

# Determination of the Equilibrium, Kinetic and Thermodynamic Parameters of the Batch Biosorption of Copper( II ) Ions onto Chaff

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**Abstract:** A new sorbent system for removing copper ions from aqueous solutions has been investigated. This new sorbent is cereal chaff, an agriculture product in middle-west region in China. Variables of the system include sorption time, pH, chaff dose and solution temperature. The experimental results were fitted to the Langmuir, Freundlich model isotherms to obtain the characteristic parameters of each model. Both the Langmuir and Freundlich isotherms were found to represent the measured sorption data best. According to the evaluation with the Langmuir equation, the maximum sorption capacities of copper ion onto chaff increased from 4.46 to 5.62 mg·g<sup>-1</sup> with temperature increasing from 293 K to 303 K. Using the thermodynamic equilibrium coefficients obtained at different temperatures, various thermodynamic parameters, such as  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ , were calculated. The thermodynamics of copper ion/chaff system indicates spontaneous and endothermic nature of the process. The pseudo first-order and pseudo second-order kinetic models were also applied to experimental data assuming that the external mass transfer limitations in the system can be neglected and biosorption is sorption controlled. The results showed that copper( II ) uptake process followed the second-order rate expression and adsorption rate constants increased with temperature. Using the second-order kinetic constants, the activation energy of biosorption was also evaluated. [Life Science Journal. 2006;3(1):81–88] (ISSN: 1097–8135).

**Keywords:** biosorption; copper( II ); chaff; equilibrium isotherms; kinetics

## 1 Introduction

Sorption has been an effective separation process for a wide variety of applications. Since applying traditional treatment techniques need enormous cost and continuous input of chemicals, which become impracticable, uneconomical, an alternative inexpensive sorbent able to drastically reduce the cost of a sorption system has always been searched. The process of heavy metal removal by biological material is called biosorption. The major advantages of biosorption include: (1) low cost, (2) high efficiency of heavy metal removal from diluted solutions, (3) regeneration of the biosorbent and the possibility of metal recovery. Other advantages of biosorption are that it avoids the generation of toxic sludge and can be used under a broad range of operating conditions (pH, temperature, metal concentration, presence of other ions in the solution, etc). These demands led to increasing interest in biosorption (Drake, 1996; Han, 2000).

In recent years, agricultural by-products such

as wheat shell, rice husk, tree fern have been widely studied for metal removal from wastewater (Teixeira, 2004; Ho YS, 2003; Basci, 2004). In this article, we selected cereal chaff as the biosorbent to adsorb copper( II ) from the aquatic systems. Firstly, chaff contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen etc, which make adsorption processes possible (Han, 2004). Secondly, obtained from agriculture as a byproduct, the chaff yield is vast. Usually, chaff is fed to livestock and poultry and did not have any other use. Biosorption for lead( II ) from aqueous solution by chaff in batch mode has been studied and the chaff can be as a adsorbent to removal lead from aqueous solution (Han, 2005).

The aim of this work was to study the possibility of the utilization of chaff for sorption of copper ions from aqueous solutions. The system variables studied included pH, biomass dose and the initial metal ions concentration at different temperature. The isotherm constants for the Langmuir, Freundlich model have been determined. The ther-

modynamics and kinetic parameters, such as  $\Delta G^0$ ,  $\Delta H^0$ ,  $\Delta S^0$  and  $E_a$ ,  $k_1$ ,  $k_2$  and so on have been calculated.

## 2 Materials and Methods

### 2.1 Preparation of biomass

Fresh biomass of chaff was collected from its natural habitats on the dead millet in the farmland, Luoyang City, Henan Province, China. The raw chaff was washed a few times with distilled water, and dried in an oven at 373 K for a period of 24 hours, then ground and screened through a set of sieves to get different geometrical sizes 104 – 120  $\mu\text{m}$ . This produced a uniform material for the complete set of biosorption tests, which was stored in an air-tight plastic container for all investigations.

### 2.2 Metal solution

The chemicals used for study were analytical grades of copper nitrate ( $\text{Cu}(\text{NO}_3)_2$ ), and nitric acid supplied by Luoyang Chemical Reagent Company (China). The stock solution ( $1000 \text{ mg}\cdot\text{l}^{-1}$ ) of copper was prepared by dissolving the salts in distilled water.

