



## Removal of Copper Using Microsize Coconut Husk Powder: Equilibrium and Kinetic Studies

A. Prasad and S. Sarveswara Rao\*

Department of Chemical Engineering, G.M.R. Institute of Technology, Rajam, Srikakulam-532 127, A.P., India

\*Department of Chemical Engineering, Andhra University, Visakhapatnam-3, A. P.

### Key Words:

Biosorption  
Copper  
Coconut husk powder  
Isotherms  
Kinetic studies

### ABSTRACT

This investigation deals with the equilibrium and kinetic studies on biosorption of copper ions from aqueous solutions using coconut husk powder in a batch process. The results indicate that biosorption of copper is increased with an increase of biosorbent dosage and decrease with biosorbent size. A significant increase in percentage removal of copper was observed as pH value is increased from 1 to 7 and the percentage removal is decreased beyond pH 7. Increased initial concentration of copper in the aqueous solution results in lower biosorption. Freundlich and Langmuir isotherm models describe the present data very well indicating favourable biosorption. The biosorption follows pseudo-first-order kinetics.

### INTRODUCTION

Industrialization brings wealth but results in environmental degradation. Presence of liquid wastes in environment causes water pollution. Many liquid wastes contain heavy metals such as copper, zinc, cadmium, lead, etc. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chains even in relatively low concentrations. Copper is found to be one of the most important metals from various industries like, electroplating of copper, petroleum industries and battery industries. Removal of toxic heavy metals from industrial wastewaters has been practiced for several decades, the conventional physico-chemical removal methods, such as chemical precipitation, electroplating, membrane separation, evaporation or resin ionic exchange, are usually expensive and sometimes not effective. Therefore, there is a need for some alternative technique, which is efficient and cost effective. Biosorption, based on living or nonliving microorganisms or plants, could be such an alternative method of treatment (Cay et al. 1995, Pehlivan et al. 2006, Gang & Weixing 1998, Lees & Davis 2000, Marina & Klasnja 2003, Mehmet et al. 2006, Nuri & Mustafa 2006). Biosorption technique is more efficient and easy to operate and does not produce any secondary effluents.

### MATERIALS AND METHODS

Adsorption of copper metal has been carried out in batch type of operation with coconut husk powder as biosorbent.

**Preparation of biosorbent:** The matured coconut husk powder has been collected from Visakhapatnam region, Andhra Pradesh, India. It was dried at room temperature in shade followed by oven at 110°C till the constant weight was attained. The resulting husk was sieved to different size

fractions using Rotap sieve shaker. The size fractions are 53, 75, 106 and 212 $\mu\text{m}$ , preserved in glass bottles for further experimental work.

**Preparation of stock solution:**  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was used in preparation of copper stock solution. All the required solutions were prepared with double-distilled water. 3.6244g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  was dissolved in 1L of distilled water to prepare 1000 mg/L of copper solution. Samples of different concentrations of copper were prepared from this stock solution by appropriate dilutions. 100mL of 1000mg/L copper stock solution was taken in a 1000 mL volumetric flask and made up to the mark with distilled water. Thus, obtained solution has concentration of 100mg/L of copper. Similarly, solutions with different metal concentrations were prepared. The initial concentration of copper in the aqueous solution was analysed by atomic absorption spectroscopy (AAS) at 340nm wavelength.

## RESULTS AND DISCUSSION

Coconut husk powder was tested for its adsorbing capacity from aqueous solution of copper. The effects of various parameters on adsorption of copper by biosorbent were studied. The measured data consist of initial and final concentrations of copper in the aqueous solution, agitation time, biosorbent size, biosorbent dosage, initial concentration of copper solution, and pH of the aqueous copper solution.

