method. The synthesized GO was observed to be multi-stacked, high degree of agglomerations with wrinkles at the edge part as depicted in Figure 4(a) by arrows. This was believed due to the introduction of defects and oxygen functional groups on the GO sheets [26] which would be beneficial for the accommodation of the Cu^{2+} at the electrode surfaces. The HRTEM results show the folded appearance of GO graphitic layers at the edges which confirmed that the GO were oxidized (Figure 4(b)). The GO sample also shows a wrinkled and crumpled surface due to the overlapping sheets which is consistent with FESEM results.

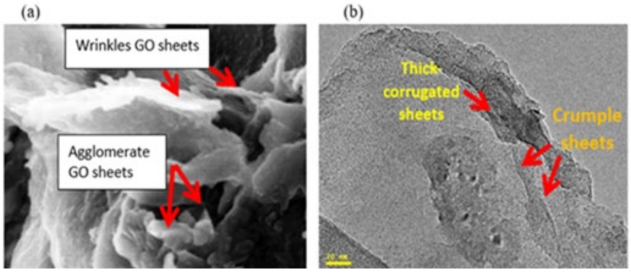


Figure 4. FESEM and HRTEM images of the folded edges of GO

3.1.1 Micro-Raman analyses of pristine GO

Micro-Raman spectroscopy was used to investigate the quality of the samples produced. Figure 5 shows the micro-Raman spectra of pristine GO. The micro-Raman spectrum of GO shows two prominent peaks, D (disorder), G (graphitic) and 2D that appear at 1354 and 1584 cm^{-1}, respectively. The intensity ratio between the D and G bands, which can be expressed as a sp2/sp3 carbon ratio, is an important measurement to quantify the disorder and defects in the lattice [29]. The result obtained is believed to be due to the edges of the graphitic layers folding up on multiple stacks GO sheets. The intensity ratio between the D- and G- peaks (ID/IG) of the pristine GO (0.48). The test configuration for this experiment is in Table 1. Nevertheless, for the experiment at Reynolds number of 2×106, the angle of attack was limited to α = 23° only.

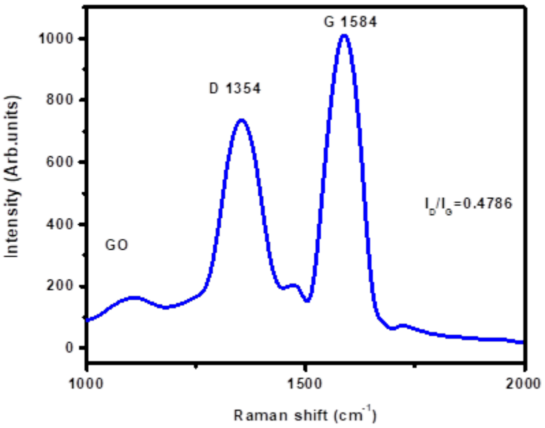


Figure 5. Micro-Raman analyses of pristine GO

3.1.2 FT-IR analyses of pristine GO

Figure 6 shows the FT-IR spectra of pristine GO. The FT-IR spectrum of pristine GO shows broad and intense peaks at ~3329 and ~1407 cm^{-1} (O-H), which indicate the absorption of water molecules in the sample [30, 31]. Generally, the O-H (hydroxyl groups) lies on the basal plane of the graphitic layers [32]. Several peaks were also observed at ~1047 and ~1648 cm^{-1}, represent the C-O (epoxy groups) and C=C of the aromatic rings, respectively. In addition, a moderate peak at ~740 cm^{-1} was observed from C=O (carbonyl groups) attaching on the edges of the GO sheets [33]. The presence of various oxygen functional groups after the exfoliation process confirmed that the GO has strong hydrophilicity.

