ISOTHERMAL, KINETIC AND THERMODYNAMIC STUDY OF BIOSORPTION OF CU (II) ION FROM AQUEOUS SOLUTION BY *ASPERGILUS NIGER*

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Abstract
Biosorption of Cu(II) ion by Aspergilus niger were investigated in a batch system. The capacity of Aspergilus niger to remove Cu(II) ion from aqueous solution were investigated under varying parameters which include: initial metal concentration, temperature and inoculum concerntration on biosorption capacity were also studied. The maximum biosorption capacity of Aspergilus niger was at 25 ppm of Cu(II), showed 100 % removal at pH 5.8 and 25 ^{o}C. Biosorption equilibrium was established in 150 minutes. The process fitted well into pseudo second order kinetic model and was best explained by Langmuir isotherm with maximum absorption capacity of 6.998 mgL^{-1}. The values of thermodynamic parameters obtained from this study, (i.e. ΔG^{o}, ΔH^{o} and ΔS° values) imply that the process is feasible and spontaneous.

Keywords*: Aspergilus niger*, biosorption, equilibrium, kinetics, thermodynamics.

Introduction

Persistence of heavy metals in the ecosystem and their incremental accumulation in the food chain make their environmental contamination to be worldwide problems. Copper, one of the important toxic metals finds its way through the waste water generated from industrial processes (such as: electroplating, mining, electrical and electronics, iron and steel production etc.) into water streams [1]. The effects of acute copper poisoning in humans and plants are very serious, in particular possible liver damage with prolonged exposure. Intake of over dosed copper by humans may cause to severe mucosal irritation, hepatic and renal damage, widespread capillary damage, gastrointestinal irritation and central nervous problems [2, 3].

High level of copper compounds in the body may lead to aging, schizophrenia, mental illness, Indian childhood cirrhosis, Wilson's and Alzheimer's diseases [4 - 6]. In the blood system, higher level of copper generates reactive free oxygen species and damage the protein, lipids and DNA [7]. Damage to marine life and vital organs such as gills, liver, kidneys, the nervous system and changing sexual life of fishes a has been attributed to high concentration of copper [8, 9]. It is therefore important to reduce the concentration of copper in industrial effluent to acceptable level before discharge into stream or other receiving water bodies.
New technologies for heavy metal removal from wastewater are desirable due to strict environmental regulations. Readily available technologies (such as; ion exchange, chemical precipitation, oxidation reduction, filtration, electrochemical techniques etc.) are most time ineffective for the removal of heavy metal ions at low concentrations (below 50 mg/L), and besides they may be expensive. Toxic sludge may also be generated with another problem of disposal.
Biosorption is an innovative technology for the removal of metal ion from aqueous solution with superior advantages [10]. Its advantages include; high efficiency and selectivity for absorbing metals in low concentrations, energy-saving, broad operational range of pH and temperature, easy reclamation of metals and easy recycling of the biosorbent. Agricultural based materials have been utilized as biosorbent for heavy metal biosorption In the recent years, these include: coconut husk and palm pressed fibres [11, 12], sea weeds [13], and bagasse ash [14].
Numerous studies have been devoted to preparation of low-cost high quality sorbents for purification of water [14 – 19]. In this study, we used *Aspergilus niger* for the preparation of biosorbent for the removal of copper (II) ion from aqueous solution in a batch process. The effect of solution pH, biosorbent dose, initial metal ion concentrations and contact time were investigated. The equilibrium parameters were analyzed with common adsorption isotherms.

Materials and Methods

Preparation of Cu (II) ion solution

Aqueous solutions of copper (II) ions of different concentration were prepared from copper nitrate ($Cu(NO_3)_2$) obtained from British Drug House, London. This was used as adsorbate and was not purified prior to use. Double distilled-deionised water was employed for the preparation of all the solutions and reagents.

Preparation of media for microbial growth

The media used in this study are potato dextrose agar and potato dextrose broth. Potato Dextrose Agar was prepared by dissolving 10 g of potato dextrose agar powder in 250 mL sterile distilled water. The mixture was then melted in a water bath and sterilized in the autoclave at 121°C for 15 m. The broth was prepared from 200 g of potato tuber, 20 g of dextrose and a drop of antibiotic. Peeled potato was weighed and boil till soft (1 h), then it was marshed and sieved; distilled water was added to the filtrate in a conical flask. Dextrose agar and lactic acid were added. The mixture was then sterilized in the autoclave at 121°C for 15 minutes.