**Effect of agitation time:** Agitation time has influence on metal uptake and percentage removal of copper. Percentage copper removed was calculated by the expression  $[(C_0 - C_t)/C_0] \times 100$ . The percentage removal of copper against the agitation time is shown in Fig. 1 for different dosages (0.5, 1.0, 1.5 and 2.0 g). The percentage adsorption was found to increase up to 40 min, but later negligible increase in adsorption was noticed. It was observed that the rate of adsorption is fast in the initial stages because of the adequate surface area of the biosorbent available for the adsorption of copper. As time increases, more amount of copper gets adsorbed onto the surface of the biosorbent and surface area available decreases. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the biosorbent capacity is exhausted. The maximum percentage of adsorption was attained at 40 minutes. The percentage removal of copper becomes almost constant after 40 min. Therefore, all other experiments were conducted at this agitation time.

**Effect of biosorbent size:** The variations in % removal of copper from the aqueous solution with particle sizes (53 $\mu\text{m}$ , 75 $\mu\text{m}$ , 106 $\mu\text{m}$  and 212 $\mu\text{m}$ ) were obtained at different biosorbent dosages at 40 minutes. The results are shown in Fig. 2 as percentage removal of copper versus biosorbent size. The percentage removal of copper was increased as the biosorbent particle size decreased from 212 to 53 $\mu\text{m}$ . This phenomenon was expected, as the size of the particle decreases, surface area of the biosorbent increases, thereby the number of active sites on the biosorbent are better exposed to the adsorbate.

**Effect of biosorbent dosage:** The percentage removal of copper against biosorbent dosage for different biosorbent sizes (53 $\mu\text{m}$ , 75 $\mu\text{m}$ , 106 $\mu\text{m}$  and 212 $\mu\text{m}$ ) are shown in Fig. 3. It is evident from the plots that the percentage removal of metal from the aqueous phase increases with increase in the biosorbent dosage. Percentage removal of copper from the aqueous solution increases from 71.43 % to 88.10 %, as dosage is increased from 0.5 to 2.0 g at a biosorbent size 53 $\mu\text{m}$ . Such behaviour is obvious because the number of active sites available for metal removal would be more as the amount of the biosorbent increases.

**Effect of initial concentration of copper in the aqueous solution:** Percentage removal of copper

versus initial concentration is shown in Fig. 4. The percentage removal of copper decreased from 90.476% to 71.03% as the initial concentration of copper in the aqueous solution increased from 21 mg/L to 183 mg/L. Such behaviour can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the biosorbent since the amount of biosorbent is kept constant.

**Effect of pH of the aqueous solution:** pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. So pH is an important factor controlling the process of biosorption. The present study was carried out over the pH range from 1 to 14 for copper initial concentration of 100mg/L and 2 g of biosorbent dosage, 53 $\mu$ m size adsorbent. The effect of pH of solution on percentage removal of copper is shown in Fig. 5. The percentage removal of the metal increased from 71.42% to 89.88% as pH is increased from 1 to 7, but decreases from 85.18 to 71.60 as pH increases from 7 to 14. In the present investigation, the maximum % removal of copper was obtained for 2 g of 53 $\mu$ m size adsorbent at 40 minutes. The principal driving force for metal ion adsorption is the electrostatic interaction, i.e., attraction between biosorbent and adsorbate. The greater the interaction, more is the biosorption of heavy metal. With an increase in interaction, the copper ions replace H<sup>+</sup> ions bound to the biosorbent for forming part of the surface functional groups such as OH<sup>-</sup> and COOH<sup>-</sup> etc.

### EQUILIBRIUM STUDIES

**Freundlich isotherm for adsorption of copper:** The Freundlich relationship is an empirical equation. However, it is easier to handle mathematically without complex calculations. The Freundlich isotherm is given by  $q_e = k_f C_e^n$ . Where,  $k_f$  and  $n$  are known as Freundlich constants obtainable from the plots of  $\log q_e$  versus  $\log C_e$  on the basis of the linear form of the equation as shown in Fig. 6. The resulting line has the correlation coefficient of 0.97. The following equation is obtained from the plot shown in Fig. 6.  $\log q_e = 0.5899 \log C_e - 0.4431$  at 303K. The slope of the above equation is 0.5899. The  $n$  value satisfies the condition of  $0 < n < 1$  indicating favourable adsorption.

