

Short communication

Equilibrium biosorption isotherm for lead ion on chaff

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Abstract

A new adsorbent system for removing lead ion from aqueous solutions has been investigated. This new adsorbent is cereal chaff, an agriculture product in middle-west region in China. Variables of the system include biosorption time, chaff dose and solution temperature. The experimental results were fitted to the Langmuir, Freundlich, Koble–Corrigan and Temkin model isotherms to obtain the characteristic parameters of each model. Both the Langmuir and Koble–Corrigan isotherms were found to best represent the measured biosorption data. According to the evaluation using the Langmuir equation, the maximum biosorption capacities of lead ion onto chaff was 12.5 mg g^{-1} at 293 K. Using the thermodynamic equilibrium coefficients obtained at different temperatures, various thermodynamic parameters, such as ΔG^0 , ΔH^0 and ΔS^0 , have been calculated. The thermodynamics of lead ion–chaff system indicates spontaneous and exothermic process. It was concluded that an increase in temperature result in a lower metal loading per unit weight of the chaff.

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1. Introduction

Adsorption has been an effective separation process for a wide variety of applications. Since activated carbon is expensive, an alternative inexpensive adsorbent able to drastically reduce the cost of an adsorption system has always been searched. The process of heavy metal removal by biological material is called biosorption. It can mainly be used for treatment of wastewater with low or medium initial heavy metal concentration. Other advantages of biosorption are that it avoids the generation of toxic sludge and can be used under a broad range of operating conditions (pH, temperature, metal concentration, presence of other ions in the solution, etc.). These demands led to increasing interest in biosorption [1,2]. The most appropriate method for assessing biosorbent capacity is the derivation of a whole adsorption isotherm. The adsorption isotherm is the equilibrium between the concentration in the fluid phase and the concentration in adsorbent particles at a given temperature.

The removal of metal ions from effluents is of importance to many countries of the world both environmentally and for water re-use. The application of low-cost adsorbents including carbonaceous materials, agricultural products and waste by-products has been investigated [3,4]. In recent years, agricultural by-products have been widely studied for metal removal from water. These include pine bark, tree tern, wheat shell, rice husk, sawdust, etc. [6–10].

Lead has been used in many industries and the removal of lead ions from wastewaters is significant [5,10]. The relatively cheap biosorbents are capable of removing significant quantities of lead ions. Chaff was chosen as biosorbent in this experiment. Firstly, as the rice husk [3], the physical characterization of chaff as a kind of food plant contains abundant floristic fiber and protein and properties the functional groups such as carboxyl, hydroxy and amidogen, etc., are in existence, which make biosorptive processes possible [11]. Secondly, the adsorbent of chaff obtained from agriculture as a by-product, furthermore, their yield is vastness. Usually, harvesting in Henan, Hebie and Shanxi Province in China, chaff was as feed to raise livestock and poultry and did not have any extensive use. So, the chaff is not only abundant but also cheap.

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The aim of this work was to study the possibility of the utilization of chaff for biosorption of lead ions from aqueous solutions. The system variables studied include biosorptive time, biomass dose, pH and temperature. The isotherm constants for the Langmuir, Freundlich, Koble–Corrigan and Temkin isotherm have been determined. The thermodynamics parameters, such as ΔG^0 , ΔH^0 and ΔS^0 , have been calculated.

2. Materials and methods

2.1. Materials

The major interest of this study was to investigate biosorption of lead by natural chaff produced China. The raw chaff was dried in an oven at 373 K for a period of 24 h and then ground and screened through a set of sieves to get different geometrical sizes 104–120 μm . This produced a uniform material for the complete set of biosorption tests, which was stored in an air-tight plastic container for all investigations.

The stock solutions of lead ion were prepared in distilled water using lead nitrate. All working solutions were prepared by diluting the stock solution with distilled water to the needed concentration.

The data obtained in batch model studies were used to calculate the equilibrium metal uptake capacity. It was calculated for biosorptive quantity of lead by using the following expression:

$$q_e = \frac{V(c_0 - c_e)}{m} \quad (1)$$

where q_e is the biomass biosorption equilibrium metal uptake capacity in mg g^{-1} , V the sample volume in mL, c_0 the initial metal ion concentration in mg L^{-1} , c_e the equilibrium metal ion concentration in mg L^{-1} and m is the dry weight of the biomass in grams.

2.2. Methods

2.2.1. Effect of biosorption time

Batch biosorption tests were done at different biosorption time at the initial concentration of lead ion 80 mg L^{-1} and chaff dose 0.4 g . The temperature was controlled with a water bath at the temperature of 293 K for all studies.