### 2.3 Methods of adsorption studies

The process of experiment was as following: put a certain mass of chaff into conical flasks, added the solute of metals of copper, vibrated for some time, when reaching the biosorption equilibrium, took out the conical flasks, and filtrated to separate the chaff and the solution. The concentration of the free metal ions in the filtrate was analyzed using flame atomic absorption spectrometer (AAS) (AAAnalyst 300, Perkin Elmer, USA). Each procedure was repeated three times and the results given were the average values.

The data obtained in batch model studies was used to calculate the equilibrium metal uptake capacity. It was calculated for each sample of copper by the following equation:

$$q_e = \frac{V(c_0 - c_e)}{m} \quad (1)$$

Where:  $q_e$  is the biomass biosorption equilibrium metal ion uptake amount in  $\text{mg}\cdot\text{g}^{-1}$ ,  $V$  is the sample volume in ml,  $c_0$  is the initial metal ion concentration in  $\text{mg}\cdot\text{l}^{-1}$ ,  $c_e$  is the equilibrium metal ion concentration in  $\text{mg}\cdot\text{l}^{-1}$ , and  $m$  is the dry weight of the biomass in g.

## 3 Results and Discussion

### 3.1 The effect of biosorption time

In this part of experiment, in order to find the time of equilibrium, we studied the effect of time to adsorb copper on chaff. Take 0.08 g chaff to sever-

al conical flasks, added containing metal ions solution 10 ml separately. The concentration of copper was  $20 \text{ mg}\cdot\text{l}^{-1}$ . Then in different intervals we analyzed the concentration of metal ions in the solution. The results were shown in Figure 1. A two-stage kinetic behavior was evident: a very rapid initial sorption over a few minutes, followed by a long period of much slower uptake. As seen from Figure 1, with the beginning of biosorption the uptake of metal ions increased quickly, then 10 minutes later, the change slowed down. So the adsorption of copper on chaff was speedy, and in ten minutes, the reaction of sorption nearly reached equilibrium. After this equilibrium period, the amount of adsorbed metals ions did not significantly change with time. So the removal efficiency was high. Furthermore the adsorption capacity of copper attained  $1.78 \text{ mg}\cdot\text{g}^{-1}$  ( $0.028 \text{ mmol}\cdot\text{g}^{-1}$ ). Hence in the following studies, we selected 30 minutes as the time of adsorption equilibrium.

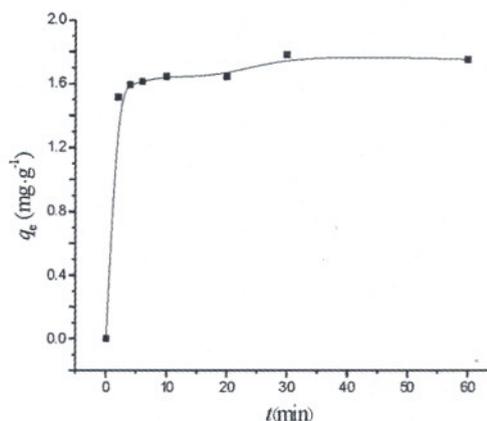


Figure 1. The effect of biosorption time

### 3.2 The effect of biomass dose

In order to find out the effect of biomass dose on biosorption of copper on chaff, studies were carried out in stirred batch experiments using known quantities of the chaff. We did the following experiments. Put different weight chaff into conical flasks, then added the solute of metals in the same concentration, which copper was  $20 \text{ mg}\cdot\text{l}^{-1}$ , and vibrated for 30 minutes. The influence of adsorbent dosage in equilibrium uptake and copper removal is depicted in Figure 2.

The increase in adsorbent dosage from 2 – 12  $\text{g}\cdot\text{l}^{-1}$  resulted in an increase from 50.7% to 77.0% in adsorption of copper(II) ions. This was because of the availability of more and more binding sites for complexation of copper(II) ions. However, copper uptakes showed a reverse trend to the percentage adsorptions (Figure 2). With increasing

adsorbent dosage from 2 to 12  $\text{g}\cdot\text{l}^{-1}$ , the adsorption of copper(II) ion per unit weight of adsorbent decreased from 5.1 to 1.2  $\text{mg}\cdot\text{g}^{-1}$ . There were many factors, which contributed to this adsorbent concentration effect. The first and most important factor was that adsorption sites remain unsaturated during the adsorption reaction. This was due to the fact that as the dosage of adsorbent is increased, there was less commensurate increase in adsorption resulting from the lower adsorptive capacity utilization of the adsorbent. The second cause may be the aggregation/agglomeration of sorbent particles at higher concentrations, which would lead to a decrease in the surface area and an increase in the diffusional path length. Put together, the following experiments were carried as the selected concentration of biosorbent 8  $\text{g}\cdot\text{l}^{-1}$ .

