

A Novel Plant-Based Biosorbent for Removal of Copper (II) from Aqueous Solutions: Biosorption of Copper (II) by Dried Plant Biomass

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ABSTRACT: Biosorption effectively removes heavy metal ions by using inexpensive biosorbents. In this study, *Portulaca oleracea* plant waste biomass was used as environmentally friendly biosorbent for the removal of copper ions from aqueous solution. This article includes the study of the effects of various important parameters on the biosorption process. Maximum biosorption was found to occur under slightly acidic conditions (pH 6). Small particle size, moderate agitation speed, and moderate temperature favor the biosorption process. The Langmuir model was most suitable, showing the biosorption capacity to be 85.470 mg/g. Pseudo-second-order model best described the kinetics of the biosorption process. Thermodynamic studies suggested the spontaneous and endothermic nature of biosorption. The results from the present study suggest that copper can be successfully removed from aqueous solution by waste portulaca plant biomass. This new biosorbent has proven to be an efficient, low-cost, environmentally friendly material.

KEYWORDS: Biosorption, copper, isotherms, plant biomass, pseudo second order, thermodynamics

1 INTRODUCTION

Heavy metal contamination of water is a major threat to the ecosystem. To meet quality standards all heavy metals must be removed from the effluents before they are discharged [1]. Copper (Cu) and its compounds are most frequently found in surface water and are spread into the environment by different natural phenomena. Excess copper compounds in the body cause vomiting, diarrhea, stomach cramps, and damage the brain, liver, spleen, kidney, etc. [2]. The presence of high copper content in the body may also have an effect on aging, schizophrenia, mental illness, Indian childhood cirrhosis, and Alzheimer's disease [3–5]. Copper in the blood system may generate reactive free oxygen species and damage proteins, lipids and DNA [6].

Biosorption is an economical and eco-friendly technique which uses biomaterials as sorbents for the removal of various pollutants from water. Biosorbents are easily available, highly efficient, cheap and

environmentally friendly materials. Biomass used for biosorption may be living or dead, while the use of dead biomass or derived products may be easier to use. Using dead biomass for water purification is eco-friendly and economical compared to other sophisticated water treatment technologies. Metal biosorption onto plant-based materials is a complex process. Plant materials displayed good adsorption capacities and some of them were comparable with commercially available activated carbons and synthetic resins. Many easily available low-cost materials, such as rape straw, *Guazuma ulmifolia* seeds, mango peel powder, garden grass, ficus leaves, coffee waste, palm fibers and coconut husk, have been used for adsorption in recent years. Reviews on low-cost adsorbents have also been published recently [7, 8]. In our earlier studies we have used plant-based material for the removal of lead, cadmium and chromium [9–11].

The present study evaluates the use of waste portulaca plant biomass (PPBM), as a low-cost, eco-friendly biosorbent with natural chemical composition for removal of Cu (II) ions from dilute aqueous solution. Portulaca is a small seasonal plant which survives for 3–4 months in summer. It becomes waste afterwards. Using dried portulaca plant powder as metal

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adsorbent for treating wastewater is the novelty of the present work. Experimental data obtained in this study were applied to different kinetic isotherm and thermodynamic models.

2 MATERIALS AND METHODS

All chemicals of analytical reagent grade procured from the standard source were used for different batch experiments. Deionized water was used in all the experiments.

2.1 Preparation of Copper (II) Solution

Stock solution was prepared by dissolving 1000 mg of copper nitrate (Merck) in one liter of deionized water. The stock solution was diluted and used for different concentrations required for the experiments. The pH values of the solution were adjusted in the range of 3–7 for different experiments by adding 1N HCl/1N NaOH.

2.2 Green Preparation of Biosorbent

Portulaca plant waste was collected from the local gardens; the collected material (stem and leaves) was washed thoroughly with water to remove dirt and finally washed with deionized water. Material was dried in the sun for 10 days, and finally in a microwave for about 30 minutes in a LG brand domestic microwave oven (LG microwave appliance model no. MS-285SD; Korea) having a temperature range of 40 °C to 100 °C (magnetrons are set at a frequency of 2450 MHz) at 70 °C. The dried plant material was then ground and sieved to get different size particles (200–600 μm). Powdered material of portulaca plant biomass (PPBM) was kept in airtight containers and used as such without any further chemical treatment.

