

# Removal of copper (II) ions from aqueous solution using acid- and alkali-treated carbonized mangosteen peel as adsorbent

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**Abstract.** The level of toxic heavy metals from the industrial effluents, seeping into neighbouring waterbodies and agricultural land, must be reduced. Biosorption is a highly effective option. Fruit peels, a typical agricultural waste, have been widely employed as low-cost biosorbents. The purpose of this study is to investigate the removal of copper (II) ions from aqueous solution using carbonized mangosteen peel. The aim of this research is to prepare the biosorbent, activate it with H<sub>2</sub>SO<sub>4</sub> or KOH, carbonize the pulverized mangosteen peel and to optimize parameters such as adsorbent dosage, agitation speed, initial metal-ion concentration, pH and contact time on percentage removal of Cu (II) ions. The adsorption isotherms have been studied using Langmuir and Freundlich isotherms, and the internal mass transfer coefficient has been investigated. Mangosteen peel was soaked in 5 mol% H<sub>2</sub>SO<sub>4</sub> or 5 mol% KOH for one day, dried, and carbonized at 300°C for 30 min. Optimal conditions of 300 rpm agitation, initial metal-ion concentration 150 mg/L, 100 mg adsorbent dosage, pH 2 for H<sub>2</sub>SO<sub>4</sub> treatment, 60 min contact time for maximum copper (II) ion uptake. The Freundlich isotherm model is found to fit the experimental data satisfactorily, with an  $R^2$  of 0.8273. The correlation coefficient of 0.9993 for pseudo-second-order model gives the best fit for kinetic data studied with an internal mass transfer coefficient of 0.9976.

## 1 Introduction

Heavy metals are toxic and hazardous contaminants which accumulate in cells that are alive, resulting in a range of disorders and diseases. Heavy metals in industrial effluents have produced ecological issues due to their toxic properties even at low quantities. Arsenic (As), copper (Cu), chromium (Cr) and lead (Pb) are among the most toxic metal ions to humans and aquatic systems [1]. Because all heavy metals cannot biodegrade, contaminants must be removed or reduced to a specified level before being discharged into bodies of water in order to fulfil environmental quality standards. Copper is used in a variety of industries, including plumbing, agriculture, electricity generated gadgets, and construction components. This may be present in nourishments, drink and medicines. Copper is often found in stormwater runoff and has been linked to damage to aquatic ecosystems, particularly fish [2]. Copper is a

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persistent, being absorbent, hazardous substance that doesn't degrade fast in the environment and is challenging to metabolise. Consumption, absorption, and accumulation in the food chain, either ecological or human may threaten the ecology or human health [3]. A affordable method for absorbing hazardous heavy metals using biosorption method. An effective biosorbent should be inexpensive, abundant, highly efficient in attracting and retaining substances, mechanically and chemically stable, and capable of being reused [4].

Mangosteen is a prominent tropical fruit in Asia. This fruit may be processed into commercial items for a number of applications, including cosmetic and therapeutic treatments, or eaten fresh. Several countries, including Taiwan, Thailand, Malaysia, Indonesia, and Sri Lanka, have a lengthy past of using this fruit in customary medical treatments [5]. Only 55 to 75 g, or around 25-30% by content of a mangosteen fruit, is palatable, while the rest 65-70% will be fruitless and commonly abandoned in waste sites [6]. Public health could result from these challenges while atmospheric production of greenhouse gasses, as well as which are harmful to the durability of the natural world and the general health of people [7].

## **2 Research methodology**

The goal of this study is to optimize the reduction of copper (II) ions utilizing activated carbon derived from mangosteen peels. It deals with solution preparation, using acid- or alkali- treated adsorbent, and finally, experiments to maximize adsorption.

### **2.1 Materials and methods**

Mangosteen peel that was collected from the nearest wet market, copper nitrate, potassium hydroxide from ChemSoln, sulphuric acid from ChemSoln and distilled water.