Isolation of microorganism: Sub-Culturing

Aspergillus niger, was obtained from the Department of Microbiology laboratory of the University of Agriculture Abeokuta. The organism was picked with a sterile wire loop from the pure culture and sub cultured by streaking onto a freshly solidified media. The microbial counting was done by slide culture technique.

Batch equilibrium studies

Adsorption isotherms were performed as earlier described [20]. Solutions of Cu (II) ion with different initial concentrations (25 – 100 mg L^{-1}) were prepared in these flasks. 1.0 x 10^3 spore ml^{-1} of *A. Niger*, 10 ml of potato dextrose broth and distilled water was used to make up the solution to mark. The solutions were kept in an isothermal shaker at constant temperature of 25 ± 1^0C for up to 72 h to reach equilibrium. Similar procedure was followed for another set of Erlenmeyer flask containing the same Cu (II) ion concentration without adsorbent to be used as a blank. The pH of the solutions was adjusted when necessary with diluted hydrochloric acid or sodium hydroxide (0.1 mol. L^{-1}). The flasks were then removed from the shaker and the final concentrations of Cu (II) ion in the solutions were determined. The concentration of Cu(II) ion in the supernatant solution after and before adsorption was determined using an atomic absorption spectrophotometer (Buck Scientific model 200 VGP). The samples were filtered prior to analysis in order to minimize interference of the biosorbent with the analysis. The amount of adsorption at equilibrium, Q_e (mg g^{-1}), was calculated by (Eq. 1).

$$Q_e = \frac{(C_o - C_e)V}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where C_o and C_e (mg/L) are the liquid-phase concentrations of Cu (II) ion at initial and equilibrium, respectively. V is the volume of the solution (L), and W is the mass of dry adsorbent used (g).

Batch kinetic studies

The kinetic experimental procedures were basically identical to those of equilibrium tests except that aqueous samples were withdrawn at a preset time interval. The withdrawn aqueous samples was then analyzed for the concentrations of Cu(II) ion. The amount biosorbed at time t, Q_t (mg g^{-1}), was calculated by:

$$Q_t = \frac{(C_o - C_t)V}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where C_o and C_t (mg/L) are the liquid phase concentrations of Cu(VI) ion at initial and any time t, respectively. V is the volume of the solution (l), and W is the mass of dry adsorbent used (g).

Results and Discussion

Effect of agitation time and concentration on biosorption of Cu (II) ion.

A series of contact time experiments for Cu(II) ion have been carried out at different initial concentration (25 – 100 mg/L) and at a temperature of 25 ^{o}C. Fig. 1 shows that the contact time necessary for Cu (II) ion with initial concentrations of 25 - 100 mg/L to reach equilibrium is about 15 minutes. The adsorption capacity at equilibrium increases from 0.46 to 2.15 mg g^{-1} with an increase in the initial Cu(II) ion concentration from 25 to 100 mg L^{-1}. It is evident that *A. Niger* is an efficient biosorbent for Cu (II) ion in aqueous solution as the process attains equilibrium gradually.

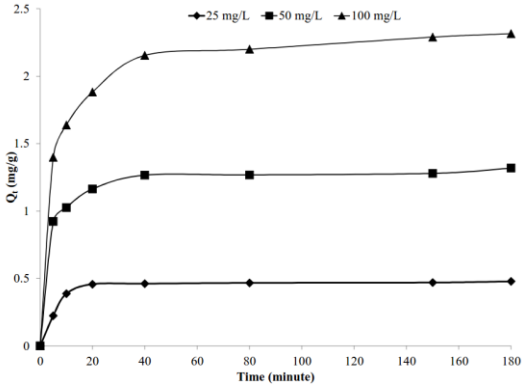


Fig. 1. The variation of adsorption capacity with biosorption time at various concentration of Cu (II) ion.

Biosorption kinetics

The rate constant of adsorption is determined from the pseudo first-order equation given by Langergren and Svenska [21]:

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where Q_e and Q_t are the amounts of Cu(II) ion biosorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_1 the rate constant adsorption (h^{-1}). Values of k_1 were calculated from the plots of ln(Q_e - Q_t) versus t for different concentrations of Cu(II) ion. The average correlation coefficient values of 0.7 depict poor fit, also the experimental Q_e values is not in agreement with the calculated ones, obtained from the linear plots (Table1, Fig. 2). This shows that the biosorption process does not fit well with first-order

kinetics, hence, it is necessary to compare the data with second order equation and subject the models to validity test using sum of error square i.e. (SSE).
Pseudo second-order equation is based on equilibrium adsorption [27] and expressed as:

$$t/Q_t = 1/k_2 Q_e^{\,2} + (1/Q_t)t \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where k_2 (g mg^{-1} s^{-1}) is the rates constant of second-order adsorption.

