

# REMOVAL OF COPPER IONS FROM AQUEOUS SOLUTION USING PALM SHELL CHARCOAL ACTIVATED BY NAOH

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**ABSTRACT:** Charcoal nanoparticles obtained through pyrolysis of palm kernel and activated by NaOH were prepared for adsorption of copper ions ( $\text{Cu}^{2+}$ ) from aqueous solutions. The effect of contact time (30–150 min) and initial adsorbate concentration (30–150 ppm) on adsorption of  $\text{Cu}^{2+}$  ions was investigated using batch adsorption experiments. Adsorption efficiency, suitability of Langmuir and Freundlich adsorption models, and kinetics of adsorption were studied. The results show that efficiency of  $\text{Cu}^{2+}$  ion removal decreased with increasing initial adsorbate concentration. Higher removal efficiencies (99%) were achieved at initial adsorbate concentration of 30 ppm and contact time of 90 min. The adsorption process was well described by the Freundlich isotherm model with an exponent (n) and equilibrium constant ( $K_f$ ) of  $9.59 \times 10^{-5}$  mg/g and 0.182, respectively.

*Keywords:* Charcoal nanoparticles, Adsorption, Freundlich isotherm, Copper ions

## 1. INTRODUCTION

Copper is one of the most toxic metals and a potential threat to human health and the environment even at very low concentrations. However, it is an essential trace element due to its roles in cytochrome c oxidase and respiratory enzymes [1]. The US Environmental Protection Agency (EPA) has set a maximum permissible copper concentration of 1.3 mg/L in drinking water [2]. At higher concentrations, copper intoxication can cause hypotension, pancreas, jaundice, melena, kidney damage, and even coma [3], [4]. Copper often occurs as a by-product in several sectors, including textiles, electroplating, paints and pigments, galvanizing, fertilizer production, the paper industry, and several areas of the chemicals sector [5], [6]. Industrial wastewater containing copper must be processed thoroughly and appropriately since it has highly adverse effects on human health and ecological systems. Liquid waste containing copper can be processed by membrane separation, electrodialysis, ion exchange, reverse osmosis, electrochemistry, and chemical precipitation [7]–[12]. However, these methods have drawbacks, including the production of toxic sludge from chemical precipitation, and difficult recovery of metal ions from the formed sludge. Furthermore, some processes are extremely costly, particularly for processing low concentrations of metal.

The adsorption process provides a good alternative, since the design and operation of the process is more economical, simple, and flexible; and adsorbent regeneration is easier [13], [14], particularly when being used to process waste at large volume and low concentration (<100 mg/L)

[15]–[18]. Consequently, there has been much research into alternative materials for affordable adsorbent, such as bagasse and fly ash [19], coir pith carbon [20], sugar beet pulp [21], tea waste [22], chitin and chitosan [23]–[26], grapefruit peel [27], and algal biomass [28]. Another affordable candidate adsorbent is charcoal derived from the pyrolysis residue of oil palm shell. This study examines the efficiency of using this material, activated with NaOH, for use in absorbing  $\text{Cu}^{2+}$ .

## 2. EXPERIMENT

### 2.1 Adsorbent Preparation

The charcoal tested for use as an adsorbent was obtained from the pyrolysis of oil palm shell at 380°C. Details of the pyrolysis procedure were explained in previous reports [29]–[31]. Prior to use, the charcoal was first crushed to particles of nanometre scale by processing in a ball mill for 40 hours. The carbon particles were then chemically activated by soaking in NaOH 0.1 N solution for 1 day, then filtered and washed with distilled water until the pH was neutral ( $\pm 7$ ). The material was then dried in an oven at 105°C until reaching a constant weight. The structure of the activated carbon nanoparticles was characterized by a Fourier-transform infrared (FTIR; Prestige-21, Shimadzu, Japan) and scanning electron microscope (SEM; JSM-6510 LA, JEOL, Ltd., Shimadzu, Japan).

### 2.2 Adsorption Test

The activated carbon nanoparticles were then used to absorb  $\text{Cu}^{2+}$  metal ions.  $\text{Cu}^{2+}$  was obtained

from  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution at several different concentrations: 30, 60, 90, 120, and 150 mg/L. Then 100 ml of a  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  solution containing  $\text{Cu}^{2+}$  was placed in an Erlenmeyer flask with 1 g of adsorbent, then stirred at 100 rpm at room temperature with a variation of contact time (30, 60, 90, 120, 150 minutes). The filtrate was then separated from the adsorbent residue by centrifuging. After adsorption, the  $\text{Cu}^{2+}$  concentration was analyzed with an atomic absorption spectrophotometer (AA-7000, Shimadzu, Japan).