2.3 Batch Experiments

The experiments were conducted in 250 ml flasks containing 200 ml of test solution on a thermostatic orbital shaker at 300 rpm speed at different temperatures. Test solutions of different desired concentrations (10–250 mg/L) were prepared by diluting the stock solution. A desired amount of biosorbent (0.02–0.2 gm) PPBM was added to different test solutions for different batch experiments. The effect of different parameters, such as solution pH, particle size, agitation speed, contact time, initial metal ion concentration, temperature and dose of PPBM, were investigated by varying only one of the operating conditions at a time while others were maintained constant. These experiments helped us to obtain the optimum condition for each parameter.

The samples were taken out of the test solution after definite time intervals till the equilibrium was reached. The biosorbent was separated by filtration with Whatman filter paper number 41 followed by centrifugation at 3000 rpm for 10 minutes. The concentration of Cu (II) in the filtrate was analyzed using an atomic adsorption spectrophotometer (GBC Avanta). Adsorption data obtained were used for different studies. Blank samples were also run under similar conditions. All the experiments were conducted in triplicate and the mean value (value ranges within ± 2) was used in the calculations.

2.4 Kinetics Experiments

Test solutions with different Cu (II) ion concentrations (10–250 mg/L) were taken using a fixed amount of biosorbent. Experiments were conducted at a fixed temperature (30 °C) at 300 rpm agitation speed. Samples were withdrawn from the solution at definite time intervals until the equilibrium was reached. Data obtained were applied to two different kinetic models.

3 RESULTS AND DISCUSSION

3.1 Effect of pH

For metal biosorption, the pH of the solution is one of the most important parameters, as the pH affects the solution chemistry, dissolution of the metal ions, activity of functional groups present, and the surface properties of the biosorbent. The ionic state of different functional groups and metal ion are also controlled by the pH of the solution [12]. Figure 1 shows the results of different batch experiments conducted by varying the metal ion concentration from 10–250 mg/L, with PPBM dose 0.2 gm and the pH varied from 3–7.

Results indicated that biosorption of Cu (II) increased with an increase in pH from 3–6 and then started decreasing for all the different Cu (II) ion concentrations. These results can be explained by the fact that at low pH, hydrogen ions are the predominant

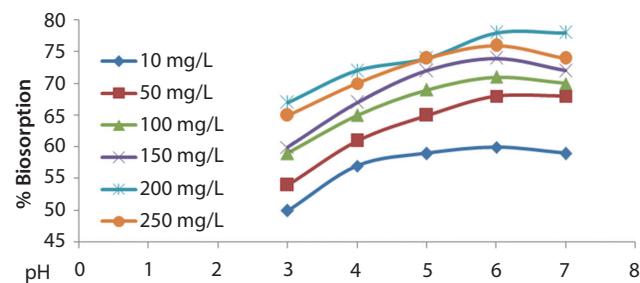


Figure 1 Effect of pH on biosorption.

species, and they compete with dominant metal ion species Cu^{2+} , $\text{Cu}(\text{OH})^+$ and $\text{Cu}(\text{OH})_2$ at the sorption sites, resulting in lower biosorption. In the present study, maximum biosorption of Cu (II) ions occurs at pH 6, so this was taken as an optimum pH and used in all other experiments. As the pH increases, the surface becomes negatively charged and the active sites of PPBM become exposed and facilitate the biosorption of Cu (II) ions on PPBM.

