



Biosorption of Copper (II) from Aqueous Solution by *Saccharomyces cerevisiae* : Kinetics and Thermodynamics

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ABSTRACT

Biosorption equilibrium, kinetics, and thermodynamics of Cu ions onto *S. cerevisiae* were studied in a batch system with respect to temperature and initial ion concentration. Biosorption efficiency increased up to Cu ion initial concentration of 75 mg/L, and then decreased with the increasing metal ion concentration. Equilibrium uptake value changed from 9.8 mg/g at 20° C to 14.5 mg/g at 50° C. Langmuir isotherm model was found to be in good correlation with data. Biosorption enthalpy indicated that the biosorption process has an endothermic nature. Pseudo first order, pseudo second order and intraparticle diffusion models were applied to the experimental data. High value of correlation coefficients (>0.99) and the comparison of the experimental equilibrium concentration of copper with value calculated from the kinetic model indicated that the Cu(II) uptake by *S. cerevisiae* was best described by pseudo second order rate model. The thermodynamic constants of biosorption namely, ΔG° , ΔH° and ΔS° were also evaluated.

Key Words: *Biosorption, Wastewater, Cu ion, Kinetic, Saccharomyces cerevisia.*

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1. INTRODUCTION

As heavy metals are toxic, nonbiodegradable and can be accumulated in living organisms, heavy metal pollution is becoming a serious environmental problem. The removal and recovery of heavy metals from wastewater is important in the protection of the environment and human health. Copper is an essential trace element found in many living organisms, but at high levels it is potentially harmful and when discharged at high concentration into natural water resources could pose a serious environmental threat to marine ecosystems. Various industries produce waste water containing dissolved copper ions, including those that carry out metal cleaning and plating, paper pulp, paper board mills, and wood pulp production sites and the fertilizer industry [1]. Many conventional methods have been investigated to remove heavy metals such as, chemical reduction, ion exchange, precipitation, reverse osmosis, and electrodialysis [2]. These methods are encountered with certain major disadvantages such as, high energy requirements, incomplete metal removal and generation of a large quantity of toxic waste sludge. As a cost-effective mean, biosorption has been extensively studied for removing wide variety of soluble heavy metals as well as some toxic organics from aqueous solutions, and many biomaterials have been tested as biosorbents including marine algae, fungal biomass, waste activated sludge, yeasts and so on [3-8].

The growing and non-living cells of microorganisms are reported to remove Cu from aqueous solutions [4,9,10]. The *S. cerevisiae* (living or non-living) is widely used as biosorbent in biosorption studies because of its many advantages. It is easy to cultivate at large scale and can be obtained from various food and beverage industries [11-13].

Biosorption capacity is influenced by many factors, including the status of *S. cerevisiae* (cell age, living or non-living), properties of metal ions (radius of ion, valence, etc.) in aqueous solution, culture conditions (carbon source, nutrition supply, composition of growth media, etc.), biosorption conditions (such as pH, temperature, contact time, co-ions in solution, initial concentration of metal and biomass, availability of metal ions and micronutrition etc.) [14-16].

Kinetic models can be helpful to better understand the mechanism of metal biosorption and to evaluate performance of biosorbents for metal removal. The magnitude of the heat effect for the biosorption process is the most important criterion to develop a thermodynamic and kinetic relationship for the biosorption process. There are some reported works dealing with the kinetics of biosorption of different ions onto *S. cerevisiae* [1,17].

In our previous study, we studied Cu binding capacities of *S. cerevisiae* as a function of environmental factors such as initial metal ion concentration, initial pH, contact time, biomass concentration, pretreatment of biomass. In this research, we mainly focused on the biosorption process isotherms, kinetics and thermodynamics. Copper was chosen for biosorption studies with regard to their wide use in industry. The effect of initial copper ion concentration and temperature that may have a strong effect on biosorption process has examined. Biosorption equilibrium and kinetics over temperature range of 293-323 K were investigated [28].

The objective of this study was to characterize pre-equilibrium kinetics of uptake of Cu(II) as well as evaluation of equilibrium isotherms constants and to examine the thermodynamics of biosorption of Cu(II). Three adsorption models, Langmuir, Freundlich and Temkin model were applied to adsorption equilibrium data. Biosorption heat was evaluated with the use of two different methods which leads to the decision about the type of adsorption. The thermodynamic constants of biosorption such as, ΔG° , ΔH° and ΔS° were also evaluated.

