



Kinetic, Equilibrium Isotherm and Thermodynamic Study of Removal of Cu (II) Metal ions by Using Sarpagandha Leaves as Bio- adsorbent

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ABSTRACT:

The ability of Sarpagandha (*Rauwolfia Serpentine*) leaves powder (SLP) to adsorb copper (II) from aqueous solutions has been investigated through batch experiments. In this study, the effect of contact time, effect of temperature, effect of adsorption dose, pH and initial concentration of metal ion on the bio adsorbent capacities. Kinetics of adsorption and adsorption isotherms has been studied. The various thermodynamic parameters such as free energy of adsorption (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were calculated. According to the experimental results, SLP is recommended as cheapest and easily available bio adsorbent to removal of toxic heavy metal ions from industrial wastewater.

Index Terms - Cu (II) metal ion, adsorption, isotherms, kinetics, thermodynamic parameters, Sarpagandha leaves powder.

I. INTRODUCTION

Industrial waste water may contain some toxic heavy metal ions like Cr, Pb, Co, Cu, Ni etc. the release of toxic heavy metal ions by various industries such as mining, electroplating, dyeing, metal processing leather tanning, cement, textile, and paint industries into the environment in quantities that pose to human health [1]. Copper metal is one of the highly toxic heavy metals essential to human life and health. Small quantities, the metal is ultimate in maintaining the health of an individual, whereas larger of the same is carcinogenic. Prolonged exposure to copper causes serious illness to human [2]. The permissible limit of Cu (II) in water is 2.5 mg/L [3]. Pulp and paper mills, fertilizers, petroleum refineries, basic steel works foundries, nonferrous metal works, motor vehicles, aircrafts plating and finishing are the major contributors of copper into the environment [4, 5]. Hence, the remedy of polluted water is the need of the hour. Ion-exchange, reverse-osmosis, electro-coagulation, chemical precipitation, neutralization and adsorption. These existing methods that are generally expensive leads to incomplete metal removal, high energy consumption and generation of toxic sludge. Utilization of low-cost adsorbents to eliminate toxic heavy metals was reported in recent years. These low-cost adsorbents include agricultural waste, domestic waste, industrial waste, forest trees [6], and many more sources.

The aim of this study was to remove the Cu metal ions from aqueous solution. The effect of various parameters such as adsorbent dose, initial metal ion concentration, contact time, pH of solution and temperature on metal ion adsorption were investigated. Various low-cost adsorbents are used for rice husk [7], wheat shell [8], teak leaves [9], seed and seed shell of mango [10], gram seed husk [11], bajra powder [12], etc. which were used to remove heavy metal ions from wastewater. The present study under taken to evaluate the efficiency of Sarpagandha leaves powder. (SLP) for adsorption of Cu (II) metal ions in aqueous solution in addition to estimate the optimum adsorption condition and the suitable adsorption isotherms with their related conditions.

In the present paper, Sarpagandha leaves powder. (SLP) as bio-adsorbent to the adsorption of Cu (II) metal ions from aqueous solutions, kinetics of adsorption equilibrium and thermodynamic studies were studied.

II. MATERIAL AND METHODS

2.1. Preparation of adsorbent:

The low-cost agricultural adsorbents were prepared from leaves of *Rauwolfia serpentine* (Sarpagandha) shrub was used. This adsorbent was used without any chemical-treatment for adsorption of heavy metal ions as well as organic dyes.

The mature and fresh leaves of *Rauwolfia serpentine* (Sarpagandha) shrub were collected from college campus and washed thoroughly by distilled water before drying to remove any dust then dried in shadow region [13]. The dried leaves were grinded to fine powder [14]. The homogeneous powder was obtained by passing through mesh of desired particle size (40 – 70 μm). The homogeneous fine powder adsorbent was stored in an air tight container for the adsorption study for further experiments.

2.2. Preparation of adsorbate:

Stock solution of analytical grades of copper sulphate was prepared by dissolving an adequate amount of the substance in distilled water solution of concentration 100 mg/L and standardized. Different concentrated solutions were obtained by diluting the stock solution. The concentrations of Cu (II) metal ion were measured at the wavelength of their maximum absorbance (λ_{max}) that was determined by UV-Visible single beam Spectrophotometer, (Bio-Era: Cal No.BI/CI/SP/SB-S-03). The pH of the Cu (II) metal ion solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH solution and measurement was done by digital pH-meter.