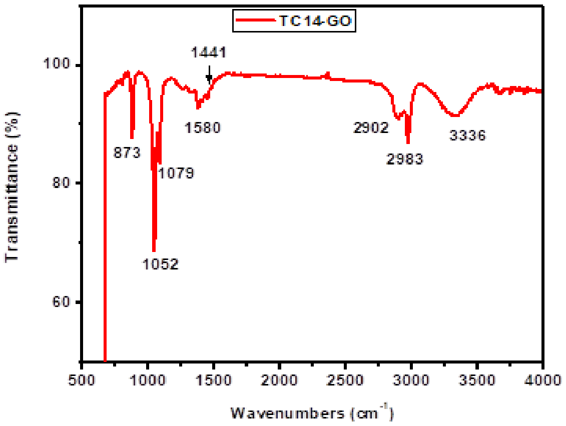


Figure 6. FTIR analysis of TC14-GO sample produced via electrochemical exfoliation method

UV-vis analysis of GO synthesized using the electrochemical exfoliation method. Figure 7 shows the UV-vis spectrum of the GO dispersions. Well-dispersed GO exhibits two characteristic features at ~230 nm, corresponding to the C-C aromatic transitions from $\pi\rightarrow\pi^*$, and a weak shoulder at ~300 nm due to C=O transitions from $n\rightarrow\pi^*$ [26]. These absorption peaks indicate the persistence of the C=C and C=O bonds after the oxidation process.

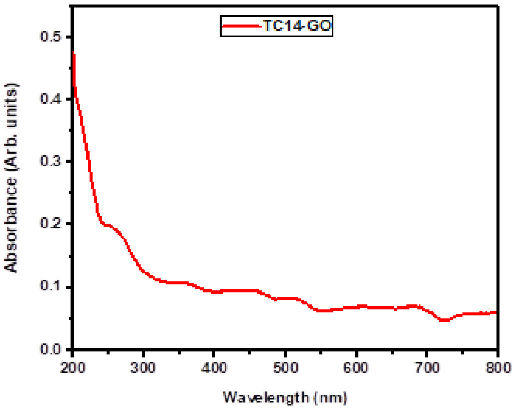


Figure 7. UV-Vis analysis of TC14-GO sample produced via electrochemical exfoliation method

3.2 Heavy metal ion removal efficiency by AAS

The traces of heavy metals namely Cu^{2+} was confirmed by AAS. The results indicated that the GO-based cathode with CMF applied to the electrodeposition system has the ability to efficiently deposit Cu^{2+} ions that were present in the solution of 89.1% (Table 1). Out of all different experimental design done, the metal ions Cu^{2+} was best removed by GO-based cathode with CMF. This then followed by GO-based cathode with the absence of CMF on the system of 88.91% removal of Cu^{2+} meanwhile bare cathode with CMF applied was only successfully to remove 78.5% of Cu^{2+} from the solution. For the system without the utilization of GO and CMF where only ~75.5% Cu^{2+} ions were removed during the same electrodeposition duration of 3 hours' time. While from time to time, as time increases from 1 to 3 hours the removal percentage were seem to increase for the whole set of experiments as shown in Figure 8. What is interesting is that the use of GO-based electrode either with the use of CMF and without CMF when electrodeposition has shown removal percentage up to 80% compared to only 58% removal of Cu^{2+} for bare cathode without GO coating. This show that high specific surface area of GO increases the accommodation of the active species (Cu^{2+}) at the electrode surfaces. For the electrode without GO coating factor the time played an important role, where the increase in time from 1 to 3 h had increased to 75.51%.

Table 1. Heavy metal removal percentage by different type of electrode with the presence and absence of CMF on electrodeposition system

Samples	**Time 1h**	**Time 2h**	**Time 3h**	**Removal (%)**
GO-based cathode with CMF	83.18 %	88.72 %	89.1 %	89.10%
GO-based cathode	81.47 %	88.65 %	88.91 %	88.91%
Cathode with CMF	60.10%	62.80%	78.50 %	78.50 %
Cathode	58.00%	61.10%	75.51 %	75.5 %

