

Kinetics and Isotherm Models of Cu^{++} Biosorption by Biomass of *Helianthus Annuus*

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Abstract-The kinetics of biosorption of Cu^{++} ions by biomass of *Helianthus Annuus* was found fast, and reached equilibrium in 20 min and followed pseudo-second order rate equation. To evaluate the biosorption equilibrium, four isotherm models were fitted to experimental data. The best model was determined by taking into account correlation coefficient (r^2) and Average Percentage Error (APE). The best adjustment from two parameter isotherms was observed to be the D-R (r^2 0.973, APE % 1.60). The mean energy of biosorption was calculated as $12.69 \text{ kJ mol}^{-1}$ from the D-R biosorption isotherm. Activation energy (E_a) of the biosorption was determined as 8.56 kJ mol^{-1} . Thermodynamic parameters such as ΔH° , ΔS° and ΔG° were calculated from the slope and intercept of linear plot of $\ln K_D$ versus $1/T$.

Keywords: Copper (II), Isotherm, *Helianthus Annuus*, Thermodynamic, Biosorption

1.Introduction

The increased use of heavy metals in many industries has resulted in the generation of large amounts of polluted aqueous effluents which contain high levels of heavy metals and cause environmental disposal problems for plants, animals and human beings (1). Natural weathering processes, waste emissions, atmospheric depositions and anthropogenic activities also contribute to the heavy metal contamination in the water bodies. Among these contaminants, copper is usually considered to be non-toxic for human at lower concentration ranges, but its presence at higher concentrations ($>5 \text{ mg/l}$) in the body has been linked many of health problems such as high fever, kidney damage, vomiting and hemolysis (2-7).

The uptake of toxic metal ions from industrial wastewaters using different adsorbents is currently of great interest (8-10). Biosorption, an alternative process, is the uptake of heavy metals from aqueous solutions by biological materials. This novel approach is competitive, effective and cheap (11).

Biomass of *Helianthus Annuus* for Cu^{++} ions are an economical material, which has been used for the uptake of Cu^{++} ions from aqueous solutions.

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In the present work, values of well-known thermodynamic and isotherm studies have been performed to elucidate the equilibrium biosorption behavior of Cu^{++} ions at different temperatures. In addition, the kinetic parameters as a function of agitation rate, pH, temperature, and particle size have been investigated.

2.Material and Methods

2.1. Biosorbent preparation

The shells of *Helianthus Annuus* were gathered after they were consumed. Fresh shells of *Helianthus Annuus* were dried in outdoors for 72 h and cut into small pieces, ground in a blender to granulate and sieved to get it separated for different particle sizes. 500 mg portions of the sample were taken for biosorption studies.

Cu^{++} solutions were prepared by diluting 400 mg L^{-1} of $\text{CuSO}_4 \cdot 6\text{H}_2\text{O}$ (Merck) stock solution with deionized water to a desired concentration range. The concentration of the Cu^{++} ions were complexometrically determined (12).

Biosorption of Cu^{++} ions on the shells of *Helianthus Annuus* was investigated in a batch reactor of 750 mL with a water-cooling jacket. The effect of pH (from 3 to 5.5), biosorbent dosage (from 0.4 to 0.9 g/400 mL), particle size (P.S) (0.25-0.5, 0.5-1 and 1-2 mm), agitation rate (A.R) (from 150 to 900 rpm) and temperature (from 15 to 55°C) on the biosorption process were studied. The initial pH values of solution were adjusted with 0.1M H_2SO_4 or 0.1M NaOH.

3. Results and discussion

3.1. Kinetics of Cu^{++} biosorption

In order to examine the mechanism of biosorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyse the rate data. The linear pseudo-first-order equation is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

where q_t and q_e are the amounts of Cu^{++} ions biosorbed at time t and at equilibrium (mg/g), respectively, k_1 is the rate constant of pseudo-first order biosorption process (min^{-1}). A plot of $\log(q_e - q_t)$ vs. t for biosorption of Cu^{++} was drawn as a

function of agitation rate, pH, temperature and particle size.