**Langmuir isotherm for adsorption of copper:** Since, the chemical forces fall off very rapidly with distance, it is probable that chemisorption does not extend beyond a single layer of adsorbate on the surface of the solid. It can be anticipated as first pointed out by Langmuir that chemisorbed adsorbate layers may be only one molecule thick. The Langmuir isotherm is the most widely used two-parameter equation. The relationship is of a hyperbolic type form  $q_e/q_m = bC_e / (1 + bC_e)$ . Where,  $C_e$  is the concentration of the adsorbate at equilibrium,  $q_e$  is the amount adsorbed at equilibrium per unit mass of the biosorbent,  $q_m$  is the maximum amount adsorbed per unit mass of the biosorbent and  $b$  is the coefficient related to affinity.  $(1/q_m)$  and  $(1/b)$  can be calculated by Langmuir isotherm as shown in Fig. 7. Further analysis of the Langmuir equation is made on the basis of separation factor, RL defined as  $RL = 1/(1 + bC_e)$   $0 < RL < 1$  indicates favourable adsorption,  $RL > 1$  indicates unfavourable adsorption,  $RL = 1$  indicates linear adsorption and  $RL = 0$  indicates irreversible adsorption. Langmuir isotherm, shown in Fig. 7, has good linearity (correlation coefficient is 0.989) indicating strong binding of copper ions onto the surface of coconut husk powder. The separation factor (RL) obtained is 0.4367, which shows favourable adsorption. The following equations are obtained from Fig. 7,  $(C_e/q_e) = 0.2430 C_e + 3.761$  at 303K.

### KINETICS OF ADSORPTION

The order of adsorbate-biosorbent interaction has been described by using various kinetic models.