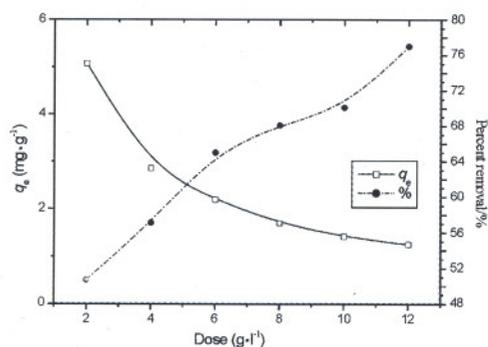


Figure 2. The effect of biomass dose

### 3.3 The effect of pH values

The most important single parameter influencing the biosorption rate and capacity is the pH of the biosorption medium. In order to examine the pH variation as well as its effect on metal ions biosorption in batch, copper ions adsorption experiments were done in the pH ranging from 2.0 to 6.5 at 293 K. The concentration of copper was 20  $\text{mg}\cdot\text{l}^{-1}$ . The adsorptive time was 30 minutes. Figure 3 showed the effect of pH values on adsorption of copper by chaff.

From Figure 3, we observed that the adsorption capacities increased with pH value at the range of 1.8 to 5.2. While, when the value of pH was higher than 5.2, the decrease of adsorption capacities were observed. The reason may be as follows: at very low pH values, the surface of adsorbent would also be surrounded by the hydrogen ions which competed with metal ions binding the sites of the biosorbent. While with the pH values increased, especially when the pH value was above 3.0, and the concentration of proton was very low, the carboxylic acid sites can be appreciably deprotonated,

the effect of proton competition was feeble, and metal ions removal was increased. As for the decrease of adsorption capacities after the pH value of 5.2, it was because when above this pH value, copper ions in solution were in two forms:  $\text{Cu}^{2+}$  and  $(\text{CuOH})^+$ . Since in the later state copper in solution would present a larger size that it would be adsorbed less easily and therefore a diminution in the biosorption capacity would be expected. Furthermore, if the pH value was over 7.0, the ions of copper would deposit, so in the course of experiment, we selected that the pH values near 5.0. Similar results were reported using wheat shell as the biosorbent at pH 2–7 (Basci, 2004).

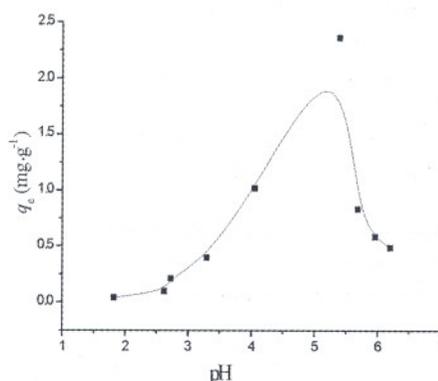


Figure 3. The effect of the value of pH on the biosorption of copper on chaff

### 3.4 The effect of initial copper concentration on temperature-dependent biosorption

The biosorption of copper by chaff at the biomass concentration of 8  $\text{g}\cdot\text{l}^{-1}$  was studied at several different initial metal concentrations ranging from 5  $\text{mg}\cdot\text{l}^{-1}$  to 30  $\text{mg}\cdot\text{l}^{-1}$  of copper at pH 5.0 and 293 K. The result was shown in Figure 4. As seen from Figure 4, equilibrium uptake increased with the increasing of initial metal ions concentrations at the range of experimental concentration. This was a result of the increase in the driving force from the concentration gradient, as an increase in the initial copper(II) ion concentrations. In the same conditions, if the concentration of metal ions in solution was higher, and the active sites of chaff were surrounded by much more metal ions, the reaction of adsorption would be carried out more sufficiently. So as it was observed, the biosorption amount for copper increased with the increase of initial metal ion concentrations.

