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# Reducing Copper (II) Ions from Aqueous Solutions Using Ficus-Activated Carbon

Muhammad Muammar Abu Jamra, Kaled Ali Abed [*], and Saleh Al-Hamali Al-Nakua

Department of Chemical Engineering, Faculty of Engineering, Alasmarya Islamic University, Zliten, Libya.
*البريد الإلكتروني: k.abed@asmarya.edu.ly

# تقليل أيونات النحاس (II) من المحاليل المائية باستخدام الفحم النشط من أغصان شجرة التين

محمد معمر أبوجمرة، خالد علي اعبيد*، و صالح الهمالي الناكوع

قسم الهندسة الكيميائية، كلية الهندسة، الجامعة الأسمرية الإسلامية، زليتن، ليبيا

**Abstract**

Heavy metals are inherent natural elements in the earth's crust and can be byproducts of industrial activities such as petrochemicals and other manufacturing processes. In this study, the adsorption of heavy metal ions Cu(II) from wastewater using Ficus Activated Carbon (FAC) and the relationship between different adsorption coefficients in the removal of heavy metal ions Cu(II) was examined. The analysis was done by using a spectrophotometer device (ONDA V-10 PLUS). The optimum conditions were a contacting time of 100 minutes at 200 rpm, with 0.4 g of FAC per 35 ml of solution, a particle size of 0.2mm, pH =6, and a temperature of 25 °C. The adsorption capacity for heavy metal ions increased with increasing temperature, pH, contact time, and concentration of heavy metal ions, but decreased with increasing particle size. The adsorption processes are therefore spontaneous thermal desorption processes, and the results demonstrated a good agreement with pseudo-second-order kinetics. The adsorbent prepared in the laboratory (FAC) was placed in a high-temperature 200 °C oven and then activated with hydrogen peroxide acid ($H_2O_2$), thus having higher removal rates. In addition, 90% of the heavy metal ions were significantly removed and made the solution the permitted values. The results show that FAC can be used as a green for the adsorption of heavy metals from water.

***Keywords:*** *Adsorption, Water, Copper ions, Activated Carbon, Pollution.*

## الملخص

في هذه الدراسة، تمت دراسة امتزاز أيونات النحاس الثقيلة Cu(II) من الماء بواسطة والكربون المنشط من أحد أنواع أشجار التين والمستخدم في تزين الحدائق العامة. تم تحضير المادة المازة في المعمل وهي (FAC) وضعت في فرن عند درجات حرارة عالية 200 $^{o}$م ومن ثم نشطت بحمض ببروكسيد الهيدروجين ($H_2O_2$). في هذا البحث تمت دراسة العلاقة بين معاملات الامتزاز المختلفة في إزالة أيونات المعدن الثقيل Cu(II). وقد استخدم جهاز الطيف المرئي ONDA V-10 PLUS في تحليل العينات. وقد بينت النتائج أنه زادت قدرة المادة المازة في امتزاز لأيونات المعادن الثقيلة مع زيادة درجة الحرارة، وقيمة الرقم الهيدروجيني، وزمن التلامس، وبينما كانت نسبة الزيادة في انتزاع الملوثات بسيطة مع زيادة كمية المادة الممتزة، وتركيز أيونات المعادن الثقيلة، ولكنها تناسبت عكسيا مع زيادة حجم الجسيمات الممتزة. تم امتصاص أيونات المعدن الثقيل بشكل ملحوظ في الظروف الحمضية في تجارب الامتزاز. كما أظهرت النتائج توافقاً جيداً مع حركيات الدرجة الثانية الظاهرة وعمليات الامتزاز هي عمليات امتصاص حرارية تلقائية. من خلال النتائج يمكننا القول إن الكربون المنشط من هذه الأغصان لديه القدرة بنسبة أعلى من 90% لإزالة أيونات Cu(II) من المحاليل المائية عند الظروف المثلى وهي زمن تلامس 100دقيقة وعدد دورات 200، و0.4 جم لكل 35 مل من المحلول وقطر الجزيئات 0.2 مم عند درجة حرارة 25 درجة مئوية و pH 6. توضح النتائج أنه يمكن استخدام FAC كمادة مازة خضراء لانتزاع أيونات النحاس الثنائية من المياه الملوثة.