The correlation coefficients of pseudo-first order equation were determined between 0.5 and 0.9 which values were lower. At all the experimental conditions, the correlation coefficients show that the biosorption system is not a pseudo-first order reaction then linear pseudo-second order equation was used in this study.

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

where k_2 is the equilibrium rate constant of pseudo-second order biosorption (g/mg.min). Fig. 1 shows typical plots t/q_t vs. t of pseudo-second order equation.

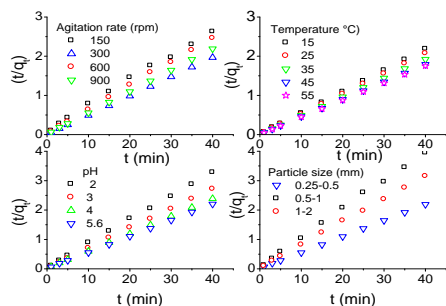


Fig. 1. The plot of the pseudo-second order equation at the different experimental conditions.

The straight lines in the plot show good agreement of experimental data with the pseudo-second order kinetic model for different agitation rates, temperatures, initial pHs and particle sizes. The correlation coefficients for the pseudo-second order equation were approximately 0.99 for all experimental conditions. This strongly suggests that biosorption is most appropriately represented by a pseudo-second order rate process.

3.1.1. Reaction kinetics and biosorption capacities as a function of agitation rate(A.R)

Biosorption studies were carried out in a batch reactor at pH 5.5. Cu^{++} concentration in the solution was 40 mg L^{-1} . The agitation rate varied from 150 to 900 rpm. The rate constants and biosorbent capacities at different agitation rates of 150, 300, 600 and 900 rpm were approximately determined as (0.036, 0.12, 0.29 and 0.48 g/mg.min) and (15.8, 16.4, 18.3 and 20.4 mg/g) respectively. Biosorption rate constants and biosorption capacities increased because of increasing kinetic energy of Cu^{++} ions, and they were maximum at 900 rpm as seen from Fig.2.

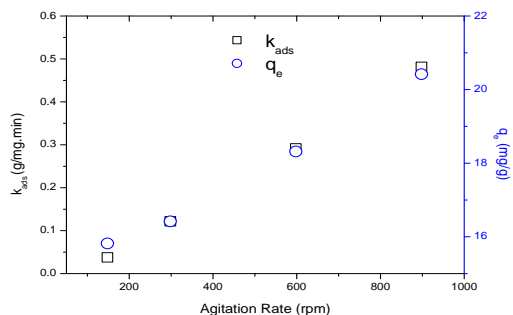


Fig. 2. Relation between q_e , k_{ads} and agitation rate ($\text{Cu}_0^{++} 40 \text{ mg L}^{-1}$, $T 288 \text{ K}$, pH 5.6, P.S 0.25-0.5 mm and biosorbent dosage 0.5g /400 mL).

3.1.2. Reaction kinetics and biosorption capacities as a function of solution of pH

Fig. 3 presents the effect of initial pH on the rate constants and biosorption capacities. In order to find out the rate constant and biosorption capacity, experiments were conducted in copper solution of 40 mg.L^{-1} . Biosorbent of 500 mg was added separately at the pH range 2-5.5. The rate constants and biosorbent capacities of Cu(II) uptake at different pHs of 2, 3, 4 and 5.6 °C were approximately determined as (0.1, 0.19, 0.23 and 0.29 g/mg.min) and (12.4, 14.8, 16.9 and 18.3 mg/g), respectively.

The rate constants and biosorption capacities were high at the pH 5.6. The pH of the aqueous solution affected on the rate constants and biosorption capacities and they increased with the augmentation of pH values.

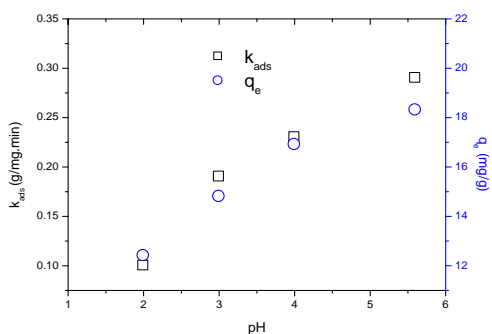


Fig. 3. Relation between q_e , k_{ads} and pH values ($\text{Cu}_0^{++} 40 \text{ mg L}^{-1}$, $T 288 \text{ K}$, A.R 600 rpm, P.S 0.25-0.5 mm and biosorbent dosage 0.5g /400 mL).

