



## Removal of Cu(II) Ions by *Leucaena Leucocephala* (Subabul) Seed Pods from Aqueous Solutions

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**Abstract:** In this method, *Leucaena leucocephala* seed pods (LLSP) have been used for removal of Cu(II) ions from aqueous solution. Batch adsorption experiments were conducted to study the effect of process parameters like pH, contact time initial Cu(II) ions concentration and adsorbent dose. The maximum adsorption of Cu(II) ions on *Leucaena leucocephala* seed pods was 94.17% at pH 5. The amount of metal adsorbed per unit weight of adsorbent increases with time and reach equilibrium after 30 minutes of shaking time for the different initial metal concentrations. The Freundlich and Langmuir isotherm equations were applied for the equilibrium adsorption data and the various isotherm parameters were evaluated. The obtained plots were linear as evident from  $R^2$  values close to unity. The data agreed very well with the pseudo second-order kinetic model.

**Keywords:** *Leucaena leucocephala*, Seed pods, Low-cost adsorbent, Langmuir isotherm, Freundlich isotherm, Adsorption kinetics.

### Introduction

Environmental pollution is the major concern faced by the society today. The pollutants generally include organic wastes and metals. The concentration of toxic metal ions like Cu(II), Cr(VI), Cd(II), As(V), Pb(II) and Ni(II) etc. has increased beyond environmentally and ecologically sustainable levels. It has resulted in severe contamination of ground and surface water. One of the more important toxic metals, copper, finds its way to the water stream from industries like electroplating, mining, electrical and electronics, iron and steel production, the non-ferrous metal industry, the printing and photographic industries and metalworking and finishing processes. The adverse health effects caused by copper, mercury

and arsenic poisoning are far more catastrophic than any other natural calamity through out the world in recent times<sup>1</sup>. Copper is not acutely toxic to humans, but its extensive use and increasing levels in the environment may cause serious health problems with prolonged exposure<sup>2</sup>. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation and possible necrotic changes in the liver and kidney<sup>3</sup>. Removal of such metal is important for survival of environment.

The use of conventional technologies, such as ion exchange, chemical precipitation, reverse osmosis and evaporative recovery, for this purpose is often inefficient and very expensive. It is therefore important to develop new methods for the removal Cu(II) and reduction of it to very low concentrations. In recent years, considerable attention has been focused on the removal of copper from aqueous solution using adsorbents derived from low-cost materials. Non conventional materials have been tested in a large scale for this purpose, such as orange peel, sawdust and bagasse<sup>4</sup>, wheat shell<sup>5</sup>, bagasse fly ash<sup>6</sup> and Rice bran<sup>7</sup> *etc.*

In this study, *Leucaena leucocephala* seed pod (LLSP) have been used as adsorbents to remove Cu(II) ions form aqueous solution. *Leucaena leucocephala* seed pods are widely available. *Leucaena leucocephala* seed pods are often considered as solid wastes of agriculture. These materials cause a significant disposal problem, it to be dumped or buried. Efforts have been made to use the cheapest and unconventional adsorbents to adsorb metal such as Cu(II) ions form aqueous solution. The optimum adsorption conditions were determined as a function of initial pH, initial metal ion concentration and time.

## Experimental

*Leucaena leucocephala* seeds are available twice a year, July to November and in February. Pods were in bunches, flat, about 8-9 cms long, brittle, reddish brown when ripe. Pods were collected from a local farm and dried in the sun for 3 to 4 days. The seeds were separated from the pods. Then the pods were ground to get desired particle size of 100 to 150  $\mu\text{m}$ . It was then soaked 1-2 h in 0.1 N NaOH solution to remove the lignin content. Excess alkalinity was then removed by neutralizing with 0.1 N HCl. The LLSP was again washed several times with distilled water till the wash water became colorless and then oven dried at 50 °C for 24 h.

### Preparation of solutions

#### *Adsorbate solution*

Stock copper(II) solution (1000 mg/L) was prepared by dissolving 3.929 g of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in 1000 mL double-distilled water. All working solutions of lower concentrations were prepared by diluting the stock solution with distilled water.

