KINETICS, EQUILIBRIUM AND THERMODYNAMICS STUDIES ON BIOSORPTION OF HEAVY METALS BY FUNGAL BIOMASS

Wajeeha Azhar[1]* and Shazia Iram[2]
Department of Environmental Sciences, Fatima Jinnah Women University,
The Mall, Rawalpindi, Pakistan.

ABSTRACT

Batch studies were conducted to assess biosorption potential of Aspergillus niger and Aspergillus flavus dead biomass, operated under various pH (5, 6 and 7), temperature (20, 30 and 40ºC) and initial metal concentration (300, 600 and 900ppm) conditions. The maximum sorption by A. flavus being a better adsorbent showed to be 257mg/g for Cr (III) at 40°C leading to 85.6% biosorption. Metal uptake was preeminent at pH 6 and decreased at pH 7. Results revealed amplifying uptake in biosorption with the increase in temperature and initial metal concentration. Kinetics and equilibrium studies were carried out in which pseudo-second-order kinetic model and Langmuir adsorption isotherm best represented the biosorption with regression coefficient values > 0.982 respectively. The calculated thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) showed that the biosorption of each of the metal ions on A. flavus was spontaneous, feasible and endothermic. A. flavus was efficient for removal of toxic metals.

KEYWORDS: *Biosorption, Kinetics, Equilibrium, Thermodynamics, fungal biomass.*

I. INTRODUCTION

Pollution of heavy metals in agricultural land has been chiefly due to the discharge of industrial effluents in agricultural soil. Industrial effluents may release into the agricultural land by a large number of processes [1,2,3]. They are in soluble form and cannot be eliminated and degraded to products which are harmless; hence they are very toxic to natural systems and persist in the ecosystem indefinitely [4,5]. There are many conventional methods which have limitations and demerits in application. Biosorption is relatively cost effective and ecofriendly technique as metal recovery is possible, highly efficient, biosorbent can be regenerated and reused as well as no additional nutrient media is required for revival of culture. There are many factors which effect the efficiency of biosorption e.g., temperature, pH, biomass concentration, metal concentration in a solution, shaking time, shaking speed and pre-treatment of the biomass. The dead cells of fungal biomass are proven to be more effective for biosorption than live cells [6,7,8].
The present study was conducted on the isolated filamentous fungi *A. niger* and *A. flavus* from the contaminated agricultural areas of Multan and Kasur, Pakistan respectively. The objectives of this study include biosorption potential of fungal strains, to check the factors effecting process, to study kinetics, equilibrium and thermodynamic parameters.

II. MATERIAL AND METHODS

2.1 Preparation of Fungal Biomass and Adsorbent

The fungal strains were isolated from the agricultural soil of Multan and Kasur, Pakistan. Biomass of the test fungi were collected by growing in Potato Dextrose broth to obtain the biomass in bulk. The dried biomass was then grinded to use as adsorbent.

2.2 Preparation of Stock Solutions of Heavy Metals as Adsorbate

All chemicals used in present study were of analytical purity. Stock solutions of heavy metals were prepared by dissolving 7.843g of Cr (III) and 3.93g of Cu (II) in 1L of distilled water.

2.3 Effect of pH, Temperature and Initial Metal Concentration

To check the effect of pH and initial metal concentration solutions were prepared of different pH (5, 6 and 7) and 300, 600 and 900ppm initial metal concentration. The process was operated at different temperature conditions i.e. 20, 30 and 40°C.

2.4 Analysis of Metal Biosorption by Fungal Biomass

Biosorption was done by adding 0.5g of fungal biomass in 100mL metal solution under different conditions to determine the effect of pH, temperature and initial metal concentration [9]. The residual metal ion was analyzed by flame atomic absorption spectrophotometer. Biosorption capacity i.e. the amount of metal ions (mg) sorbed by fungal biomass (g) was calculated by using Eq. 1.

$$Q = (C_i - C_f)\, V/m \quad (1)$$

where Q is the metal ion bioadsorbed (mg g-1) of biomass, Ci and Cf are initial and final metal ion concentration (mgL-1), m is the mass of fungi biomass in the reaction mixture (g) and V is volume of the reaction mixture (L).

III. RESULTS AND DISCUSSION

Biosorption capacity of A. niger and A. flavus was investigated at different conditions of pH (5, 6 and 7), initial metal concentration (300, 600 and 900ppm) and temperature (20, 30 and 40°C). In this study the kinetic, equilibrium and thermodynamics studies were done for the isolate (A. flavus) showing the better uptake capacity for metal ions. The metal uptake capacity by A. niger and A. flavus is shown in the Table 1.