3.2 Effect of Particle Size

Biosorption is a surface phenomenon; smaller particle size of biosorbent provides larger surface area hence influences the uptake of metal ion. Different batch experiments were conducted by using a metal ion concentration of 200 mg/L, PPBM dose 0.2 gm and pH 6 with varying biosorbent particle sizes (200 μm to 600 μm). Results are shown in Figure 2, which shows that smaller particle size has greater biosorption. The smaller particle size offers relatively larger effective surface area and hence higher adsorption occurs at equilibrium. Since 200 μm -sized PPBM particles resulted in higher biosorption of Cu (II) ions from aqueous solution, they were subsequently used in all other experiments.

3.3 Effect of Agitation Speed

Agitation influences the distribution of the solute in the bulk solution and the formation of external boundary film. Biosorption increases with the agitation speed. High speed reduces the boundary-layer resistance and increases the mobility of the system [13]. Experiments were done with varying agitation speed (50–400 rpm), PPBM dose of 0.2 gm and Cu (II) ion concentration of 200 mg/L at pH 6. The effect of agitation speed is shown in Figure 3. Maximum biosorption capacity of PPBM was found to be at 300 rpm and remained constant after that. This speed was considered as optimum speed and maintained for all other experiments.

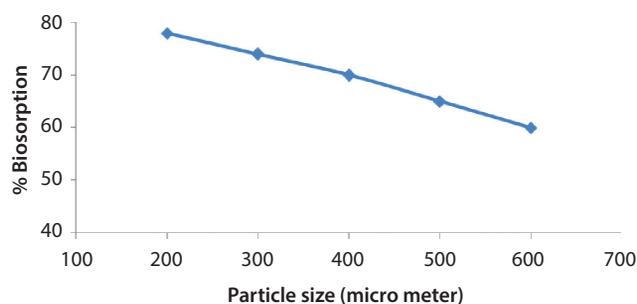


Figure 2 Effect of particle size on biosorption.

3.4 Effect of Contact Time and Metal Ion Concentration

Different experiments were conducted by varying metal ion concentration from 10–250 mg/L and contact time from 15–75 minute, and the PPBM dose was fixed as 0.2 gm. Results are shown in Figure 4, which clearly shows that biosorption increases with an increase in contact time and becomes constant after 60 minutes, showing that equilibrium has been achieved. This time is defined as equilibrium time, which reflects the maximum biosorption capacity of the biosorbent under pre-set operating conditions [14]. Results also indicated that equilibrium time is independent of initial Cu (II) ion concentration. Major biosorption occurs in the initial 15 minutes. This might be due to large numbers of vacant binding sites available in the beginning, initially resulting in rapid biosorption of copper ions.

3.5 Effect of Temperature

Temperature of the solution plays an important role in the biosorption of metal ions. Experiments were done at three different temperatures: 20, 30 and 40 °C. Biosorption of the Cu (II) increases with the increase in temperature, as shown in Figure 5. This shows the endothermic nature of the biosorption process. This increase may be either due to an increase in active binding sites available on the surface or due to a decrease in thickness of boundary layer surrounding

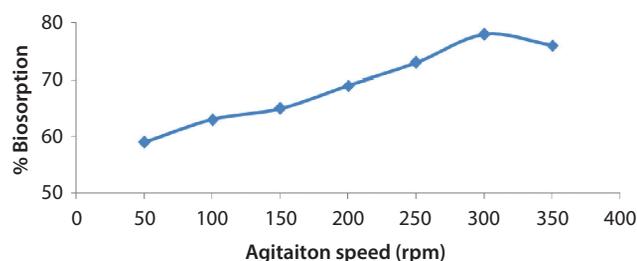


Figure 3 Effect of agitation speed on biosorption.

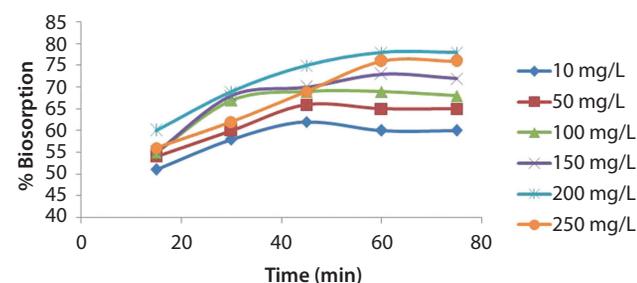


Figure 4 Effect of contact time and metal ion concentration on biosorption.

the biosorbent [15]. Increased temperature may favor the transport of copper ions within the pores of biosorbents [16].