2. EXPERIMENTAL

2.1. Preparation of the Microorganism

S. cerevisiae 251 TP(3-2) was obtained from the Hifzissihha Center in Turkey. It was maintained by transferring to fresh agar-malt slants each month and storing at 4 °C. Agar-malt extract contained (g/L): malt extract 3.0; yeast extract 3.0; peptone 5.0; glucose 10; agar 20; pH 4.5. The yeast was subcultured on agar-malt extract slants at the start of each experiment. Culture was grown in an incubator at 30 °C for 24 hour. For the seed culture, the inoculum from the fresh slant culture were transferred aseptically to previously sterilized 500 mL growth medium. The growth medium contained (g/L): glucose 50.0, yeast extract 5.0, $(\text{NH}_4)_2\text{SO}_4$ 5.0 (Sigma Aldrich, $\geq 99.0\%$), KH_2PO_4 12.0 (Aldrich, 99.99%), CaCl_2 0.5 (Sigma, Anhydrous, $\geq 96.0\%$), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ 1.0 (Sigma, 99.5%), $(\text{NH}_4)_2\text{SO}_4$ 5.0 (Sigma Aldrich, $\geq 99.0\%$), yeast extract 5.0, CaCl_2 0.5. The pH of the medium was adjusted to 4.5 with 0.5 M H_2SO_4 (Sigma, $\geq 98.0\%$). The growth medium of 30 °C was agitated using a magnetic stirrer at 440 rpm. After approximately 19 h corresponding to the mid exponential growth phase, solid phase from liquid was separated using a centrifuge at 3000 rpm and solid phase was washed several times with deionized (DI) water. Non-living biomass were obtained by autoclaving cultures at 121°C for 15 min and were dried at room temperature. The dried biomass were ground and sieved through a 200 mm mesh and stored in a desiccator and used in the biosorption experiments.

2.2. Biosorption Experiments

Biosorption experiments were performed by using 250 ml flasks containing 50 ml Cu(II) solution in a shaking water bath of 140 rpm. Cu(II) solutions were prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Sigma, $\geq 98.0\%$) salt and DI water. The initial pH value of the solutions was adjusted with 1 M H_2SO_4 . Biosorption experiments were conducted temperatures (20-50°C) and initial Cu(II) concentrations (20-200 mg/L). All experiments were conducted in duplicate and mean values were used in the analysis of data. The metal concentration in the filtrate was analyzed using an Atomic Adsorption Spectrophotometer (Model ATI UNICAM 929).

3. RESULTS AND DISCUSSION

3.1. Effect of Initial Cu(II) Concentration

Biosorption experiments were carried out at different initial copper concentrations ranging from 20 to 200 mg/L. Variation of metal uptake values with respect to time is given in Figure 1 for different initial copper ion concentrations.

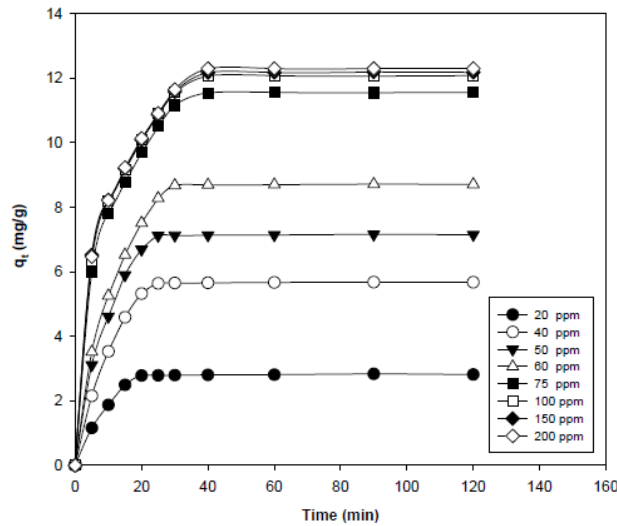


Figure 1. The effect of initial Cu(II) concentration on biosorption (pH=5.0, T= 30°C, Biomass concentration= 3 g/L, 140 rpm).

Adsorption occurred in two steps: an initial fast step in first 10 minutes and slower second step which continued

until equilibrium was reached. Characteristic values determined from Figure1 are given in Table 1.

Table 1. Characteristic values of biosorption for different initial Cu(II) concentrations.

