Kinetic and Thermodynamic Studies in Removal of Cu (II) by Biosorption on *Pleurotus ostreatus*

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Abstract

The use of adsorbents of biological origin has emerged in the last decade as one of the most promising alternatives for the control of environmental pollution caused by heavy metals. A number of methods, viz. chemical precipitation, evaporation, electroplating, ion exchange, membrane, processes, etc. exist for the removal of heavy metals from liquid wastes. All these methods are expensive and have shortcomings such as in complete removal of metal, limited tolerance to pH change, moderate or not metal selectivity, and production of toxic sludge or other products that also need disposal. Fruiting bodies of macrofungi (mushrooms) may be considered ideal for the purpose of biosorption of heavy metals because their potentiality for heavy metal uptake have already been proved. In this study, batch biosorption experiments were carried out for the removal of Cu (II) from its aqueous solution using P.ostreatus as biosorbent. The kinetics and thermodynamic results were evaluated. The experimental data were analysed using three sorption kinetic models the pseudo first, pseudo second order and the intraparticle diffusion equations to determine the best fit equation for the biosorption of Cu(II) ions onto P. ostreatus. Pseudo second order model provided the best description of data with a correlation coefficient 0.97-0.99 for different initial metal concentrations and temperatures. The activation energy of biosorption (Ea) was determined as 21.45 kj/mol using the Arrhenius equation. Using the thermodynamic equilibrium coefficients obtained at different temperatures, the thermodynamic constants of biosorption (ΔG^o, ΔH^o and ΔS^o) were also evaluated.

Keywords: Biosorption, Copper, Mushroom, kinetic, thermodynamic.

1. Introduction

Heavy metals are continuously released to aquatic environment as a mainly result of urbanization, industrialization and agricultural/mining activities [1]. Heavy metal contamination of industrial water is a significant problem in the modern world. The water pollution with metal cations has dramatically increased in the last fifty years as a consequence of expansion of industrial activities [2].

Copper, a widely used metal in industry, is an essential trace element for human health and play an important role in carbohydrate and lipid metabolism and in the maintenance of heart and blood vessel activity. The adult human body contains 100–150 mg of Cu (II)' but excess amounts in the body can be toxic [3]. In aqueous environments, the specification of the metal is dependent both on ligand concentration and pH. While the cupric ion (Cu (II)) is the metallic form most toxic to flora and fauna, it is also a nutrient necessary for algal growth [1].

If allowed to enter the environment excessive amounts of Cu (II) can cause serious potential health issues such as nausea, headache dizziness, respiratory difficulty, hemolytic anemia, massive gastrointestinal bleeding, liver and kidney failure, and death [4–9]. The world health organization (WHO) recommended a maximum acceptable concentration of Cu (II) in drinking water of 1.5 $mg.L^{-1}$[5].

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In recent year, increasing concern about the effect of toxic metals in the environment has resulted in more strict environmental regulations for industrial applications that discharge metalbearing effluents [10]. Removal of metal ions from wastewater in an effective manner has become an important issue [2]. Efficient methods for the removal of metals have resulted in the development of new separation technologies. Precipitation, adsorption, ion exchange, flocculation, absorption, electrochemical processes and/membrane processes such as electrodialysis, nanofiltration and reverse osmosis are commonly applied for the treatment of industrial effluents [2, 5, 7, 9, 11–19]. However, these techniques have several disadvantages such as high chemical cost, low removal efficiency, low selectivity, high-energy requirements, and generation of secondary toxic slurries. Among these various treatment techniques, activated carbon adsorption is one of the most commonly used due to its high efficiency and easy operation. However, it is expensive and may also require complexing agents to improve its ability to remove inorganic matter [11, 20, and 21]. Thus, there is a need to develop a cost effective and an efficient technique for metal removal from wastewaters. That is biosorption. Biosorption is considered as an alternative process for the removal of heavy metals, metalloid species, and compounds from aqueous solution by biological materials. Compared with conventional methods for the removal of toxic metals from wastewater, the biosorption process offers potential advantages such as low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed of, and high efficiency in detoxifying very dilute effluents [13, 19-23, 25-28]. Large number of studies was reported in literature on biosorption of [4, 8, 10, 12, 17, 20, 21, 23–38] heavy metals onto different microbial and plant biomass.

