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Biosorption of chromium (VI) onto (*Eriobotrya japonica*) loquat bark from aqueous solution

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ABSTRACT

The present study investigated the effectiveness of an inexpensive and ecofriendly loquat bark as a biosorbent for the possible removal of toxic chromium ions from aqueous solution. In this study, the effects of biosorbent dose, pH, initial concentration, contact time, and temperature were examined. The biosorption data were fitted well by Langmuir isotherms. Thermodynamic analysis revealed that the adsorption behavior of Cr(VI) onto loquat bark biosorbent was an endothermic process, resulting in higher biosorption capacities at higher temperatures. The negative values of ΔG° and positive values of ΔH° revealed that the biosorption process was spontaneous and endothermic. The mean free energy (E) for the biosorption of Cr(VI) was determined from the Dubinin-Radushkevick equation indicated that the biosorption of chromium species onto loquat bark mainly proceeds through binding surface functional groups.

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INTRODUCTION

Heavy metals are recognized as long-term hazardous contaminants because of their high toxicity, accumulation and retention in human body. Chromium (VI) is one of the toxic heavy metals and carcinogenic properties. Major sources of chromium (VI) in environment are electroplating, leather tanning, textile dyeing, paints, and metal finishing industries. The conventional methods for the removal of chromium and other heavy metals from water and wastewater include chemical precipitation^[1], ion exchange^[2], electrochemical precipitation^[3], membrane separation^[4], and adsorption^[5]. All these methods are in this case either economically unfavorable or technically complicated and thus used only in special cases. Each of these methods has some limitations in practice. Problems with the aforementioned methods make it necessary to develop easily available

inexpensive, ecofriendly, and equally effective alternatives for water and wastewater treatment. Biosorption of heavy metals by agricultural waste materials, which are produced in large quantities as a solid waste is one of these alternative treatment methods^[6-10].

In the present work, thermodynamic parameters, isotherm models, and the mean free energy for the biosorption of Cr(VI) by loquat bark have been investigated and used to explain the possible surface binding of Cr(VI) by loquat bark.

EXPERIMENTAL

Preparation of Cr(VI) stock solution

An Cr(VI) stock solution 1000 mg·L⁻¹ was prepared by dissolving a known quantity of potassium dichromate [K₂Cr₂O₇, Merck, Germany] in 1000 mL

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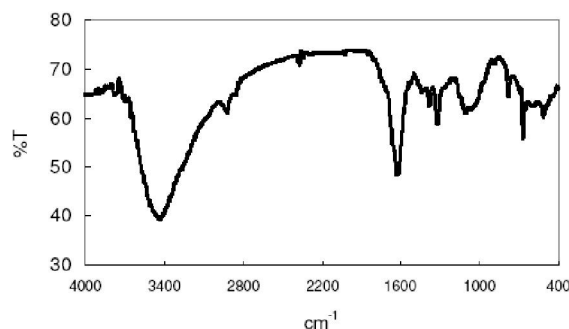


Figure 1 : FTIR of loquat bark

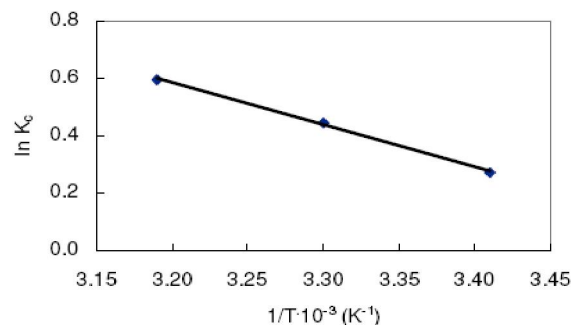


Figure 3 : Plot of $\ln K_c$ versus $1/T$

of double distilled water. The working solutions for the experiments with different concentrations of Cr(VI) were prepared by appropriate dilutions of the stock solution immediately prior to their use. Standard acid 0.1 M HNO₃ and a base solution 0.1 M NaOH were used for pH adjustment. All of the reagents were of analytical grade and used without further purification.

