Research Article [Araştırma Makalesi]



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# Biosorption studies for removal of Cu (II) ions onto Saccharum bengalense an efficient and eco-friendly biosorbent

[Etkili ve çevre dostu bir biyoabsorban olan Saccharum bengalense'nin üzerindeki Cu (II) iyonlarının uzaklaştırılması için biyoabsorbsiyon çalışmaları]

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#### ABSTRACT

Objective: In this research work, a low-cost biosorbent derived from the pulp of Saccharum bengalense (SB) was used as an adsorbent material for the removal of Cu (II) ions from aqueous solution

Methods: A batch adsorption method was experimented for biosorptive removal of copper ions from the aqueous solution.

Results: Nearly 90% removal of copper is possible at initial pH 6.0, under the batch test conditions. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) adsorption isotherms have been applied to describe the biosorption of Cu (II) by SB. It was found that biosorption of Cu (II) by SB followed Langmuir and Freundlich model. The monolayer adsorption capacity of SB as obtained from Langmuir isotherm at 40 °C was found to be 10.42 mg/g at 323K. The Cu (II) adsorption data was analyzed by applying pseudo-first-order and pseudo-second-order kinetic models. The intra- particle diffusion model was applied to investigate the rate-determining step. It was found that the biosorption of Cu (II) ions on SB followed pseudo second-order rate kinetics. Thermodynamic parameters such as free energy change ( $\Delta G^{\circ}$ ), enthalpy change ( $\Delta H^{\circ}$ ) and entropy change ( $\Delta S^{\circ}$ ) have been calculated respectively revealed the spontaneous, feasible and endothermic nature of adsorption process.

Conclusion: The results of the present investigation suggested that biosorbent SB can be used as an economically feasible and environmentally friendly biosorbent for the removal of Cu (II) from aqueous solutions.

Key Words: Isotherms, Saccharum bengalense, kinetics, thermodynamics, low cost Conflict of Interest: Authors have no conflict of interest.

# ÖZET

Amaç: Bu araştırma çalışmasında, sulu çözeltiden Cu (II) iyonlarının uzaklaştırılmasında, adsorban madde olarak Saccharum bengalense (SB) lizatından elde edilen düşük maliyetli bir biyosorban kullanılmıştır.

Metod: Sulu çözeltiden bakır iyonlarının uzaklaştırılmasında bir grup adsorbsiyon yöntemi denenmistir.

Bulgular: Test koşulları altında başlangıç pH'sı 6.0 olduğunda bakırın yaklaşık %90'ının uzaklastırılması mümkün olmustur. Cu (II)'nin SB tarafından biyoabsorbsiyonunu tanımlamak için Langmuir, Freundlich ve Dubinin-Radushkevich (D-R) adsorbsiyon izotermleri uygulanmıştır. Cu (II)'nin SB tarafından biyoabsorbsiyonunun Langmuir ve Freundlich modelini takip ettiği gösterilmiştir. Langmuir izoterminden 40 °C'de elde edilen SB'nin tek katmanlı adsorbsiyon kapasitesi 323K'de 10.42 mg/g olarak bulunmuştur. Cu (II) adsorbsiyon verileri, pseudo-first-order ve pseudo-second-order kinetik modelleri kullanılarak analiz edilmiştir. Hız kısıtlayıcı basamağı belirlemek amacıyla partikül için difüzyon modeli uygulanmıştır. SB üzerindeki Cu (II) iyonlarının biyosorbsiyonunun, pseudo-second-order hız kinetiklerini izlediği bulunmuştur. Serbest enerji değişimi ( $\Delta G^{\circ}$ ), entalpi değişimi ( $\Delta H^{\circ}$ ) ve entropi değişimi ( $\Delta S^{\circ}$ ) gibi termodinamik parametreler hesaplanarak, adsorbsiyon sürecinin sırasıyla spontan, uygulanabilir ve endotermik doğasını ortaya çıkartmıştır.

Sonuç: Bu araştırmanın sonuçları, sulu çözeltilerden Cu (II)'ın uzaklaştırılmasında biyoabsorban SB'nin, ekonomik olarak uygulanabilir ve çevreye dost bir biyoabsorban olarak kullanılabileceğini önermiştir.