Mushrooms serve as delicacies for human consumption and as neutriceuticals “food that also cures”. Mushrooms, the fruiting bodies of basidomycetous fungi, contain substances of various kinds that are highly valued as medicines, flavaring and perfumes [37, 38]. It considered healthy food as it is low in calories, fat and cholesterol, while rich in protein, carbohydrate, fibers, vitamins and minerals. Mushrooms are saprophytic, growing on dead organic matter of vegetative origin. Therefore, they can utilize almost all agricultural wastes as substrates. *P. ostreatu*s is an edible mushroom [39, 40]. *P. ostreatus* grows on wood on nature, usually on dead standing trees or fallen logs. It has a relatively large size, whitish gills and exceptionally small stem. It fruits in fall and winter and has a brownish cap [39, 41].

In none of the literature studies, the biosorption of Cu (II) ions onto *P. ostreatus* was investigated. In this study, *P. ostreatus* was studied as a biosorbent for the removal of Cu (II) ions from aqueous solutions and the biosorption rate were determined as a function of initial Cu (II) ion concentration and temperature. The kinetic and thermodynamic parameters were investigated to evaluate the biosorption capacity of *P. ostreatus* as a function of operating parameters.

2. Material and Methods

2.1. Collection and preparation of biomass samples

In the present study, *P. ostreatus* was used as a biosorbent for the removal of Cu (II) ions from aqueous solutions. Samples of biomass were collected from dense forests covering area of Erzurum, Atatürk University Campus, Turkey, in April and May of 2008. All samples were washed in distilled water and then dried in the open air. The dried biomass were cut into small pieces, ground in a motor to a very fine powder and sieved to select particles of less than 0.5 mm (mesh size 125-250 μm) for use as a biosorbent in batch studies. The surface area of biosorbent was measured by the BET method at 77 K using a Quantachrome QS-17 model apparatus. The surface areas of the biosorbent were defined as 0.835 and 0.384 m^2g^{-1}, before and after biosorption, respectively.

2.2. Synthetic wastewater preparation

Synthetic wastewater solutions were prepared by dissolving analytical grade $CuSO_4.5H_2O$ in distilled water to obtain 1000 $mgL^{-1}$of Cu (II) solution. The solution was diluted to the required concentration for experiments. The pH of the solution was measured and observed as 5.4 ± 0.5 and no chemicals were added to change pH.

2.3. Batch biosorption experiments

The biosorption of Cu (II) ions on the *P.ostreatus* biomass was investigated in batch biosorption-equilibrium experiments. The effect of different Cu (II) ions concentration (100-250 mgL^{-1}), temperatures (25-55 ^oC) on biosorption rate were studied. Solution pH was adjusted with 0.1 M HCl and NaOH solutions. The mixture was shaken in a mechanical shaker (Thermolyne ROSI 1000). Samples were taken at known time intervals. Preliminary experiments showed that biosorption is fast

and the removal rate is negligible after 30 min. Therefore, contact time of 30 min. was used for batch test. After each experiment, the mixture was filtered through Whatman filter paper No. 1 and analyzed for Cu (II) ion. The Cu (II) ion concentration in the supernatant solution was determined complexometrically [42]. The metal concentration in the liquid phase was determined at beginning (Co) and equilibration (Ce) in mgL^{-1}. The following equation was used to compute biosorbent uptake capacity at equilibrium *qe* (mg g^{-1}): $q_e = (C_o - C_e)\frac{V}{M}$

M is the dry mass of biomass in grams and V is the volume of solution in liters.