#### *Thiosulphate solution*

2.482 g of sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) was taken in a 1 liter volumetric flask and diluted up to the mark using distilled water. The concentration of the solution was 0.01 M.

#### *Starch solution*

1 g of the starch was taken in a 250 mL beaker and 100 mL hot water was added with continuous stirring.

#### *Potassium iodide solution (10%)*

10 g of the potassium iodide was taken in a 100 mL volumetric flask and diluted up to the mark using distilled water.

### Batch adsorption studies

Batch adsorption experiments were carried out by shaking 10 g/L of adsorbent dose with 50, 150, 250 mg/L of the copper solution concentration at room temperature. The initial pH values of the solution were previously adjusted with 0.1 M HCl or NaOH using Equipronics EQ-610 pH meter. At the end of the predetermined time interval, the adsorbent was removed by centrifugation. The amount of copper was analyzed by iodometric titration method.

### Detection of copper by iodometric titration

25 mL of Cu(II) ions containing solution was pipette out into glass stopper bottle. To it  $\text{NH}_4\text{OH}$  was added drop by drop till little bluish precipitate appears. Then acetic acid was added drop by drop till the solution become clear.  $2/3$  drops excess of acetic acid was added to make the solution distinctly acidic. Finally 10 mL 10% KI was added. Then the librated iodine equivalent to concentration of Cu(II) ions in solution was titrated with 0.001 M  $\text{N}_2\text{S}_2\text{O}_3$  solution using starch indicator. At the end point dark blue color changes to colorless<sup>8</sup>.

## Results and Discussion

### Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. It affects both the surface charge of adsorbent and the degree of ionization of the metal in solution<sup>9</sup>. The effect of initial pH on Cu(II) ions adsorption onto LLSP has been studied by varying it in the range of 1-6 using 50 mg/L initial copper concentration and 10 g/L adsorbent dose with 30 min contact time. The optimum pH was found to be pH 5.0. The Figure 1 represents results showed that the percent removal increases from pH 1 to 5. The maximum removal was 94.17% at pH 5. This may be attributed to the competition between the hydrogen and copper ions on the sorption sites, at low pH values. At pH values higher than 6, insoluble copper hydroxide starts precipitating from the solutions making true sorption studies impossible<sup>10</sup>. Consequently, the working pH value for copper removal onto LLSP was chosen as 5.0 and the other adsorption experiments were performed at this pH value.

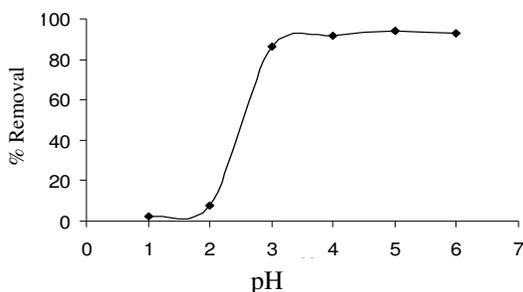
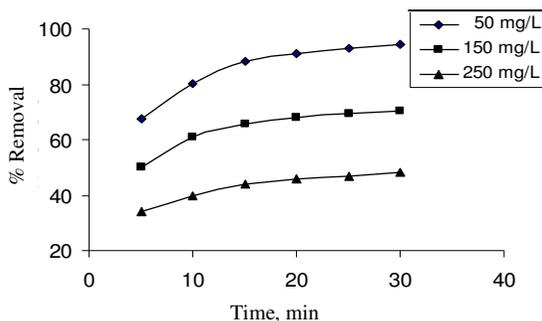