**الكلمات الدالة:** الامتزاز، الكربون المنشط، أيونات النحاس، التلوث، المياه.

## 1. Introduction

Water is absolutely essential for the existence of life on the planet. Not only does it have a crucial role in the sustenance of all living organisms, but it is also the lifeblood that nourishes and supports our delicate ecosystems. Without this precious resource, the very essence of life would simply vanish into oblivion. Furthermore, water serves as an indispensable asset for essential sectors such as agriculture, providing the foundation for bountiful harvests and nourishing our crops. Additionally, it is a vital component for various industries, acting as a catalyst for growth and innovation. (Adnan et al., 2024; and Charlier et al., 2024).

The industrial revolution has led to a growing population and increased pollution of rivers, lakes, oceans, and groundwater. As a result, many of these bodies of water can no longer purify themselves, which is a concern for countries worldwide (Zamora-Ledezma et al., 2021). Wastewater refers to liquid waste or water that has been negatively impacted by human activities. This can include effluents released from residential, commercial, industrial, and agricultural areas, which may contain various pollutants at varying levels of concentration. Industrial wastewater refers to the release of any and all effluents from industrial operations into the sewage system (Çelebi et al., 2020; and Singh et al., 2023).

Water is utilized in the industrial sector as it is incorporated into various products. This includes its use in cooling systems, where it is essential for dissipating the heat produced by internal processes or equipment (Singh et al., 2023). Water is widely recognized as a vital and essential resource for the development and extraction of coal, natural gas, oil, and uranium. It is utilized in industrial settings as a solvent, encompassing a wide array of chemicals that can dissolve or dilute other substances. The discharge of untreated industrial wastewater has significant repercussions, impacting both the environment and human health. Untreated wastewater poses a threat to human health by enabling the spread of diseases such as cholera, malaria, liver disease, and Hepatitis C. Beyond its effects on human health, untreated wastewater also disrupts aquatic ecosystems by promoting the growth of algae and plants due to the presence of fertilizers and agricultural waste. This damages aquatic life, including fish populations, and fosters the proliferation of disease-carrying insects such as mosquitoes and snails (Aljfairi et al., 2019; Elgarahy et al., 2021; and Singh et al., 2023) .

The hazard posed by heavy metals comes from their capacity to accumulate in living organisms and become harmful when their concentrations exceed the rates at which they dissolve in the body. The liver plays a vital role in eliminating heavy metals and other toxins from the human body. It is important to note that only small percentages of these heavy metal concentrations have a harmful impact on human health and well-being (Jaishankar et al., 2014 and Sarma et al., 2015). Copper, designated as a transition element with an atomic number of 29 and an atomic weight of 63.55, exhibits a density of 8.9 g/cm$^3$ at 20°C. In aqueous solutions, copper (II) is characterized by its distinctive blue hue and can adopt oxidation states of +1 and +2. The element has a melting point of 1357 K and a boiling point of 2835 K, indicating its stability at high temperatures. Copper's malleable and ductile properties enable it to be shaped easily, making it vital for various applications, including electrical wiring, culinary utensils, plumbing, construction materials, electroplating alloys, and in the petroleum refining industry. Moreover, copper compounds play a significant role in agriculture, functioning as fungicides, insecticides, and fertilizers, thereby enhancing plant growth (Agarwal et al., 1990).

Adsorption is the capacity possessed by specific solids to extract particles from a liquid or gaseous state in which they are immersed. The particles subsequently transition to a solid state, enabling the solids to effectively remove unwanted materials from the liquid or gaseous state (Chakraborty et al., 2022). The interaction between gas or liquid and solid materials is influenced by both the physical structure (porosity) and chemical composition of the solid. This process involves the transfer of mass from the gas or liquid state to the surface of the solid material through various attraction forces. The substance that suffers from adsorption on the surface is called "Adsorbate" (Chakraborty et al., 2022; and Saleh et al., 2022).