III. EXPERIMENTAL METHODOLOGY

Batch adsorption techniques was used to investigate the adsorption of Cu (II) metal ions from aqueous solution. The SLP with different adsorbent dose (0.25, 0.50, 0.75 and 1.0 gm) were added in each separate conical flask containing 50 mL of 100 mg/L Cu (II) solution. After adsorption time solution was filtered and 10 ml of sample solution was transferred to 100 ml beaker; and 5 ml of 25 % aqueous citric acid solution was added to it. The solution was made slightly alkaline by the addition of dilute ammonia solution and then boiled to remove excess of ammonia. 15 ml of 4% EDTA solution was added then it was cooled to room temperature and transferred to a separating funnel. 10 ml of 0.2 % aqueous sodium diethyl di-thiocarbamate solution was added with constant shaking for 45 seconds. A yellow brown colour was developed into the solution.

20 ml of butyl acetate (ethanoate) was added into the funnel and the solution shakes for 30 seconds. The organic layer acquires yellow coloration. The whole content agitated for 15 seconds the phase obtained were allowed to separate. The lower aqueous layer was removed. 20 ml of 5 % sulphuric acid (v/v) was added with constant shaking for 15 seconds, it was cooled thus separate organic phase. The absorbance was determined at 560 nm. The operating parameters for each set of experiment are summarized in "Table: 1".

Table 1: Variation of experimental operating parameters

Parameters	Values Investigated
Contact time in min.	10, 20, 30, 40, 50, 60 and 24hrs.
Amount of adsorbent gm/50ml	0.5, 1.0, 1.5, 2.0
Initial concentration of Cu (II) solution (mg/L)	25, 50, 75, 100
Adsorption temperature (K)	305.2, 310.2, 315.2, 320.2, 325.2
pH	2, 3, 4, 5, 6, 7, 8, 9, 10, 11

The amount of Cu (II) metal ions adsorbed (mg/g) was calculated using the formulae reported by Vanderborcht and Van Griekenm, and then the kinetic adsorption parameters were calculated.

$$q = \frac{V(C_0 - C_t)}{M} \quad (1)$$

Where, ' q ' is the amount of Cu (II) metal ions adsorbed from the solution (mg/g), ' C_0 ' is the concentration before adsorption (mg/L), and ' C_t ' is concentration after adsorption. ' V ' is the volume of adsorbate (L) and ' M ' is the weight of the LSP adsorbent (gm).

The percentage adsorption of Cu (II) metal ions was calculated by following equation;

$$\text{Percentage adsorption} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (2)$$

Where, ' C_0 ' and ' C_e ' are the initial and equilibrium concentrations respectively.

IV. RESULTS AND DISCUSSION

4.1. Effect of contact time:

The effect of contact time on the removal of Cu (II) metal ions from the aqueous solution using SLP adsorbent was studied. The results are shown in "Fig.1". The rate of adsorption of Cu (II) metal ions was found to be quite rapid. A series of experiments were carried out to establish the equilibrium time for the effective removal of Cu (II) ions using the adsorbent. By fixing the adsorbent dosage, batch experiments were carried out at changing interval times. From the graph results obtained 71.71 % of removal of Cu (II) metal ions was found at time of 60 mints.

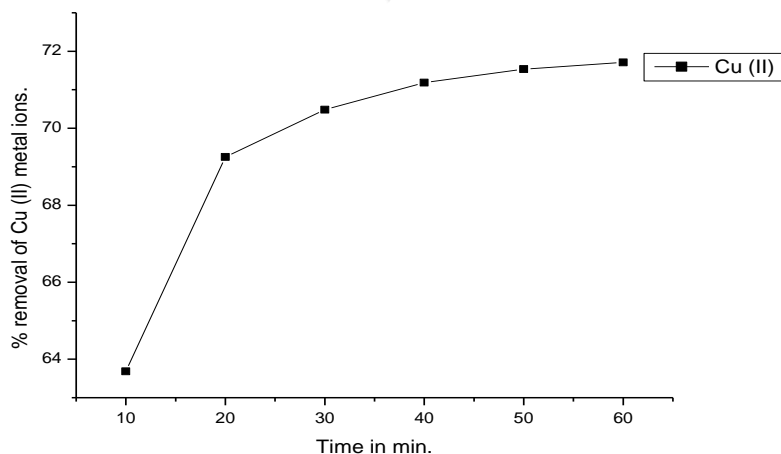


Fig.1: Effect of contact time on the removal of Cu(II) using the SLP adsorbent.