Preparation of biosorbent

Loquat bark (LB) used as biosorbent was collected from Royal Scientific Society, Jordan and washed repeatedly with double distilled water to remove soluble impurities and other adhered particles. Loquat bark was first air-dried and then dried in an oven at 333 K for 24 hours to get rid of the moisture and volatile impurities. The dried LB pieces were ground using a grinding mill (Retsch RM 100) and sieved to get size fraction < 44 μm for biosorption experiments.

Batch experiment

Biosorption studies were performed at constant pH 3.0 with initial concentration of Cr(VI) (40 mg·L⁻¹) and biosorbent dose of 2 g·L⁻¹ at temperature 303 K. 100-mL flasks containing the solutions were agitated on a shaker at 350 rpm constant shaking rate for 120 min to ensure equilibrium was reached and filtered through fil-

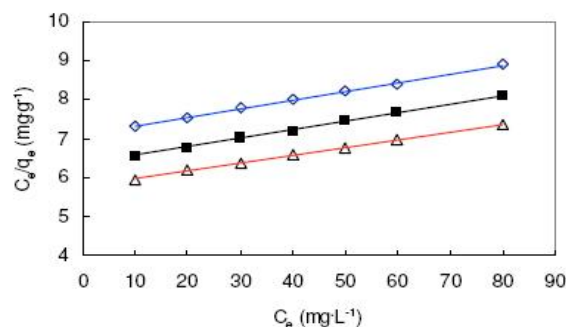


Figure 2 : Langmuir adsorption isotherm at pH 3.0 and T 303 K

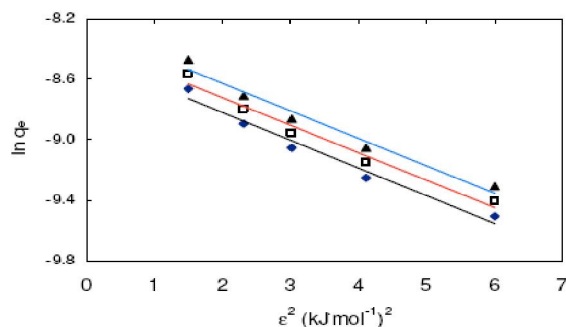


Figure 4 : Plot of $\ln q_e$ vs ϵ^2

ter paper (Schleicher and Schull 589), and the supernatant was analyzed for chromium by a sequential plasma emission spectrometer (ICPS-7510, Shimadzu). Each experiment was run in triplicate and mean values were reported.

The effect of pH on biosorption of Cr(VI) onto the LB biosorbent was investigated by varying the solution pH from 1.0 to 6.0. The effects of contact time, temperature and biosorbent concentration on uptake of Cr(VI) were then examined.

The biosorption capacity (mg·g⁻¹) of the biosorbent for each concentration of Cr(VI) at equilibrium was calculated using equation (1).

$$q_e = \frac{C_i - C_e}{M} \times V \quad (1)$$

where C_i and C_e are the initial and equilibrium concentrations of Cr(VI) ion (mg·L⁻¹). V is the volume of the solution (L) and M is the mass of biosorbent (g) used.

RESULTS AND DISCUSSION

FTIR spectra of LB biosorbent

Characterization of LB biosorbent was carried out with Fourier Transform Infrared spectroscopy (FTIR) to identify the functional groups in the 4000–400 cm⁻¹,

TABLE 1 : Langmuir constants for Cr(VI) biosorption onto LB at different temperatures

T	Langmuir constants		
	Q_m	$B \times 10^{-3}$	R^2
293	44.64	3.21	0.9994
303	46.51	3.42	0.9994
313	50.25	3.49	0.9994

(Figure 1). The spectra indicated a number of absorption peaks showing the complex nature of LB. The broad and strong band in loquat bark at 3427 cm^{-1} is attributed to hydroxyl (-OH) and amine (-NH) stretching. $2924\text{-}2854\text{ cm}^{-1}$ interval is symmetric vibration of (-CH) stretching. A strong band at 1620 cm^{-1} is due to stretching vibration of C=O. The bands at 1107 and 1059 cm^{-1} are indicative of the C-O-C and -OH. The bands at 1317 and 1383 cm^{-1} are indicative of the N-H stretching of the primary and secondary amides. The band at 1317 cm^{-1} indicates the C-O of carboxylic acids. $1000\text{-}500\text{ cm}^{-1}$ interval is C-H and C-C band vibration. The analysis of FTIR spectra showed the presence of many functional groups able to interact with Cr(VI) ions.