The equilibrium uptake at different temperatures were also showed in Figure 4 with respect to initial metal ion concentration (5–30  $\text{mg}\cdot\text{l}^{-1}$ ). It was clear that the uptake increased with increasing temperature. The increase of the equilibrium up-

take at increased temperature indicated that the adsorption of copper(II) ions to chaff was endothermic by nature. The endothermic nature of metal adsorption has also been reported previously for adsorptive removal of copper(II) by tree fern (Ho YS, 2003) and wheat shell (Basci, 2004).

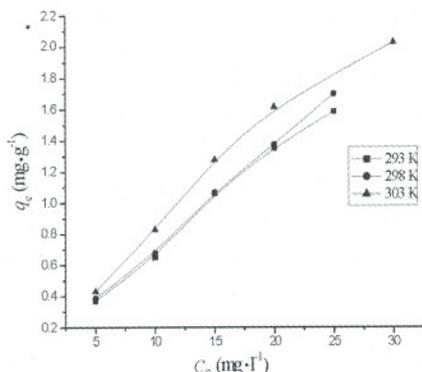


Figure 4. Equilibrium quantities of copper at different initial concentrations at different temperature

### 3.5 Application of adsorption model

Adsorption isotherms show the distribution of solution between the liquid and solid phases. Many different isotherm models have been proposed for the adsorption of solutes in a liquid solution on a solid surface. And it can be described by several mathematical relationships such as the standard Langmuir and Freundlich models. In this article, Langmuir and Freundlich models were both applied to the adsorption data.

Langmuir model is probably the most popular isotherm models due to its simplicity and its good agreement with experimental data. It can be described by the linearized form (Langmuir I, 1916):

$$\frac{1}{q_e} = \frac{1}{K_L q_{max}} \cdot \frac{1}{c_e} + \frac{1}{q_{max}} \quad (2)$$

Where  $q_{max}$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the maximum amount of metal ion per unit weight of chaff and  $K_L$  is the equilibrium adsorption constant.  $c_e$  is the equilibrium metal ion concentration in  $\text{mg} \cdot \text{l}^{-1}$  and  $q_e$  is the biomass biosorption equilibrium metal ion uptake capacity in  $\text{mg} \cdot \text{g}^{-1}$ . By plotting  $1/q_e$  versus  $1/c_e$ ,  $q_{max}$  and  $K_L$  can be determined.

As to Freundlich model, the equilibrium established between the adsorbed metal ions ( $q_e$ ) and that remained free in the solution ( $c_e$ ) is represented by the Freundlich adsorption isotherm, which has the general form (Freundlich, 1906),

$$q_e = K_F \cdot c_e^{1/n} \quad (3)$$

A linear plot of this equation is as the following form,

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (4)$$

This equation gives an intercept  $K_F$  denoting the adsorption and slope, the value of  $1/n$  indicating the intensity of adsorption.

The data obtained in different temperature were applied to the Langmuir and Freundlich model and the results were shown in Table 1.  $SD$  is the residual standard deviation of regressive lines.

Table 1. The application of Langmuir and Freundlich model to the adsorption of copper on chaff at different temperatures

T/(K)	Langmuir constant				Freundlich constant			
	$K_L$ ( $\text{l} \cdot \text{mg}^{-1}$ )	$q_{max}$ ( $\text{mg} \cdot \text{g}^{-1}$ )	R	SD	$K_F$	n	R	SD
293	0.0437	4.46	0.987	0.160	0.188	1.130	0.990	0.097
298	0.0484	4.51	0.982	0.180	0.210	1.134	0.976	0.153
303	0.0533	5.62	0.996	0.074	0.344	1.359	0.975	0.155

From Table 1, as the  $R > 0.97$  and  $SD < 0.2$ , it could be concluded that the adsorption of copper on chaff was both fitted well to Langmuir model and Freundlich model. It could be observed that with the temperature increasing, the value of equilibrium adsorption constant became bigger and the maximum amount of metal ion per unit weight of chaff increased, too. When the temperature was lower than 300 K, the adsorption capacity rose with temperature increase. It could also be observed that with the temperature increasing, the values of  $K_F$  and  $n$  rose. This also indicated that

with the temperature increasing, the ability of adsorption increased. It was consistent with the result obtained from Langmuir model.

$K_F$ , one of the Freundlich constants has been used as a relative measure of adsorption capacity,  $n$ , the other Freundlich constant was related to intensity of adsorption. From Table 1, all measured values of  $K_F$  showed easy uptake of copper with high adsorptive capacity of chaff and significant differences in sorption capacities due to temperature. In general, the values of  $K_F$  increased with temperature from 293 K to 303 K. The obtained values of

$n$  indicated a higher adsorb ability of the copper at all temperatures studied.