### 3. RESULTS AND DISCUSSION

#### 3.1 Study of Adsorption Process

##### 3.1.1 Effect of contact time on $\text{Cu}^{2+}$ removal efficiency

The relationship between contact time and removal of  $\text{Cu}^{2+}$  ions is shown in Figure 1.

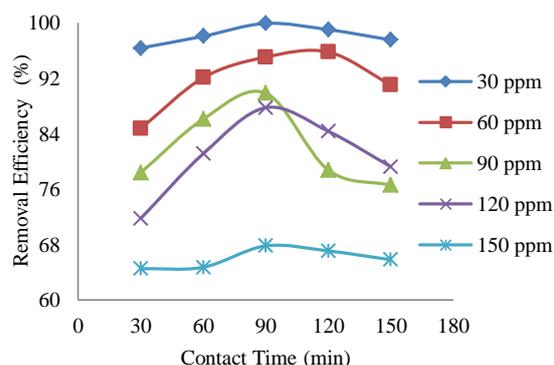


Fig.1 Effect of contact time on  $\text{Cu}^{2+}$  removal efficiency

Figure 1 shows that  $\text{Cu}^{2+}$  adsorption rate increased until approximately 90 mins, then subsequently declined. The same tendency is observed for all initial adsorbate concentrations. The results show increasing removal of  $\text{Cu}^{2+}$  from 30–90 minutes.

The results show that the optimum contact time of 90 min can achieve 99%  $\text{Cu}^{2+}$  removal. After 90 minutes, removal rates showed a significant decline. The adsorbent reached saturation at 150 minutes. Subsequently, the  $\text{Cu}^{2+}$  adsorption capability continued to decline, likely due to the scarcity of unoccupied adsorption sites since most sites were already bound to Cu molecules. The rate at which adsorbate binds to the adsorbent tends to decline over time as the active centers on the adsorbent surface become saturated [32], [33]. Munandar et al.[34] reported that adsorbent capability increased at the beginning of the time interval and decreased at the next time interval; the

optimum contact time was obtained at 4<sup>th</sup> hour and it decreased at next hour until saturation at 8 hours of treatment.

##### 3.1.2 Effect of initial $\text{Cu}^{2+}$ concentration on removal efficiency

The relationship between initial Cu concentration and removal of  $\text{Cu}^{2+}$  ions is shown in Figure 2.

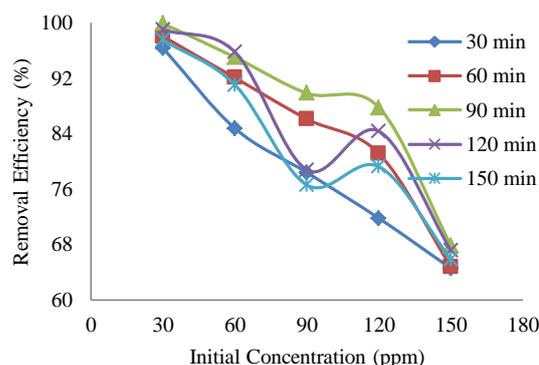


Fig. 2 The effect of initial  $\text{Cu}^{2+}$  concentration on removal efficiency

Figure 2 shows that  $\text{Cu}^{2+}$  removal efficiency differs for each time interval and initial concentration. The highest (99.9%) and lowest (64.5%) removal efficiencies were obtained for Cu solutions of 30 and 150 ppm, respectively. The higher the concentration of  $\text{Cu}^{2+}$  solution the lower the removal percentage, since the dose of adsorbent remains constant while the amount to absorb increases, so the removal of  $\text{Cu}^{2+}$  metal ion decreases [33]. Similar results were also obtained by Munandar et al. [34], showing that the higher the concentration, the lower the removal percentage. Their findings showed that at a concentration of 47 mg/l, removal efficiency was 94%, which decreased to 46% at an initial concentration of 482 mg/L. Another study found that for adsorption process, the highest adsorption efficiency occurred within a concentration range of <60 mg/L [35].

##### 3.1.3 Effect of Contact Time on $\text{Cu}^{2+}$ Adsorption Capacity

Figure 3 shows the relationship between contact time and capacity for  $\text{Cu}^{2+}$  adsorption. Figure 3 shows that, at a contact time of 90 minutes, the achieved adsorption capacities are 3.10, 5.6, 8.6, 10.1, and 9.9 mg/g for initial concentrations of 30, 60, 90, 120, and 150 ppm, respectively. However, the highest adsorption capacity is obtained at an initial concentration of 120 ppm. The data show that optimum adsorption capacity occurs at 90 min for every initial concentration of the  $\text{Cu}^{2+}$  solution. At 30–90 min contact time, the amount of  $\text{Cu}^{2+}$  adsorbed