### **2.2 Preparation of adsorbent**

In this study, the collected mangosteen peels were washed and sun-dried for two weeks. The peels were then divided into two groups and activated using either  $H_2SO_4$  or KOH solutions. Next, they underwent a low-temperature heating process (2 hours at  $120^\circ C$ ) followed by further heating in a furnace (30 minutes at  $300^\circ C$ ) for carbonization. The resulting material was sieved to a specific size range (0.45-1.18 mm) for further experiments on copper adsorption.

### **2.3 Preparation of adsorbate**

Anhydrous copper nitrate was dissolved in one litre of filtered water to create a stock solution of copper (1000 mg/L). To achieve the required concentration, the stock solution was diluted with roughly 100 mL of pure water. To obtain KOH-treated adsorbent, the pH of the stock solution was raised to 10 using 0.1M KOH solution. Similarly, 0.1M  $H_2SO_4$  is used to raise the pH of the stock solution to 4 in order to produce  $H_2SO_4$ -treated adsorbent.

### **2.4 Experimental procedure**

#### **2.4.1 Effect of adsorbent dosage**

In this experiment, the effect of adsorbent dosage on the uptake of Cu(II) ions by activated

mangosteen peels was investigated under controlled conditions. Three different dosages (150 mg, 100 mg, and 50 mg) of the adsorbent were tested. The experimental parameters including agitation speed (200 rpm), metal ion concentration (150 mg/L), contact time (60 minutes), and pH conditions (pH 2 for H<sub>2</sub>SO<sub>4</sub>-activated peels and pH 8 for KOH-activated peels) were kept constant throughout the study.

Each dosage of activated mangosteen peels was added to a mixture containing 47.24 ml of Cu(II) stock solution diluted with 52.76 ml of distilled water. The mixtures were agitated for 60 minutes to ensure equilibrium. After agitation, samples were analysed using a UV-Vis Spectrophotometer to quantify the amount of Cu(II) ions adsorbed by the mangosteen peels at each dosage level.

This experimental design allowed for a systematic evaluation of how varying the amount of adsorbent affects its efficiency in removing Cu(II) ions from solution, providing valuable insights into the optimal conditions for utilizing mangosteen peels as a potential adsorbent for heavy metal ions. The same steps were followed for each parameter using the one-factor-at-a-time method.

### 2.4.2 Efficiency of Copper (II) ions

This formula (Equation 1) compares the initial concentration of copper ions in the solution with the concentration remaining after the removal process. It quantifies how effectively the treatment or purification method has reduced the copper ion content in the solution. This measurement is crucial in evaluating the effectiveness of various methods employed to purify or remediate copper-contaminated solutions, providing quantitative feedback on the success of the treatment in reducing copper ion levels.

$$\text{Removal Efficiency (\%)} = \frac{\text{Initial Concentration} - \text{Final Concentration}}{\text{Initial Concentration}} \times 100 \quad (1)$$

## 3 Results and discussion

### 3.1 Batch adsorption study

One factor at a time strategy was used in the trials to investigate each parameter that affected the percentage elimination of copper (II) ions utilizing activated carbon generated by mangosteen peels that had been treated with KOH or H<sub>2</sub>SO<sub>4</sub>.

#### 3.1.1 Effect of adsorbent dosage

Increasing the amount of adsorbent from 10 mg to 100 mg enhanced the removal of copper for both peels treated with H<sub>2</sub>SO<sub>4</sub> and KOH, as illustrated in Figure 1(a). This trend continued up to 100 mg, identified as the optimal dosage for both types. Acid-treated peels were consistently more effective due to their improved pore structure for better copper ion penetration and presence of acidic groups (stronger attraction to copper ions) [8].