H^+ ions at lower pH values concentration compete with Cu^{++} ions for the biosorption sites, and resulting in the reduced uptake of Cu^{++} ions. As the value of solution pH increased, the biosorbent surface became more and more negatively charged and therefore the biosorption of positively charged Cu^{++} and Cu(OH)^+ species were more favourable.

3.1.3. Reaction kinetics and biosorption capacities as a function of solution of temperature

The effect of the temperature on the rate constants and biosorption capacities was shown in Fig.4. The rate constants and biosorbent capacities of at different temperatures of 15, 25, 35, 45 and 55 °C were approximately determined as (0.29, 0.33, 0.37,0.39 and 0.46 g/mg.min) and (18.3, 19.6, 21.3, 22.7 and 23.3 mg/g), respectively. It was thought that kinetic energy of Cu^{++} ions increased with the increase of the temperature. Hence, collision frequency between biosorbent and Cu^{++} ions increased and then Cu^{++} ions were electrostatically biosorbed on the surface of biosorbent particles.

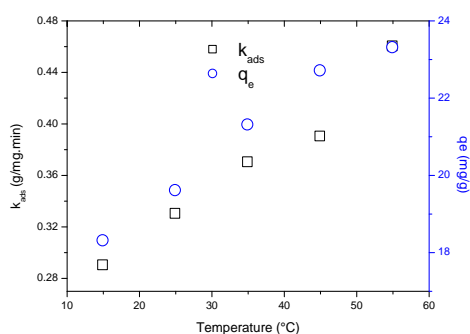


Fig. 4. Relation between q_e , k_{ads} and temperature (Cu_o^{++} 40 mg L^{-1} , pH 5.5, A.R 600 rpm, P.S 0.25-0.5 mm and biosorbent dosage 0.5g /400 mL).

3.1.4. Reaction kinetics and biosorption capacities as a function of particle size(P.S)

The effect of P.S on the rate constants and biosorption capacities was shown in Fig.5.

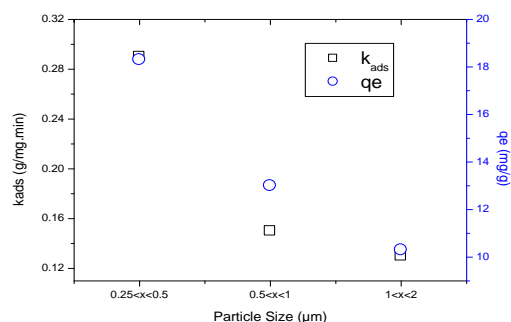


Fig. 5. Relation between q_e , k_{ads} and particle size (Cu_o^{++} 40 mg L^{-1} , pH 5.5, A.R 600 rpm and biosorbent dosage 0.5g /400 mL).

The rate constants and biosorbent capacities of at different particle sizes of 0.25-0.5, 0.5-1 and 1-2 mm were determined as (0.29, 0.15 and 0.13 g/mg.min) and (18.3, 13 and 10.3 mg/g), respectively. The rate constants and biosorption capacities increased with the decrease of the

particle size due to increase of the biosorbent surface area per unit particle size as seen from Fig.5.

3.2. Equilibrium Isotherms

At pH 5.5, biosorption isotherm experiments were carried out with accurately weighted amount of the biosorbent (0.4–0.9 g L^{-1}) that were continuously stirred at 600 rpm. The temperature was controlled at 15°C. Agitation was provided for 40 minutes. Experimental isotherm data were fitted to four different models of biosorption isotherms: Freundlich, Langmuir, Temkin, D-R from two parameter isotherms.