4.2. Effect of initial metal ion concentration:

An adsorption study was carried out to fix the initial concentration by changing the metal ion concentration and by constant adsorbent dosage, pH and contact time. A series of Cu (II) metal ion concentration 25, 50, 75 and 100 ppm were mixed in

separate flasks with 1.0 g of SLP adsorbent. This mixture was agitated for 60 min at a pH of 6.1. The results obtained are shown in “Fig.2”. From the graph results was clear that the removal of Cu (II) ions from aqueous solution decreases as the Cu (II) ion concentration increases. It is due to the lack of adsorption sites in the SLP adsorbent. The maximum removal of Cu (II) ions was found at metal ion concentration of 10 ppm.

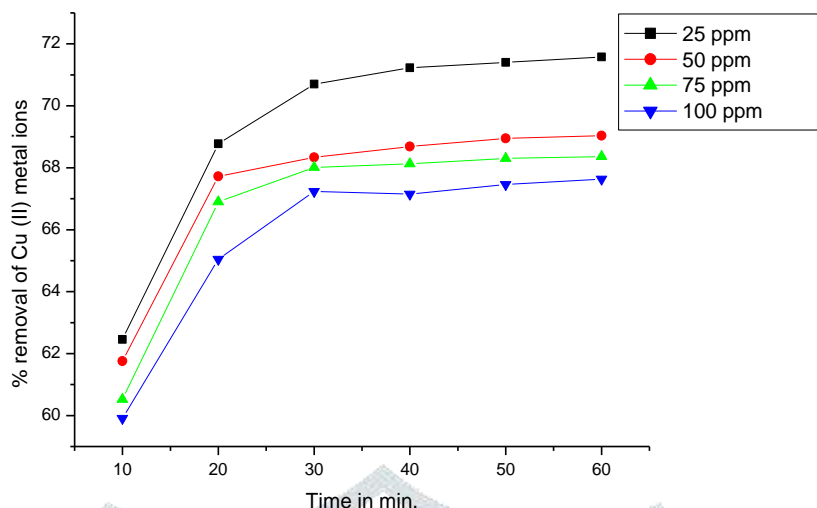


Fig. 2 Effect of initial metal ion concentration on the removal of Cu(II) using the SLP adsorbent.

4.3. Effect of adsorbent dosage:

A series of experiments were carried out to ascertain the adsorbent dose for the efficient removal of Cu (II) ions by the SLP adsorbent. The experiments were conducted by 0.5, 1.0, 1.5 and 2.0 g of the adsorbents for batch studies. The results obtained are shown in “Fig.3”. From the graph, it was found that removal of Cu (II) ions from aqueous solution was effective for 2.0 g SLP and similar was fixed as optimum adsorbent dosage.

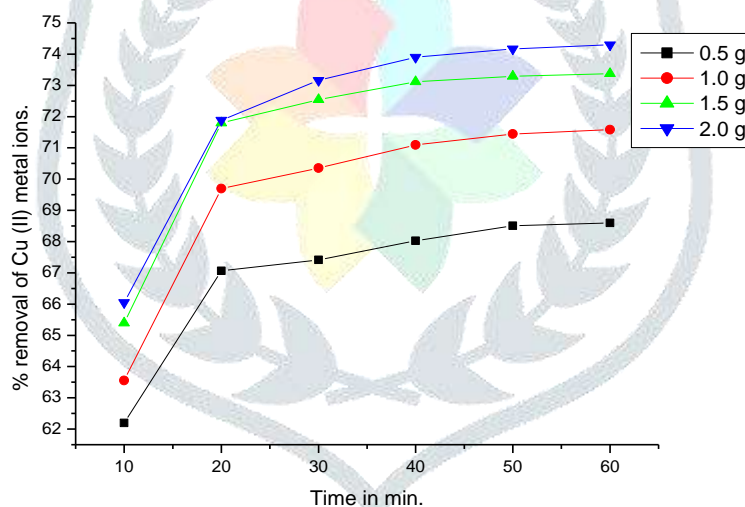


Fig. 3 Effect of adsorbent dosage on the removal of Cu(II) using the SLP adsorbents