C ₀ (mg/L)	C _e (mg/L)	q _e (mg/g)	t _e (min)	BE*	IBR** (mg/g.min)
20	11.68	2.81	20	41.95	0.84
40	23.02	5.67	25	42.51	1.30
50	28.41	7.14	25	43.01	1.93
60	33.82	8.70	30	43.58	1.67
75	40.43	11.56	40	46.18	2.60
100	63.60	12.08	40	36.30	2.67
150	114.34	12.18	40	24.22	2.62
200	164.21	12.30	40	18.35	2.54

* : Biosorbition Efficiency

** : Initial Biosorption Rate

It was observed that the time for which equilibrium was attained, t_e, depends on the initial copper ion concentration. For this concentration range, it varied from 20 to 40 minutes. At low concentrations of metal ions, the number of available binding sites on the yeast surface was high and hence biosorption of metals was very effective resulting in shorter time of contact to reach equilibrium. Throughout this study, the equilibrium values were taken to be the values corresponding to 2 hours of contact time to be in confidence. The uptake capacity q_e increased from 2.80 to 11.60 mg/g when the initial concentration changed from 20 mg/L to 75 mg/L, and became almost constant for the initial Cu(II) ion concentration higher than 75 mg/L.

The increases in the uptake capacity for increasing initial copper ion concentration may be due to higher probability of collision between metal ions and biosorbent particles and also due to the higher concentration gradient. After 75 mg/L initial Cu(II) ion

concentration, increasing initial concentration leads to decrease in biosorption efficiency. This may be attributed to the saturation of binding sites on the biomass surface leading to increased number of unadsorbed Cu(II) ions because of the lack of binding sites on the biomass at higher concentrations than 75 mg/L in these experimental conditions. Although most of the researchers found that the metal uptake increased with an increase in initial metal ion concentration, there are also some studies in which saturation has been observed at higher initial metal ion concentrations [5, 17-19].

3.2. Effect of Temperature

The influence of temperature on the removal of copper ion was shown in Figure 2 as a function of contact time.

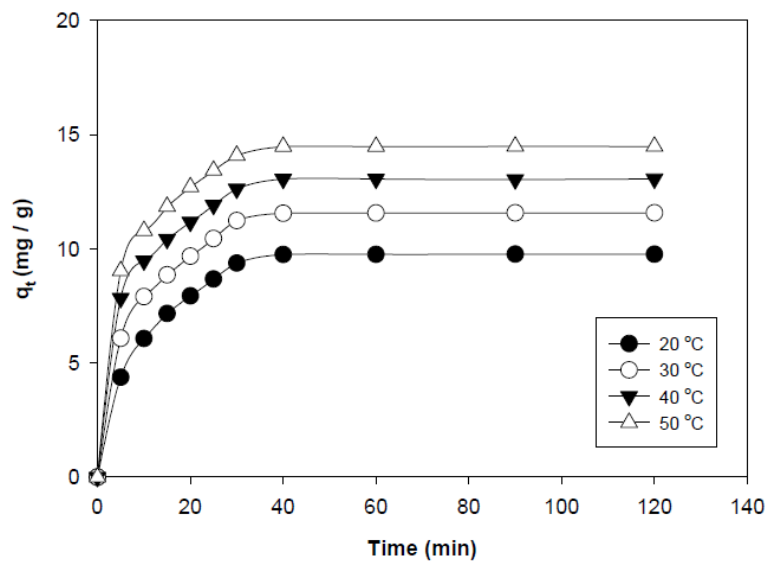


Figure 2. The effect of temperature on biosorption (pH= 5.0, $C_0=75$ mg/L, Biomass conc= 3 g/L, 140 rpm).

In the experimental temperature range (20-50°C), although temperature effects the equilibrium uptake values, the time to reach to equilibrium values remains constant. With rising temperature, equilibrium uptake value changed from 9.8 mg/g at 20°C to 14.5 mg/g at 50°C. This indicates that biosorption process of Cu(II) ions is endothermic. Previous studies related to biosorption of heavy metals indicated that the effect of temperature on biosorption depends on metal-biosorbent systems [20]. Similar results were observed for copper on different biomaterials [21,22].