increases, since the adsorbent has a certain timeframe for maximum absorption efficiency. After 90 min, the amount of  $\text{Cu}^{2+}$  adsorbed decreases, since the bonds between clusters in the adsorbent and the metal adsorbate keep weakening, and the adsorbate is finally released back into the solution [36]. The results show that every 1 g dose of adsorbent achieves maximum  $\text{Cu}^{2+}$  adsorption at initial adsorbate concentration of 120 ppm. The adsorption of  $\text{Cu}^{2+}$  decreases at an initial concentration of 150 ppm, as the constant dose of adsorbent, is unable to hold the increased weight of the adsorbate. Zhan et al.[37] reported similar results, in which at an initial concentration of 0.25–8 mmol/L, adsorption capacity increased at a concentration of 0.25–5 mmol/L and subsequently decreased at a concentration of 6–8 mmol/L.

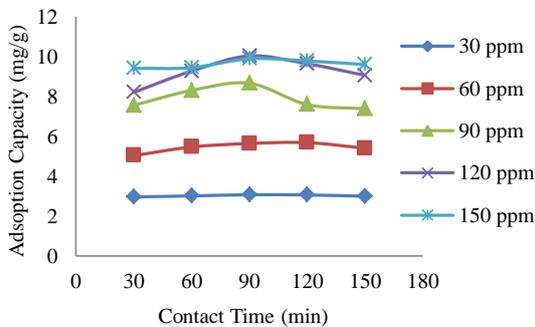
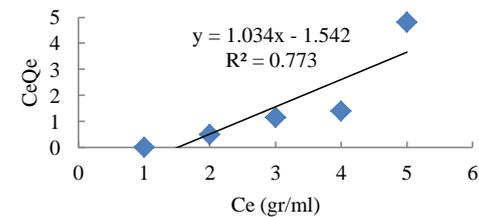


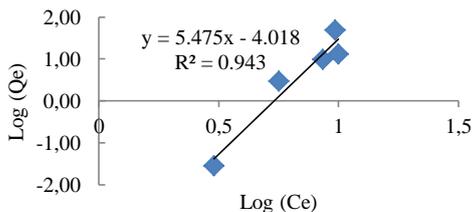
Fig. 3 Effect of contact time on the capacity for  $\text{Cu}^{2+}$  adsorption

### 3.2 Adsorption Isotherms

The Langmuir and Freundlich models were employed in order to determine the adsorption isotherms.



(a)



(b)

Fig. 4 Langmuir (a) and Freundlich (b) isotherms for  $\text{Cu}^{2+}$  adsorption

The Langmuir and Freundlich equations are shown in Figure 4 a–b. The Langmuir isotherm represents the relationship between  $C_e$  and  $C_e/Q_e$ , whereas the Freundlich isotherm is obtained through the relationship between  $\log C_e$  and  $\log Q_e$ .

Figure 4 shows that  $\text{Cu}^{2+}$  adsorption by the activated carbon nanoparticles tends to follow the Freundlich isotherm, with higher coefficient of determination ( $R^2=0.943$ ) than in the Langmuir model ( $R^2=0.773$ ). Table 1 shows the values of constants and parameters from the Langmuir and Freundlich models for  $\text{Cu}^{2+}$  adsorption.

Table 1 shows that, for Langmuir model, maximum adsorption capacity ( $q_m$ ) of 0.96 L/mg with Langmuir constant ( $k_l$ ) -0.67 mg/g was obtained. Meanwhile, in the Freundlich model, empirical constant ( $K_f$ ),  $9.59 \times 10^{-5}$  mg/g and exponent ( $n$ ) of 0.182 were obtained.

Table 1 Constants and parameters values of Langmuir and Freundlich models for  $\text{Cu}^{2+}$  adsorption

Langmuir			Freundlich		
$R^2$	$q_m$ (L/mg)	$k_l$ (mg/g)	$R^2$	$n$	$K_f$ (mg/g)
0.773	0.96	-0.67	0.943	0.182	$9.59 \times 10^{-5}$

### 4. CONCLUSION

Activated carbon nanoparticles obtained through pyrolysis of oil palm shell provide a highly effective adsorbent for removing low concentrations (30 ppm) of  $\text{Cu}^{2+}$  from aqueous solution. Following activation of the nanoparticles by NaOH and mixing at 100 rpm,  $\text{Cu}^{2+}$  adsorption efficiencies at 90 min were 99.9, 95.04, 89.83, 87.75, and 67.82 % for initial  $\text{Cu}^{2+}$  concentrations of 30, 60, 90, 120, and 150 ppm, respectively. The adsorption trend follows the Freundlich isothermal model, with a higher value of the coefficient of determination ( $R^2=0.997$ ) than the Langmuir model.

### 5. ACKNOWLEDGMENTS

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