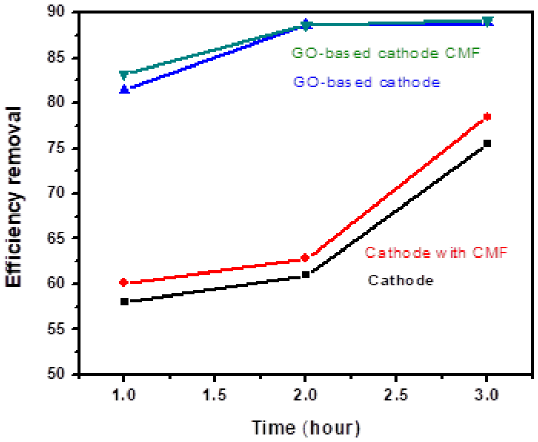
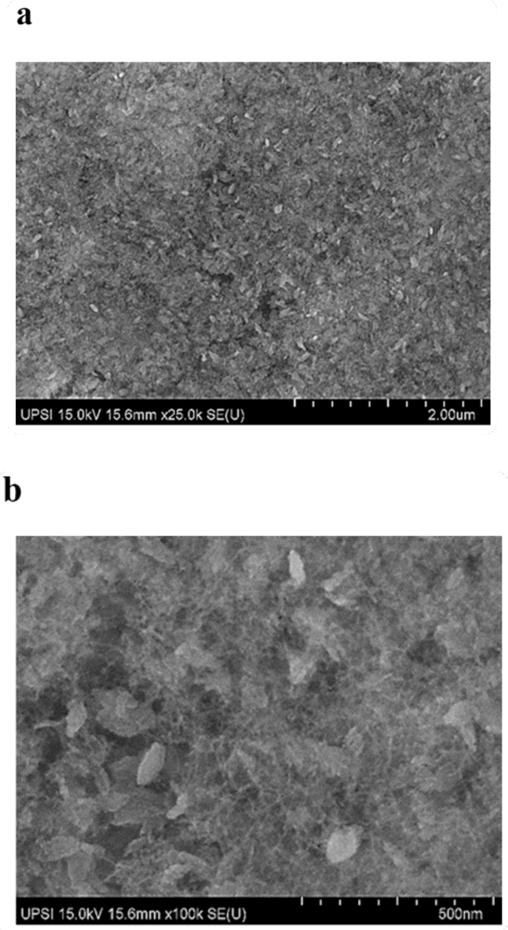


Figure 8. Removal percentage of Cu (II) by different type of electrode with the presence and absence of CMF on electrodeposition system

Although only a slight increase of about 78.50% is observed with the presence of CMF on the electrodeposition system, but this value is believed to be more significant if the magnetic field value is increased from only 23 G to 1000 G. This is evidenced by the efficacy of heavy metal removal percentage by different type of electrodes with the presence and absence of CMF on electrodeposition system were shown in Table 1. Therefore, it can be concluded that the prepared GO-based cathode with CMF applied during the electrodeposition process has a great potential for efficient removal of heavy metal ions. This was believed due to high specific surface area of GO that increases the accommodation of the active species (Cu^{2+}) at the electrode surfaces. In the meantime, it was found that the presence of CMF of 23G parallel to cathode surfaces enhances the convection and mass transport of Cu^{2+} charged species to the electrode as compared to the absence of the CMF on electrodeposition system. This phenomenon was due to MHD effect of CMF which based on the Lorentz force that increases the Cu^{2+} deposition efficiency by reducing the diffusion layer thus increases the ions transfer into the electrical double layer. This is due to the GO has a high surface area, which increased the surface area of the cathode as well as the possibility of involve van der Waals interaction and π–π stacking.