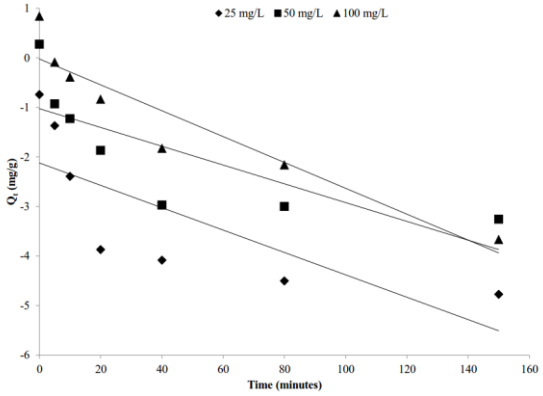


Fig. 2. First order kinetics for the biosorption of Cu(II) ion by *A. niger*.

A second-order kinetics model will give a linear relationship for the plot of t/Q_t versus t. The values of Q_e and k_2 will can be estimated from the slope and intercept of the plot. The model is more likely to be able to predict the behaviour of the process over the whole range of adsorption. Fig. 3 shows a good agreement between experimental and calculated Q_e values (Table 1). The correlation coefficients for the second-order kinetic model are about 0.9 indicating the applicability of this kinetic equation and the second-order nature of the biosorption process of Cu(II) ion on the adsorbent.

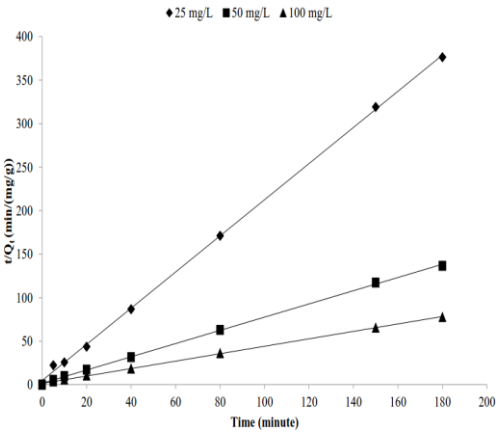


Fig. 3. Pseudo-second order kinetics for the biosorption of Cu(II) ion by *A. niger*.

Test of kinetic models

The validity of the two kinetic models can also be verified by the sum of error squares (SSE, %) along with R^2 values. The biosorption kinetics of Cu (II) ion on adsorbent prepared from *Aspergilus Niger* was tested at different initial concentrations. The validity of each model was determined by the sum of error squares (SSE, %) given by Eq. 5,

$$SSE(\%) = \sqrt{\frac{\sum (Q_{e,\exp} - Q_{e,cal})^2}{N}} \quad \ldots\ldots\ldots\ldots \quad (5)$$

where N is the number of data points. The higher is the value of R^2 and the lower is the value of SSE; the better will be the goodness of fit. Table 1 lists the calculated results. It is found that the biosorption kinetics of Cu (II) ion on adsorbent prepared from *A. Niger* can be best described by the pseudo second-order kinetic model.

Table 1. Pseudo first and second-order adsorption rate constants for biosorption of Cu(II) by *A. niger*

Conc. mg/L	pseudo first order model				pseudo second order model			
	$Q_{e\ exp}$ mg/g	$Q_{e(cal)}$ mg/g	k_1	R^2	k_2 g/(mg min)	$Q_{e(cal}$ mg/g	R^2	% SSE
25	0.48	1.023	0.02	0.6	0.038	0.48	0.99	0.193
50	1.32	1.019	0.02	0.6	0.876	1.32	0.99	0.106
100	2.32	1.026	0.03	0.9	2.967	2.36	0.99	0.456

The Elovich equation.

The Elovich equation is based on equilibrium adsorption and it is generally expressed as shown by eq. 6 [22]:

$$Q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}), β is the desorption constant (g mg^{-1}) during the experiment. If the adsorption fits the Elovich model, a plot of Q_t vs ln(t) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β)ln(αβ).
The graph of the Elovich model for the biosorption of the Cu(II) ion by *A. Niger* at 25 ^{o}C is shown in Fig 4. The values of R^2 for the parameters of the Elovich model show that the data fit well for Cu(II) ion biosorption thereby suggesting that the process involved chemisorption.