Anahtar Kelimeler: İzoterm, Saccharum bengalense, kinetik, termodinamik, düşük maliyet Çıkar Çatışması: Yazarların çıkar çatışması yoktur.

# Introduction

Higher concentration of heavy metals caused contamination of water bodies. The most commonly encountered heavy metals in water bodies are arsenic, cadmium, mercury, nickel, lead, chromium and copper. Aquatic life is destroyed due to anthropogenic sources like industrial, domestic agricultural and mining activities of man. Copper is an essential nutrient to humans and also biocidal to certain organisms. Copper in high concentrations (>5mg/L ) in water is a serious environmental pollutant and can be toxic to aquatic species [1]. The major contributors of higher concentrations of Cu (II) in water bodies are the industrial metal used for electrical wiring, wood pulp production, plumbing, board mills, air conditioning tubing and roofing etc. Convential methods like adsorption, ion exchange, reverse osmosis, evaporation, membrane filtration and chemical precipitation for removing metal ions from waste waters suffer from drawbacks such as the disposal of the residual metal sludge, high capital and operational cost [2]. Natural plant based biomaterials and are accessible in huge quantities have potentials as alternate and cost effective sorbents [3].

Saccharum bengalense (SB) ('Kana' or 'Sarkanda' in urdu) is distributed from north and North West India to Pakistan and Afghanistan [4]. A valuable fiber biomass in large quantities can be extracted from the upper leafsheaths of the flowering Culm that may offer a good basis for the selection of SB economic and alternative biosorbent. The aim of the present research work is to investigate the biosorption capacity  $q_e(mg/g)$  of SB for Cu (II) metal ions. The Cu (II) adsorption data was analyzed by applying pseudo-first-order and pseudo-second-order and intra- particle diffusion. Mechanism of adsorption was explained by applying adsorption isotherms.

# **Materials and Methods**

# Biosorbent-Saccharum bengalense

The biosorbent SB was collected in the form of large pieces from the bank of the river Satluj, Bahawalpur, Pakistan. To remove dust or other particles, these large pieces were washed with deionized water and dried under shade then were knife-milled. The particles size 100µm were obtained. Finally the samples were oven dried (at 333 K) and stored in air tight plastic bottles and labeled as SB and were used without any chemical treatment [5].

# Copper synthetic wastewater

Analytical grade Cu  $(NO_3)_2$  supplied by Merck was used as an adsorbate. The stock solution of Cu (II) was prepared by dissolving desired amount of Cu  $(NO_3)_2$  in 1000 mL of distilled water. The standard solution of different concentrations of Cu (II) was prepared by appropriate dilution of stock solution.

# Batch adsorption procedure

Batch adsorption experiments were carried out in a se-

ries of Erlenmeyer flasks of 250 mL capacity, sealed with glass stoppers and para film to prevent contamination. The effect of influencing factors, such as adsorbent dosage, effect of pH, time and temperature were studied. For each experiment, 50 mL solution containing Cu metal ions, of known concentration, was used. For adsorption isotherms, Cu containing solutions of different known concentrations  $C_0(mg/L)$  were agitated with a known amount of adsorbent until equilibrium was achieved. The kinetics of adsorption were determined by analyzing adsorptive uptake (q, mg/g) of the Cu (II) ions from the aqueous solutions at different time intervals. All experiments were performed in triplicate and an average of three values reported. The deviation was found to be 2% of the average value. After the equilibrium period, the suspensions were filtered via filter paper Whatman 42. The concentrations of Cu metal ions were determined by atomic absorption spectrometry. A Perkin-Elmer 2380 Atomic Absorption Spectrophotometer, with air-acetylene flame, was used for the determination of copper concentration.

The percentage removal efficiency of adsorbent (%R) for copper metal was calculated as follows:

% Removal (R %) = 
$$\left(\frac{C_o - C_e}{C_o}\right)$$
 X 100 (1)

The adsorption capacity of SB for copper metal at equilibrium  $q_a$  (mg/g) was calculated as follows:

$$q_{e}(mg/g) = \left(\frac{C_{o} - C_{e}}{m}\right) V$$
(2)

The amount of Cu metal adsorbed onto SB biomass at any time t,  $q_{\rm c}$  (mg/g) was calculated as follows:

$$q_t(mg/g) = \left(\frac{C_o - C_t}{m}\right) v \tag{3}$$

Where  $C_0$  is the initial copper ions concentration (mg/L),  $C_e$  is the concentration of copper ions at equilibrium (mg/L),  $C_t$  is the concentration of copper metal ions at time t (mg/L). V is the volume of solution in liters (L) and m is the amount of biomass SB powder in grams (g).