The objective of this study was to assess the efficiency and practical applicability of locally sourced, low-cost adsorbents for the removal of copper ions from aqueous solutions. Specific objectives included the preparation of these adsorbent materials and the optimization of various factors affecting the adsorption process. These factors include the effect of contact time, initial copper (Cu) concentration, solution pH, adsorbent dosage, and temperature. Additionally, the study aimed to investigate and analyze the adsorption kinetic process.

## 2. Materials & Methods

### 2.1. Materials and Preparation

The Ficus-activated carbon was used as an absorbent material. Firstly, the twinges were collected from locally garden in Zliten Figure (1) Almontzah garden, then it washed with distilled water to get rid of any impurities, after that it dried at 110°C for 72 hrs. The FAC was then crushed in a mill and filtered using sieves of varying sizes (150 to 450 μm).

**Figure 1. Ficus Tree**

The standard solution of ($Cu^{+2}$) was prepared by dissolving precisely measured quantities of copper sulfate pentahydrate ($CuSO_4.5H_2O$) in distilled water. Hydrochloric acid HCl 0.1M and sodium hydroxide NaOH 0.1M were used to regulate the pH levels of the specimens. Throughout all experimental procedures, distilled water serves as the solvent. All chemicals utilized in this study were of analytical grade.

The standard solution of copper, with a concentration of 1000 ppm, was created by dissolving 3.935 g of Cu $SO_4.5H_2O$ in 1000 mL of distilled water and subsequently mixing it slowly. Furthermore, to achieve the desired concentration of 5,10, 20, and 30 ppm, a volume of 0.5, 1 ,2 , and 3 mL of the 1000 ppm standard solution was added to 4 flasks containing 100 mL of distilled water (Alshuiref et al., 2017).

The adsorption of heavy metals (copper sulfate) on FAC has been investigated using batch technology. A specified quantity of FAC adsorbent, such as 1 gram, was measured against 100 milliliters of copper solutions with concentrations of 5, 10, 20, and 30 ppm. After filtration with FILTER-LAB Cod paper PN1248110, the remaining concentrations of copper (II) were assessed using a spectrophotometer device (ONDA V-10 PLUS) at the designated wavelength of 466 nm as it shown in Figure (2). Then the calibration curve was obtained at a wavelength of 466 nm.

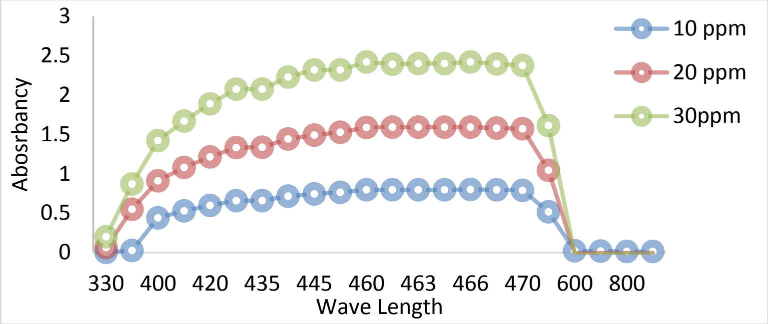

**Figure 2. Absorbency vs. wave length**

Figure (3) below shows the calibration curve. The effect of several factors such as pH, initial concentrations, temperature, induction rate, adsorbent dosage, and contact time on adsorption has been studied.

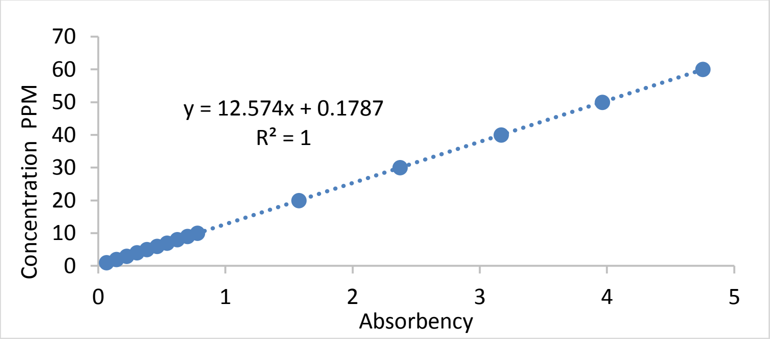

**Figure 3. The calibration curve**

The removed Cu(II) ions percentage and adsorption capacity were calculated using Eqns. (1 and 2);