3.3 Physical characterization of graphene oxide-based cathode as compared to bare cathode after electrodeposition of cu^{2+} in the presence and absence of constant magnetic field

The Cu electrodeposited in the presence of CMF parallel were homogenous and smooth as shown in Figures 9 (a)-(b) than those obtained without CMF as shown in Figures 9 (c)-(d). This due to the MHD effect on electrodeposited surface which effect on the size crystallite. In fact, increase of processing time in the presence of CMF which more Cu ions can get to reach the cathode surface and the homogenous and smooth surface it comes from effect MHD on the Cu ions which more a regular movement resulting in the regulation of deposition on the surface. On the other hand, Figures 9 (c)-(d) with absence CMF dendrite growth which mean MHD can stop dendrite growth [33]. Figures 10 (a)-(b) shown EDX spectrum led to know of the type of the elements. The Figure 10 (a) show a ratio of 48.10% and the percentage of oxygen and carbon 41.83 %, 10.07%.



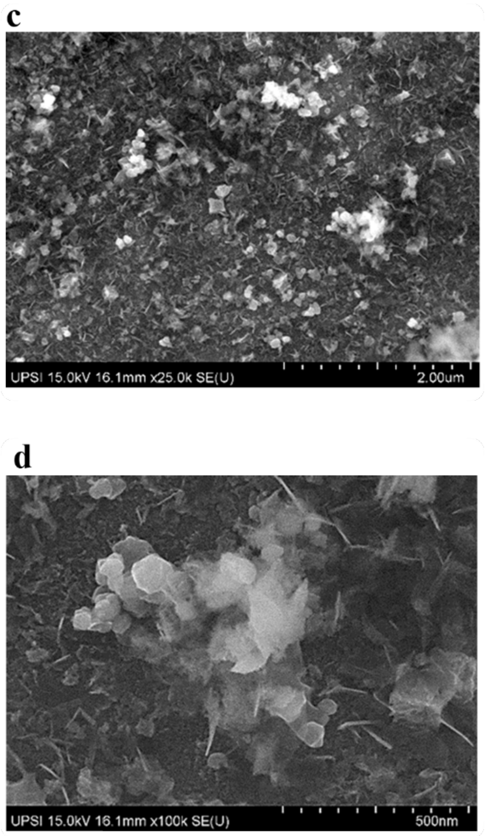


Figure 9. FESEM images of; (a)-(b) GO-based cathode with CMF and (c)-(d) GO-based cathode without CMF

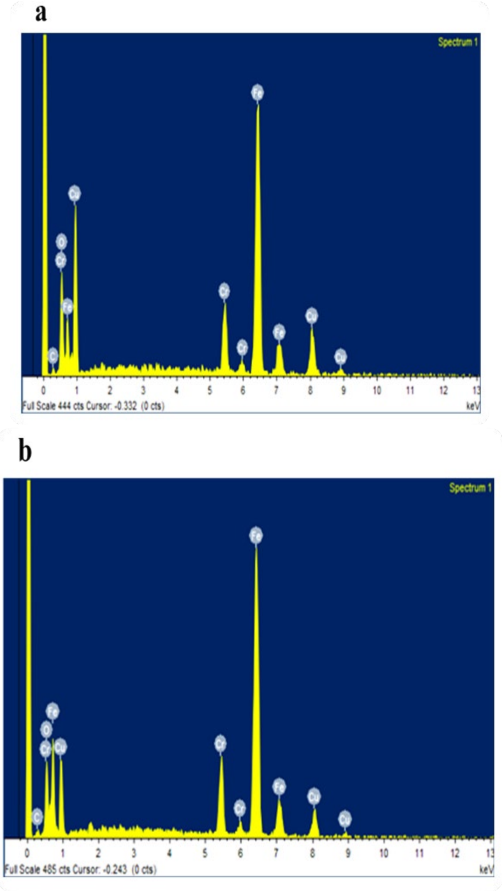


Figure 10. EDX images of; (a) Cu deposit on GO-based cathode with CMF and (b) Cu deposit on GO-based cathode without CMF