3.6 Effect of Biosorbent Dose

Batch experiments were conducted by varying the biosorbent dose from 0.02 to 0.20 gm. Optimum values for all other parameters were used. The results shown in Figure 6 clearly indicate that the increase in the PPBM dose increases the percentage removal of copper; removal becomes constant after a particular dose (0.2 gm). Increase in the percentage removal of Cu (II) with increased PPBM dose may occur due to the increase in the surface area and in the number of potential binding sites [17].

3.7 Biosorption kinetics

The rate of the uptake of metal ion by the biosorbent is an important parameter; it depends on many factors such as initial concentration of metal ion, interaction between the metal ion and active sites of biosorbent. The kinetics of Cu (II) ions on the PPBM was analyzed using two simple kinetic models: pseudo first order and pseudo second order. Experiments were done to study the rate of the biosorption process and to know the rate controlling step. Two models were applied to the complete range of contact time for different initial copper (II) ion concentrations.

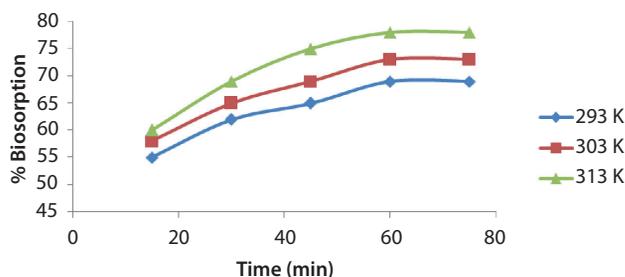


Figure 5 Effect of temperature on biosorption.

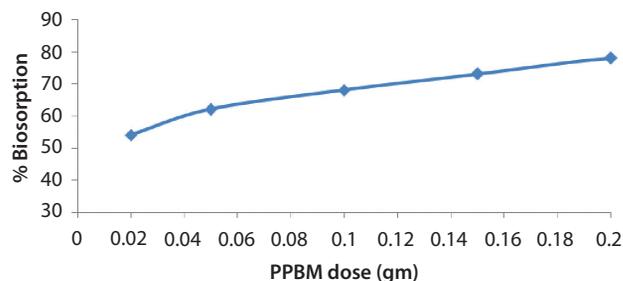


Figure 6 Effect of biosorbent on biosorption.

3.8 Pseudo-First-Order Model

The Lagergren pseudo-first-order model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites [18, 19], i.e., rate of change of solute uptake with time is directly proportional to the difference in the saturation concentration and the amount of solid uptake with time. The general form of this model is expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

where q_e and q_t are amount of metal ion (mg/g) at time t and at equilibrium respectively and k_1 is the rate constant of pseudo-first-order adsorption. The integrated form of the equation is:

$$\frac{q_t}{q_e} = 1 - e^{(-k_1 t)} \quad \text{Or} \quad \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

A graph of $\log(q_e - q_t)$ versus t was plotted and the rate constant k_1 and equilibrium amount of metal ion q_e was obtained from the slope and the intercept of the plot (Figure 7). The calculated value of k_1 was 0.067 min^{-1} and q_e was 106.740 mgg^{-1} respectively. Correlation coefficient for the pseudo first order was 0.9416. Low correlation coefficient value showed that the process of biosorption of copper (II) onto PPBM was not entirely explained by pseudo-first-order kinetic reaction.