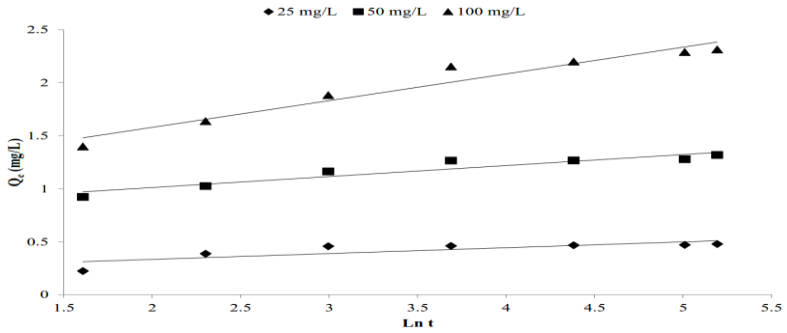


Fig. 4. The Elovich model for the biosorption of the Cu(II) ion by *A. Niger*.C

Table 2. The Elovich and intraparticle diffusion model parameters for the biosorption of the Cu(II) ion by *A. Niger*

concentration (mg L^{-1})	Elovich			Intraparticulate		
	β (g mg^{-1})	α	R^2	k_{id}	a	R^2
25	18.158	3.129	0.99	0.027	0.198	0.93
50	9.621	236.875	0.99	0.067	0.605	0.94
100	3.959	17.731	0.99	0.129	0.913	0.95

The intraparticle diffusion model.

The intraparticle diffusion model is expressed as in eq. 7 [20]:

$$R = K_{id} t^{a} \quad \text{..... (7)}$$

The linearised form of eq. 7 is written as follow:

$$\log R = \log K_{id} + a \log t \quad \text{..... (8)}$$

where R is the percentage metal ion biosorbed, t is the contact time (min), "*a"* is the gradient of linear plots, K_{id} is the intraparticle diffusion rate constant (min^{-1}), "*a*" depicts the adsorption mechanism. K_{id} is taken as a rate factor, i.e. percentage metal ion biosorbed per unit time.

If the mechanism of adsorption fits the intraparticle diffusion model, then a plot of 1og R against 1og t will yield a straight line (Fig. 5) with a slope *"a"* and an intercept of 1og K_{id}. The intraparticle diffusion model for the adsorption of the Cu(II) ion by *A. Niger* at 25 ^{o}C is shown in Fig. 5 below. The curves show a kind multi-linearity for the biosorption process, which implies that the adsorption process involves more than one kinetic stage (or sorption rates) [23]. The values of K_{id} were calculated from the slope of such plots and the R^2 values (Table 2) led to the conclusion that the intraparticle diffusion process also contribute to the rate-limiting step.

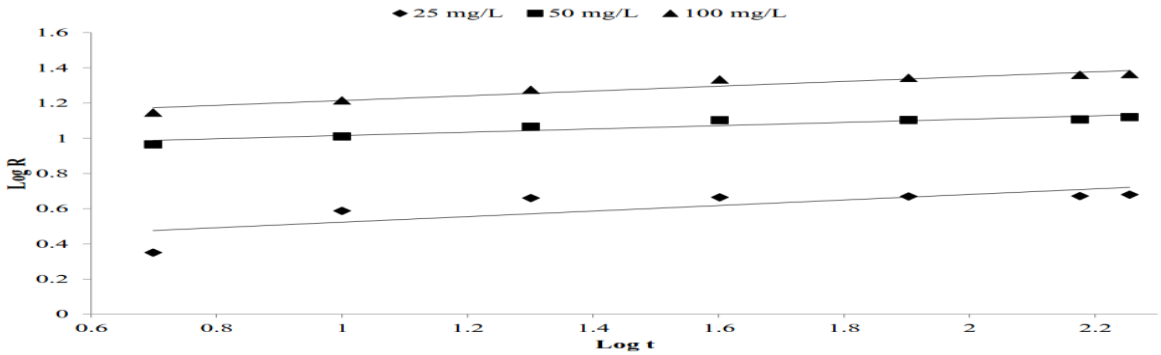


Fig. 5. Intraparticle diffusion model for the biosorption of the Cu(II) ion by *A. Niger*

Table 3. Isothermal parameters for the biosorption of the Cu(II) ion by *A. Niger*