2.2.2. Effect of biomass dose

Batch biosorption tests were done at different biomass dose at the initial concentration of lead ion 80 mg L^{-1} and the chaff dose 0.1 – 0.6 g in 50 mL solution. The temperature was controlled with a water bath at the temperature of 293 K for all studies.

2.2.3. Equilibrium studies

A volume of 50 mL of lead ion solution with a concentration in the range 8 – 96 mg L^{-1} was placed in a 125 mL conical flask. An accurately weighed chaff sample 0.4 g with

particle size 104 – $120 \mu\text{m}$ was then added to the solution. A series of such conical flasks was then shaken at a constant speed of 100 rpm in a shaking water bath with temperatures 293 , 298 and 303 K , respectively. After shaking the flasks for 30 min , the chaff was separated by filtration through a $0.45 \mu\text{m}$ membrane filter to remove particulates and the filtrate was analyzed for the remaining lead ion concentration by atomic absorption spectrophotometer (AAS, AAAnalyst300, Perkin-Elmer).

3. Results and discussion

3.1. The effect of biosorption time

The results of biosorption at different shaking time are shown in Fig. 1. As can be seen from the Fig. 1, with the beginning of biosorption, the uptake of metal ions increased quickly, after 10 min , the change became slow. The biosorption process of lead on chaff was speedy and in 10 min , the process of biosorption nearly reached equilibrium. After this equilibrium period, the amount of adsorbed metals ions did not significantly change with time. So the removal efficiency was high. From Fig. 1, we selected 30 min as the time of biosorption equilibrium.

3.2. Effect of chaff dose on lead biosorption

The results of different chaff dose for lead biosorption are shown in Fig. 2. With the biomass dose of chaff increasing, the biosorption quantity per gram of chaff decreased. This was because that the amount of lead ions was changeless in the system; the more the chaff dose used, the little the biosorptive quantity adsorbed for per gram chaff. The flowing experiments were carried as the selected concentration of biosorbent was 8 g L^{-1} .

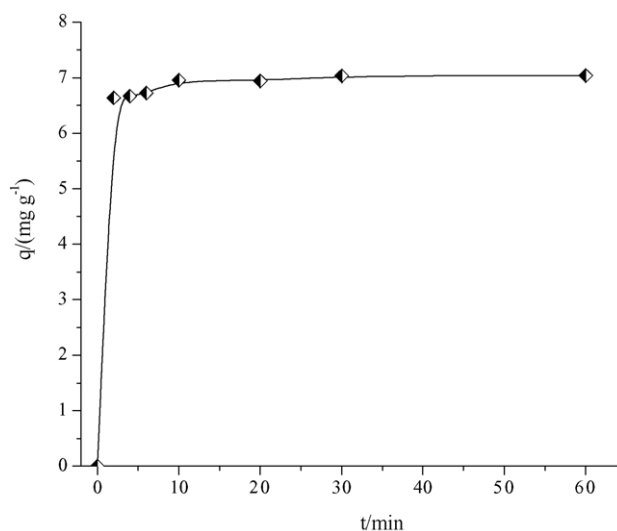


Fig. 1. The effect of biosorptive time on lead biosorption.

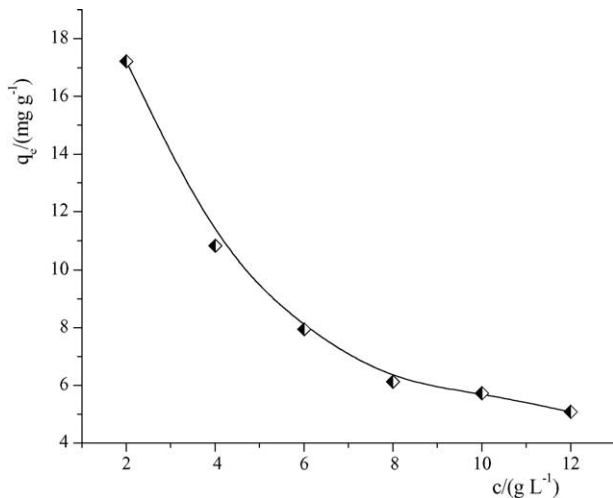


Fig. 2. The effect of biomass dose lead biosorption.

3.3. Effect of pH on lead biosorption

The results of different pH for lead biosorption are shown in Fig. 3.