3.9 Pseudo-Second-Order Model

The pseudo-second-order model is based on sorption capacity of solid phase:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (3)$$

where k_2 is rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{ min}^{-1}$). The integrated linear form of the equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

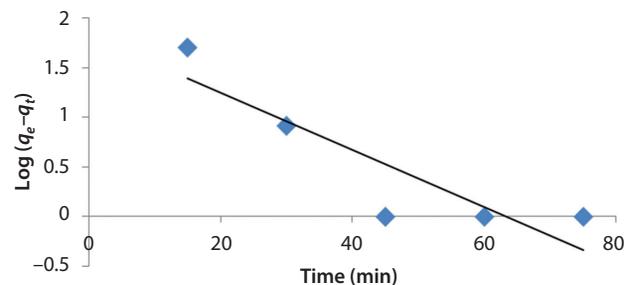


Figure 7 Pseudo-first-order reaction kinetics.

This is the linear form of Ho’s second-order model. The plot between t/q_t versus t shows the kinetic data of adsorption of copper (II) ions on biosorbent. The rate constant k_2 and equilibrium amount of metal ion q_e can be obtained from the slope and the intercept of the plot (Figure 8). The excellent linearity with high correlation coefficient (R^2) 0.999 during the entire process can be properly explained by this model. The values of k_2 and q_e were calculated as $0.001 \text{ g mg}^{-1} \text{ min}^{-1}$ and $169.492 \text{ mg g}^{-1}$ respectively. The calculated values explain that the process favors the pseudo-second-order model in comparison to the pseudo-first-order one.

3.10 Isotherms

An adsorption isotherm is characterized by certain constants; their values express the surface properties and affinity of the adsorbent. The adsorption isotherm indicates distribution of metal ions between the liquid phase and the solid phase at equilibrium.

3.11 Langmuir Isotherm

The Langmuir expression is valid for monolayer adsorption onto a uniform surface with a finite number of identical biosorption sites (homogenous) without any interaction between adsorbed ions [20]. The Langmuir expression is given by the following equation:

$$\frac{1}{Q_e} = \frac{1}{qbC_e} + \frac{1}{q} \tag{5}$$

where Q_e = Cu (II) ions concentration at equilibrium (mg/g);

q = maximum metal uptake per unit mass of PPBM (mg/g) adsorption capacity;

b = Langmuir constant (L) related to energy of sorption;

C_e = Concentration of Cu (II) ions in aqueous phase.

Here b reflects quantitatively the affinity between the PPBM and Cu (II) ions. The values of q and b are

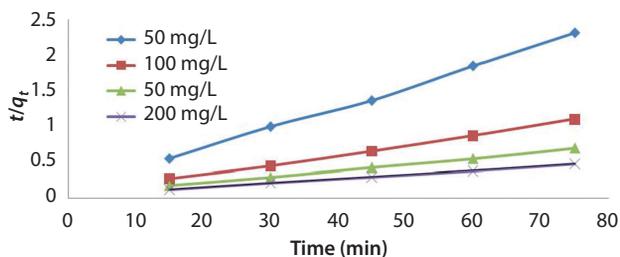


Figure 8 Pseudo-second-order reaction kinetics.

the characteristics of the Langmuir model. They can be determined by linearizing the above equation.

$$\frac{C_e}{Q_e} = \frac{1}{qb} + \frac{1}{qC_e} \tag{6}$$

A plot of $1/Q_e$ versus $1/C_e$ gives a straight line of slope $1/qb$ and intercept $1/(q)$. The value of Q_e is given from the following equation:

$$Q_e = (C_i - C_e) / (m / v) \tag{7}$$

where C_i = initial concentration of Cu (II) ions in the solution (mg/L);

C_e = concentration of Cu (II) ions at equilibrium;
 v = initial volume of Cu (II) ions solution used (L);

m = mass of PPBM used (g).

Figure 9 shows the compiled results for the Langmuir isotherm. The result of regression analysis for calculating the parameters of Langmuir shows that q is 85.470 mg g^{-1} and adsorption equilibrium constant b is 0.008 L mg^{-1} . These values prove that the Langmuir isotherm describes the biosorption phenomenon completely.