Table 1. Metal uptake capacity of *A. niger* and *A. flavus.*

Adsorbent	***Aspergillus niger***		***Aspergillus flavus***	
Adsorbate	**Cu (II) mg/g**	**Cr (III) mg/g**	**Cu (II) mg/g**	**Cr (III) mg/g**
Effect of Initial Metal Concentration				
300ppm	200	210	192	239
600ppm	409	426.4	433.2	458
900ppm	665	677.36	682	732
Effect of pH				
5	75.617	80.1	233	242
6	85.456	116.68	239	248.8
7	75.057	112.88	232.7	239
Effect of Temperature				
20°C	119	122	229	232
30°C	145	157	233	242.7
40°C	159	163	242.4	257

A comparative study was performed to check the biosorption efficiency by *A. niger* and *A. flavus* for the Cu (II) and Pb (II). It was evaluated that the *A. flavus* has a better uptake capacity as compared to *A. niger* for both of the metal ions [10]. In current study experiments performed to check the effect of pH revealed the best pH at 6 for the biosorption of Cu (II) and Cr (III) metal ion by *A. flavus* as it alters the solution chemistry. In a study *Aspergillus flavus*, *Trichoderma harzianum* and *Aspergillus niger* from solid waste leachate were isolated and checked against Cu, Zn, Hg and Pb. The optimum conditions were determined to be at pH 6 [11]. In another study pH

6 was found the optimum pH for the biosorption of Pb (II) and Cd (II) for pretreated fungal biomass. Cereal chaff was used as a biosorbent and was evaluated that biosorption increased with the increase in pH until the optimum pH 6 [12].

Temperature is one of the factors which may affect the sorption efficiency above the range of 35°C. however biosorption increases with the increase in temperature [13]. In present study the effect of temperature revealed the increase in biosorption with the increase in temperature due to the increased collision frequency between sorbate and sorbent. As a result the kinetic energy increased and the biosorption sites of the adsorbent became active and the capability to adsorb also increased. *A. flavus* showed the uptake capacity with the value of 242mg/g and 257mg/g for Cu (II) and Cr (III) respectively at 40°C. Lead removal by *A. flavus* was investigated in a study. The effect of pH, temperature and biosorbent concentration was checked and it was found that the maximum uptake was 144.5mg/g at 4 pH and 40°C [14]. In a study biosorption of Pb, Cu and Cd by Phanerochaete chrysosporium was studied. Results revealed that the biosorption increased with the increase in initial metal concentration [15]. In another study of cadmium biosorption by biomass seaweed and chromium biosorption by Termitomyces clypeatus it was suggested that the biosorpion increased with the increase in metal concentration [16,17].

3.1 Biosorption Kinetics

A number of kinetic models are required to create the mechanism of a biosorption process. In order to examine the kinetics of the biosorption of these metal ions on *A. flavus* biomass, two kinetic models were employed. One of such models is the Langergren pseudo-first-order and pseudo-second-order.

The study of biosorption kinetics enables to describe the rate of adsorption by adsorbent and this rate controls the solid liquid interface. In all the experiments performed to investigate the biosorption potential of *A. flavus* and it was noted that biosorption has two phases so biphasic kinetics was observed in this process. First phase was rapid and metals adsorbed rapidly on the adsorbent resulting in a fast biosorption process and eventually leading to the equilibrium stage. Second phase is the slow phase in which biosorption is relatively slower. The first phase is instantaneous stage of biosorption while the second phase is the gradual biosorption. The biosorption of each of the metal ions achieved equilibrium within 180min although their rate of adsorption was different depending on the metal ion.

The kinetic models were employed on the sorption of *A. flavus*. For pseudo-second-order model t/qt was taken against time (min) whereas for pseudo-first-order log (qe – qt) was taken on y-axis. On comparison of the R^2 values for each of the metal ion biosorption pseudo-second-order model was the best model to predict the dynamic biosorption of Cu (II) and Cr (III) shown in Table 2. Models were employed for the data depicting the effect of temperature, pH and initial metal concentration. In a study the biosorption was performed in which Cu (II) uptake by *S. cerevisiae* was best described by pseudo-second-order model [18].