Langmuir		Freudlinch		Temkin		Dunbini- Radushkevich	
Q_{max}	6.998	K_F	5.368	b_T	381.04	Q_{max}	25.49
b	0.010	n	6.223	a_T	0.226	β	2×10^{-5}
R_L	0.631					E	158.11
R^2	0.982	R^2	0.853	R^2	0.968	R^2	0.891

Adsorption Isotherms:

Adsorption isotherms represent the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbents surface at a given condition. A number of isotherm models have been developed to describe equilibrium relationships. An adsorption isotherm is characterized by certain constants the values of which express the surface properties and affinity of the sorbent and can also be used to compare biosorptive capacity of biomass for different metal ions. Out of several isotherm equations, four have been applied for this study, the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R) isotherms. Their linearized form for the Cu(II) ion uptake by *A, Niger* at 25 °C were shown in Figs. 6 to 9. The adsorption constants evaluated from the isotherms with the correlation coefficients are given in Tables 3.

Langmuir isotherm can be used to show how favorable is the biosorption process in a batch adsorption process. Q_{max} is the maximum adsorption capacity of the material (mg g^{-1}) assuming a monolayer of adsorbates uptake by the adsorbent and *b* the Langmuir affinity constant (L mg^{-1}). The values of R^2 in Table 3 for Langmuir Isotherm show a better fitting. The values of R_L in this study are presented in Table 3 and it implied that the process is favourable.

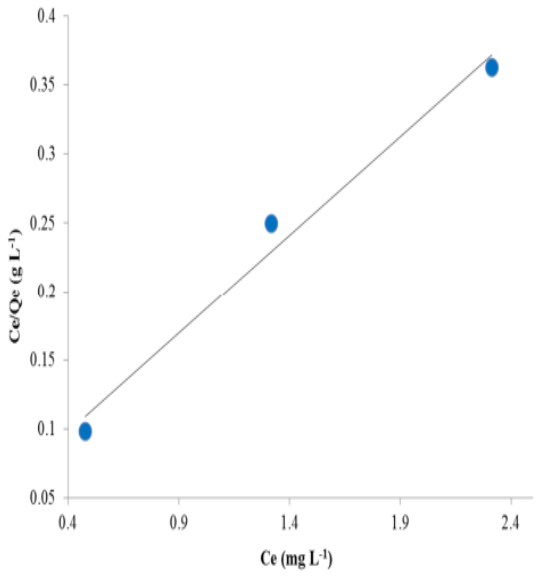


Fig. 6. Linearized Langmuir Adsorption Isotherm for the biosorption of the Cu(II) ion by *A. Niger*

K_F, ((mg g^{-1}) (L g^{-1}))$^{1/n}$ and n are Freundlich constants, which are related to the sorption capacity and adsorption intensity of the adsorbent respectively. The value of K_F from this study showed a higher affinity for Cu(II) ion, and somehow a better fitting, the value of 1/n showed that the surface is heterogeneous (Table3; Fig 7).

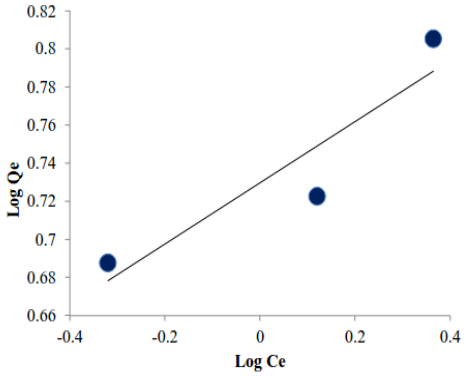


Fig. 7. Linearized Freundlich Adsorption Isotherm for the biosorption of the Cu(II) ion by *A. Niger*

The interactions between adsorbents and metal ions to be adsorbed are accounted for by Temkin isotherm. It is based on the assumption that the free energy of sorption is a function of the surface coverage [24]. The constant b_T is related to the heat of adsorption and a_T is the equilibrium binding constant (L/min) corresponding to the maximum binding energy. The values b_T in this study (Table 3) show that the process is not purely chemisorption confirming the heterogeneous nature of the surface [20].