Micro-Raman spectra of GO and Cu deposited on GO-based cathode with CMF and without CMF are presented in Figure 11. Based on the spectra the GO with substrate from stainless steel exhibits three peaks in the range of 50-3000 cm^{-1}. The D-band which shows the disorder and defect level was seen at 1359 cm^{-1}. G-band at 1581.72 cm^{-1} was decreased and reason the Raman spectra depends on many factors like type of substrate, laser intensity, wavelength etc. the second beak was 2D at 2692 cm^{-1}. The third peak was at 680 cm^{-1} which was come from substrate Fe. The Raman spectra for GO-based Cathode was presence Cu_2O at wave length the 598 cm^{-1} and 1070 cm^{-1}. Raman spectra for GO-based cathode with CMF are presented in Fig. exhibits four peaks in the range of 500-3000 cm^{-1}, the most memorable is 635 cm^{-1} this peak to presence of CuO. The peaks at 1090 cm^{-1} carbonate grope, the D-band was observed at 1350 cm^{-1} are associated with C and G-band has slight shift from 1581.72 to 1575 cm^{-1} [34] is considered to be the representation of C-C as well as due to stretching of sp^2 C-C band present in GO [35].

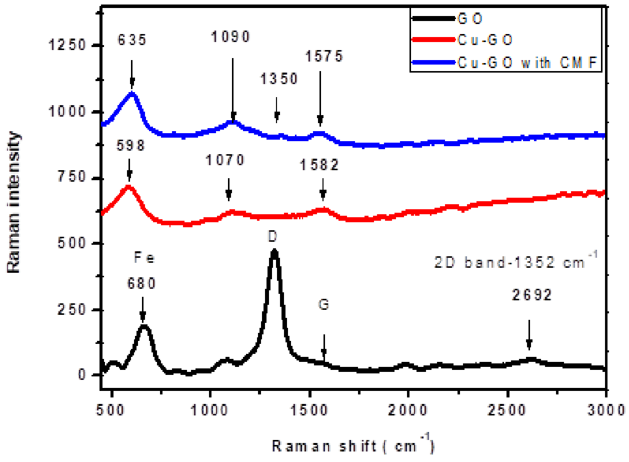


Figure 11. Micro-Raman analyses of pristine GO deposit on stainless steel substrate, Cu deposited on GO-based cathode without CMF and with CMF

The Cu electrodeposited in the presence of CMF were thick and homogenous as shown in Figure 12 (a) than those obtained without CMF the Cu electrodeposited was discontinuous and irregular manner as shown in Figure 12 (b). Moreover, the presence of CMF can be observed increase Cu electrodeposited as in Figure 12 (a). The effect CMF was clear and can be seen from FESEM photos. Figures 12 (c)-(d) shown EDX spectrum led to know of the type of the elements, the EDX spectrum taken the same time FESEM.

Figure 13 shows the Micro-Raman of Cu deposited on stainless steel cathode with CMF and without CMF. Based on the spectra the Cu electrodeposited on substrate from stainless steel with CMF exhibits some peaks in the range of 100-1000 cm^{-1}. The group of peaks located at around 154, 220, 412, 535 and 635 cm^{-1} these peaks come from copper oxide. The peaks at 154,220 and 412 cm^{-1} were presence Cu_2O for both electrodes. The Cu_4O_3 was presence at 535 cm^{-1} [36]. It is clear similarity between the two curves with a slight difference in Raman intensity which was more intensity when there was a magnetic field. In addition to the curve when there was a magnetic field was all the more pronounced peaks.