It was shown in Fig. 3 that there was an increase in lead ions adsorption per unit weight of chaff biomass with the increasing of pH values from 2.0 to 6.2, just that in the pH ranging from 2.0 to 4.0, the increase rate was very quick and in the flowing it was slower. This phenomenon suggested that with the increasing of pH, the adsorption capacities increased. The reason may be as follows: at very low pH values, the surface of adsorbent would also be surrounded by the hydrogen ions, which compete with metal ions binding the sites of the biosorbent. While with the pH values increased, especially, when the pH value was higher 4.0, the concentration of proton was very low, the carboxylic acid sites can be appreciably deprotonated and so the effect of proton competition was feebleness, metal ions removal is increased. In the following

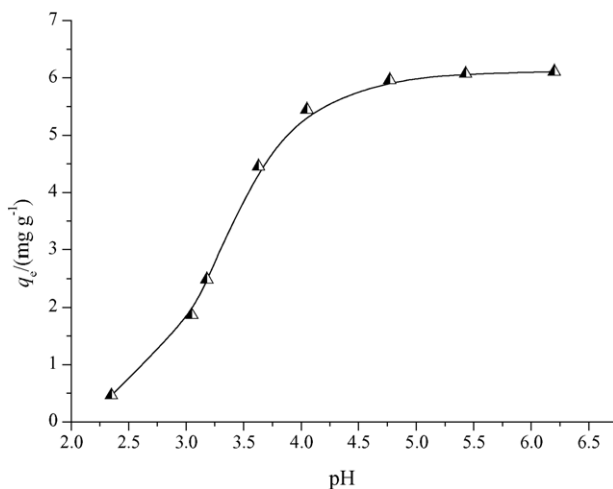


Fig. 3. The effect of pH on lead biosorption.

experiments, values of pH during lead biosorption process were controlled near 5.5.

3.4. Equilibrium studies

The equilibrium quantities of lead on chaff are illustrated in Fig. 4 at different equilibrium concentrations with 293, 298 and 303 K.

The equilibrium adsorption isotherm is fundamentally important in the design of adsorption systems. Equilibrium studies in adsorption give the capacity of the adsorbent. It is described by adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the adsorbent. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. In order to investigate the adsorption isotherm, four equilibrium models were analyzed. These included the Langmuir, the Freundlich, Koble–Corrigan and Temkin isotherms.

3.4.1. Langmuir isotherm

The Langmuir adsorption isotherm is probably the most widely applied adsorption isotherm. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. The saturated monolayer isotherm can be represented as [12]:

$$q_e = \frac{q_{\max} K_L c_e}{1 + K_L c_e} \quad (2)$$

The above equation can be rearranged to the following linear form:

$$\frac{1}{q_e} = \frac{1}{K_L q_{\max}} \cdot \frac{1}{c_e} + \frac{1}{q_{\max}} \quad (3)$$

where c_e is the equilibrium concentration (mg L^{-1}), q_e the amount of metal ion adsorbed (mg g^{-1}), q_{\max} the q_e for a

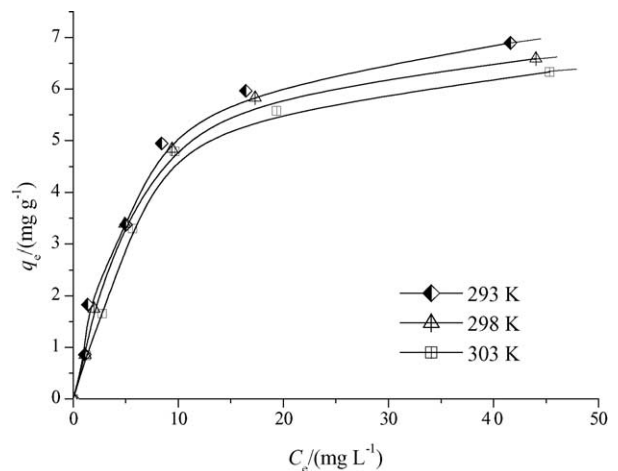


Fig. 4. Equilibrium quantities of lead at different equilibrium concentrations.

complete monolayer (mg g^{-1}), a constant related to adsorption capacity and K_L is the constant related to the affinity of the binding sites and energy of adsorption (L mg^{-1}). A plot of $1/q_e$ versus $1/c_e$ should indicate a straight line of slope $1/K_L q_{\text{max}}$ and an intercept of $1/q_{\text{max}}$. So, q_{max} and K_L can be determined.