While the Freundlich model does not describe the saturation behaviour of the sorbent,  $q_{\max}$ , the mono-component Langmuir constant represents the monolayer saturation at equilibrium or the total capacity of chaff for copper. From Table 1, the values of  $q_{\max}$  increased with temperature till 303 K. At 303 K, the maximum loading capacities of chaff was determined as  $5.62 \text{ mg}\cdot\text{g}^{-1}$ . The other mono-component Langmuir constant  $K_L$  indicated the affinity for the binding of copper. Its value was the reciprocal of the concentration at which half of the saturation of the adsorbent was attained (or copper amount of  $q_{\max}/2$  was bound). A high  $K_L$  value indicates a high affinity. The higher values of  $K_L$  obtained at 303 K also implied the strong bonding of copper to chaff at this temperature. But for adsorption Pb(II) on chaff, the results were inverse to the effect of temperature. The adsorptive capacity decreased which implied the weaker bonding of lead to chaff with temperature increasing (Han, 2005).

### 3.6 Estimation of the specific surface area $S$ of chaff

The solubility of a metal is an essential property to enable the metal to penetrate into the porous structure of chaff. The concentrations of metal species (i. e.  $\text{CuOH}^+$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}(\text{OH})_3^-$ , and  $\text{Cu}(\text{OH})_4^{2-}$ ) were too small to affect the concentrations of  $\text{Cu}^{2+}$  in this study. Although many metal species can be viewed as potential adsorbates in the uptake of  $\text{Cu}^{2+}$  from solution, the data presented in this study suggested that, under experimental conditions ( $\text{pH} = 5.0$ ), the species responsible for the adsorptive removal of  $\text{Cu}^{2+}$  was the predominant one in the species distribution, namely the  $\text{Cu}^{2+}$  (Ho YS, 2003; Basci, 2004). Thus, biosorption could be explained by elucidating the mechanism whereby the  $\text{Cu}^{2+}$  molecules were accommodated by chaff surface.

Monolayer coverage of the surface by the metal ions can be used for the calculation of the specific surface area  $S$  according to following equation (Ho YS, 2003):

$$S = \frac{q_{\max} NA}{M} \quad (5)$$

where  $S$  is the specific surface area,  $\text{m}^2\cdot\text{g}^{-1}$  chaff;  $q_{\max}$  is monolayer sorption capacity, gram metal per gram chaff;  $N$  is Avogadro number,  $6.02 \times 10^{23}$ ;  $A$  is the cross sectional area of metal ion,  $\text{m}^2$ ;  $M$  is molecular weight of metal. For  $\text{Cu}^{2+}$  ion, the molecular weights are 63.5 and the cross sectional

area  $\text{Cu}^{2+}$  has been determined to be  $1.58\text{\AA}^2$  ( $\text{Cu}^{2+}$  radius is  $0.71\text{\AA}$ ) in a close packed monolayer. Therefore, the specific surface areas can be calculated for  $\text{Cu}^{2+}$ . Table 2 listed the  $S$  values at three different temperatures.

**Table 2.** Specific surface areas for copper ion

$T(\text{K})$	$q_{\max}(\text{mg})$	$S(\text{m}^2\cdot\text{g}^{-1})$
293	4.46	0.67
298	4.51	0.68
303	5.62	0.69

From Table 2, the maximum specific surface area of chaff towards  $\text{Cu}^{2+}$  binding was  $0.67 \text{ m}^2\cdot\text{g}^{-1}$ ,  $0.68 \text{ m}^2\cdot\text{g}^{-1}$ ,  $0.69 \text{ m}^2\cdot\text{g}^{-1}$  with the temperature 293 K, 298 K, 303 K, respectively.

### 3.7 $K_R$ values at different initial concentrations

The effect of isotherm shape can be used to predict whether a sorption system is 'favourable' or 'unfavourable' (Ho YS, 2003). The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter  $K_R$ , which is defined by the following relationship (Ho YS, 2003):

$$K_R = \frac{1}{1 + K_L c_0} \quad (6)$$

where  $K_R$  is a dimensionless separation factor,  $c_0$  is initial concentration ( $\text{mg}\cdot\text{l}^{-1}$ ) and  $K_L$  is Langmuir constant ( $\text{l}\cdot\text{mg}^{-1}$ ). The parameter  $K_R$  indicates the shape of the isotherm accordingly:

Values of $K_R$	Type of isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

The values of  $K_R$  at 293 K, 298 K and 303 K were given in Table 3. The  $K_R$  values indicate that sorption was more favorable for the higher initial copper concentrations than for the lower ones. It was apparent that the sorption of copper on chaff was favorable with the conditions used in this study.