$$\text{Re}\ \% = \frac{c_o - c_e}{c_o} * 100 \qquad \text{.....} \quad (1)$$

$$q = \left(\frac{c_o - c_e}{w}\right) * V \qquad \text{.....} \quad (2)$$

where q is the adsorption capacity (mg/g), V is the volume of copper ions solution, $C_e$ is the equilibrium concentrations of copper in solution (mg/L), $C_o$ is the initial concentrations of copper in solution (mg/L), and w is the weight of the adsorbent (g) (Aljfairi et al., 2019; and Alshuiref et al., 2017) .

## 3. Results & Discussion

### 3.1. Optimum conditions

The optimum conditions were selected on the basis of previous studies (Alshuiref et al., 2017). A contacting time of 100 mins. at 200 rpm, with 0.4 g of FAC per 35 mL of solution, a particle size of 0.2 mm, pH =6, and a temperature of 25 °C.

### 3.1.1. Effect of contact time variation:

The contact period, which can range from 30 to 400 mins., affects the removal and adsorption capability of Cu(II) ions. Investigations were conducted at certain time intervals of 30, 60, 100, 130, 190, 250, and 400 mins. in the optimum condition. The adsorbent's amount and particle size stayed constant at 0.4 g and 0.2 mm, respectively. Throughout the study, the pH level and temperature were maintained at 6 and 25 °C.

The data presented in Figure (4) shows that the percentage of Cu(II) removed was raised by increasing the contact time until reaching equilibrium. Equilibrium was observed after 100 minutes with 85% removal % of heavy ions of copper.

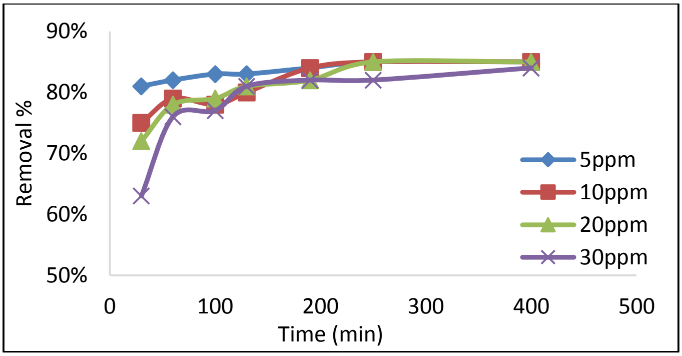

**Figure 4. Impact of changing contact time on Cu (II) removal percentage**

### 3.1.2. Effect of adsorbent dose variation:

The effect of adsorbent quantity on the adsorption of Cu(II) was investigated at the optimum condition. The mass of the adsorbents ranged from 0.2 to 1 g. The results presented in Figure (5) indicate that the percentage of Cu(II) removal slightly increases as the adsorbent dose rises. This improvement is attributed to the enhanced surface area of the adsorbent materials FAC. which provides more active sites for the adsorption of additional Cu(II) ions. Furthermore, the Figure (5) clearly shows that more than 90% of ions can be removed from the solution even at low concentrations (5 and 10 ppm) under the specified operating conditions.

In general, a dose of 0.4 g of FAC achieves a relatively high removal percentage. However, for synthetic solutions with higher concentrations, such as those found in tannery wastewater, a greater quantity of FAC is necessary to provide a larger surface area for effective adsorption. The findings indicate that the optimal adsorbent dose is 0.4 g.