Figure 1. Effect of pH on adsorption of Cu(II) ions on LLSP

### Effect of contact time

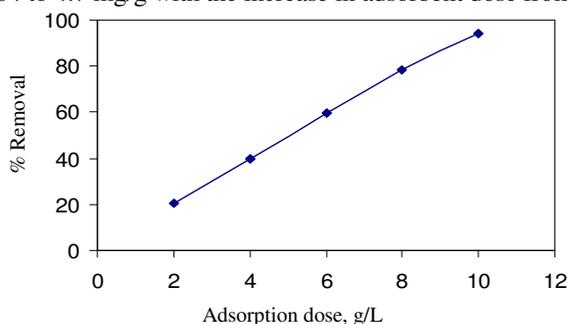
The effect of contact time on the amount of Cu(II) ions adsorbed was investigated using 50, 150 and 250 mg/L initial concentration of Cu(II) ions with 10 g/L LLSP at pH 5. The equilibrium was attained in about 30 min. The extent of removal of Cu(II) ions by LLSP was found to increase, reach a maximum value with increase in contact time shown in Figure 2. The percentage of Cu(II) ions removal increases at equilibrium from 48% to 94.17% as Cu(II) ions concentration decreases from 250 mg/L to 50 mg/L for 10 g/L of adsorbent dose, even though the sorption equilibrium was achieved during the same period of 30 minutes.



**Figure 2.** Effect of contact time on adsorption of Cu (II) by LLSP

### *Effect of adsorbent dose*

The effect of varying doses 2 to 10 g/L of LLSP was investigated using 50 mg/L of initial Cu(II) ions concentration at initial pH 5.0. Figure 3 shows an increase in percentage removal of copper with the increase in dose of adsorbent. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites<sup>11</sup>. In contrast, the adsorption capacity of Cu(II) ions on LLSP decreases from 5.04 to 4.7 mg/g with the increase in adsorbent dose from 2 to 10 g/L.



**Figure 3.** Effect of adsorbent dose on adsorption of Cu(II) ions by LLSP

### *Isotherm models*

The study of the adsorption isotherm is fundamental and plays an important role in the determination of the maximal capacity of adsorbents. The experimental data were fitted to the Freundlich and Langmuir isotherm equations. The constant parameters of the isotherms equations were calculated for each isotherm.

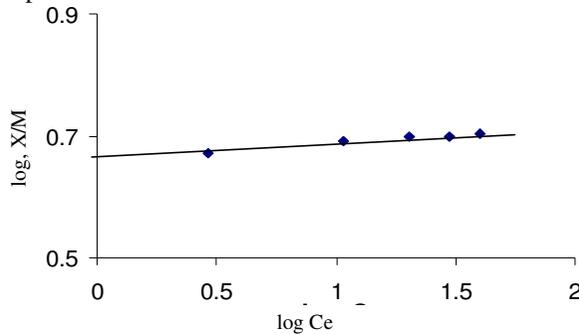
### *Freundlich isotherm*

The Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The logarithmic linear form of Freundlich isotherm may be represented as follows<sup>12</sup>:

$$\log q_e = \log K_f + 1/n \log C_e \quad (1)$$

Where,  $q_e$  is the amount of metal ion adsorbed per gram of adsorbent (mg/g).  $C_e$  is the equilibrium concentration of metal ion in solution (mg/L),  $K_f$  and  $n$  are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively.

Linear plot of  $\log q_e$  versus  $\log C_e$  indicates that the adsorption of Cu(II) ions on LLSP follows the Freundlich isotherm (Figure 4). The linearity of Freundlich plot suggested the formation of homogenous monolayer of copper(II) on the outer surface of the adsorbent, the adsorption coefficient  $K_f$  of Cu(II) ions on LLSP was found to be 4.562 L/g. Table 1 shows the Freundlich adsorption isotherm constant and correlation coefficient. The value of  $1/n$  was found to be lie between zero and one, indicating that copper(II) is favorably adsorbed by LLSP at all studied parameters.