# Characterization of Biosorbent

The biomass SB was characterized by elemental analysis, FT-IR and BET surface area analysis.

# Elemental analysis

An elemental analysis was accomplished by *Perkin Elmer* 2400 Series II CHNS/O Elemental Analyzer using sulfanilamide as the standard.

# Surface area analysis

BET surface area and single point surface area of SB was determined from the  $N_2$  adsorption isotherm at 77 K in the range of relative pressure  $10^{-6}$  to 1.0 with a surface area and pore size analyzer (Autosorb 1, Quantachrome Instruments).

# **IR-Analysis**

A potassium bromide (KBr) disc method was used to scan the FTIR spectra in 4000-600 cm<sup>-1</sup> ranges by using FTIR spectrophotometer (Tensor 27, Bruker Germany).

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Figure 1. (a) FTIR of SB (b) Cu-loaded SB.

# **Results and Discussion**

#### Characterization of SB

SB composed of cellulose molecules and surrounded by hemicellulosic materials (glucomannans, galactans, and arabogalactans), ligninand pectin [5]. The results of elemental analysis showed that SB contain 41.23% of Carbon, 4.2% of nitrogen and 0.9% of Hydrogen [6]. The BET surface area and single point surface area of SB was measured 9.43 m<sup>2</sup>/g and 5.78 m<sup>2</sup>/g, respectively [5-6].

In the FT-IR spectrum of SB, from Figure 1a, the intense peak at 1039 cm<sup>-1</sup> along with the weak peak at 1240 cm<sup>-1</sup> and the shoulder at 1159 cm<sup>-1</sup> are C-O stretching vibration of ethers and alcohols. The band at 1601 cm<sup>-1</sup> is due to carbonyl groups of aldehydes and ketones. The absorption band at 1730 cm<sup>-1</sup> is attributed to the vibrations by carbonyl groups of ester and carboxylic acid groups [7]. The single peak at 2913cm<sup>-1</sup> is due to C-H stretching vibration of CH, CH<sub>2</sub> and CH<sub>3</sub> groups present in lignin. The broad band centered at 3356 cm<sup>-1</sup> is a characteristic band of O-H stretching vibration. Thus, SB mainly consists of compounds having oxygen containing functional groups [6,8]. Comparing and assignments of SB FT-IR spectra before and after Cu (II) adsorption is too important to indicate the functional groups responsible for Cu (II) binding. Regarding FT-IR for SB after Cu (II) uptake, it was found that oxygen containing functional groups like phenolic –OH, carboxy –COOH and methoxy –OCH<sub>3</sub> groups are affected after uptake process as shown in figure 1b. This was confirmed from shifts in their position or band intensity from 3359 cm<sup>-1</sup> to 3345 cm<sup>-1</sup>, 2913 cm<sup>-1</sup> to 2926 cm<sup>-1</sup>, 1039 cm<sup>-1</sup> to 1035 cm<sup>-1</sup> and from 1730 to 1603 cm<sup>-1</sup> [6-7,9].

# Effect of the adsorbent dosage

Amount of adsorbent is an important factor affecting  $Cu^{2+}$  adsorption process, as it specifies the adsorbent capacity for a typical concentration of contaminant. Figure 2a showed that with increase in the adsorbent dosage, from 0.1 to 1.0 g / 50mL, the amount of adsorbed Cu (II) ions



Figure 2. (a) Effect of adsorbent dose, (b) Effect of pH Effect; for biosorption of Cu (II) ions on SB at 50 °C.

increases from 71% to 91%. The extent of adsorption increased with the increase in adsorbent dosage due to availability of more adsorption sites on SB [10-11].