3.2.1. Non-linear regression analysis

All the model parameters were evaluated by non-linear regression using STATISTICA software. The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data (13). Apart from the correlation coefficient (r^2), average percent error (APE%) was also used to measure the goodness of fit. APE calculated according to Eq. (3) indicated the fit between the experimental and predicted values of Cu^{++} concentration.

$$\text{APE}(\%) = \frac{\sum_{i=1}^N \left| \frac{(\text{C})_{\text{experimental}} - (\text{C})_{\text{predicted}}}{(\text{C})_{\text{experimental}}} \right|}{N} \times 100 \quad (3)$$

where N is the number of experimental data.

3.3. Two-parameter models

3.3.1 Langmuir isotherm

The Langmuir biosorption isotherm has been used to quantify the performance of different biosorbents. In its formulation, binding to the surface was primarily by physical forces and all sites possess equal affinity for the biosorbate. It may be represented by Eq.(4).

$$Q = \frac{Q_{\max} b_L C_f}{1 + b_L C_f} \quad (4)$$

where Q_{\max} is the maximum metal uptake (mg/g) and b_L the Langmuir equilibrium constant (L/mg). The constant b_L represents affinity between the biosorbent and biosorbate. Values of b are reflected in the steep initial slope of a sorption isotherm, indicating desirable high affinity. Among two-parameter models, high correlation coefficients and low APE (%) were observed in Langmuir model as seen from Fig.6 and Table 1. Relations between observed and predicted values were shown in Fig.6.

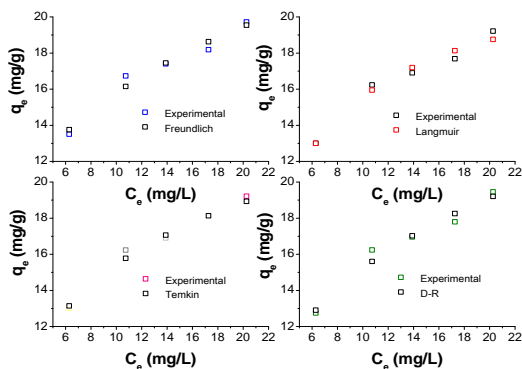


Fig.6. The predicted values versus observed values for isotherms (Cu_o^{++} 40 mg.L^{-1} , T 15°C, A.R 600 rpm, P.S 0.25-0.5 mm and the solution of 400 mL).

3.3.2. Freundlich isotherm

The Freundlich is originally in empirical nature, but was later interpreted for heterogeneous surfaces. It is assumed that the stronger binding sites are occupied first and the binding strength decreases with the increasing degree of site occupation. It may be represented by Eq.(5).

$$Q = K_F C_e^{1/n_F} \quad (5)$$

where K_F is the Freundlich constant and n_F is the Freundlich exponent. From two-parameter models, correlation coefficient and APE (%) of Freundlich model were shown in Fig.6 and Table 1.

Table 1. Values of the parameters of the two-parameter models and correlation coefficients

Isotherms	Value	r^2	APE(%)
Freundlich			
K_f (L/g)	7.83	0.968	1.7
n_f	3.3		
Langmuir			
Q (mg/g)	23.845	0.972	1.6
B (L/g)	0.2038		
D-R			
B_D (mol^2/kJ^2)	0.0031		
Q_D (mol/g)	0.000963	0.973	1.6
E (kJ/mol)	12.69		
Temkin			
b_{T_e}	2.416	0.956	1.7
a_{T_e} (L/g)	6833.69		

3.3.3. Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of biosorption is linear rather than logarithmic. Freundlich equation.

The heat of sorption of all the molecules in the layer would decrease linearly with coverage due to biosorbate/biosorbent interactions. The Temkin isotherm was given by Eq.(6).

$$Q = \frac{RT}{b_{T_e}} \ln(a_{T_e} C_e) \quad (6)$$

where b_{T_e} is Temkin constant related to heat of sorption (J/mol), a_{T_e} Temkin isotherm constant (L/g). R the gas constant (8.314 J/mol K) and T the temperature (K). The correlation coefficient and APE (%) of model were shown in Fig.6 and Table 1.