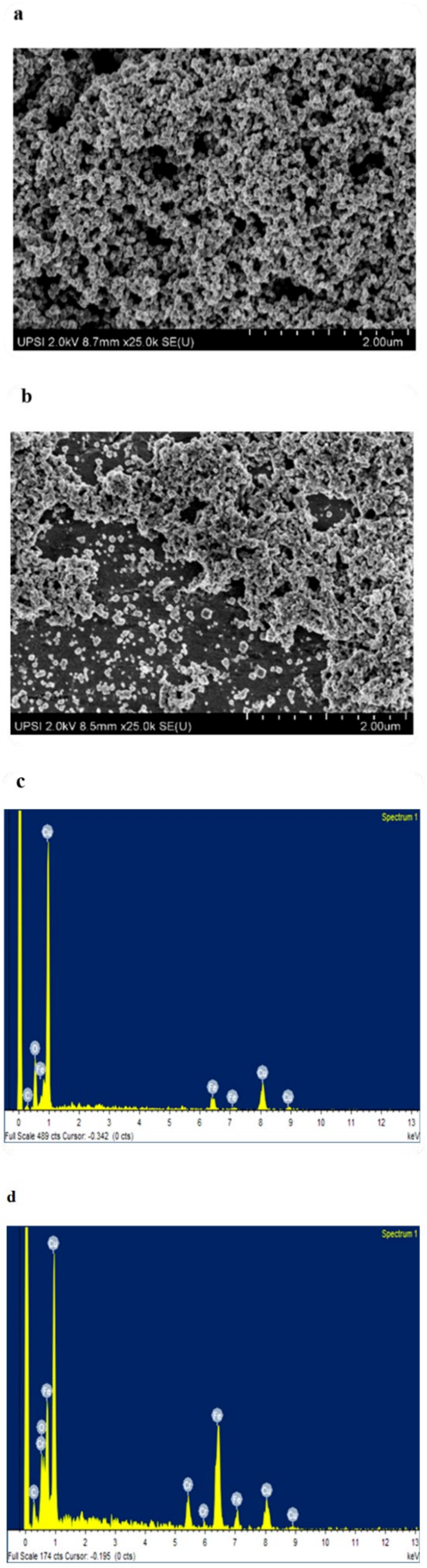


Figure 12. (a)-(b) FESEM (a) cathode with CMF and (b) cathode without CMF and EDX images of; (c) Cu deposit on cathode with CMF and (d) Cu deposit on GO-based cathode without CMF

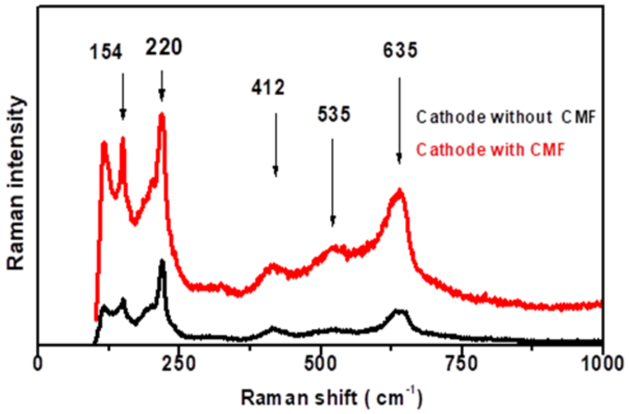


Figure 13. Micro-Raman analyses of the Cu coating in the presence and absence of CMF

3.4 Suggested Mechanism

The electrodeposition mechanism of Cu^{2+} on the GO-based cathode with CMF, GO and GO-Cu^{2+} chemical structures are illustrated in Figure 14. The electrodeposition of Cu^{2+} mechanism on the cathode surface was believed to include the electrostatic attraction, ion exchange, chemical interaction between metal the oxygen-containing functional groups of carboxyl, hydroxyl and epoxy groups on GO ions as well as with the defect sites in the cathode surface. This phenomenon is also widely discussed for the adsorption mechanism between GO and Cu^{2+}. Despite this obvious difference with the use of electrodeposition is the approach of using adsorption requires a large quantity of adsorbent, adsorption process is done for a long time, most of these adsorbent materials show lower adsorption capacity owing to the limitation of active sites particularly for low cost adsorbent such as peat, biomaterials, rice husk, peanut hulls, zeolites, chitosan, expensive production cost, complicated methodology, such as functionalization of adsorbents and the separation of the adsorbent would be difficult after adsorption.