On the other hand, further increase in adsorbent amount from 1.1-2.0 g/ 50 mL, the amount of adsorbed Cu (II) ions decreases from 85% to 72%. This decrease may be due to the overlapping or aggregation of adsorption sites also the time required to reach the equilibrium decreased at higher doses of SB [6]. It is obvious that the amount of SB for further adsorption experiments was selected as 0.5 g /50mL. Similar results have been reported by a number of earlier researchers studying Cu metal biosorption on different biosorbents [31-34].

#### Effect of pH

In this study, the effect of pH in the solution on biosorption of copper by SB was studied at pH range 2-10 with the adsorbent dose of 0.5 g /50mL. It was observed that biosorption of copper by SB was highly pH dependent. From Figure 2b, it is clear that the maximum removal was 88% at pH 6. Increased in percentage removal effeciency of Cu ions in acidic conditions is due to the fact that as the pH of the medium is increased, the competition between Cu (II) ions and H<sup>+</sup> ions decreases as a result Cu<sup>+2</sup> ions adsorb on the SB surface [12]. Above pH 6.0, Cu (II) ions react with hydroxide ions and precipitate as copper hydroxide [10]. The optimum pH for further adsorption experiments was selected as 6.0. Similar results have been reported by a number of earlier researchers studying Cu metal biosorption on different biomasses [29-36].

# Effect of contact time: Adsorption Kinetics

Effect of contact time for biosorption of  $Cu^{+2}$  ions on SB was carried out from 10-80 minutes. For Cu (II) ions, the maximum percentage removal efficiency was 87% at 30 minutes. The percentage removal efficiency of  $Cu^{+2}$  ions on SB decreased after 30 minutes. In the beginning the fast adsorption rate is due to fact that at the initial stage more binding sites are available, and the Cu (II) ions can attach easily on these sites. After this, due to slower diffusion of adsorbate, the rate of adsorption become slow [6]. Similar results have been reported by a number of earlier researchers studying Cu metal biosorption on different adsorbents [29-31,35-36]

The efficiency of the biosorption process was determined by applying the pseudo-first-order (PFO), pseudo-second-

| Kinetics Model  | Parameters                    |   |                              |                |
|---|-------------------------------|---|------------------------------|----------------|
| 1. Pseudo-First-order   | q <sub>e</sub> (cal.)<br>mg/g | K <sub>r</sub> (min.⁻¹)                               | q <sub>e</sub> (exp)<br>ma/a | R <sup>2</sup> |
| $\ln (q_e - q_t) = \ln qe - k_f t$  |                               |   |                              |                |
|   | 12.75                         | 0.131   | 4.0                          | 0.409          |
| 2. Pseudo-second-order  | q <sub>e</sub> (cal.)         | K <sub>s</sub> (gmg <sup>-1</sup> min <sup>-1</sup> ) | q <sub>e</sub> (exp)         | R <sup>2</sup> |
| $\frac{t}{a} = \frac{1}{ t  a ^2} + \frac{t}{a}$  | mg/g                          |   | mg/g                         |                |
| $\mathbf{q}_{\mathrm{t}} = \mathbf{K}_{\mathrm{s}} \mathbf{q}_{\mathrm{e}} = \mathbf{q}_{\mathrm{e}}$ | 4.12                          | 0.072   | 4.0                          | 0.999          |
| 3. Intra- particle diffusion Model  | С                             | $K_{id}$ (mg g <sup>-1</sup> min <sup>-1/2</sup> )    | q <sub>e</sub> (exp)         | R <sup>2</sup> |
| $q_t = K_{id} \sqrt{t} + C$   | mg/g                          |   | mg/g                         |                |
|   | 2.8                           | 0.14  | 4.0                          | 0.863          |

Table 1. Kinetics parameters for biosorption of Cu (II) on SB

order (PSO) and intra-particle diffusion kinetic models.