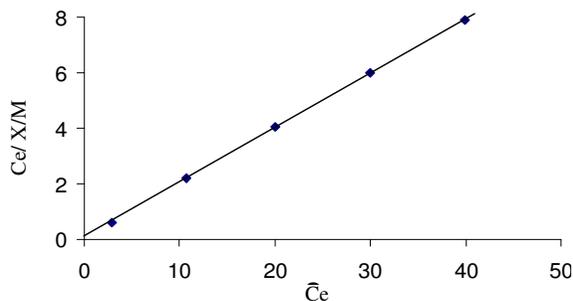
**Figure 4.** Freundlich adsorption isotherm of Cu(II) ions adsorption by LLSP (Cu(II) ions concentration: 50 mg/L, pH: 5, agitation time: 30 min)

#### Langmuir isotherm

The Langmuir isotherm model however makes a number of assumptions such as monolayer-based sorption. It also assumes that all the binding sites on the sorbent are free sites, ready to accept the sorbent from solution<sup>13</sup>. The Langmuir isotherm is represented in the linear form as<sup>14</sup>:

$$C_e / q_e = 1/b Q_0 + C_e / Q_0 \quad (2)$$

Where,  $q_e$  is the equilibrium CV concentration on adsorbent (mg/g) and  $C_e$  is the equilibrium concentration of CV (mg/L).  $Q_0$  and  $b$  is Langmuir constants related to the capacity and energy of sorption respectively. The values  $Q_0$  and  $b$  were determined from slopes and intercepts of the Langmuir plot of  $C_e / q_e$  vs.  $C_e$  for adsorption of Cu(II) ions on LLSP (Figure 5). The values of  $Q_0$  and  $b$  and correlation coefficient for Langmuir isotherm are presented in Table 1. The values of  $Q_0$  and  $b$  were found to be 5 mg/g and 1.33 mg/L respectively. The low value of  $b$  for Cu(II) ions in this case was suggestive of greater affinity of adsorbent for Cu(II) ions. A good metal adsorbent in general should have a high  $Q_0$  as well as a low  $b$ <sup>15</sup>.



**Figure 5.** Langmuir adsorption isotherm of Cu(II) ions adsorption by LLSP (Cu(II) ions concentration: 50 mg/L, pH: 5, agitation time: 30 min)

**Table 1.** Langmuir and Freundlich isotherm parameters for Cu(II) uptake by LLSP

Cu(II) Conc.	Freundlich Constants			Langmuir Constants		
	$K_f$	$1/n$	$R^2$	$Q_0$ mg/g	$B$ , l/mg	$R^2$
50 mg/L	4.562	0.01057	0.9840	5.000	1.3333	0.9999

### Adsorption kinetic study

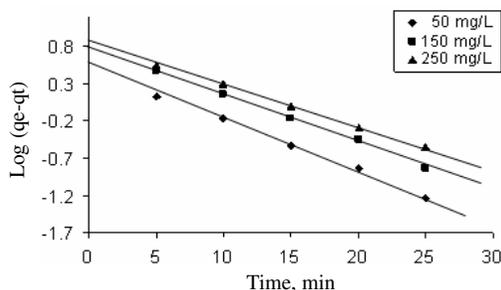
Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process. Pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion kinetic models were used. The conformity between experimental data and the model predicted values were expressed by correlation coefficient ( $R^2$ ). A relatively high  $R^2$  value indicates that the model successfully describes the kinetics of Cu(II) ions adsorption.

### Pseudo-first-order model

The pseudo-first-order (Lagergreen) rate expression generally expressed as follows<sup>16</sup>:

$$\text{Log}(q_e - q_t) = \text{log } q_e - k_1 t/2.303 \quad (3)$$

Where,  $q_e$  and  $q_t$  are the amounts of Cu(II) ions adsorbed ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$  (min), respectively and  $k_1$  the rate constant of pseudo first order adsorption ( $\text{min}^{-1}$ ). The plots of  $(q_e - q_t)$  versus  $t$  for 50, 150 and 250 mg/L concentration of Cu(II) ions are shown in Figure 6. The linear relationship of the plot indicates the validity of equation. The calculated  $q_e$ ,  $K_1$  and regression correlation coefficient  $R^2$  values are summarized in Table 2. It was observed that, even though the correlation coefficient  $R^2$  of the first order equation is considerably high (0.9970-0.998). The calculated  $q_e$  values from first order kinetic plot wear far two small as compared to the experimental values and does not shows good agreement between calculated and experimental  $q_e$  Values. This shows that the adsorption of Cu(II) ions on LLSP is not a first order reaction. It was observed that the rate constant  $K_1$  decreases with increase in initial Cu(II) ions concentration.