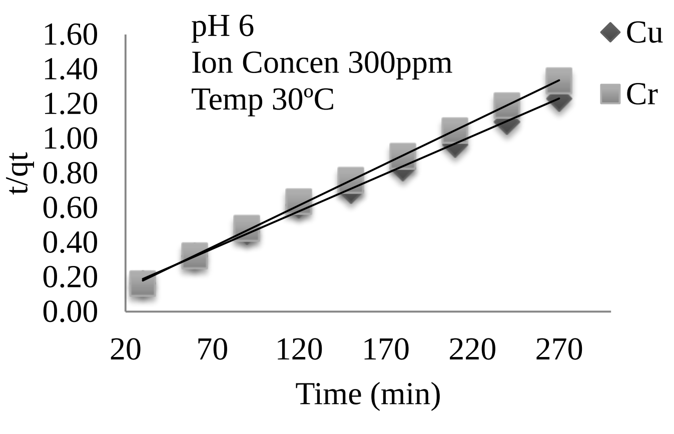

Figure 1. Pseudo-second-order kinetics for the biosorption of Cu (II) and Cr (III) ions by *A. flavus*. (Effect of pH)

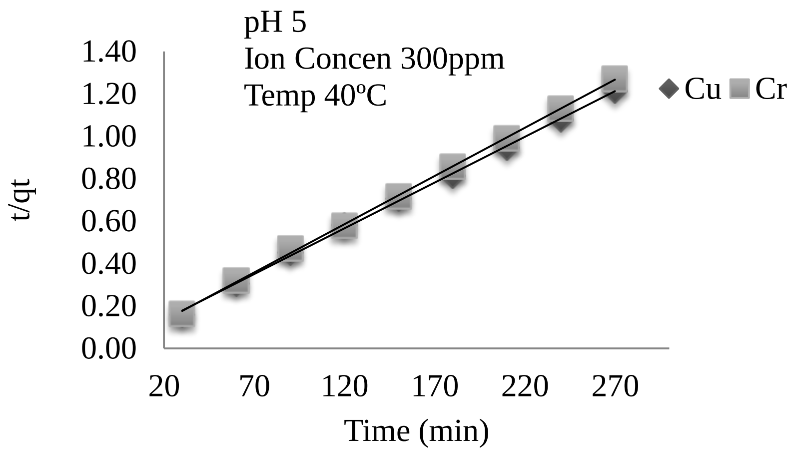

Figure 2. Pseudo-second-order kinetics for the biosorption of Cu (II) and Cr (III) ions by *A. flavus*. (Effect of Temperature)

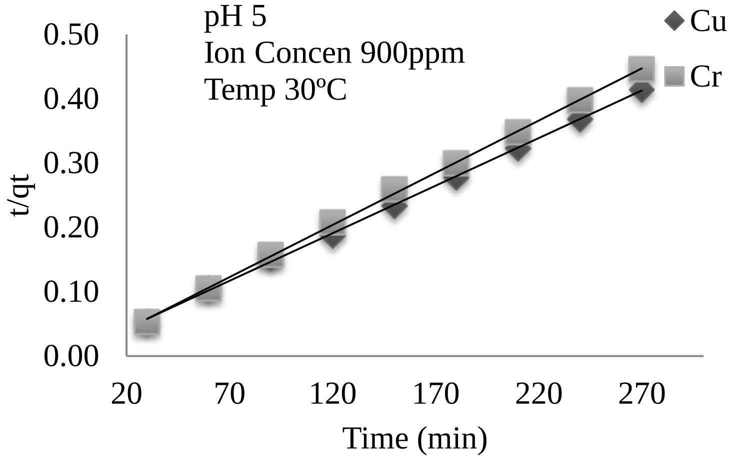

Figure 3. Pseudo-second-order kinetics for the biosorption of Cu (II) and Cr (III) ions by *A. flavus*. (Effect of Initial Metal Concentration)

3.2 Equilibrium Studies

Adsorption isotherms provide a relationship between the amount of metal ions in the solution and the amount of metal ions adsorbed on the surface of adsorbent at equilibrium. To calculate the biosorption of metal ions and equilibrium of the process different models of equilibrium were applied.

3.2.1 The Langmuir Adsorption Isotherm

The Langmuir model was chosen for the judgment of most adsorption competence resultant to entire monolayer coverage on the surface of biomass. The Langmuir model takes a postulation that the adsorption takes place at definite homogenous sites inside the adsorbent. In all the results the biosorption increased with the increase in temperature. After 180 min equilibrium was almost attained. The increase in biosorption with the increase in temperature is because of the increase in the kinetic energy of sorbent particles. Hence the collisions increase between the sorbent and adsorbate and eventually causes the increase in sorption. There may be one other reason of increase in biosorption with increase in temperature. That can be explained in a way that may be the sorption sites become active on the rise of temperature. On comparison of R^2 values it was evaluated that Langmuir was the best model to predict the nature of the adsorbent. This investigation suggested the monolayer adsorption due to high regression coefficients values i.e. > 0.982. The regression coefficients values for Langmuir adsorption isotherm is given in Table 2.