The pseudo-first-order model predict that the adsorption rate is proportional to the number of available sites [13]. Pseudo-second-order (PSO) is based on the assumption that adsorption rate is proportional to the square of the number of unoccupied sites [14]. Simplest and mostly applied linear form of the pseudo-first-order (PFO) pseudosecond-order (PSO) and intra-particle diffusion (IPD) kinetic models are given in equations 4,5 and 6.

$$\ln (q_e - q_t) = \ln q_e - k_f t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{K_{iq_e}^2} + \frac{t}{q_e} \qquad (5)$$

$$q_t = K_{id} \sqrt{t} + C \qquad (6)$$

Where  $q_t$  and  $q_e$  (mg/g) are the amount of Cu<sup>+2</sup> ions adsorbed on per unit amount of SB at time t and equilibrium, respectively; and  $k_f$  (min<sup>-1</sup>) is the pseudo-first-order rate constant of the sorption process.  $k_s$  (mg/g min) is the pseudo-second-order rate constant of the sorption process. kid is the intraparticle diffusion rate constant (mg g<sup>-1</sup> min<sup>-1/2</sup>) and *C* is the intercept.

Linear plots of  $\ln (q_e - q_t)$  versus t can be plotted to evaluate PFO kinetic model and to determine  $q_e$  and rate constant from intercept and the slop, respectively.

The PSO kinetic model parameters  $k_s$  and  $q_e$  can be calculated from the intercept and the slope of the linear plot of t/q, versus t.

If the intraparticle diffusion is involved in the adsorption process then plot of  $q_t$  (mg g<sup>-1</sup>) versus the square root of time ( $t^{1/2}$ ) should be linear and lines pass through the origin [6,15].

To adjudicate which kinetic model is best fitted on experimental data, here are two indicators for pseudo-first-order and, pseudo-second-order kinetic and Intra particle diffusion models, i.e.,  $R^2$  value and comparison of experimental and calculated qe values.

The kinetic parameters for the adsorption of Cu (II) ions onto (S.B) are summarized in Table 1 and shown in Fig. 3(a-c).

From figure 3a and table 1 it is clear that, for pseudo – first- order, calculated  $q_e$  values did not agree well with experimental  $q_e$  values and the value of correlation coefficients ( $R^{2}=0.409$ ) was low.

Results showing that the adsorption of Cu (II) on SB followed the pseudo-second-order kinetic model at all time intervals. The calculated  $q_e$  (4.1 mg/g) value agrees with experimental  $q_e$  (4.0 mg/g) value and the correlation coefficient (R<sup>2</sup>= 0.999) value for the pseudo-second-order kinetic plots were closed to unity as shown in Fig.3 (b).

The correlation coefficients ( $R^2 = 0.863$ ) for the intra-particle diffusion model are lower than that of the pseudosecond-order kinetic model, whereas this model indicates that the adsorption of Cu (II) ions on SB did not follow the intra-particle diffusion model as shown in figure 3(c).As the plots of  $q_t$  (mg g<sup>-1</sup>) versus the square root of time ( $t^{1/2}$ )



**Figure 3. (a)** Pseudo-First-order kinetics model **(b)** Pseudo-secondorder kinetics model, **(c)** Intra-particle diffusion Kinetic model, for biosorption of Cu (II) ions on SB at 50 °C.

did not pass through the origin [7,16].

#### Adsorption Isotherms

Mechanism of biosorption of Cu<sup>+2</sup> on SB surface was analyzed using different isotherm model, Freundlich, Langmuir, and Dubinin–Radushkevich (D-R) isotherm equations.

The Langmuir adsorption isotherm model is based on the assumption that adsorption takes place at specific homogeneous sites within the adsorbent [17].

### Langmurian form [18-19]

$$\frac{c_e}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{c_e}{q_m} \tag{7}$$

Klotz equation [7]

$$\frac{1}{q_e} = \frac{1}{K_L \cdot q_m \cdot C_e} + \frac{1}{q_m} \tag{8}$$

The linear form of the Freundlich adsorption model is [20]

$$\ln q_{e} = \ln K_{F} + \frac{1}{n} \ln C_{e} \tag{9}$$

The linear form of (D–R) isotherm model [21-22] is

$$\ln \mathbf{q}_{e} = \ln \mathbf{q}_{m} - \beta \epsilon^{2} \qquad (10)$$
  

$$\epsilon = RT \ln \left(1 + \frac{1}{c_{e}}\right) \qquad (11)$$
  

$$Es = \frac{1}{\sqrt{2\beta}} \qquad (12)$$

Where  $C_{e}$  (mg/L) was the concentration of Cu (II) at equilibrium,  $q_{e}$  (mgg<sup>-1</sup>) is the adsorption capacity at equilibrium,  $q_{m}$  the monolayer adsorption capacity of the adsorbent (mg g<sup>-1</sup>);  $K_{L}$  the Langmuir constant (L mg<sup>-1</sup>) related to the free energy of adsorption.