Percent removal of Cu (II) is $\frac{(C_o - C_e)}{C_o}100$

2.4. Adsorption kinetic model

The pseudo-first order kinetic model [5] has the following form

$$\frac{dq}{dt} = k_1(q_{eq} - q_t) \quad (1)$$

where q_{eq} and q_t (mg g^{-1}) is the amount of adsorbed Cu(II) on the biosorbent at equilibrium(mg g^{-1}) and at time(t), espectively, and k_1 is the rate constant of pseudo-first order adsorption process(min^{-1}). The integrated form of Eq.(6) is

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2{,}303}t \quad (2)$$

A straight line of $\log(q_{eq} - q_t)$ versus t suggests the applicability of this kinetic model, q_{eq} and k_1 can be determined from the intercept and slope of the plot, respectively.

The pseudo-second-order kinetic model was used to describe the experimental data of heavy metals adsorption on biomass.

The pseudo-second order kinetic model as developed by Ho and McKay [43] has the following form;

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

where k_2 (g mg^{-1}min^{-1}) is the equilibrium rate constant of pseudo-second order biosorption(g mg^{-1}min^{-1}). Eq. (4) can be rearranged and linearized to obtain:

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

The plot t/q_t versus t should give a straight line if second-order kinetics are applicable and q_e and k_2 can be determined from the slope and intercept of the plot, respectively.

Intra-particle diffusion model [25] is given by Eq.(5)

$$q_t = k_{\text{int}}t^{1/2} \quad (5)$$

where k_{int} is the intraparticle diffusion rate constant, (mg g^{-1} min$^{-1/2}$).

2.5. Adsorption thermodynamics

The thermodynamic parameters of the adsorption process were determined using the following equations:

$$K_C = C_a / C_e, \quad (6)$$

$$\Delta G^o = -RTInK_C, \quad (7)$$

$$InK_C = \Delta S^o / R - \Delta H^o / RT, \quad (8)$$

where K_C is the distribution coefficient for the adsorption. $\Delta H^o, \Delta S^o$ and ΔG^o are the changes in enthalpy, entropy, and Gibb's free energy, R is the gas constant(8.314 J mol^{-1}K^{-1}), T is absolute temperature, C_a(mg L^{-1}) is the amount of Cu (II) adsorbed per unit mass of the adsorbent and C_e(mg L^{-1}) is the equilibrium adsorbate concentration in the aqueous phase. The values of ΔH^o and ΔS^o were determined from the slopes and intercepts of the plots of InK_c versus $1/T$ (7).

2.6. Activation parameters

From the pseudo-second-order rate constant k_2, the activation energy E_a for the adsorption of Cu (II) on *Agaricus campestris* was determined using the Arrhenius equation:

$$Ink_2 = InA_o - E_a / RT \quad (7)$$

where E_a is the activation energy kJ mol^{-1}, R is the gas constant and A_o is the Arrhenius constant. By plotting Ink_2 versus $1/T$ and from the slope and the intercept, values of E_a and A_o can be obtained. The magnitude of activation energy may give an idea about the type of adsorption. Two main types of adsorption may occur, physical and chemical. In physical adsorption, the equilibrium is usually rapidly attained and easily reversible, because the energy requirements are small.

3. Result and Discussion

3.1. Adsorption kinetics

Adsorption kinetics decribes the solute uptake rate which intern controls the residence time and hence the size of the adsorption equipment. Fig. 1 shows the plot between amount adsorbed, *qe* (mg g^{-1}) versus time for different copper concentrations. From the Fig. 1, it was observed that *qe* value increased with increase in copper concentration. However, the adsorption rates was observed to be very high within the first 5 min. and thereafter; the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after 25 min. The equilibrium time is independent of copper concentration. Initially, the adsorption sites are open and the metal ions interacts easily with the site and hence a higher rate of adsorption is observed in the first 5 min. Further, the driving force for adsorption-the concentration difference between the bulk solution and the solid liquid interface is higher initially and this results a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent.