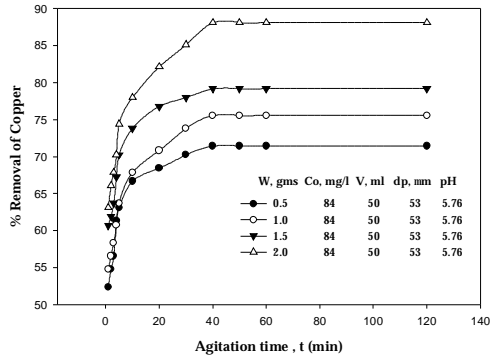


Fig 1. Effect of agitation time on percentage removal of Copper

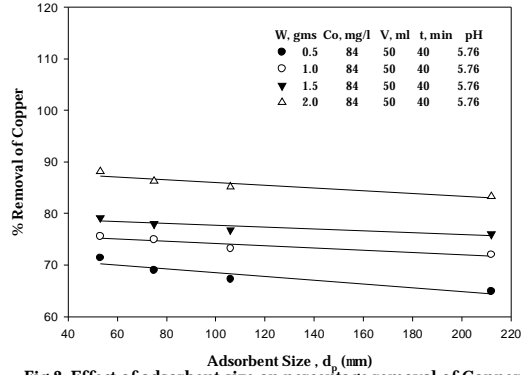


Fig 2. Effect of adsorbent size on percentage removal of Copper

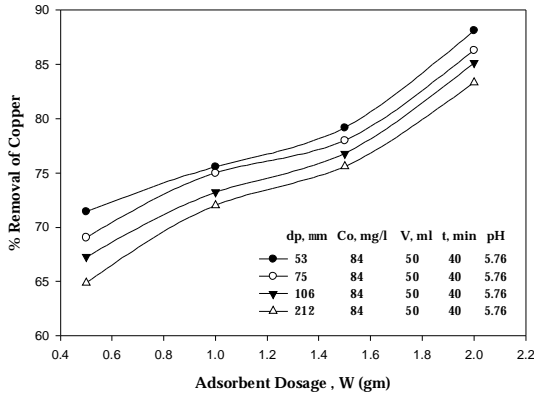


Fig 3. Effect of adsorbent dosage, W (gm) on percentage removal of Copper

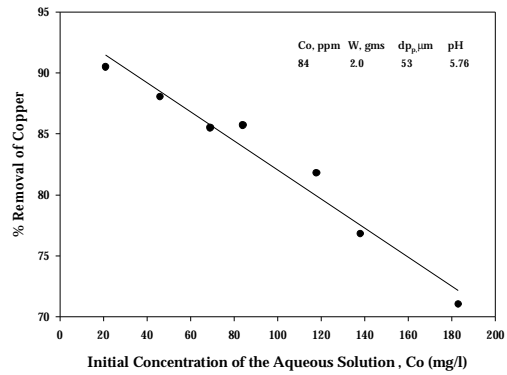


Fig 4. Effect of Initial Concentration on % Removal of Copper

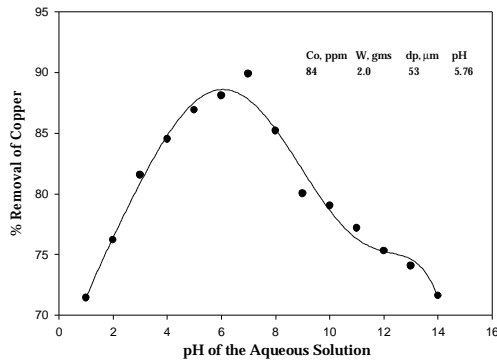


Fig 5. Effect of pH of the aqueous solution on percentage removal of Copper

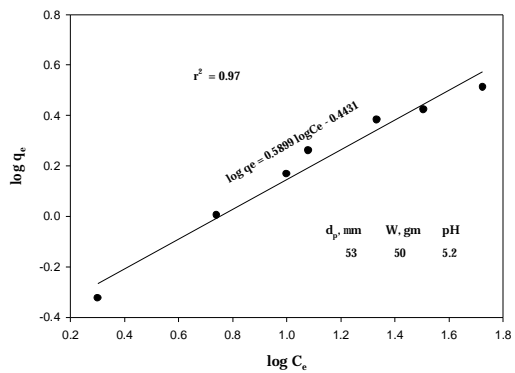


Fig 6. Freundlich isotherm

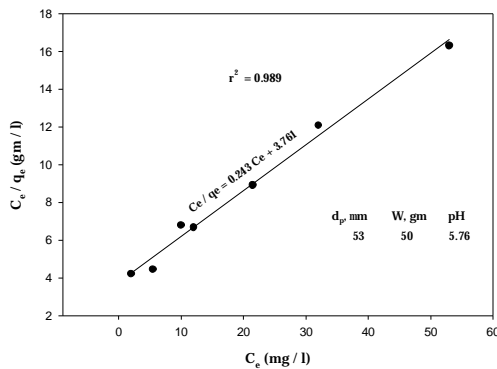


Fig 7. Langmuir isotherm

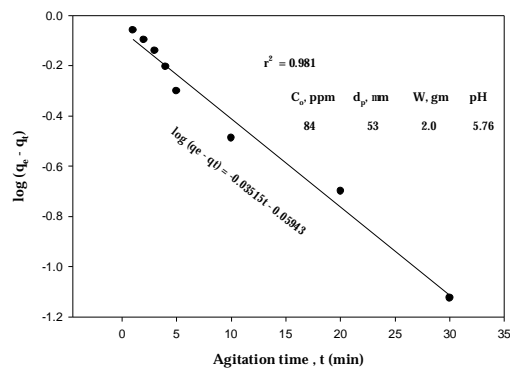


Fig 8. First order kinetics for adsorption of Copper

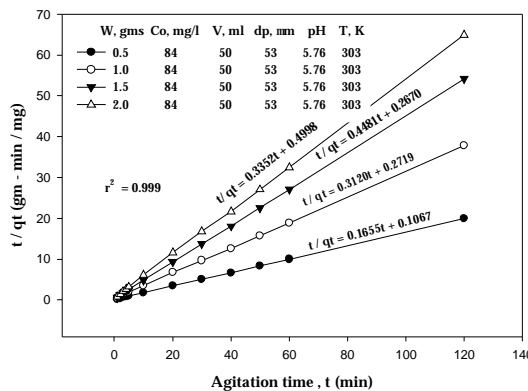


Fig 9. Second order kinetics for adsorption of Copper

On the other hand, several authors have shown that pseudo second order kinetics can also describe these interactions very well in certain cases. The first order rate equation is  $(dq_t/dt) = k_{ad}(q_e - q_t)$ . Where,  $q_e$  and  $q_t$  are the amounts adsorbed at  $t$  min at equilibrium and  $K_{ad}$  is the rate constant of the first order adsorption process. Plot  $\log(q_e - q_t)$  vs  $t$  gives a straight line for first order kinetics, which allows computation of the adsorption rate constant,  $K_{ad}$ . It is shown in Fig. 8. Second order kinetics (pseudo first order kinetics), is given by  $(dq_t/dt) = k(q_e - q_t)^2$  is applicable, where  $K$  is the second order rate constant. The following second order rate equations are obtained from the Fig. 9.  $(t/q_t) = 0.1655t + 0.1067$ ,  $(t/q_t) = 0.3120t + 0.2719$ ,  $(t/q_t) = 0.4481t + 0.2670$ ,  $(t/q_t) = 0.3352t + 0.4998$ .