Table 2. Regression coefficients of isotherms

Parameters	Langmuir		Freundlich		Pseudo-first-order		Pseudo-second-order	
	Cu (II)	Cr (III)	Cu (II)	Cr (III)	Cu (II)	Cr (III)	Cu (II)	Cr (III)
Effect of pH								
5	0.985	0.995	0.896	0.898	0.853	0.846	0.999	0.993
6	0.987	0.998	0.896	0.899	0.894	0.881	0.997	0.999
7	0.993	0.988	0.898	0.897	0.884	0.898	0.997	0.999
Effect of Initial Metal Concentration(ppm)								
300	0.988	0.998	0.897	0.899	0.870	0.872	0.999	0.995
600	0.980	0.992	0.895	0.897	0.818	0.894	0.997	0.997
900	0.994	0.998	0.898	0.899	0.804	0.787	0.999	0.999
Effect of Temperature								
20°C	0.974	0.995	0.893	0.898	0.824	0.821	0.999	0.998
30°C	0.988	0.977	0.897	0.893	0.872	0.875	0.999	0.995
40°C	0.979	0.995	0.894	0.798	0.820	0.819	0.998	0.999

3.2.2 The Freundlich Isotherm

The values of regression coefficient for Freundlich model are shown in Table 2 and are below 0.982 and hence Freundlich does not seem to fit the data of biosorption of Cu (II) by *A. flavus*. Freundlich isotherm depicts the heterogeneity of the adsorbent but the results are not depicting heterogeneity in the data of biosorption of Cu (II) and Cr (III) by A. flavus. In one of the earlier studies biosorption kinetics, equilibrium and thermodynamics was studied on the biosorption of Cu (II) ions onto S. cerevisiae. Equilibrium uptake value changed from 9.8 mg/g at 20º C to 14.5 mg/g at 50º C. Langmuir adsorption isotherm model was found to be the best model to predict the correlation of the data [18]. The biosorption was done by macrofungus (Amanita rubescens) biomass for Pb II) and Cd (II). The effect of pH, temperature and contact time was investigated. Freundlich, Langmuir and Dubinin–Radushkevich isotherms were employed to check the biosorption and it was found that maximum biosorption capacity was found to be 38.4 and 27.3mg/g, for Pb II) and Cd (II) respectively, at optimum conditions of pH 5.0, 30min contact time, 4g/L biomass, and at 20°C. Langmuir adsorption isotherm fitted the best on the data as compared to Freundlich model [19].

3.3 Thermodynamic Parameters of Sorption

The temperature variation affects the biosorption process as it is one of the major factors effecting metal binding. Biosorption is reversible process. Adsorbent can be regenerated. The character of each side of the equilibrium evaluates the effect which temperature has on the point of equilibrium. The increase in temperature holds the endothermic side while on the contrary side is for the exothermic condition [20,21]. The increase in biosorption may be defended by the increase in collisions between sorbent and sorbate and hence kinetic energy increases and results in rapid uptake of metal ions. Three temperature ranges (293, 303 and 313K) were taken to calculate the free energy. Thermodynamic aspects of a sorption process are obligatory to wrap up whether the course is spontaneous or not. The ΔG° (free energy change) is a sign of spontaneity of a reaction. In addition, both entropy change and standard enthalpy factors should be measured in order to establish the standard free energy of the process. If ΔG° is negative, it shows the spontaneity of reaction. It can be determined from the following equation:

$$\Delta G° = -RT \ln K_c \quad (2)$$

where R is a Gas constant (8.314 J.mol-1 K-1), T is absolute temperature and Kc can be calculated from the following relationship:

$$K_c = C_{ad} / C_e \quad (3)$$

Relation between ΔH°, ΔG° and ΔS° can be expressed by the following equation:

$$\Delta G° = \Delta H° - T\Delta S° \quad (4)$$

Where values of ΔH° and ΔS° can be determined from the slope and the intercept of the plot of Lnb versus 1/T.