The electrochemical mechanism for electrodeposition of metal is very simple where the cathodic deposition is [37] as follow Eq. (3) [38]:

$$Cu^{+2} + 2e = Cu \tag{3}$$

Water treatment using electrodeposition technique to enhancement of Cu^{2+} ions removal.it is wonderful of methods used water treatment to disarmament Cu^{2+} ions from water. When the electric current passé between electrodes the Hydrogen H^{+} liberated from GO, which gives an opportunity for the Cu^{2+} ions to bond. The possible explanation for efficient Cu^{2+} removal from GO-based cathode with CMF electrodeposition system could be that when the current passed through between the electrode H^{+} was released from the –COOH or –OH on the GO surface to the solution. This then gave an opportunity for the Cu^{2+} to bond with –COOH or –OH leading to Cu-OOC, Cu^{+}-OC and Cu-2OC and low reaction probability with the epoxy group [38]. This reaction also then led to the release of H+ into the solution (see Eqs. (4)-(6)):

$$Cu^{+2} + COOH \rightarrow Cu - OOC + H^{+} \tag{4}$$

$$Cu^{+2} + COH \rightarrow Cu^{+} - OC + H^{+} \tag{5}$$

$$Cu^{+2} + 2COH \rightarrow Cu - 2OC + 2H^{+} \tag{6}$$

The released H^{+} then led to a decrease in solution pH as shown by the measurement of the pH solution taken against the sample solution using a GO-based cathode with the presence and absence of CMF on the electrodeposition system. Available for both sets of experiments using GO-based electrode with the presence and absence of CMF shows the pH value as low as 3.71 after 3 hours Cu^{2+} depositing time on cathode surface. This value decreases from 4.98-4.89 pH value after 1 hour of experiment is then carried out to 4.00-4.01 pH value after 2 hours of electrodeposition process were shown in Table 2.

Table 2. The changing of solutions pH value during ED process utilizing (23 G)/SS typical plates

Samples	Solution pH after 1h	Solution pH after 2h	Solution pH after 3h
GO-based cathode with CMF	4.98	4.00	3.71
GO-based Cathode	4.89	4.01	3.71

The magnetic field parallel to electric field which were introduced during the copper electrodeposition for efficient help to enhance the mass transport process of Cu^{2+} then offered better chance of Cu^{2+} to contact with graphene-based cathode electrode and to efficiently deposit on the cathode surface. As the efficiency of the electrochemical process significantly depended on the relationship between the electron transfer at the cathode electrode surface and particles mass transfer of the substrate therefore impose of 23 G of CMF is seen to significantly improve the mass transform to improve the effectiveness of electrodeposition of $Cu^{2\ +}$ and water purification.

The magnetic field was directed perpendicularly to the electric field (E) and parallel to the surface of the cathode. This configuration was designed to generate a Lorentz force, which is essential for the magnetohydrodynamic (MHD) assisted deposition process. The Lorentz force acts on the charged copper ions, influencing their movement within the electric field and enhancing their deposition efficiency on the cathode surface. This innovative approach leverages the synergistic effects of electric and magnetic fields to improve the performance of heavy metal removal from aqueous solutions.

Moreover, the interaction between GO and Cu^{2+} happened in the presence of oxygen sites because the skeletal carbon less affinity for metal ions on the contrary oxygen atoms. As well as the presence of oxygen this may be one of the reasons to increase the electrochemical deposition [39]. The sp^2 Hybridization, electronic configuration wonderful, extraordinary electron transfer feature, so-called ballistic conductivity, and the number and location of jobs oxygen from Graphene help to enhance and accelerate the process of electron transport through electrochemical treatment [40]. GO has ability to removal Cu^{2+} by sufficient quantity of oxygen function groups (–COOH or –OH) on the surface, adsorption of metal ions GO is primarily surface complex, ion exchange, and due to the electrostatic attraction [41, 42]. The copper oxide CuO, Cu_2O and CU_4O_3 were formed by the following electrochemical reaction on cathode surface as stated in “Zulfiqar’s study” shown in the Eqs. (7)-(9) [43].

$$2Cu^{2+} + 2e^{-} + 2OH \rightarrow Cu_2O + H_2O \quad (7)$$

$$Cu^{2+} + 2OH \rightarrow Cu(OH)_2 \quad (8)$$

$$Cu(OH)_2 \rightarrow CuO + H_2O \quad (9)$$

The Cu^{2+} can be bound to GO was deposited on cathode as shown in the Eqs. (4)-(6). This reaction mechanism is affected by the equilibrium pH value.