#### 3.1.2 Effect of agitation speed

Agitation speed significantly impacted copper removal (Figure 1(b)). For both H<sub>2</sub>SO<sub>4</sub>- or KOH-treated peels, increasing speed from 100 rpm to 300 rpm boosted removal due to better diffusion of copper ions. However, 300 rpm was the optimal speed as higher speeds caused detachment of weakly bound copper ions. This resulted in maximum removal efficiency of

99.71% for  $H_2SO_4$ -treated peels and 92.29% for KOH-treated peels.



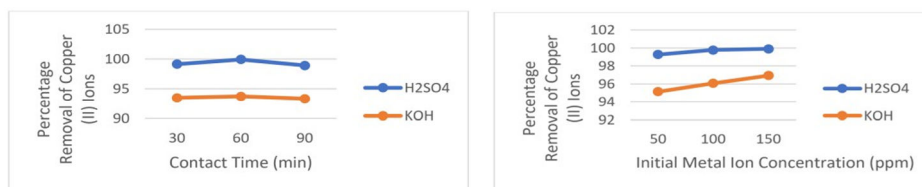
**Fig. 1.** (a) The effect of adsorbent dosage on %removal of Cu (II) ions and (b) shows the effect of agitation speed on Cu (II) ions.

### 3.1.3 Effect of contact time

Increasing contact time up to 60 minutes significantly improved copper removal for both peel types (Figure 2(a)).  $H_2SO_4$ -treated peels achieved a higher maximum removal (99.95%) compared to KOH-treated peels (93.73%), suggesting a stronger chemisorption process for acid treatment. After 60 minutes, removal efficiency declined due to site saturation. Overall, 60 minutes were determined as the optimal contact time for two of the peels. This aligns with other studies on biosorption.

### 3.1.4 Effect of ion metal concentration

The effect of initial metal ion concentration on % removal of Cu(II) ions is shown in Figure 2(b). As concentration increased from 50 mg/L to 150 mg/L, removal efficiency went up for both peels (more copper ions competing for sites). At even higher concentrations, competition became less important [9]. The increased concentration gradient at 150 mg/L also aided removal. Overall, 150 mg/L was best for both peels (almost 100% removal for  $H_2SO_4$ -treated, good removal for KOH-treated). Acid treatment worked better at higher concentrations because individual copper ions penetrated the peels easier, unlike bulky complexes formed with KOH treatment [12].



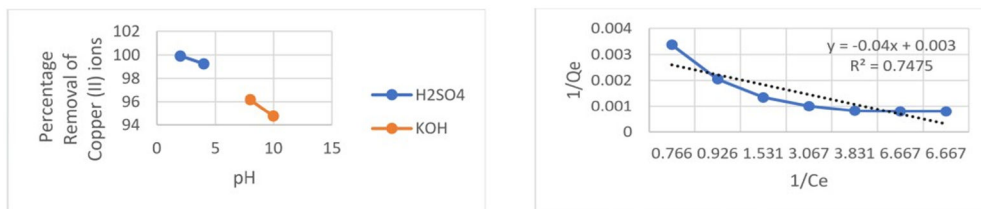
**Fig. 2.** (a) The effect of contact time on % removal of Cu (II) ions and (b) shows the effect of initial metal ion concentration removal of Cu(II) ions.

### 3.1.5 Effect of pH

The type of treatment on the mangosteen peels and the solution's pH significantly impacted copper removal (Figure 3(a)).  $H_2SO_4$ -treated peels worked best at a lower pH (2) due to stronger attraction between positively charged peels and negatively charged copper ions [10]. KOH-treated peels performed better at a slightly basic pH (8) for the same reason. At even higher pH (10), both types of peels became negatively charged, repelling copper ions and reducing removal efficiency.

### 3.1.6 Langmuir adsorption isotherm

Analyzing copper adsorption on mangosteen peels, the Langmuir model in Figure 3(b) showed a good fit ( $R^2 = 0.7475$ ). While the peels can capture a good amount of copper (25 mg/g), the low Langmuir constant (1.003) suggests a relatively weak attraction between copper and the peels, potentially leading to slower and less efficient adsorption at lower copper levels.