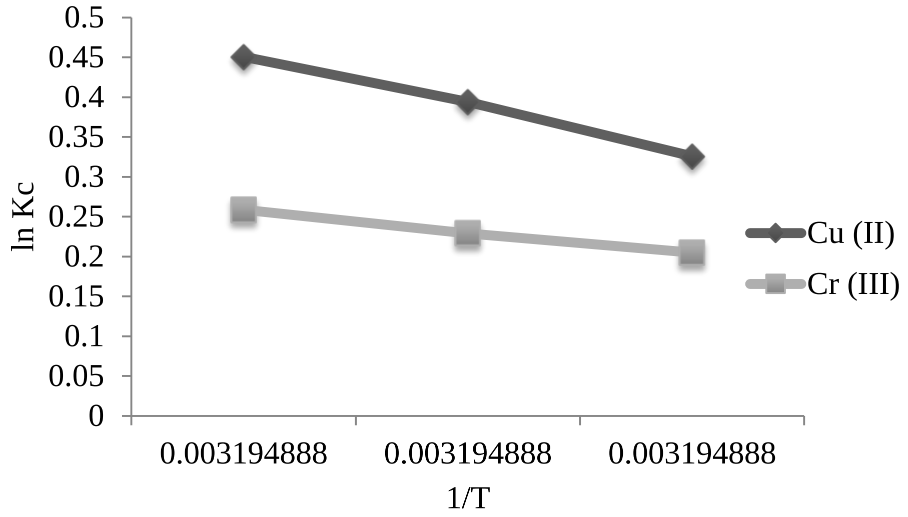

Figure 4. Plot of ln Kc vs. 1/T for the sorption of Cu (II) and Cr (III) on *A. flavus*

The values of ΔH° and ΔS° were calculated from the slope and intercept of the linear plot of ln Kc vs 1/T. The plots between ln Kc vs 1/T is shown in Fig. 4.

Table 3. Thermodynamic parameters for the biosorption of Cr (III) and Cu (II) by *A. flavus*.

Metal Ion	**ΔH° ($kJmol^{-1}$)**	**ΔS° ($kJmol^{-1}$)**	**R^2**	**ΔG ($Jmol^{-1}$)**		
				293 K	**303 K**	**313 K**
Cu (II)	0.515	-0.062	0.997	-793.336	-992.532	-1172.55
Cr (III)	0.284	-0.026	0.996	-558.038	-651.334	-533.136

The negative values of ΔG° showed the process spontaneity and feasibility of the metal biosorption on A. flavus. The positive values of ΔH° depicted the endothermic nature of the biosorption process. This may also due to the increase in biosorption with increase in temperature. The values of ΔS° were calculated negative for metal ions. The values depicted that the biosorption process is uniform. The negative values of ΔS° showed the increase in uniform behavior of biosorption process. The values of ΔH°, ΔS°, ΔG° and R2 are shown in Table 3. In an earlier investigation Cr (IV) biosorption was carried out on A. niger. Three different ranges of temperature taken were 22, 33 and 50°C. The values of ΔG° were evaluated as -7.403, -7.780 and -8.106 (Jmol-1) respectively. The ΔH° and ΔS° were calculated from the slope and intercept of the plot between ln Kc and 1/T. The values were shown to be 7.366 × 10-4kJmol-1 while ΔS° was calculated to be 0.0251kJmol-1. The positive values of ΔH° and ΔS° showed the endothermic nature of the reaction and increasing randomness at the liquid/solid interface during the process of biosorption of Cr (IV) [22].

In an earlier investigation the thermodynamics studies were done on the biosorption of Cd (II), Pb (II) and Zn (II) by Cocos nucifera. The values of ΔH° and ΔS° were found to be 9.878 and 47.7854 respectively for Cd (II), 2.308 and 8.1153 for Pb (II) and 5.421 and 13.68 for Zn (II) [23].

IV. CONCLUSIONS

It can be concluded from the present investigation that *A. flavus* has efficient potential for the metal uptake from solution as compared to *A. niger*. The optimum conditions were found to be pH 6, 40°C and it was noted that biosorption increased with the increase in temperature and initial metal concentration. The kinetics study revealed the pseudo-second-order model to be better fitted with regression coefficients values higher than 0.982 as compared to pseudo-first order model. Langmuir adsorption isotherm best represented the equilibrium data with high R^2 values as compared to Freundlich isotherm. The thermodynamic studies depicted the process spontaneity with negative values of ΔG°. Positive values of ΔH° revealed the endothermic nature of the process and negative values of ΔS° represented the uniform behavior of the process which increased with increasing biosorption.

V. ACKNOWLEDGMENTS

The author appreciates the twas "The academy of sciences for the developing world" ICTP Campus – Strada Costiera 11 – 34151 Trieste – Italy, assistance for this work.

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AUTHORS

Wajeeha Azhar has done her BS (HONS) in Botany from Lahore College for Women University, Lahore, Pakistan and recently completed M.Phil in the field of Environmental Science from Fatima Jinnah Women University, The Mall, Rawalpindi, Pakistan.

Shazia Iram has been appointed as Professor of Environmental Science in Fatima Jinnah Women University, The Mall, Rawalpindi, Pakistan.