3.4.2. Freundlich isotherm

In 1906, Freundlich studied the adsorption of a material onto animal charcoal [13]. This fairly satisfactory empirical isotherm can be used for non-ideal adsorption and is expressed by the following equation:

$$q_e = K_F c_e^{1/n} \quad (4)$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. The Freundlich model is more widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model. Eq. (4) can be linearized in logarithmic form and Freundlich constants can be determined.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (5)$$

3.4.3. Koble–Corrigan isotherm

Koble–Corrigan model is another three-parameter empirical model for the representing equilibrium adsorption data. It is a combination of the Langmuir and Freundlich isotherm-type models and is given by Eq. (6) [14]:

$$q_e = \frac{A c_e^n}{1 + B c_e^n} \quad (6)$$

where A , B and n are the Koble–Corrigan parameters, respectively.

Three isotherm constants, A , B and n can also be evaluated from the linear plot represented by Eq. (7) using a trial and error optimization method.

$$\frac{1}{q_e} = \frac{1}{A} \cdot \frac{1}{c_e^n} + \frac{B}{A} \quad (7)$$

The structure of chaff is cellulose-based, and the surface of cellulose in contact with water is negatively charged. Lead compounds used in this study will dissolve to give the cationic metal and this will undergo attraction on approaching the anionic chaff structure. So, it is expected that lead ion will have a strong adsorption affinity for chaff.

3.4.4. Temkin isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm [15]:

$$q_e = \frac{RT}{b_t \ln(a_t c_e)} \quad (8)$$

where R is the general gas constant, T the absolute temperature (K), and b_t and a_t represent isotherm constants, respectively.

3.4.5. Determination of equilibrium model constants about lead–chaff system

An adsorption isotherm is characterized by certain constants which values express the surface properties and affinity of the adsorbent and can also be used to find the biosorptive capacity of biomass. The equilibrium data were fitted to the Langmuir, Freundlich, Koble–Corrigan and Temkin isotherm models.

The Langmuir, Freundlich, Koble–Corrigan and Temkin adsorption constants evaluated from the isotherms at different temperatures and their correlation coefficients (R) and residual standard deviations (S.D.) are also presented in Table 1 according to Eqs. (3), (5), (7) and (8). High-regression correlation coefficients (>0.945) and lower S.D. values (<0.500) were found in good agreement as in the case of the four isotherms at the temperatures and lead concentration range studied. The applicability of all the isotherm models to the lead(II)–chaff system implies that both monolayer biosorption and heterogeneous surface conditions exist under the experimental conditions used. The biosorption of lead(II) ions on the biomass is thus complex, involving more than one mechanism.

Langmuir constant, q_{max} , represents the monolayer saturation at equilibrium. The other monocomponent Langmuir constant K_L , indicates the affinity for the binding of lead(II) ions. A high K_L value indicates a high affinity. Values of

Table 1
Isotherm constants for lead ion biosorption onto chaff at different temperatures

	T (K)		
	293	298	303
Langmuir			
K_L (L mg^{-1})	0.0920	0.0723	0.0700
q_{max} (mg g^{-1})	12.5	11.9	10.4
R	0.996	0.989	0.998
S.D.	0.041	0.064	0.029
Freundlich			
K_F	1.102	1.105	0.954
n	1.74	1.83	1.73
R	0.952	0.954	0.948
S.D.	0.274	0.269	0.280
Koble–Corrigan			
n	4.45	1.50	1.09
A	0.696	0.826	0.728
B	0.141	0.131	0.086
R	0.991	0.999	0.998
S.D.	0.057	0.018	0.025
Temkin			
a_t	1.85	1.58	1.29
RT/b_t	1.66	1.66	1.66
R	0.989	0.991	0.983
S.D.	0.394	0.347	0.448

q_{\max} and K_L for different temperatures were calculated from the Langmuir plots and the results are listed in Table 1. The biosorption capacity of biosorbent also decreased slightly on increasing the temperature. The value of q_{\max} obtained at 293 K (maximum uptake 12.5 mg g⁻¹). A higher value of K_L also implied strong bonding of lead(II) to the chaff at this temperature.

The Freundlich model does not describe the saturation behavior of the biosorbent. Table 1 also shows the Freundlich adsorption isotherm constants and the correlation coefficients (R) and residual standard deviations (S.D.). The values of K_F and n determined from the Freundlich model changed slightly with the rise in temperature. As $1 < n < 10$, indicating that lead(II) ions are favorably adsorbed by chaff at all the temperatures studied [17].

Relevant adsorption parameters were also calculated according to the three-parameter isotherm of Koble–Corrigan at different temperatures. Examination of the data shows that the Koble–Corrigan isotherm is an appropriate description of the data for lead ion biosorption over the concentration ranges studied. Koble–Corrigan constants n decreased with increasing temperature. The constant n is 1.09 for 303 K, and it indicates the isotherm is approaching the Langmuir form.