The values for these parameters are calculated from Figure 4(a) and are given in Table 2.

 $K_F$  (L g<sup>-1</sup>) and n (dimensionless) are the Freundlich adsorption isotherm constants, being indicative of the extent of the adsorption and the degree of non-linearity, respectively.

Where  $\beta$  is a constant connected with the mean free energy of adsorption per mole of the adsorbate (mol<sup>2</sup> kJ<sup>-2</sup>), ' $\epsilon$ ' is the Polanyi potential and *T* (K) is the absolute temperature. *Es* biosorption mean free energy (kJ/ mol). Hence by plotting ln*q*<sub>e</sub> versus  $\epsilon^2$ , it is possible to generate the value of *q*<sub>m</sub> from the intercept and the value of  $\beta$  from the slope [23].

The graph of lnCe versus  $\ln q_e$  for the adsorption was plotted to generate the intercept value of  $K_F$  and the slope value of *n*, respectively as shown in Figure 4(b).

From figure 4a it is clear that for Langmuir model the calculated  $q_m$  value for SB is comparable with experimental  $q_m$  value. Also on the basis of R<sup>2</sup> value it is indicated that the adsorption of copper onto SB followed the Langmuir isotherm model.

Low R<sup>2</sup> value 0.856 indicates that the adsorption onto the heterogeneous systems is quite unfavorable. The value of 'n' was calculated to be '1.46' for SB.



**Figure 4.** Linear adsorption Isotherm for biosorption of Cu (II) ions on SB (a) Langmuir Isotherm; (b) Freundlich isotherm; (c) Dubbin–Radushkevich (D–R) at 50 °C.

| Table 2. | Adsorption | Isotherms | parameters | for | biosor | ption | of | Cu | (II) | on | SB |
|----------|------------|-----------|------------|-----|--------|-------|----|----|------|----|----|
|----------|------------|-----------|------------|-----|--------|-------|----|----|------|----|----|

| Adsorption isotherm | Constant parameters |                        |        |                         | R <sup>2</sup> |
|---------------------|---------------------|------------------------|--------|-------------------------|----------------|
| Langmuir Isotherm   | q <sub>m</sub>      |                        | K      |                         |                |
|                     | (mg/g)              |                        | (L/mg) |                         |                |
|                     | 10.42               |                        | 0.011  |                         | 0.937          |
| Freundlich Isotherm | Κ <sub>F</sub>      |                        | n      |                         |                |
|                     | 0.302               |                        | 1.555  |                         | 0.825          |
| (D–R) Isotherm      | β                   | q <sub>DR</sub> (mg/g) |        | E <sub>s</sub> (kJ/mol) |                |
|                     | 7.00E-06            | 2.33                   |        | 0.267                   | 0.972          |

For D-R model the calculated  $q_{DR}$  value for SB is 2.4 mg/g, which is not comparable with experimental  $q_{DR}$  value (2.33 mg/g) as shown in figure 4c. On the basis of qDR and  $R^2$  values, it is indicated that the adsorption of copper onto SB did not follow the Dubinin–Radush-kevich isotherm. The mean free energy of biosorption (Es) was found to be 0.267 kJ/mol for SB.

### Effect of Temperature: Thermodynamics

Figure 5 showed that the biosorption of Cu (II) ions by SB observed to be temperature dependent over the temperature range tested (10–50  $^{\circ}$ C). The percentage removal of Cu (II) onto SB significantly increased with increasing temperature. It is due to either higher affinity of SB sites for Cu (II) or an increase in binding sites on biosorbent as a result of reorientation of SB surfaces components.