Effect of pH

The effect of pH on biosorption of Cr(VI) onto LB was studied by varying the initial pH 1-6 of 20 ml Cr(VI) solution at concentration 40 mgL^{-1} by adjusting the pH with 0.1 M NaOH and 0.1 M HNO_3 . The LB dosage of 5 gL^{-1} was mixed with the solution in a 250 ml. flask and then shaking the mixture at 120 rpm and at 303 K. After shaking the flasks for 30 min, the reaction mixtures were separated by filtration. Then, the residue of Cr(VI) in the filtered solutions were measured by AAS. In addition the pH of the aqueous solution was also measured. Maximum adsorption by loquat bark was observed at pH 3.0. Thus, the results showed that of Cr(VI) rises from 1 to 3 and starts decreasing. Accordingly, the optimum pH for the maximum adsorption of Cr(VI) onto LB was found at 3.0.

Effect of contact time

The effect of contact time on the extent of the adsorption of Cr(VI) onto LB, 40 mgL^{-1} initial chromium concentration at pH 3.0 and temperature 303 K showed that the Cr(VI) adsorption rate is high at the beginning and decreased slowly till the saturation levels were com-

TABLE 2 : Thermodynamic parameters of LB for Cr(VI) biosorption

T	K_c	ΔG°	ΔH°	ΔS°
K		kJ mol^{-1}	kJ mol^{-1}	$\text{J K}^{-1}\text{ mol}^{-1}$
293	1.312	-0.663	12.283	44.211
303	1.564	-1.126		
313	1.811	-1.546		

pletely reached at the equilibrium point 60 min.

Effect of biosorbent dose

To determine the effect of biosorbent dose, different amounts $1\text{-}10\text{ mgL}^{-1}$ of biosorbent were suspended in 20 ml chromium solution in which the concentration of chromium was 40 mgL^{-1} under optimized conditions of pH 3.0 and contact time 60 min. From experimental results obtained, we found an optimum dose of 5 gL^{-1} is used for all the experiments.

Effect of Cr(VI) concentration

The effect of Cr(VI) concentration on LB slurry was investigated at different chromium concentrated solutions. The results showed that the contact time for the equilibrium adsorption remains unchanged and shows maximum biosorption at 40 mgL^{-1} .

Sorption isotherm

Adsorption data is generally described by adsorption isotherms, Langmuir isotherms. These isotherms relate the amount of solute adsorbed at equilibrium per weight of adsorbent, q_e to the adsorbate concentration at equilibrium C_e . The Langmuir isotherm model represents one of the first theoretical treatments of non-linear sorption and suggests that adsorption occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. The Langmuir isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{1}{Q_m} C_e \quad (2)$$

where q_e is the milligrams of chromium adsorbed per gram of the adsorbent, C_e is the chromium concentration in the final solutions (mgL^{-1}), Q_m (gg^{-1}); and b (Lg^{-1}) are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum biosorption capacity denoted by Q_m represents monolayer coverage of Cr(VI) with biosorbent and b implies the enthalpy of biosorption which should vary with tempera-

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TABLE 3 : Dubinin-radushkevick parameters for the biosorption of Cr(VI) to loquat bark (LB)

T	K_E	q_m	E	R^2
K	($\text{mol}^2\text{K}^{-1}\text{J}^{-2}$)	(mol g^{-1})	(kJ mol^{-1})	
293	$1.83 \cdot 10^{-3}$	0.21	5.31	0.975
303	$1.82 \cdot 10^{-3}$	0.23	7.12	0.977
313	$1.80 \cdot 10^{-3}$	0.26	9.70	0.976

ture. A linear plot, (Figure 2), is obtained by plotting C_e/q_e against C_e over the entire range of lead concentration investigated.