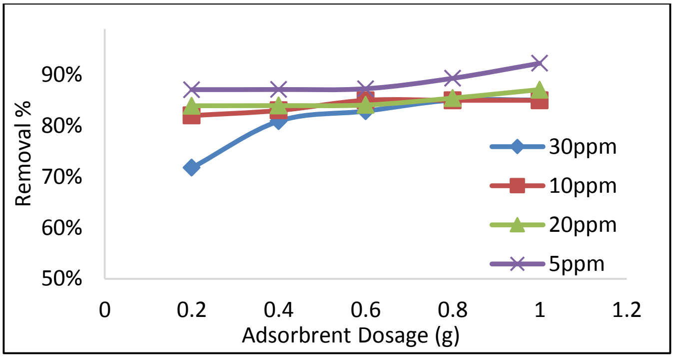

**Figure 5. Adsorbent dose variation's impact on Cu (II) removal percentage**

### 3.1.3. Effect of temperature:

The effect of temperature on the adsorption of Cu(II) from 35 mL solutions with a known concentrations of samples were investigated at the optimum conditions and a temperature of 8, 12, 15, 20, 25, 40, and 60 °C. The results presented in figure 6 indicate that the removal percentage increases very gradually as the temperature rises from 8 to 25°C.

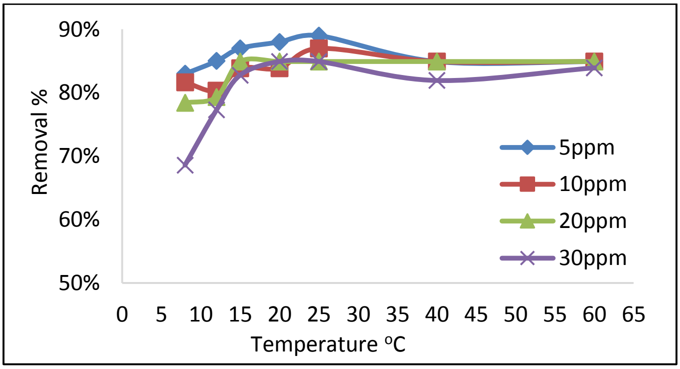

**Figure 6. Temperature variation's impact on the proportion of Cu (II) removed**

Adsorbate molecules move more quickly when the temperature of the solution rises because it increases the kinetic energy of the adsorbate particles. As a result, the time it takes for these particles to reach the adsorbent surface is shortened, which speeds up the removal of adsorbate. Above 25°C, however, temperature has no discernible effect on the percentage of adsorption removal.

### 3.1.4. Effect of pH:

The pH of the solution is regarded as one of the key factors influencing the adsorption process using FAC. Therefore, the effect of initial solution pH on the removal of copper ions from aqueous solutions was investigated. This study was conducted under the optimum conditions, while varying the solution pH from 2 to 9 (2, 3, 4, 5, 6, 7, 8, and 9).

As shown in Figure (7), increasing the pH from 2 to 7 results in a rise in the amount of copper adsorption. However, pH values above 7 do not significantly affect the removal percentage. The impact of pH on the adsorption process is evident from the fluctuation in adsorption quantities. The larger concentration of $H^+$ ions at lower starting pH, which compete with Cu (II) ions for accessible adsorption sites, is responsible for the improved removal efficiency. Conversely, as pH increases, the solution becomes more basic, leading to a decrease in copper ions available for adsorption and reduced competition with hydrogen ions.

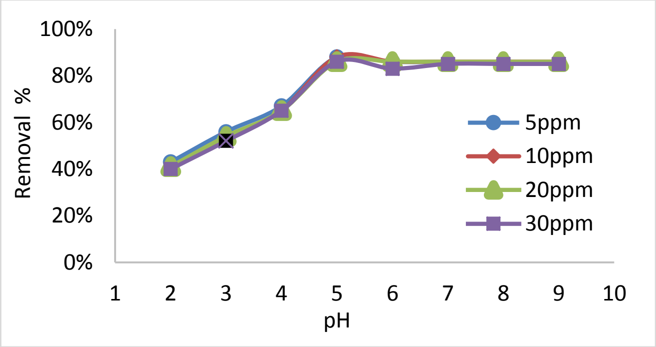

**Figure 7. Impact of pH change on Cu (II) removal %**

### 3.1.5. Effect of particle size:

The difference in the particle size is considered one of the main factors that affect the adsorption process using FAC. The effect of the difference in the size of the adsorbent of the initial solution on the removal of copper ions from the aqueous solution was studied. This study was conducted under optimum condition, with a particle size ranging from 0.5 to 2, which is as follows. (0.5, 1, 1.5, and 2). As shown in the Figure (8), increasing the particle size from (0.5 to 2.5 mm) leads to a decrease in the absorption of copper from the aqueous solution. That is, as the particle size increases, the absorption of copper decreases.