### 3.8 Thermodynamic parameters of biosorption

The original concepts of thermodynamics assumed that in an isolated system, where energy cannot be gained or lost, the entropy change was the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change,  $\Delta G^0$ , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if  $\Delta G^0$  is a negative quantity.

**Table 3.**  $K_R$  values based on the Langmuir isotherm

$C_0$ (mg·l <sup>-1</sup> )	293 K	298 K	303 K
5	0.821	0.805	0.790
10	0.696	0.674	0.652
15	0.604	0.579	0.556
20	0.534	0.508	0.484
25	0.478	0.452	0.429
30	0.433	0.408	0.385

Value of  $\Delta G^0$  can be determined from the following equation (Ho YS, 2003; Tewari, 2005)

$$\Delta G^0 = -RT \ln K_L \quad (7)$$

The change of enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) can be obtained from the slope and intercept of a van't Hoff equation of  $\Delta G^0$  versus  $T$  (Tewari, 2005; Aksu, 2002),

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (8)$$

Where  $\Delta G^0$  is standard free energy change, J;  $R$  is universal gas constant, 8.314 J·mol<sup>-1</sup>·K and  $T$  is absolute temperature, K.

Values for the biosorption process obtained from Eq. (7) and Eq. (8) are listed in Table 4.

**Table 4.** The  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$  values of copper and copper adsorption on chaff at different temperatures

$T/K$	293	298	303
$\Delta G^0$ (kJ·mol <sup>-1</sup> )	-19.3	-19.9	-20.5
$\Delta H^0$ (kJ·mol <sup>-1</sup> )		14.6	
$\Delta S^0$ (kJ·mol <sup>-1</sup> K <sup>-1</sup> )		0.116	

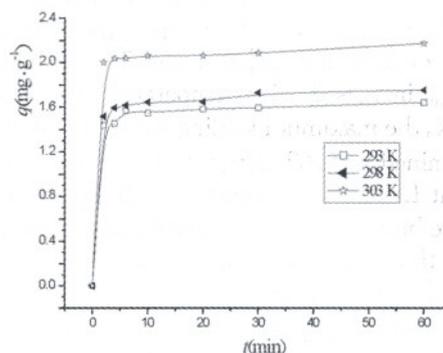
The negative values of  $\Delta G^0$  confirm the feasibility of the process and the spontaneous nature of sorption with high preference of copper (II) on chaff. The value of  $\Delta H^0$  is positive, indicating that the sorption reaction is endothermic. The positive value of  $\Delta S^0$  reflects the affinity of the chaff for copper ion and suggests some structural changes in copper and chaff (Gupta, 1998). In addition, positive value of  $\Delta S^0$  shows the increasing randomness at the solid/liquid interface during the sorption of copper ion on chaff.

### 3.9 Kinetic parameters of biosorption

In order to calculate the kinetic parameters, the change of the amount of metal ion per unit weight of chaff with adsorbing time increasing at different temperatures was shown in Figure 5.

From Figure 5, we observed that the value of  $q_e$  increased with time and in the same condition of adsorption, the higher temperature was, the higher

of the capacity quantities of chaff were. Hence as to copper adsorption, it took advantage of higher temperature.



**Figure 5.** The effect of temperature and time on biosorption of copper

#### 3.9.1 Kinetic modeling

There were several reports on the use of different kinetic models to adjust the experimental data of heavy metals adsorption on biomass. One of them was the pseudo-first-order Lagergren model that considered that the rate of occupation of adsorption sites was proportional to the number of unoccupied sites (Aksu, 2005):

$$\frac{dq}{dt} = k_1(q_e - q) \quad (9)$$

Where  $q_e$  and  $q$  are the amounts of adsorbed metal ions on the biosorbent at equilibrium and at any time  $t$ , respectively, and  $k_1$  is the Lagergren rate constant of the first-order biosorption. The range of  $t$  is from 0 to  $t$  and  $q$  is from 0 to  $q_e$ . It can be described by the linearized form as following:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (10)$$

Linear plots of  $\log(q_e - q)$  versus  $t$  indicate the applicability of this kinetic model. However, before application Eq. (10), the value of  $q_e$  must be pre-estimated by extrapolating the experimental data to  $t = \infty$ .