The essential features of the Langmuir isotherm can be used to predict the affinity between biosorbent and metal ions; this is expressed in terms of a dimensionless constant called the separation factor or equilibrium parameter R_L , which is indicative of the isotherm shape that predicts whether an adsorption system is favorable or unfavorable. R_L is defined by the following equation:

$$R_L = 1 / (1 + bC_0) \tag{8}$$

where b is Langmuir constant and C_0 is initial concentration of Cu (II) ion. The value of R_L indicates the isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), and unfavorable if ($R_L > 1$) [21]. This factor was calculated for copper ions and was found to be 0.379. From this value it is confirmed that PPBM is a favorable biosorbent for copper ions.

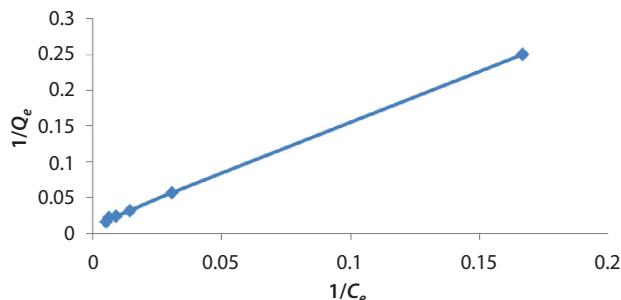


Figure 9 Langmuir isotherm model.



3.12 Freundlich Isotherm

The Freundlich expression is an empirical equation based on adsorption on a heterogeneous surface with the interaction between metal ions and exponential distribution of active sites and their energies. The Freundlich isotherm is:

$$Q_e = KC_e^{1/n} \quad (9)$$

where K = Freundlich constant, indicating the adsorption capacity;

n = Freundlich constant, indicating the adsorption intensity.

The above equation is rearranged in linear form to give:

$$\log Q_e = \log K + 1/n \log C_e \quad (10)$$

From the plot of $\log Q_e$ versus $\log C_e$, K and n are determined from the intercept and slope respectively. K is a constant related to the bonding energy, $1/n$ is the heterogeneity factor and n is a measure of the deviation from linearity of biosorption. The value of n indicates the degree of nonlinearity between solution concentration and biosorption. Value of K is 1.052 mg g^{-1} and value of n is 1.321, indicating physical biosorption of copper ions on PPBM. The result is represented in Figure 10.

The calculated values of different constants shown in Table 1 indicate that PPBM is a good biosorbent for the uptake of copper ions from aqueous solution. These results showed that the equilibrium biosorption data conformed well to all the isotherms; however, higher value of R^2 indicates that Langmuir is the favored model.

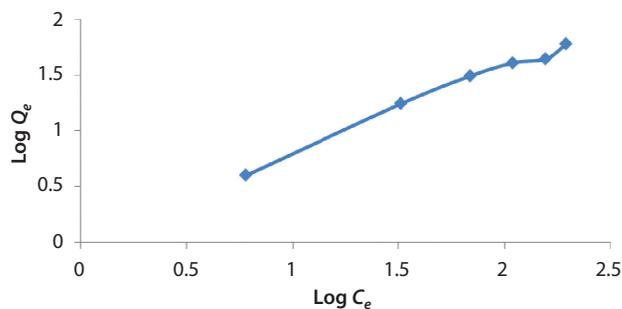


Figure 10 Freundlich isotherm model.

Table 1 Calculated values for different isotherm models.

Langmuir			Freundlich		
q	b	R^2	K	n	R^2
85.740 mg g^{-1}	0.008 L mg^{-1}	0.9997	1.052 mg g^{-1}	1.321	0.9882

3.13 Biosorption Thermodynamics

Temperature is an important parameter for the biosorption of metal ions when dealing with the thermodynamics of the biosorption process, since it is directly related to the kinetic energy of metal ions. A slight change in temperature should cause a change in the amount of metal removed or sorbed by the biosorbent. Thermodynamic parameters reflect the feasibility and spontaneous nature of the biosorption process.