3.3. Adsorption Isotherms

Adsorption isotherms show the distribution of solute between the liquid and solid phases at equilibrium conditions. To develop an equation which accurately represents the results from the analysis of the equilibrium data is important for the design of an adsorption-based process. Freundlich, Langmuir and Temkin isotherm models were used to correlate our experimental equilibrium data. Linearized form of

$$\text{Langmuir isotherm is: } \frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}}$$

Where C_e is the concentration of metal ion remaining in solution at equilibrium ($\text{mg}\cdot\text{L}^{-1}$); q_e is the amount of metal ion adsorbed per unit weight of adsorbent ($\text{mg}\cdot\text{g}^{-1}$); q_{\max} is the amount of metal ion adsorbed per unit weight of adsorbent in forming complete monolayer on the surface of adsorbent ($\text{mg}\cdot\text{g}^{-1}$).

The linearized Freundlich isotherm is :

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$$

Linearized form of Temkin isotherm is:

$$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$$

The applicability of Freundlich, Langmuir and Temkin sorption isotherms have been checked by plotting $\ln q_e$ versus $\ln C_e$ and C_e/q_e versus C_e and q_e versus $\ln C_e$ respectively. The values of parameters in these three sorption isotherms were determined. Table 2 summarizes the isotherm constants and their correlation coefficients for each of these isotherm models. As it is seen from Table 2, biosorption of Cu(II) follows Langmuir model well according to the correlation coefficient. Biosorption capacity of Cu(II) ions (q_{\max}) increases with increase in temperature and varies from 13.95 to 18.05 mg Cu(II)/g of biomass. Thus maximum Cu(II) biosorption capacity, 18.05 mg Cu(II)/g of biomass was observed at 50°C supporting the results of [17] and [23]. In each of temperature values, experimental q_e was found to be smaller than the calculated values of q_{\max} from Langmuir isotherm. This indicates that the surface of microorganism is not fully covered.

Table 2. Parameters for Langmuir, Freundlich and Temkin isotherms.

Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
T (°C)	R ²	q _{max}	K _L × 10 ⁻³	R ²	K _F	1/n	R ²	A _T	B _T
20	0.94	13.95	27.2	0.77	0.89	0.55	0.84	0.23	709.58
30	0.95	15.34	32.0	0.75	1.15	0.52	0.81	0.26	673.65
40	0.95	16.72	38.1	0.73	1.50	0.50	0.79	0.32	650.25
50	0.96	18.05	45.9	0.70	1.91	0.47	0.77	0.40	637.06

Biosorption heat (ΔH) can be calculated by using various methods. One method is the use of Langmuir parameters. Langmuir parameter can be expressed as a function of temperature with the use of an Arrhenius type equation. Its linearized form is:

$$\ln b = -\frac{\Delta H}{R} \frac{1}{T} + \ln b_0 \tag{4}$$

where b₀ is constant, ΔH is the heat of adsorption (kcal/mol), R is the universal gas constant (1.987 kcal/mol.K) and T is absolute temperature (K) The heat of adsorption was calculated from the slope of the ln b versus 1/T plot as 3.28 kcal/mol (Figure3). Regression coefficient of this plot was 0.997.

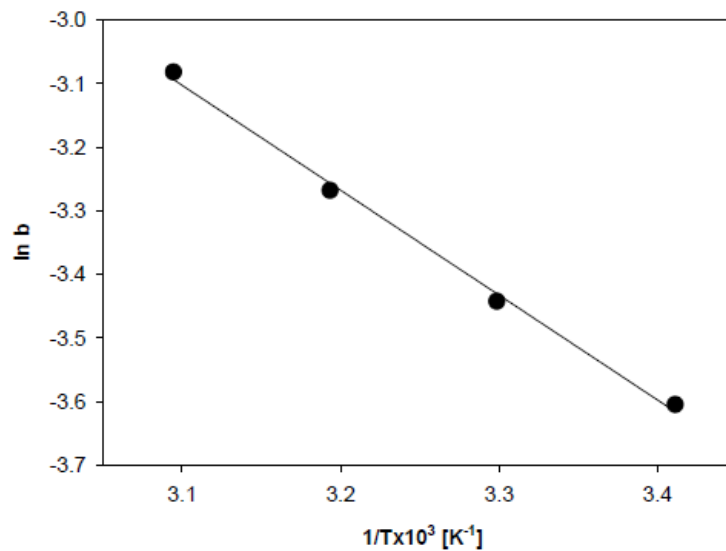


Figure 3. ln b versus 1/Tx10³ plot.