Langmuir parameters Q_m and b , together with the regression coefficients R^2 determined from the plot given in TABLE 1, confirm a good agreement between the theoretical model and experimental results obtained. Q_m values are computed from slope while b values from the intercept. Langmuir Q_m and b values increased with temperature, showing that the adsorption capacity and intensity of adsorption are enhanced at higher temperatures.

Thermodynamic parameters

To study the effect of temperature on the uptake of Cr(VI), the process was carried out at three operating temperatures, (293, 303, and 313) K with 40 mg L^{-1} of initial Cr(VI) concentration at pH 3.0. The biosorption capacity was found to be varied with temperature. When increase in temperature from 293 to 313 K, the biosorption capacity increased. Higher uptake at higher temperature may be attributed to the availability of more active sites on the surface of LB.

Temperature dependence of the biosorption process is related with several thermodynamic parameters including Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), which are used to decide whether the biosorption is a spontaneous process or not. In the present work, the thermodynamic behavior of the biosorption of Cr(VI) ions onto LB is evaluated as follows. The changes in Gibbs energy, ΔG° , of the biosorption process is related to the equilibrium constant by the following equation.

$$\Delta G^\circ = -RT \ln K_c \quad (3)$$

where K_c is the equilibrium constant calculated from the following equation.

$$K_c = \frac{C_{Ac}}{C_e} \quad (4)$$

where C_{Ac} and C_e are the equilibrium concentration of Cr(VI) (mg L^{-1}) onto LB biosorbent and in solution, respectively. The obtained values of K_c at temperatures, (293, 303, and 313) K are listed in TABLE 2.

The enthalpy change, ΔH° and entropy change, ΔS° were obtained from the van't Hoff equation.

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (5)$$

where T is the absolute temperature (K); R is the gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$). ΔH° (kJ mol^{-1}) and ΔS° ($\text{J mol}^{-1}\text{K}^{-1}$) were calculated from the slope and intercept of a linear plot of $\ln K_c$ versus $1/T$. The plot shown in figure 3 is linear over the entire range of temperatures investigated.

Dubinin-Radushkevick equation^[11] used to determine the possible adsorption mechanism, which assumes a constant sorption potential¹² is presented in equations (6 and 7):

$$\ln q_e = \ln q_m - K_E \varepsilon^2 \quad (6)$$

$$\varepsilon = RT \ln(1 + 1/C_e) \quad (7)$$

where ε is the Polanyi potential, q_m (mol g^{-1}) is the monolayer capacity, C_e (mol dm^{-3}) is the equilibrium concentration and K_E (mol^2KJ) is the constant related to sorption energy. The parameters q_m and K_E can be obtained from the intercept and slope of the plot as shown in figure 4.

The mean energy of sorption, E is calculated by equation (8):

$$E = (-2K_E)^{-1/2} \quad (8)$$

Dubinin-Radushkevick parameters and mean free energy are given in TABLE 3. The magnitude of E is estimated the type of sorption reaction. An energy range from 8 to 16 kJ mol^{-1} indicates ion-exchange reaction¹³. Therefore the mean energy of sorption, E values obtained from 5.31 to 9.71 kJ mol^{-1} that are practically in the ion-exchange energy range, support the sorption of chromium ions onto loquat bark mainly proceeds by binding surface functional groups.

CONCLUSION

The results in this paper demonstrate that raw loquat bark (LB) is an effective adsorbent and can be successfully used as a biosorbing agent for the removal

of Cr(VI) ions from water. The thermodynamic parameters, ΔH° , ΔS° , and ΔG° values of Cr(VI) ion adsorption onto raw loquat bark show endothermic heat of adsorption, favored at higher temperatures. The positive value of ΔS° revealed an increase in randomness of the solid/solution interface during the adsorption of Cr(VI) ions. Regression coefficients R^2 were found to be more than 0.999 revealing the best fit for the biosorption data by the Langmuir and Freundlich isotherm models. The mean free energy (E) for the biosorption of Cr(VI) was determined from the Dubinin-Radushkevich equation indicated that the biosorption of chromium species onto loquat bark mainly proceeds through binding surface functional groups.

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