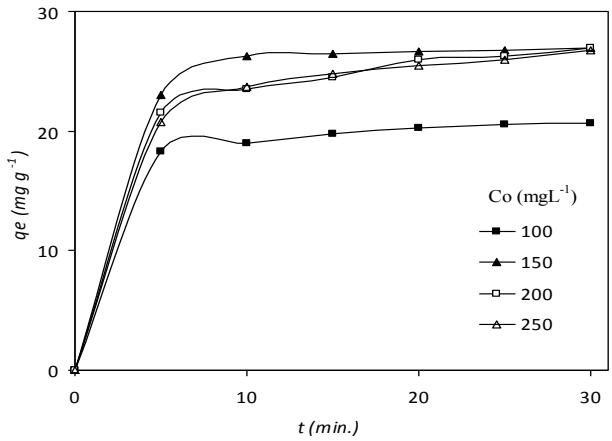

Figure 1: Plot of the adsorption of Cu (II) onto *P.ostreatus* against contact time (adsorbent concentration = 0.2 g per 50 mL; initial pH 5.4, T = 298 K).

Kinetic analyses were made at different copper concentrations and temperatures by using pseudo first order, pseudo second order and intraparticle diffusion equations. The results of the various kinetics parameters including k_2, q_{eq} and R^2 are shown in Table 1. It is clear from the Table 1 that coefficient of correlation (R^2) for the pseudo second order kinetic model at the different initial concentration and temperatures studied is higher in comparison to pseudo first order model, and the estimated values of q_{eq} for the pseudo second order kinetic model of *P. ostreatus* were also closer to the experimental q_{eq} values than those obtained from the pseudo first order kinetic model (Table 1). The parameters of the

intraparticle diffusion model were also presented in Table 1. Low R^2 values indicated apparently that the model did not fit the data well. It gives an indication that intraparticle diffusion model did not control the rate which consisted with the results taken from the pseudo second order that the biosorption may be a rate limiting step. The maximum removal for all metalic species occured in 30 min. where the uptake was 20.65, 27. 27 and 26.75 mgg^{1}, respectively for experimental data. The values, which were derived for the reaction rate constant for pseudo first, second order and intraparticle diffussion equations are shown at Table 1. The results indicated that pseudo first (k_1), pseudo second (k_2) and intraparticle diffusion (k_{int}) rate constant were affected by initial Cu (II) ions concentration and temperatures. At all Cu (II) concentration, the values of k_2 decrease from 0.0432 to 0.012 g mg^{-1}min^{-1}. as the Cu (II) concentrations increases from 100 to 250 mgL^{-1}. The reason for the decrease in the rate constant with increasing Cu (II) concentrations may be the competition among Cu (II) ions for the same binding sites on *P.ostreatus* biomass, while the values of k_2 increases from 0.0432 to 0.0979 g mg^{-1} min^{-1} as the temperature increases from 298 to 328 K indicating that the Cu (II) adsorption on *P.ostreatus* is an endothermic. This is due to higher frequency of interactions (ie; high energy levels) among the Cu (II) ions and the adsorbent particles at high temperature. As seen in Table 1, the values of q_{eq} increase both with increase in concentration and temperature. The first order rate constant (k_1) and $q_{eq,cal}$ determined from the model are not in good agreement with the experimental values of $q_{eq,exp}$. In the view of these results, it can be said that the pseudo second order kinetic model provided a good correlation for the biosorption of Cu (II) onto *P. ostreatus* at different Cu (II) concentration in constrast to the other models. This suggests that the rate limiting step in this sorption process may be chemisorption involving valent forces through the sharing or exchange of electrons between sorbet and sorbate, as also reported by Ho and McKay [43].

Table 1. Pseudo first order, Pseudo-second-order and Intraparticle diffusion equations kinetic parameters for the biosorption of Cu (II) onto *P. ostreatus* at different copper (*Co*) concentrations and temperatures (*T*)