**Figure 6.** Lagergren plots for the adsorption of Cu(II) ions on LLSP (Cu(II) ions concentration: 50, 150 and 250 mg/L, adsorbent: 10 g/L, pH: 5)

### Pseudo-second-order model

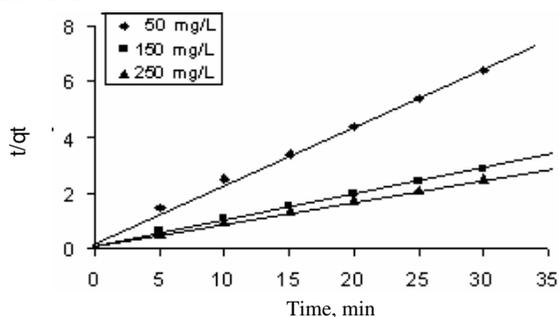
The pseudo-second-order equation is also based on the sorption capacity of the solid phase. It predicts the behavior over the whole range of data. Further more, it is in agreement with chemisorptions being the rate controlling step and is expressed as<sup>17</sup>:

$$t/q_t = 1/K_2 q_e^2 + t/q_e \quad (4)$$

Where,  $K_2$  ( $\text{g/mg min}$ ) is the rates constant of second-order adsorption. The initial sorption rate,  $h$  ( $\text{mg/ g. min}$ ), at  $t = 0$  is defined as:

$$h = K_2 q_e^2 \quad (5)$$

The plot of  $t/q$  versus  $t$  (Figure 7) shows a linear relationship.  $q_e$  and  $K_2$  can be determined from the slope and intercept of the plot. The values of the calculated  $q_e$ ,  $K_2$ ,  $h$  and correlation coefficients  $R^2$  are also presented in Table 2. The calculated  $q_e$  values from first order kinetic plot wear shows good agreement with experimental  $q_e$  values. The correlation coefficients of all examined data were found very high ( $R^2 > 0.9997$ ). This shows that the model can be applied for the adsorption process and confirms that the sorption of Cu(II) ions onto LLSP follows the pseudo-second-order kinetic model. The  $q_e$  values increases with increase in initial Cu(II) ions concentration, while  $K_2$  values increases with increase in initial Cu(II) ions concentration.



**Figure 7.** Pseudo second-order adsorption of Cu(II) ions on LLSP (Cu(II) ions concentration: 50, 150 and 250 mg/L, adsorbent: 10 g/L, pH: 5)

**Table 2.** Comparison between adsorption rate constants,  $q_e$  estimated and coefficient of correlation associated to the Lagergren pseudo first order and to pseudo second order kinetic models

Cu(II) Conc. mg/L	$q_{e,exp}$ mg/g	Pseudo first order kinetic model			Pseudo second order kinetic model			
		$K_{1,ads}$ $\text{min}^{-1}$	$q_{e,cal}$ mg/g	$R^2$	$K_{2,ads}$ g/mg min	$q_{e,cal}$ mg/g	$H$ mg/g min	$R^2$
50	4.7	$14.96 \times 10^{-2}$	2.754	0.9970	$6.56 \times 10^{-2}$	5.385	1.9040	0.9997
150	10.57	$14.39 \times 10^{-2}$	6.026	0.9984	$5 \times 10^{-2}$	10	5	0.9999
250	12	$12.33 \times 10^{-2}$	6.607	0.9984	$4.26 \times 10^{-2}$	12.5	6.6666	0.9997