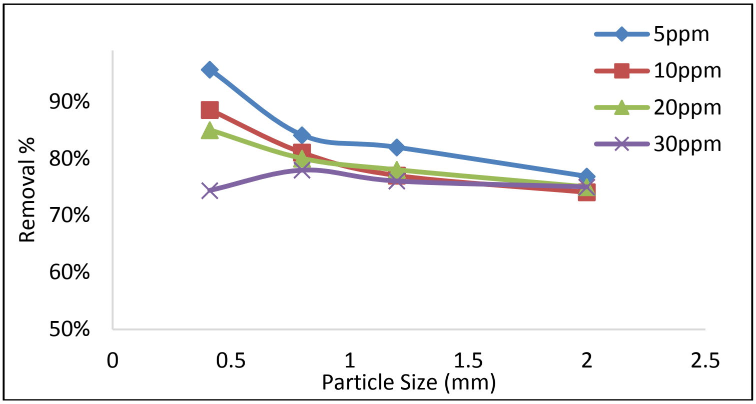

**Figure 8. Impact of fluctuating particle size on Cu (II) removal %**

## 3.2. Kinetics adsorption process

The investigation of kinetics provides insights into the mechanisms of adsorption reactions and the pathways involved. Kinetics describes the residence time of adsorbate molecules on the adsorbent surface, which helps estimate solute uptake. The adsorption process occurs in three steps, with the slowest step determining the overall kinetics of adsorption. These steps are: i) the movement of ions to the external surface of the adsorbent from the bulk solution, ii) the transport of pollutants through the liquid film that adheres to the adsorbent surface, and iii) the interaction of the adsorbate with the surface atoms of the adsorbent, resulting in chemisorption. Various adsorption systems are used to characterize the kinetics of the adsorption process, with the pseudo-first-order and pseudo-second-order models being the most commonly employed. (Purkait et al., 2023; Aljfairi et al., 2019; Alshuiref et al., 2017; and Ibrahim et al., 2016).

### 3.2.1. Pseudo first order:

The kinetics of adsorption were investigated for a known volume and concentration of Cu (II) solutions 35 mL and 20 ppm respectively, at the optimum condition. The obtained results are presented in Figure (9) for pseudo first order kinetic model by using Eqns. (3) and (4);

$$\frac{dq(t)}{dt} = K_1 \,(q_e - q_t) \qquad \text{.....} \quad (3)$$

$$\ln(q_e - q_t) = -K_1\, t + \ln(q_e) \qquad \text{.....} \quad (4)$$

where $K_1$ ($min^{-1}$) is the rate constant of the pseudo-first-order adsorption $q_t$(mg/g) denotes the amount of adsorption at time t (min) and $q_e$ (mg/g) is the amount of adsorption at equilibrium (Purkait et al., 2023; Aljfairi et al., 2019; Alshuiref et al., 2017; and Ibrahim et al., 2016).

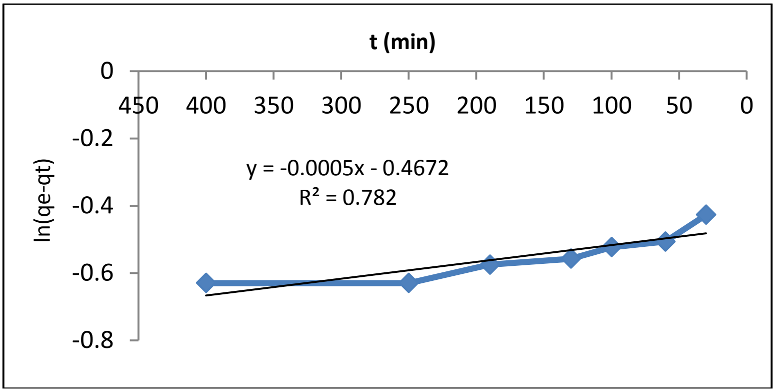

**Figure 9. Cu (II) adsorption pseudo first order kinetics diagram**

### 3.2.2. Pseudo second order:

Pseudo-second-order kinetics assumes that the rate-determining step is a chemical reaction involving valence forces related to the exchange of ions. The most commonly used form of the pseudo-second-order equation can be expressed as follows:

$$\frac{t}{qt} = \frac{1}{K_2 * qe^2} + \frac{t}{qe} \quad \text{.....} \quad (5)$$

where $K_2$ (g/(mg min)) is the rate constant. $K_2$ and $q_e$ can be obtained from the intercept and slope by plotting Eqn. (6) (Aljfairi et al., 2019; and Ibrahim et al., 2016).

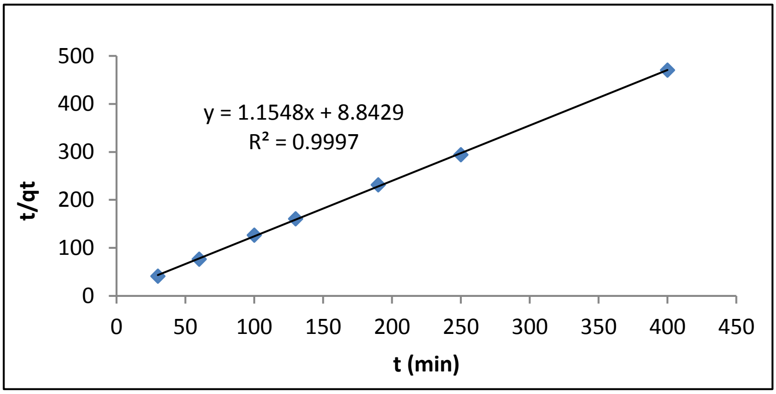

**Figure 10. Pseudo second order adsorption kinetics graph for Cu (II)**

The reported $R^2$ values from Figures (9 and 10) indicated that the experimental results show a better fit to pseudo second order model. Hence, the copper adsorption follows pseudo second order.

### 3.3. Gibbs free energy

It is a thermodynamic property that combines the entropy and enthalpy of a system only to determine whether the change is spontaneous or not. The change in Gibbs free energy can be found by Eqn. (7) as mentioned by Alshuiref et al. (2020).

$$\Delta G = -RT\ln K_L \qquad \text{.....} \quad (7)$$

Based on the calculation presented in Table (1) below the magnitude of ΔG for the adsorption of Cu (II) by FAC seems to be spontaneous.

**Table 1. Gibes energy values**

| Temp (K) | $\Delta G°$ |
|---|---|
| 285.15 | -1786.67 |
| 288.15 | -1806.93 |
| 293.15 | -1841.36 |
| 298.15 | -1874.38 |

## 4. Conclusion

In this work, the use of low-cost adsorbents in wastewater treatment is addressed. For this purpose, a Ficus Activated Carbon (FAC) was examined. It was used successfully as adsorption agent to remove copper (II) from aqueous solutions. Adsorption was affected by various factors such as temperature, initial concentration, different amounts of activated carbon FAC, adsorbent dose, contact time, pH, and the adsorption kinetics were studied. Based on the results of this study, the following conclusions can be drawn:

- The contact time greatly affects the removal of copper by adsorption, as the removal was rapid at first and then decreased until the equilibrium state began to reach 100 minutes.
- The efficiency of adsorption removal is influenced by the quantity of adsorbent added to the solution. As the amount of adsorbent increases, the removal efficiency also rises. The findings indicate that the optimal dosage of the sorbent is 0.4 g.
- The efficiency of adsorption removal is gradually influenced by temperature. As the temperature rises, the removal rate also increases, with the optimal temperature identified as 25°C.
- pH plays an important role in removing copper from wastewater. The difference in the amount of adsorption indicated the effect of pH on the absorption process, as increasing the pH from 2 to 9 leads to an increase in the copper removal rate. It was found that the optimum pH of the solution for copper(II) removal is between 6 and 7.

- Adsorption kinetic investigations showed that the copper adsorption process adhered to a pseudo-second-order kinetic model. Also, the adsorption processes are spontaneous thermal desorption processes.

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