Pseudo first order equation					
T (K)	Co (mg L^{-1})	q_{eqexp} (mg g^{-1})	k_1 (min^{-1})	R^2	q_{eqcal} (mg g^{-1})
298	100	20.65	0.183	0.88	9.20
298	150	27	0.124	0.85	4.51
298	200	27	0.100	0.97	9.86
298	250	26.75	0.100	0.99	9.15
308	100	20.75	0.612	0.86	3.88
318	100	21	0.448	0.97	2.69
328	100	21.25	0.550	0.93	2.10
Pseudo second order equation					
T (K)	Co (mg L^{-1})	q_{eqexp} (mg g^{-1})	k_2 (g mg^{-1}min^{-1})	R^2	q_{eqcal} (mg g^{-1})
298	100	20.65	0.043	0.99	21.36
298	150	27	0.045	0.99	27.70
298	200	27	0.013	0.99	29.10
298	250	26.75	0.012	0.99	29.10
308	100	20.75	0.056	0.99	21.32
318	100	21	0.068	0.99	21.36
328	100	21.25	0.098	0.99	21.60
Intra particle diffusion equation					
T (K)	Co (mg L^{-1})	q_{eqexp} (mg g^{-1})	k_{int} (mg g^{-1}min$^{1/2}$)	R^2	q_{eqcal} (mg g^{-1})
298	100	20.65	0.787	0.97	20.88
298	150	27	1.045	0.70	27.51
298	200	27	1.933	0.70	27.24
298	250	26.75	2.091	0.89	27.09
308	100	20.75	0.586	0.96	20.90
318	100	21	0.479	0.99	20.99

328	100	21.25	0.378	0.94	21.36

3.2. Thermodynamic parameters

The change in Gibbs free energy (ΔG^o) for adsorption of Cu (II) ions onto *P. ostreatus* biomass were calculated from Eq.(8). ΔH^o and ΔS^o values were also determined from the slope and the intercept of the plot of *ln Kc* versus *1/T* (Fig.2) and listed in Table 2.

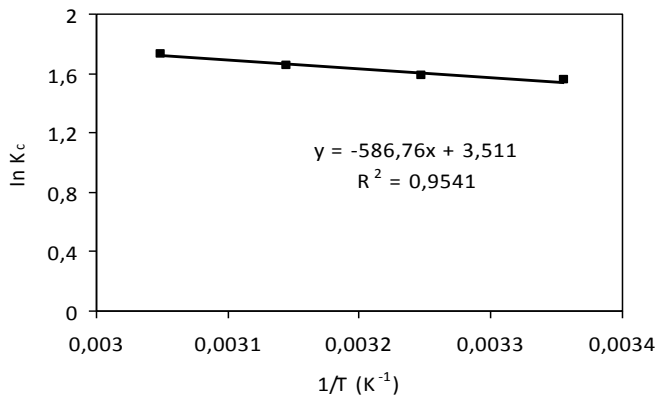

Figure 2. Plot of lnKc against 1/T for the adsorption of Cu (II) onto *P.ostreatus*

Table 2. Thermodynamic parameters of *P.ostreatus* biomass at Cu (II) concentration of 100 mgL^{-1}, pH=5.4

T (K)	ΔG^o ($kjmol^{-1}$)	ΔH^o ($kjmol^{-1}$)	K_c	ΔS^o (J/molK)
298	-3.85	4.87	1.55	29.63
308	-4.06		1.58	
318	-4.38		1.65	
328	-4.73		1.73	

The distribution coefficient (*Kc)* indicates the capability of *P. ostreatus* biomass to retain the solute and also the extent of movement in a solution phase and hence it is a useful parameter for comparing the adsorption capacity of any metal ion under the same experimental conditions obtained thermodynamic parameters are given in Table 2. The values of ΔG^o were found to be (-3.85, -4.06, -4.38 and -4.73) $kjmol^{-1}$ at all temperatures (T= 298, 308, 318 and 328 K). As shown in the Table 2, the negative values of ΔG^o imply the spontaneous nature of the adsorption process and a better adsorption is actually obtained at higher temperature (T=308 K). After this temperature, it was observed on slightly increase in ΔG^o. The ΔG^o value determines the rate of the reaction, the rate increases as ΔG^o decreases, and hence the energy requirement is fulfilled, the reaction proceeds. Generally, the change in free energy for physisorption is between -20 and 0 kJ mol^{-1}, but chemisorption is a range of -80 to -400 $kjmol^{-1}$[8]. The values of ΔG^o obtained in this study was in the range of (-3.85 – -4.73) $kjmol^{-1}$ and so the adsorption was predominantly physical adsorption. The positive value of ΔH^o (4.87 kj mol^{-1}) confirms the endothermic process, meaning the reaction consume energy. The positive value of ΔS^o (29.63 j/mol K) suggests the increased randomness at the solid/solution interface during the adsorption of Cu (II) onto *P.ostreatus*. In adsorption of Cu (II), the adsorbed solvent molecules, which are displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate ions, thus allowing for the prevalence of randomness in the system. Also, in the case of physisorption which may also contribute to the total adsorption process can cause increase in entropy because of the water molecules released from the hydrated ions or water molecules present on the surface during the adsorption process.