The second model is the pseudo-second-order model reaction. The observed kinetics can be modeled that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Ho YS, 1999):

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (11)$$

Where  $k_2$  is the rate constant of second-order biosorption ( $g \cdot mg^{-1} \cdot min^{-1}$ ), which corresponds to the integrated rate law for a second-order reaction, is obtained:

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 \cdot t \quad (12)$$

Eq. (12) can be rearranged and linearized to obtain:

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

The plot  $t/q$  versus  $t$  should give a straight line if second-order kinetics is applicable and  $k_2$  and  $q_e$  can be determined from the slope and intercept of

the plot, respectively. Furthermore, the value of  $q_e$  may not be known.

### 3.9.2 Kinetic parameters

Aiming at evaluating the biosorption kinetics of copper and copper ions on chaff, the pseudo-first-order kinetic model and pseudo-second-order model were used to fit the experimental data. The initial concentration of copper and copper was  $20 \text{ mg} \cdot \text{l}^{-1}$ . The result was shown in Table 5.

**Table 5.** The application of kinetic model to the biosorption of copper on chaff

T(K)	First-order kinetic model			Second-order kinetic model		
	$k_1(\text{min}^{-1})$	$q_e(\text{mg} \cdot \text{g}^{-1})$	R	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$q_e(\text{mg} \cdot \text{g}^{-1})$	R
293	0.0260	0.27	0.980	0.939	1.65	1.000
298	0.0286	0.23	0.951	1.305	1.73	1.000
303	0.0316	0.20	0.940	3.685	2.09	1.000

From Table 5 we came to a conclusion that the biosorption data of copper on chaff was perfectly fitted the second-order kinetic model. The linear coefficients were all 1.000, which indicated that the linearity was good. Furthermore the value of  $q_e$  obtained from the Eq. (13) fitted the experiment data well. The value of  $k_2$  was increased with the increased temperature, which indicated that the rate of reaction became speedy.

According to the Arrhenius-type correlation (Tewari, 2005; Aksu, 2002; Ho YS, 1999):

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \quad (14)$$

where  $k_0$  is the temperature independent factor in  $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ,  $E_a$  is the activation energy of the reaction of biosorption in  $\text{kJ} \cdot \text{mol}^{-1}$ ,  $R$  is the gas constant,  $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$  and  $T$  is the sorption absolute temperature, K. The linear form is:

$$\ln k = -\frac{E_a}{RT} + \ln k_0 \quad (15)$$

Linear plots of  $\ln k$  versus  $1/T$  should give a straight line. The value of  $E_a$  can be obtained from the slope of the line. According to the Eq. (15), the activation energy of biosorption of copper on chaff was evaluated as  $100.3 \text{ kJ} \cdot \text{mol}^{-1}$  by the value of the rate constant of second-order biosorption. This value was of the same magnitude as the activation energy of activated chemisorption. The result also suggested that the process of the chaff adsorbing copper was endothermic.

## 4 Conclusion

The Freundlich and Langmuir adsorption models were used for the mathematical description

of the biosorption equilibrium of copper(II) ions to chaff depending on temperature. The isotherm constants evaluated from the isotherms were used to compare the biosorptive capacity of the dried biomass. It was seen that the isotherm constants decreased with temperature increasing. The obtained results showed that the adsorption equilibrium data fitted very well to both the models in the studied concentration range at all the temperatures studied. The equilibrium sorption of copper ions was determined from the Langmuir equation and was found to be  $5.62 \text{ mg} \cdot \text{g}^{-1}$  at 303 K. Various thermodynamic parameters, such as  $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ , were calculated. The suitability of the pseudo first and second order kinetic models for the sorption of copper(II) ions onto biomass was also discussed. It was decided that the biosorption kinetics of copper(II) ions to chaff obeyed the pseudo second-order adsorption kinetics. With the pseudo second-order kinetic constants increasing with temperature, the activation energy of biosorption was evaluated as  $100.3 \text{ kJ} \cdot \text{mol}^{-1}$ . The thermodynamics and kinetics of copper ion/chaff system indicated spontaneous and endothermic nature of the process.

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