**Fig. 3. (a)** The effect of pH on % removal of Cu (II) ions and **(b)** shows the Langmuir Plot for Adsorption of Cu (II) ions.

### 3.1.7 Freundlich adsorption isotherm

The Freundlich model reflects copper adsorption on peels. The Freundlich model in Figure 4(a) showed a better fit with higher  $R^2 = 0.8273$ ). The Freundlich constant ( $n > 1$ ) suggests strong attraction between copper and peels, leading to more copper adsorbed at higher copper concentrations. This indicates a heterogeneous peel surface favoring the Freundlich model over Langmuir.

### 3.1.8 Pseudo first order

The experiment was conducted on the rate of copper adsorption on mangosteen peels using kinetic models. Figure 4(b) depicts a plot consistent with a pseudo-first-order adsorption process ( $q_e = 8.36$  mg/g), indicating that the rate of copper uptake is mainly determined by the remaining copper concentration in the solution, not the availability of binding sites on the peels. This suggests that as adsorption progresses, the remaining active sites on the peels become progressively occupied, leading to a gradual decrease in the adsorption rate over time (downward slope in the plot) [11].



**Fig. 4. (a)** Freundlich plot for adsorption of Cu (II) ions and **(b)** shows the Pseudo-First-Order plot for adsorption of Cu (II) ion.

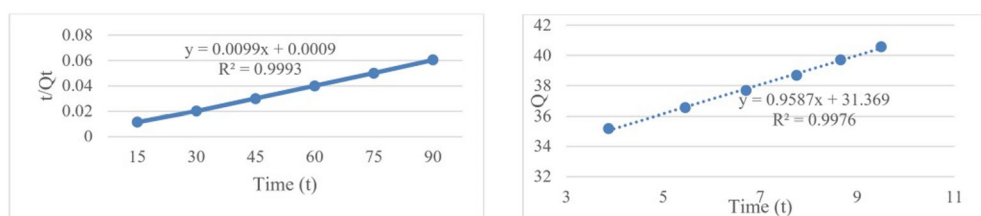
### 3.1.9 Pseudo second order

A better fit is provided by the pseudo-second-order model (Figure 5(a)) with  $R^2 = 0.9993$ . This model suggests that the rate of adsorption is primarily controlled by the availability of unoccupied binding sites on the peels. This aligns with the idea that chemisorption, involving

chemical bond formation between copper and the peels, is the rate-limiting step. The high adsorption rate observed in the first 60 minutes supports this notion, as readily available sites are quickly filled. As the experiment progresses and these sites become occupied, the adsorption rate slows down and plateaus.

### 3.1.10 Internal mass transfer coefficient

Intraparticle diffusion, the movement of copper ions inside the peels, also affects adsorption rate (Figure 5(b)). A value less than 1 (0.9976) suggests chemisorption might be involved alongside diffusion. This aligns with the increasing mobility of copper ions at longer times, potentially due to chemical bond formation (chemisorption) within the peels. The constant  $K_i$  was 0.9587 mg/min.



**Fig. 5.** (a) Pseudo-Second-Order plot for adsorption of Cu (II) ions and (b) shows the internal mass transfer coefficient for removal of Cu (II) ions.

## 4 Conclusion

In this study, the following parameters were shown to be ideal for extracting copper (II) ions from mangosteen peels using  $H_2SO_4$ -treated activated carbon: 300 rpm agitation speed, 150 mg/L metal ion concentration, 100 mg adsorbent dosage, pH of 2, and 60 minutes of contact time with 99.99% reduction. The equilibrium data match well by the Freundlich isotherm model, as indicated by its  $R^2$  of 0.8273. The optimal plot for kinetic research was determined to be the pseudo second-order model's correlation value of 0.9993, with an internal mass transfer coefficient of 0.9976. The research presented here suggests that additional kinds of activated carbon by mangosteen peels that has been handled with acids and alkalis be used in the removal of copper (II) ions from aqueous solution.

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