Another method for calculating biosorption heat is using equilibrium constants. The apparent equilibrium constant (K_c[']) is defined as:

$$K_c' = \frac{C_{ad,eq}}{C_{eq}}$$

Where C_{ad,eq} is the concentration of metal ion on the adsorbent at equilibrium. The apparent equilibrium constants (K_c[']) at different initial metal ion concentrations found and extrapolated to zero and so K_c⁰ value evaluated. The K_c⁰ value evaluated from the C_{ad,eq}/C_{eq} versus C_{eq} plot. The K_c⁰ value was used in the following equation to determine the Gibbs free energy of biosorption (ΔG).

$$\Delta G = -RT \ln K_c^0$$

$$\Delta G = \Delta H - T\Delta S$$

$$\ln K_c^0 = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{5}$$

ΔH and ΔS values were obtained from the slope and intercept of ln K_c⁰ versus 1/T plot as 3.32 kcal/mol and 0.0102 kcal/mol, respectively (Figure 4). Regression coefficient of this plot was 0.999. From the ΔH and ΔS values, ΔG was obtained as 0.2816 kcal/mol at 25°C. The positive value of ΔS confirms the increased randomness at the solid-solution interface during biosorption.

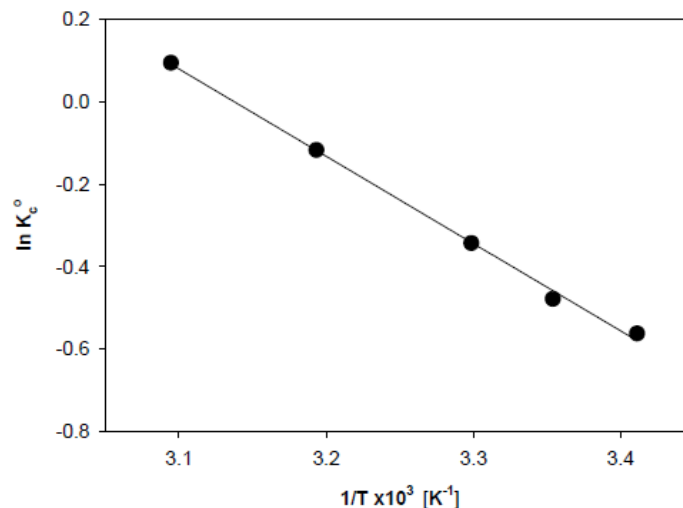


Figure 4. $\ln K_c^0$ versus $1/T$ plot.

The two biosorption heat (ΔH) values calculated from Langmuir constants ($\Delta H = 3.28$ kcal/mol) and equilibrium constants ($\Delta H = 3.32$ kcal/mol) are almost equal. In literature the values of ΔH calculated using free energy changes, equilibrium constants and Langmuir constants were found to be almost equal [24], [16], [25].

Positive heat of adsorption value indicates that biosorption of copper on *S. cerevisiae* was endothermic. This was also supported by the increase of uptake capacity with increasing temperature (Figure 2). The heat of physical adsorption is no more than 1 kcal.mol⁻¹ and that of chemical adsorption is 20-50 kcal.mol⁻¹ [26]. In our study, adsorption heat has a value between, physical and chemical adsorption. Most probably both types of adsorptions are involved during biosorption process. Similar results were reported for biosorption of Pb(II) ions on *Z. ramigera* and Ni(II) ions on *R. arrhizus* [16].

3.4. Kinetic Studies

Kinetic models can be helpful to better understand the mechanism of metal biosorption and to evaluate performance of biosorbents for metal removal. The plots in Figure 2 represent amount of Cu(II) adsorbed (q_t) versus time for four different temperature at fixed initial Cu(II) ion concentration (75 mg/L). It was observed that significant proportion of Cu ions in solution was removed within first 20 minutes. Afterwards, there were slower rates of uptake to about 40 minutes and no further significant adsorption was observed beyond this period.

The three models, namely a pseudo-first order process, a pseudo-second order process and an intraparticle diffusion process models were tested with the use of the corresponding equations given in the literature [27]. These equations are given as follows:

For pseudo-first order chemical sorption:

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

For pseudo-second order chemical sorption:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

For intraparticle diffusion:

$$q_t = k_i t^{0.5}$$

Where k_1 , k_2 and k_i are the equilibrium rate constants for the first order, second order and intraparticle diffusion, respectively. Figure 5 and Figure 6 shows the corresponding plots for two different kinetic model equations. Desorption experiments in our previous study indicated that percent removal of Cu(II) ion from the loaded biomass was 93% [28]. This may be attributed to the chemical adsorption to some extent. This supports the above argument.