4.4. Effect of pH:

Uptake of Cu (II) metal ions by adsorbents is significantly influenced by pH of the solution. Since pH determines the surface charge of the adsorbent and degree of ionization and speciation of adsorbate. The results obtained are shown in “Fig. 4”. As the pH of the solution increased, a significant increase in the equilibrium capacity of Cu (II) removal by the SLP adsorbents was observed from the graph. As a higher initial pH (>8), precipitation of Cu (II) ions was found. From the graph, it was clear that the adsorption was effective at pH value of 6 with the SLP adsorbent used. pH 6 was fixed as optimum pH for the present study.

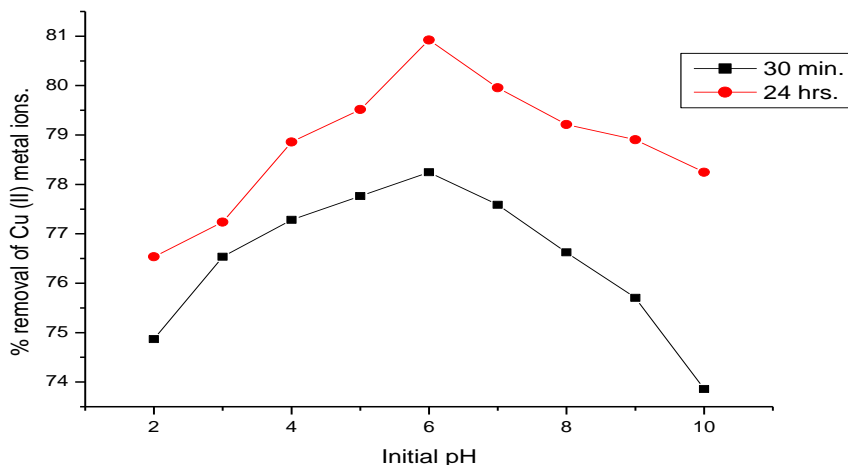


Fig. 4 Effect of pH on the removal of Cu(II) using the SLP adsorbent.

4.5. Effect of temperature:

The effect of temperature on the removal efficiency of Cu (II) metal ions from the aqueous solution using SLP adsorbent was studied. The results are shown in Fig.5. A series of experiments were carried out to establish the equilibrium temperature for the effective removal of copper ions using the SLP adsorbent. By constant adsorbent dosage, contact time, pH and initial concentration, batch adsorption experiments were carried out at different temperatures. From the graph 67.06 % of removal of Cu (II) metal ions was found at a temperature of 305.2 k. Optimum conditions for the removal of Cu (II) ions from aqueous solutions are presented in “Table:3”.

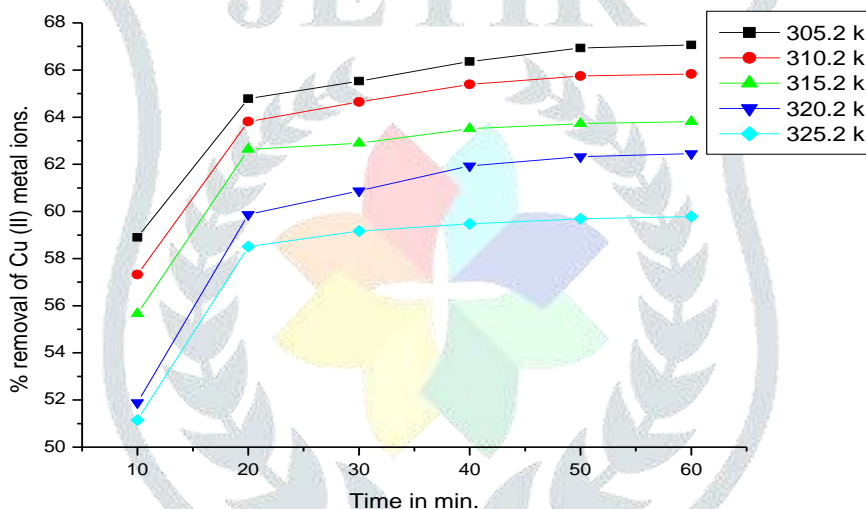


Fig. 5 Effect of temperature on the removal of Cu(II) using the SLP adsorbent.