Energy and entropy can be determined using equilibrium constant (K), which is temperature dependent. The change in temperature causes a change in thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 . These parameters contribute to understanding the biosorption mechanism. The changes in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) associated with the adsorption were determined using the following equations:

$$\Delta G^0 = -RT \ln K \quad (12)$$

where R is universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$) and T is absolute temperature (K). The equilibrium constant may be defined as:

$$K = C_{Ae} / C_e \quad (13)$$

where C_{Ae} and C_e are the equilibrium concentration (mg L^{-1}) of the metal ions on the adsorbent and in the solution respectively.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (14)$$

where ΔG^0 is the change in free energy, kJ mol^{-1} , ΔH^0 the change in enthalpy, kJ mol^{-1} and ΔS^0 is the change in entropy, kJ mol^{-1} .

$$\log K = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \quad (15)$$

A straight line is obtained when $\log K$ was plotted against $1/T$ (Figure 11), slope and intercept gave ΔH^0 and ΔS^0 . The negative value of ΔG^0 (Table 2), indicates the feasibility and spontaneous nature of the

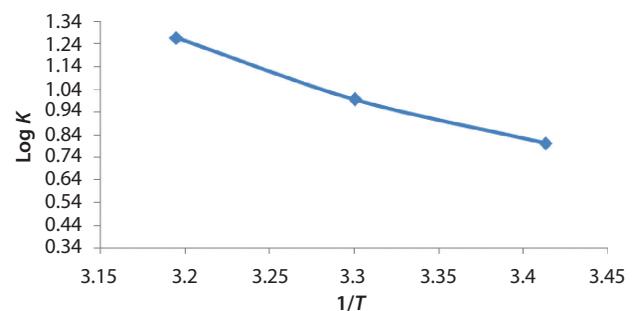


Figure 11 Plot of $\log K$ vs $1/T$.

Table 2 Thermodynamic parameters at different temperatures.

Temperature (K)	K	ΔG (KJ mol ⁻¹)	ΔH (KJ mol ⁻¹)	ΔS (KJ mol ⁻¹)
293	2.23	-1.949	17.710	0.0669
303	2.70	-2.505		
313	3.55	-3.293		

Table 3 Biosorption capacity of different biosorbents used for copper (II) ions.

Biosorbent	Biosorption capacity (mg g ⁻¹)	Reference
Pomelo peel	21.1	[22]
Teak leaves	23.0	[23]
Water hyacinth	99.42	[24]
Watermelon shell	111.10	[25]
Banana peel	20.37	[12]
Paper mill waste	5.5	[26]
Coffee waste	70.00	[13]
Peanut shell	25.4	[17]
Wheat bran	24.5	[27]
Mangrove barks	6.95	[28]
Chestnut shell	12.56	[21]
Hyacinth roots	22.7	[29]
<i>Pinus sylvestris</i> biomass	28.83	[30]
Pomegranate peel	1.32	[31]
Present study	85.470	

biosorption. This also showed that the material used has higher affinity at higher temperatures. The positive value of ΔH^0 indicates that biosorption of Cu (II) on material is an endothermic process. The positive value of ΔS^0 shows that there is an increase in randomness at the solid/solution interface during the process. It also reflects the affinity of the biosorbent for copper ions and suggests some structural changes in biosorbent and copper ions.

4 CONCLUSIONS

Raw material PPBM obtained from *Portulaca oleracea* waste plant biomass used in the present study has been shown to have fairly high adsorbent capacity for copper metal ion and has proved to be an effective adsorbent for copper ions from aqueous solution without any pretreatment. The adsorption process is found to be dependent on various process parameters such as pH, particle size, agitation speed, contact time, metal ion concentration, temperature and adsorbent

dose. The maximum adsorption was at pH 6 and equilibrium was achieved in 60 minutes. Biosorption increased with decreasing particle size of PPBM material. Kinetic studies showed that biosorption followed pseudo-second-order model. Experimental equilibrium data conformed well to both the isotherm models but data were better represented by the Langmuir model and the sorption capacity of plant biomass was found to be 85.470 mg g⁻¹. Thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 (free energy change, enthalpy, and entropy) were also evaluated and it was found that the biosorption was spontaneous and endothermic in nature.

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