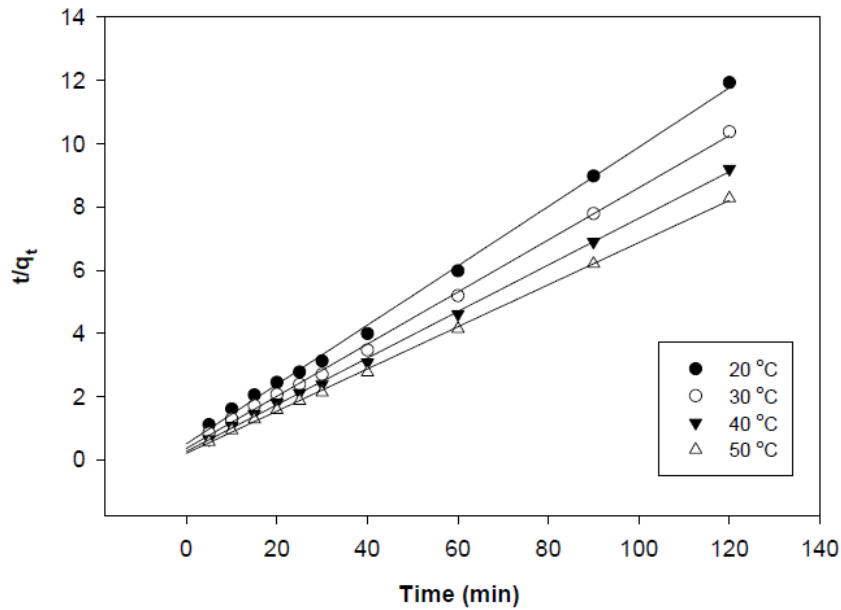


Figure 5. t/q_t versus t plot for pseudo-second order kinetics.

The calculated parameter values from Figure 5 and similar linear plots for the other kinetic models are given in Table 3 along with the coefficients of correlations. As seen from Table 3, the regression coefficients from linear plots of pseudo-second order equation are better than those obtained for the pseudo-first order equation and also the calculated q_e values for second order agreed well

with experimental ones. Therefore these values suggested that sorption of copper ions followed the pseudo-second order kinetic model which means that rate of binding of copper ions to the adsorption sites was proportional to the squares of number of unoccupied sites.

Table 3. Parameters for the effect of temperature for *Saccharomyces cerevisiae*.

T	Pseudo-first order			Pseudo-second order			Intraparticle diffusion		
	R_1^2	k_1	q_e	R_2^2	$k_2 \times 10^{-3}$	q_e	R_i^2	k_i	$q_{e,exp}$
20	0.92	0.13	14.49	0.99	18.1	10.36	0.97	1.35	9.77
30	0.95	0.14	17.43	0.99	19.8	12.12	0.97	1.38	11.58
40	0.91	0.15	18.45	0.99	21.7	13.55	0.98	1.31	13.07
50	0.92	0.15	18.72	0.99	22.7	14.97	0.97	1.37	14.49

T (°C); q_e (mg/g); k_1 (L/min); k_2 (g/mg.min); h (mg/g.min); k_i (mg/g.min^{0.5})

The values of pseudo-second order rate constants (k_2) increased from 1.81×10^{-2} to 2.27×10^{-2} g/mg.min for increasing solutions temperature between 20-50°C. Sorption rate constant may be expressed as a function of temperature in an Arrhenius form as:

$$k_2 = k_0 \exp\left(-\frac{E}{RT}\right)$$

Where k_0 is the temperature independent factor in g/mg.min and E is activation energy of sorption (kcal/mol). From the intercept and slope of the straight line plots of $\ln k_2$ against $1/T$, k_0 and E values were determined to be 0.2216 g/mg.min and 1.46 kcal/mol, respectively. Therefore k_2 is expressed as follows:

$$k_2 = 0.2216 \exp\left(-\frac{1.46}{RT}\right)$$

CONCLUSION

Copper removal from aqueous solution by *S. cerevisiae* was shown to be affected by changes in solution temperature and initial Cu(II) ion concentration. Biosorption isotherm was well described by Langmuir model of favorable type and the calculated heat of adsorption value of 3.28 kcal/mol indicated that adsorption is of endothermic nature. Pseudo-second order kinetics provided the best correlation of experimental data.

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