Thermodynamic Parameters such as Gibb's free energy change ΔG^0 , enthalpy change ΔH^0 and entropy change ΔS^0 were determined using the following equations [15-18].

$$K_c = \frac{C_{ad}}{C_e} \tag{3}$$

$$\Delta G^0 = - RT \ln K_c \tag{4}$$

Were,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \tag{5}$$

$$\log K_c = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \tag{6}$$

Where, K_c is the equilibrium constant, C_{ad} is the amount of metal ion adsorbed per liter of the solution at the equilibrium, C_e is the equilibrium concentration (mg/L) of the metal in the solution, T is the temperature in Kelvin and R is the gas constant (8.314 J/mole). The values of ΔH^0 and ΔS^0 were determined from the slopes and intercepts of the plot of $\log K_c$ against $\frac{1}{T}$ respectively. Thermodynamic parameter values are shown in “Table 2”.

Table:2. Thermodynamic parameter values with Copper metal ion solution

Temp (K)	ΔG^0 KJ/mole	ΔH^0 KJ/mole	ΔS^0 J/mole
305.2	- 2.180	- 16.067	- 45.523
310.2	- 1.953		
315.2	- 1.725		
320.2	- 1.498		

325.2

- 1.270

The negative value of ΔG^0 confirms that the feasibility of the reaction and spontaneous nature of the adsorption. The ΔG^0 values obtained in this study for the Cu (II) metal ions are < -10 KJ/mole, which indicate that physical adsorption was the predominant mechanism in the adsorption process. The negative value of ΔH^0 suggests that the adsorption to be in agreement with the exothermic nature of interaction. [19, 20]. The negative value of ΔS^0 suggests that the decreased disorder and randomness at the solid solution interface with adsorbent while the adsorption there are some structural changes in the Cu (II) ion and the adsorbent occurs.

V. ADSORPTION ISOTHERMS

The most widely used isotherms for solid-liquid adsorption are the Langmuir and Freundlich adsorption isotherms [21]. Langmuir isotherm model is valid for monolayer adsorption on to surface containing a finite number of identical sites. The data of the equilibrium studies for adsorption of Cu (II) metal ion on SLP follow the following form of Langmuir model.

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_0}\right) * C_e + \frac{1}{bQ_0} \quad (7)$$

Where, C_e is the equilibrium concentration (mg/dm³), q_e is the amount of Cu (II) metal ions adsorbed at equilibrium (mg/g). Q_0 and b are Langmuir constants related to adsorption capacity (mg/g) and energy of adsorption (dm³/mg). The values of Q_0 and b are calculated from the slope and intercept of plot of $\frac{C_e}{q_e}$ against C_e respectively [22, 23]. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L . Which is a dimensionless constant referred to as separation factor or equilibrium parameter [24].

$$R_L = \frac{1}{1+bC_0} \quad (8)$$

Where, C_0 is initial concentration in ppm and b is Langmuir constant related to the energy of adsorption. R_L Value indicates the adsorption nature to be either unfavorable if $R_L > 1$, linear if $R_L = 1$, favorable if $0 < R_L < 1$ and irreversible if $R_L = 0$ [25].

Freundlich adsorption isotherm gives the relationship between the equilibrium liquid and solid phase capacity based on multilayer adsorption.

$$\log \frac{x}{m} = \frac{1}{n} \log C_e + \log K_f \quad (9)$$

The constant K_f is an approximate indicator of adsorption capacity, while $\frac{1}{n}$ is a function of the strength of adsorption in the adsorption process [26]. If $n = 1$ then the partition between the two phases is independent of the concentration. If value of $\frac{1}{n}$ is below one, are it indicates a normal adsorption on the other hand, $\frac{1}{n}$ being above one indicates co-operative adsorption [27]. A plot of $\log \frac{x}{m}$ against $\log C_e$ gives a straight line with an intercept on the ordinate axis. The value of n and K_f can be obtained from the slope and the intercept of the linear plot. The value of n is greater than one ($1 < n < 10$), that means favorable adsorption [28]. Isotherm parameter values are shown in "Table 3".