**CONCLUSIONS**

The following conclusions are made from this study. The optimum agitation time for the equilibrium metal adsorption is 40 minutes. The percentage removal of copper from the aqueous solution increases with a decrease in the particle size of the biosorbent. The percentage removal of copper from aqueous solution is augmented with increase in weight of the biosorbent. With higher the concentration of copper in the aqueous solution, lower the percentage removal of copper from the aqueous solution. Percentage removal of copper from the aqueous solution is increased significantly with

increase in pH value from 1 to 7 and removal decreases for pH beyond 7. In the range of variables studied, percentage removal varies from 52.38% to 88.10%. The data are well represented by Freundlich and Langmuir isotherms indicating favourable adsorption of copper by the biosorbent. The kinetic studies show that the adsorption of copper is better described by pseudo-first-order kinetics.

## REFERNCES

- Cay, L., Holan, Z.R. and Volesky, B. 1995. Biosorption of heavy metals by Turkish tea waste (fibrous). *Hazardous Material*, 62: 190-199.
- Pehlivan, E., Cetina, S. and Yanik, B.H. 2006. Equilibrium studies for the sorption of zinc and cadmium from aqueous solutions using sugar beet pulp and fly ash. *Journal of Hazardous Materials*, 135(1-3): 193-199.
- Gang, Sun and Weixing Shi 1998. Removal of heavy metal ions from aqueous solution using sunflower stalks. *Hazardous Materials*, 96: 190-199.
- Lees and Davis, A. P. 2000. Removal of copper and cadmium from aqueous solution by seafood processing waste sludge. *Water Research*, 22: 651-658.
- Marina Sciban and Klasnja, Mile 2003. Removal of heavy metals from wastewater by adsorption onto wood saw dust. *CEJOEM*, 9(4): 337-343.
- Mehmet Emin Argun, Sukru Dursun, Celalettin Ozdemir and Mustafa Karatas 2006. Heavy metal adsorption by modified oak sawdust. *Thermodynamics and Kinetics of Hazardous Materials*, 130: 190-199.
- Nuri Unlu and Mustafa Ersoz 2006. Adsorption characteristics of heavy metal ions onto a low cost biopolymeric sorbent from aqueous solutions. *Journal of Hazardous Materials*, 136(2): 272-280.