3.3.4. Dubinin-Radushkevich (D-R) isotherm

Another popular equation for the analysis of isotherms is that proposed by Dubinin. He has reported that the characteristic sorption curve is related to the porous structure of the biosorbent. The isotherm is given by Eq.(7).

$$Q_e = Q_D \exp(-B_D \varepsilon_D^2) \quad (7)$$

$$\varepsilon_D = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

where Q_D is the D-R constant (mol/g); B_D the D-R constant (mol^2/kJ^2) and ε_D the Polanyi potential. The mean energy of sorption, E, is calculated by Eq.(9).

$$E = \frac{1}{\sqrt{2B_D}} \quad (9)$$

The D-R constants and mean free energy were given in Table 1. The magnitude of E is useful for estimating the type of biosorption. The E values obtained were around 12.69 kJ/mol, which are in the energy range of an ion-exchange reaction from 8 to 16 kJ/mol (14). This supports the fact that biosorption may be an ion Exchange reaction. From two-parameter models, correlation coefficient and APE (%) of D-R were shown in Table 1. D-R isotherm was defined as a suitable model because of the higher correlation coefficient and lower APE (%).

3.4. Thermodynamic Parameters

The changes in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the biosorption process were obtained using the following equations;

$$\Delta G^\circ = -RT \ln K_d \quad (10)$$

$$\ln K_d = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{R} \right) \left(\frac{1}{T} \right) \quad (11)$$

The values of $\log K_d$ were defined as follow:

$$K_d = \frac{F_e}{1-F_e} \quad (12)$$

Where F_e is the fraction biosorbed at equilibrium, R is the ideal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The enthalpy change (ΔH°) and the entropy change (ΔS°) are calculated from a plot of $\ln K_d$ versus $1/T$ (Fig. 7 (a)) and the values of them were given in Table 2.

Table 2. Thermodynamic parameters and values

ΔH° kJ/mol	ΔS° kJ/mol.K	ΔG° (kJ/mol)		
		288 K	298 K	308 K
13.19	0.048	-0.63	-1.114	-1.594

The negative value for the Gibbs free energy for Cu^{++} ions shows that the biosorption process is spontaneous and the degree of spontaneity of the reaction increases with the increase of temperature.

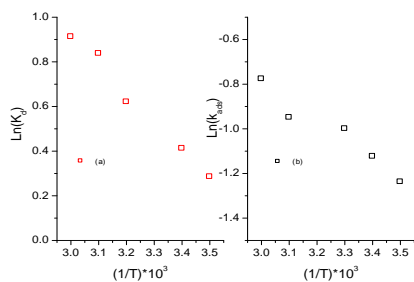


Fig.7. The plot $\ln K_d$ (a) and $\ln k_{ads}$ (b) versus $(1/T)$.

The biosorption process seems to be endothermic (ΔH° 28.23 kJ/mol). This result also supports that the biosorption capacity increases with the increase of temperature. Table 2 also shows that the (ΔS°) values were positive (entropy increases as a result of biosorption). This occurs as a result of redistribution of energy between the biosorbate and the biosorbent. Before biosorption occurs, the Cu^{++} ions near the surface of the biosorbent will be more ordered than in the subsequent adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing biosorption by producing a positive value of ΔS° and the randomness will increase at the solid-solution interface during the process of biosorption. Biosorption is thus likely to occur spontaneously at normal and high temperatures because $\Delta H^\circ > 0$ and $\Delta S^\circ > 0$.

4. Conclusion

In the present study, the isotherms, thermodynamic and kinetic investigations of Cu^{++} biosorption were studied using the two parameter isotherm models. The kinetic studies showed that pseudo-second-order equations were able to provide a realistic description of the biosorption kinetics of Cu^{++} ions. Isotherm studies indicated that the D-R isotherm model (r^2 0.973 and APE (%) 0.160) were suitable, but the others isotherm model were not able to describe the biosorption equilibrium of Cu^{++} ions. The value of the biosorption energy was determined using the D-R isotherm model. The

value of biosorption energy, E , gives an idea of the nature of biosorption. The activation energy of the Cu^{++} biosorption was calculated using Arrhenius equation. The dependence of Cu^{++} biosorption on temperature was investigated and the thermodynamic parameters ΔH° , ΔS° and ΔG° were calculated. The result shows an endothermic heat of biosorption, but a negative free energy value, indicating that the process of Cu^{++} biosorption is favored at high temperatures.

5. References

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