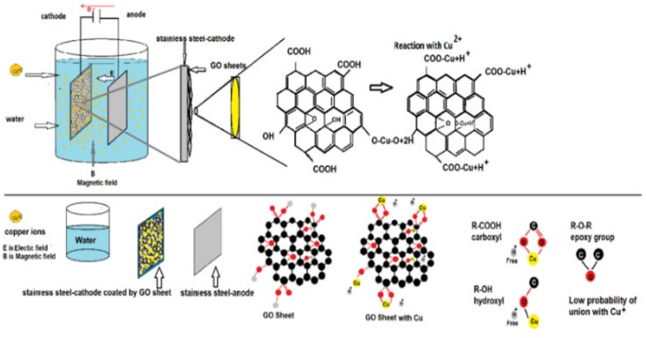


Figure 14. The schematic diagram shows the mechanism of the electrodeposit system for treatment by using GO and CMF and show chemical bonds between GO sheet and Cu^{2+}

In this study provide compelling evidence for the effectiveness of graphene oxide GO-based electrode with CMF assisted electrodeposition system in the removal of heavy metals from water via electrodeposition system. The proposed mechanism, which involves the electrostatic attraction between the negatively charged GO sheets and positively charged heavy metal ions.

The successful application of GO in heavy metal removal has far-reaching implications for the field of water treatment. As industrial effluents and environmental pollution continue to be a global concern, the development of efficient and eco-friendly treatment technologies is imperative. GO-based electrode with CMF assisted electrodeposition, with their high surface area and tunable surface chemistry, present a promising avenue for the remediation of contaminated water bodies. Furthermore, the integration of GO-coated electrode with electrodeposition system opens up possibilities for the selective removal and recovery of heavy metals, which could lead to the development of sustainable and resource-efficient water treatment systems.

Despite the promising results, several challenges must be addressed to translate these findings into practical applications. The stability of GO-coated electrode in aqueous solutions under varying pH and ionic strength conditions is a critical factor that could affect its performance in large-scale applications. Additionally, the potential release of GO nanosheets into the environment and their ecotoxicological impact necessitate further investigation to ensure the safety and sustainability of GO-based water treatment technologies.

To propel the field forward and address current limitations, future research should be directed toward several key areas. Firstly, efforts should be made to enhance the stability and selectivity of GO-based electrode, potentially through chemical modification or the synthesis of composites with other functional materials. Secondly, it is crucial to investigate the influence of various operational parameters on the removal efficiency and energy requirements of the electrochemical process to optimize performance. Furthermore, comprehensive environmental impact assessments must be conducted to evaluate the fate and potential effects of GO nanosheets in the environment, ensuring the safety and sustainability of GO-based water treatment technologies. Lastly, strategies for the regeneration and reuse of GO-based electrodes should be explored to minimize costs and waste, contributing to the economic viability and eco-friendliness of the technology.

4. CONCLUSIONS

In conclusion, it was clear influence of GO in raising the efficiency of the electrodeposit system to remove copper ions from water. In addition, it was clear through pictures the effects of magnetic fields on the morphology of the electrodeposited. Also, the external magnetic field affects the type of chemical bonding of the copper ions as shown Cu_4O_3 as well as the chemical bonds of carbon. GO was a catalyst to increase the efficiency of the electrochemical cell and the reason is to increase the surface area of the cathode and Contain quantity of oxygen function groups (–COOH or –OH) on the surface, which increased the uptake of ions between the sheets and electrodeposit process. This is due to the GO has possibility of involve van der Waals interaction and π–π stacking. These tests are considered a new branch of research in the use of GO cheap as well as the magnetic field in the electrochemical water treatment system.

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