Table: 3. Isotherm parameter values with Copper [Cu (II)] metal ions.

Adsorbent	Langmuir constants				Freundlich constants		
	Q_0 (mg/g)	b (L/g)	R_L	R^2	n	K_f	R^2
SLP	416.66	0.018	0.357	0.999	1.274	0.00638	0.989

Since R_L values lie between 0 to 1 for Cu (II) metal ion studies indicates that the adsorption of Cu (II) metal ion is favorable. The data reveal that the Langmuir model yields better fit than the Freundlich model. The values of n suggest that deviation from linearity, if $n = 1$ the adsorption is homogenous and there is no interaction between adsorbed species. The values of n greater than unity, ($1 < n < 10$), that means favorable adsorption.[29].

VI. ADSORPTION KINETICS

Pseudo first order kinetic model assumed that the rate of solute up take with time was directly proportional to difference in saturation concentration and the adsorbed amount.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (10)$$

Where, q_t and q_e are the amount of dye removed (mg/g) at contact time t (min) and at equilibrium k_1 is the pseudo first order rate constant (min⁻¹).

After integrating with the boundary conditions at $t = 0$, $q_t = 0$ and at $t = t$, $q_t = k_2$ is equilibrium rate constant for pseudo second order adsorption (g/mg min). q_t and rearranging equation (10), the rate law for a pseudo first order reaction become.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303R} t \quad (11)$$

The plot of $\log(q_e - q_t)$ versus t gave a straight line with slope $-\frac{k_1}{2.303R}$ and intercept $\log q_e$. Removal rate were calculated from the slope and results are given in "Table:2".

Second order kinetic model was

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (12)$$

After integrating with the boundary conditions at $t = 0$, $q_t = 0$ and at $t = t$, $q_t = q_t$ and rearranging equation (12), the rate law for a second order reaction become.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (13)$$

The plot of $\frac{t}{q_t}$ versus t gave a straight line with slope $\frac{1}{q_e}$ and intercepts $\frac{1}{k_2 q_e^2}$ the calculated values of k_2 , q_e values are given in

“Table: 2:.

Table: 4. Comparison of the experiments and the kinetic model of Cu (II) metal ion on SLP adsorbent.

Metal ion	Pseudo-First order			Second order		
	$K_1 (min^{-1})$	$q_e (mg/gm)$	R^2	$K_2 (gm/mg.min)$	$q_e (mg/gm)$	R^2
Cu (II)	0.0306	909.28	0.995	1.089×10^{-3}	714.28	0.999

Present work investigates that the adsorption of Cu (II) on all adsorbents was better represented by pseudo second order kinetics as presented in “Table:4”.

VII. CONCLUSION

The study reveals that SLP can act as good adsorbents for the adsorption of Cu (II) metal ion. The 6.1 is the optimum pH for adsorption. On the basis of above studies, the following conclusions may be drawn. SLP is a non-toxic agricultural material has been successfully used adsorption of Cu (II) metal ion from aqueous solutions. Adsorption of Cu (II) metal ion decreased with increasing temperature, with maximum adsorption of Cu (II) metal ion (67.06 %) at 305.2 K.

Process of adsorptive separation was exothermic in nature and thus lower temperature favors adsorption of Cu (II) metal ion. The kinetics of the adsorption of Cu (II) metal ion was the best described by the second order model. Negative values of ΔG^0 confirms that the feasibility of the reaction and spontaneous nature of the adsorption. The negative values of ΔH^0 and ΔS^0 suggests that the adsorption to be in exothermic nature of interaction and decreased disorder at the solid solution interface with adsorbent. The experimental data for the adsorption of Cu (II) metal ion on SLP fits well for the Langmuir adsorption isotherm model than Freundlich isotherm model. The investigation showed that SLP adsorbent was agricultural waste, abundant, cheap, readily available and environment-friendly effective adsorbent, which could be used as potential adsorbent for adsorption of Cu (II) metal ion from aqueous solution and polluted water.

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