3.3. Activation Parameters

Fig. 3 shows the corresponding linear plot of ln k_2 aganist *1/T* with a correlation coefficient of 0.97. The value of activation energy for the adsorption of Cu (II) on *P.ostreatus* at different temperature was calculated and its value was found tobe 21.45 kj/mol. Since the *Ea* value is in between (5 - 20) $kj.mol^{-1}$, physisorption is the predominant adsorption mechanism for Cu (II) removal by *P. ostreatus* biomass. The values of *Ea*<40 $kjmol^{-1}$ generally indicate diffusion controlled process.[44]. We can therefore conclude that the *Ea* value calculated from and data suggest a diffusion-controlled process, which is a physical step in the adsorption process.

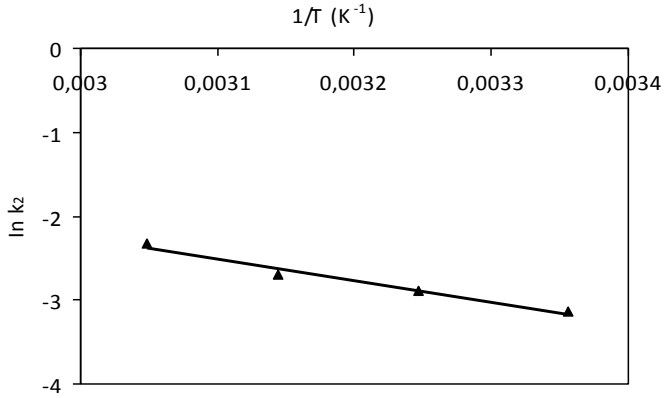

Fig. 2: Plot of $\ln k_2$ against 1/T for the adsorption of Cu (II) onto *P.ostreatus.*

4. Conclusions

In the present study, the thermodynamic and kinetic investigations of Cu (II) adsorption on *P.ostreatus* were studied. The biosorption rate has been shown to be affected by initial Cu (II) concentration, temperature. At the end of a reaction time of 30 min. The biosorption capacity was obtained as 20.65 mg g^{-1}. The results indicated that pseudo first (k_1), pseudo second (k_2) and intraparticle diffusion (k_{int}) rate constants were affected by initial Cu (II) ions concentration and temperatures. The pseudo second order kinetic model provided the best correlation with the experimental data whereas the pseudo first order model did not fit the experimental data well. The values of k_2 decreased with increasing initial Cu (II) concentrations due to competition among the Cu (II) ions for the same binding sites on *P. ostreatus* surfaces at high Cu (II) concentrations (hindering effect), while the values of k_2 increased with increasing temperature due to higher energy levels and frequency of interactions among the adsorbote and adsorbent species at high temperature. Cu (II) concentrations below 100 mgL^{-1} are prefered for high rates of biosorption. The value of adsorption energy, *Ea*, gives an idea of the nature of adsorption. The activation energy of the Cu (II) adsorption was calculated using Arrhenius equation.

From the value of activation energy of the process and ΔG^o obtained in this study, it is suggested that the adsorption of Cu (II) by *P.ostreatus* is physical adsorption. Thermodynamic parameters indicated that adsorption of Cu (II) on *P.ostreatus* was endothermic and spantaneous. Positive value of entropy shows the spontaneity and feasibility of adsorption process.

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