The corresponding Temkin parameters of a_t and b_t/RT for different temperatures are also given in Table 1 for lead–chaff system. The constant a_t also decreased with temperature increasing.

From Table 1, the Koble–Corrigan and Langmuir isotherms exhibit higher R values and lower S.D. values, which is a considerably better fit compared with Freundlich and Temkin isotherms.

3.5. K_R values at different initial concentrations

The effect of isotherm shape can be used to predict whether an adsorption system is ‘favorable’ or ‘unfavorable’ [16]. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R , which is defined by the following relationship [7]:

$$K_R = \frac{1}{1 + K_L C_0} \quad (9)$$

where K_R is a dimensionless separation factor, C_0 is initial concentration (mg L⁻¹) and K_L is Langmuir constant (L mg⁻¹). The parameter K_R indicates the shape of the isotherm accordingly:

Values of K_R	Type of isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

The values of K_R at 293, 298 and 303 K are given in Table 2. The K_R values indicate that adsorption is more favor-

Table 2

K_R values based on the Langmuir isotherm

C_0 (mg L ⁻¹)	293 K	298 K	303 K
8	0.576	0.634	0.641
16	0.405	0.464	0.472
32	0.254	0.302	0.309
48	0.185	0.224	0.229
64	0.145	0.178	0.182
96	0.102	0.126	0.130

able for the higher initial lead concentrations than for the lower ones. It is apparent that the adsorption of lead on chaff is favorable with the conditions used in this study.

3.6. Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change, ΔG^0 , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^0 is a negative quantity.

The biosorption process of metal ions can be summarized by the following reversible process, which represents a heterogeneous equilibrium. The apparent equilibrium constant (K'_c) of the biosorption is defined as [17,18]:

$$K'_c = \frac{c_{ad,e}}{c_e} \quad (10)$$

where $c_{ad,e}$ is the concentration of metal ion on the adsorbent at equilibrium. The value of K'_c in lowest experimental lead concentration can be obtained [18]. The K'_c value is used in the following equation to determine the Gibbs free energy of biosorption (ΔG^0) [17].

$$\Delta G^0 = -RT \ln K'_c \quad (11)$$

The enthalpy (ΔH^0) and entropy (ΔS^0) can be obtained from the slope and intercept of a van't Hoff equation of ΔG^0 versus T [7,17,18],

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (12)$$

where ΔG^0 is standard free energy change (J), R the universal gas constant (8.314 J mol⁻¹ K⁻¹) and T is the absolute temperature (K).

Values and the standard Gibbs free energy for the biosorption process obtained from Eq. (11) are listed in Table 3. The negative values of ΔG^0 confirm the feasibility of the process and the spontaneous nature of biosorption with a high preference of lead(II) on chaff. The standard enthalpy

Table 3

Thermodynamic parameters of lead biosorption on chaff

T (K)	293	298	303
ΔG^0 (kJ mol ⁻¹)	-4.54	-4.46	-4.23
ΔH^0 (kJ mol ⁻¹)		-13.6	
ΔS^0 (kJ mol ⁻¹)		-0.031	

and entropy changes of biosorption determined from the Eq. (12) were $-13.6 \text{ kJ mol}^{-1}$ and $-0.031 \text{ kJ mol}^{-1} \text{ K}^{-1}$, respectively. The negative value of ΔH^0 suggests the exothermic nature of biosorption. The negative value of ΔS^0 confirms the decreased randomness at the solid–solution interface during biosorption.

4. Conclusion

Chaff is able to adsorb lead ion from aqueous solutions. The lead ions binding capacity of biosorbent was affected by biosorption time, temperature and chaff dose. The biosorption time of equilibrium is shorter about 30 min. It was noted that an increase in the temperature resulted in a lower metal loading per unit weight of the biosorbent. The experimental results were analyzed by using the Langmuir, Freundlich, Koble–Corrigan and Temkin equations, thus correlation coefficients and standard deviation for fitting the Langmuir and Koble–Corrigan equations were significantly better than those for the Freundlich and Temkin equation. Biosorption capacity decreases slightly with increasing temperature. The biosorption quantity of lead ions was 12.5 mg g^{-1} at 293 K from the Langmuir equation. Various thermodynamic parameters, such as ΔG^0 , ΔH^0 and ΔS^0 , have been calculated. The thermodynamics of lead ion–chaff system indicates the spontaneous and exothermic process of lead ion biosorption.

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