Thermodynamic parameters such as change in free energy ( $\Delta G^{\circ}$ ), enthalpy ( $\Delta H^{\circ}$ ) and entropy ( $\Delta S^{\circ}$ ) for adsorption of Cu (II) onto SB were calculated using following equations [23-25]

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{13}$$

$$KD = C_{Ac}/C_{e}$$
(14)

$$\Delta G^{\circ} = -RT \ln K_{\rm D}. \tag{15}$$

$$lnK_{D} = \frac{-\Delta G^{0}}{RT} = \frac{-\Delta H^{0}}{RT} + \frac{\Delta S^{0}}{R}$$
(16)

Where KD ( $C_{Ac}/C_e$ ) is the distribution coefficient, *R* is the universal gas constant (8.314 J/mol K), *T* the temperature (K), Ce (mg/L) was the concentration of Cu (II) at equilibrium (mgL-1) and CAc(mg/L) was the concentration of Cu (II) in solution (mgL<sup>-1</sup>). Thermodynamic parameters were calculated by using figure 5 and results were discussed in Table 3.

The negative values of  $\Delta G^{\circ}$  confirm the thermodynamic feasibility of the process and spontaneous nature of adsorption on SB [25-26]. The positive value of  $\Delta H^{\circ}$  (9.936 kJ/mol) indicated the endothermic nature of the adsorption, while the positive values of  $\Delta S^{\circ}$ (0.047 kJ/mol. K) reflected the increase in randomness for solid-solution interface and affinity of the ad-

 Table 3.
 Thermodynamic parameters for sorption of Cu (II) on SB

| 1/T (K <sup>-1</sup> ) | $\ln K_{\rm D}$ | ∆G⁰<br>(kJmol⁻¹) | Parameters                       |
|------------------------|-----------------|------------------|----------------------------------|
| 0.003534               | 1.381           | -3.249           |                                  |
|                        |                 |                  | ∆Hº (kJmol⁻¹)                    |
| 0.003413               | 1.752           | -4.267           | + 9.936                          |
| 0.0033                 | 1.874           | -4.722           |                                  |
|                        |                 |                  | $\Delta S^{0}(kJmol^{-1}K^{-1})$ |
| 0.003195               | 1.780           | -4.631           | +0.047                           |
| 0.003096               | 1.738           | -4.667           |                                  |
| 0.003003               | 1.564           | -4.331           |                                  |



Figure 5. Thermodynamic parameters of activation for biosorption of Cu (II) ions on SB at different temperatures.

#### sorbent material [27,28].

# Comparison of SB for biosorption of Cu with other biosorbents

SB has been compared in terms of biosorption capacity, time of contact and solution pH with other biosorbents in order to observe its potential as an alternative to these materials. Table 4 shows such a comparison [29-36].

# Conclusion

In this research work SB has been investigated as a potential biosorbent for the removal of Cu (II) ions from aqueous solution. Nearly 90% removal of Cu (II) ions is possible at initial pH 6.0, under the batch test conditions. Adsorption Isotherm analysis showed that the biosorption of Cu (II) by SB followed Langmuir model. The kinetic data showed that the pseudo-second-order kinetic model was rate controlling for metal ions adsorption process. The adsorption capacity increased with increase in temperature indicating endothermic nature of adsorption process. It can be concluded that SB is an effective biosorbent for the removal of Cu (II) ions from wastewater.

 
 Table 4.
 Comparison of biosorption performance of SB for Cu (II) ions with some other biosorbents

| Biosorbent                | q <sub>max</sub><br>(mg/g) | рН   | Equilibrium<br>time<br>(min) | Ref.    |
|---------------------------|----------------------------|------|------------------------------|---------|
| Saw dust                  | 1.79                       | 7.0  | 180                          | [29]    |
| Orange Peel               | 3.65                       | 5.92 | -                            | [30]    |
| Aspergillus oryzae        | 4.4                        | 6.0  | 360                          | [31-32] |
| Lignite                   | 6.35                       | -    | -                            | [31]    |
| Powder activated carbon   | 4.45                       | 5.0  | -                            | [33-34] |
| Granular activated carbon | 5.08                       | 5.0  | -                            | [33-34] |
| Ceratophyllum demersum    | 6.17                       | <6   | 20                           | [35]    |
| wheat shell               | 8.34                       | 5.0  | 120                          | [36]    |
| Sacharum bengalense       | 10.4                       | 6.0  | 30                           | Present |
|                           |                            |      |                              | Study   |

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#### **Conflict of Interest**

There are no conflicts of interest among the authors.

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