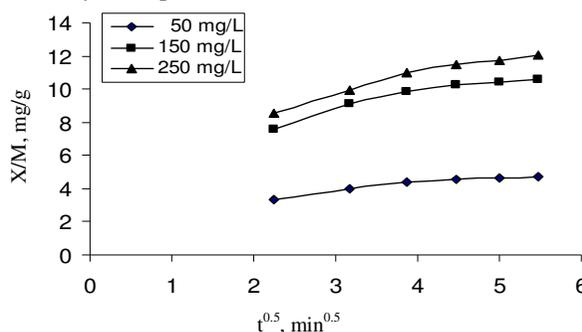
#### Intra-particle diffusion study

When the intra-particle mass transfer resistance is the rate limiting step, then the sorption process is described as being particle diffusion controlled. Webber and Morris<sup>18</sup> provided the rate,  $q_t$ , for intra-particle diffusion by:

$$q_t = K_{id} t^{0.5} \quad (8)$$

Where,  $q_t$  is the amount of copper(II) adsorbed (mg/g) at time  $t$  (min) and  $K_{id}$  is the intra-particle diffusion rate constant ( $\text{mg/g min}^{0.5}$ ). The amount of Cu(II) ions adsorbed at equilibrium ( $X/M$ , mg/g) against  $t^{0.5}$  is shown in Figure 8. It presents intra-particle plot for Cu(II) ions onto LLSP for different Cu(II) ions concentrations. The figure shows three linear portions, the first part of curve is attributed to transport of the adsorbate from the aqueous phase to the surface of the adsorbent (external diffusion or film diffusion). In second part transport of the adsorbate from the particle surface into interior sites by diffusion (internal

diffusion). The final linear parts indicate effect of adsorption of the solute on active sites on the interior surface of the pores. The diffusion rate parameters were shown in Table 3. The data indicate that intra-particle diffusion controls the sorption rate. Simultaneously, external mass transfer followed by intra-particle diffusion.



**Figure 8.** Intra-particle diffusion plot of Cu(II) ions on LLSP (Cu(II) ions concentration: 50, 150 and 250 mg/L, adsorbent: 10 g/L, pH: 5)

**Table 3.** Intra-particle diffusion rate parameters for adsorption of Cu(II) ions

Cu(II) ions Conc. mg/L	Rate constants, Intra-particle rate parameter, mg/g·min <sup>0.5</sup>		
	$K_1$	$K_2$	$K_3$
50	3.3585	1.4739	0.3484
150	7.6766	3.3777	0.8060
250	9.212	3.4545	1.044

#### Desorption of Cu(II) ions from sorbent

Desorption studies will help to recover the Cu(II) from sorbent and it also will help to regenerate the sorbents so that it can be used again to adsorb the metal ions<sup>19</sup>. Moreover, it will help to elucidate the nature of adsorption process. Desorption experiments were carried out by using 0.1 N HCl, 0.1 N HNO<sub>3</sub>, 0.1 N H<sub>2</sub>SO<sub>4</sub> and acetic acid. The % desorption after 60 minutes contact time shown in Table 4.

**Table 4.** Desorption of Cu(II) ions from LLSP

	% Desorption of Cu(II) ions with			
	0.1 N HCl	0.1 N HNO <sub>3</sub>	0.1 N H <sub>2</sub> SO <sub>4</sub>	Acetic acid
water	63.09%	84.16%	74.05%	31.54%
	2.4%			

## Conclusion

From the experimental data of adsorption of copper(II) on *Leucaena leucocephala* seed pod powder surface, the following points can be concluded.

1. *Leucaena leucocephala* seed pod, an agricultural waste, could be used as potential adsorbent for the removal of copper(II).
2. The adsorption of copper(II) on LLSP was dependent on the pH, initial copper(II) concentration, quantity adsorbent dose and contact time.
3. The maximum removal obtained at pH 5.
4. The percent removal of copper(II) by the new adsorbent is fairly high. The maximum 94.17 % removal was possible among the whole range of initial concentration used in this study.

- 5 Kinetic of metal ions adsorption obeyed the pseudo-second-order models, which suggest chemisorption as the rate-determining step in adsorption process.
6. The amount of metal ions adsorbed increased with increase initial metal ion concentration.

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