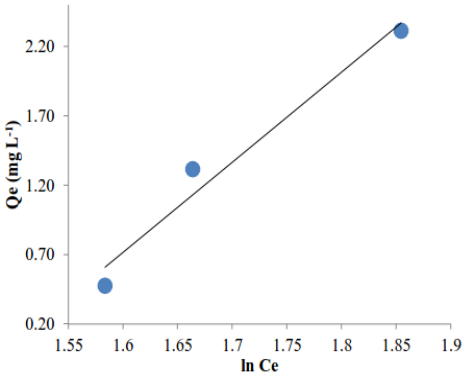


Fig. 8. Linearized Temkin Adsorption Isotherm for the biosorption of the Cu(II) ion by *A. Niger*

The Dubinin-Radushkevich model [25] was chosen to estimate the heterogeneity of the surface energies and also to determine the nature of biosorption processes as physical or chemical. The value of the constant, β, gives an idea about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate. Q_m is the theoretical saturation capacity (mol g^{-1}), and ε is the polanyi potential. The magnitude of E showed that the sorption process is dominated by physiorption [26].

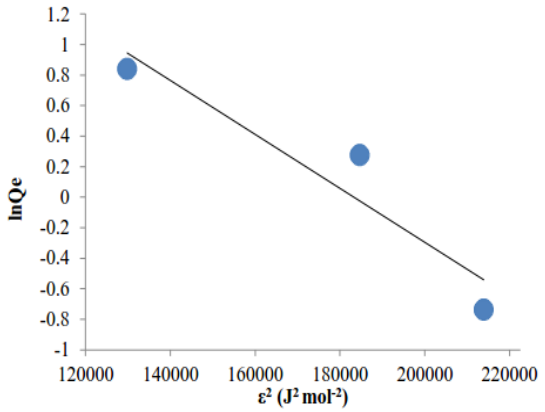


Fig. 9 Linearized Dubinin – Radushkevich Adsorption Isotherm for the biosorption of the Cu(II) ion by *A. Niger*

Biosorption thermodynamics

Distribution of the metal ion between the solution and the biosorbent is an equilibrium process, the equilibrium constant K_D could easily be written as:

$K_D = \frac{M^{n+}{}_{solution}}{M^{n+}_{Biosorbed}}$, in other word, the equilibrium constant, $K_D = \frac{C_e}{q_e}$.

This constant can be used to estimate the thermodynamic parameters owing to its temperature dependence. The thermodynamic parameters i.e. ΔG°, ΔH° and ΔS° were estimated from the following relations:

$$\Delta G^o = -RT \ln K_D \quad \text{..... (18)}$$

$$\Delta G^o = \Delta H^o - T\Delta S \quad \text{..... (19)}$$

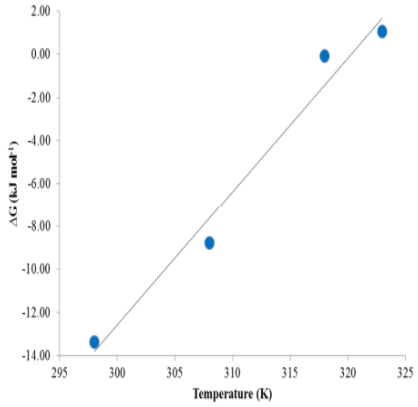


Fig. 10. Plot of ΔG^o against the temperature for the biosorption of Cu (II) ion by *A. Niger*

A plot of ΔG^o against the temperature, (Fig. 10) gives a straight line graph with intercept as ΔH^o and slope as ΔS^o. The thermodynamic parameters are presented in Table 4.

Table 4. Thermodynamic parameters for the biosorption of Cu (II) ion by *A. Niger*

Temperature (K)	ΔG (kJ mol^{-1})	ΔS (kJ mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	R^2
298	-13.373	-0.62	-198.3	0.974
308	-8.775			
318	-0.078			
323	1.066			

The negative values of ΔG°, free energy change of the process implies a thermodynamically feasible and spontaneous biosorption process. However, the decrease in ΔG° values as the temperature increased implied a decline in feasibility of biosorption as temperature is increased. The ΔH° parameter was also found to be negative indicating exothermic nature of the biosorption processes. The negative ΔS° value means a decrease in the randomness at the solid/solution interface during the biosorption process.

Conclusions

The present investigation showed that *A. Niger* can be effectively used as a material for biological removal of Cu(II) ion from aqueous solution over a wide range of concentration and pH. The biosorption process follows a monolayer Langmuir adsorption type isotherm. The value of the maximum adsorption capacity, Q_o, (6.998 mg g^{-1}) is comparable with the values observed for other biosorbent reported in earlier studies. Kinetic

data is best explained with pseudo second-order kinetic model.

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