Biosorption of Pb(II), Zn(II), and Cd(II) from Aqueous Solutions by (*Eriobotrya japonica*) Loquat Bark

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Abstract*- The present study investigated the effectiveness of an inexpensive and eco-friendly loquat bark as a biosorbent for the possible removal of toxic lead, zinc, and cadmium ions from aqueous solutions. In this study, the effects of biosorbent dose, pH, initial concentration, contact time, and temperature were examined. The linear Langmuir and Freundlich models were applied to describe the equilibrium isotherms, and both models fitted well. The monolayer adsorption capacity of of Pb(II), Zn(II) and Cd(II) on loquat bark was found as 55.770, 29.447 and 28.802 mg g^{-1}, respectively, at pH 4 and 30°C. Dubinin-Radush Kerich (D-R) isotherm model was also applied to equilibrium data. The mean free energy of adsorption of Pb(II), Zn(II) and Cd(II) (5.596, 3.748 and 3.549 kJ/mol) onto loquat bark, respectively, may be carried out via physisorption mechanism. Loquat bark (LB) was found to remove Pb(II), Zn(II), and Cd(II) ions efficiently from aqueous solutions with selectivity in the order of Pb(II) > Zn(II) > Cd(II).

Keywords*- *Metal Ions; Biosorption; Loquat Bark; Aqueous Solutions; Isotherms

I. INTRODUCTION

Heavy metals are recognized as long-term hazardous contaminants because of their high toxicity, accumulation and retention in human body. Lead ranks second in the list of prioritized hazardous materials issued by US Agency for Toxic Substances and Disease Registry. Lead poisoning in human beings causes severe damage to the kidney, nervous system, liver and brain [1]. Major sources of lead, zinc, cadmium in environment are battery manufacturing, dyeing, plastic, metal plating, oil refining, melting of sulfides ore, and fossil fuels. The conventional methods for the removal of lead, zinc, and cadmium from water and wastewater include reverse osmosis, ion exchange, chemical precipitation electro dialysis, chemical oxidation and reduction, and filtration. 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, eco-friendly, and equally effective alternatives for water and wastewater treatment. It has been reported that some agro-wastes such as rice husk [2], wheat bran [3], lignite [4], and barley straws [5], have the capacity to adsorb and accumulate toxic heavy metals. Biosorption of heavy metals by bark samples, which are produced in large quantities as a solid waste is one of these alternative treatment methods. The use of different barks as biosorbents [6-13], has also been reported.

The aim of the present work was to investigate the efficiency of loquat bark as biosorbent for removal of Pb(II), Zn(II), and Cd(II) from aqueous solutions. Laboratory batch isotherms studies were conducted to evaluate the biosorption capacity of loquat bark. The effect of contact time, initial concentration, pH and temperature were studied.

II. MATERIALS AND METHODS

A. Materials

Pb(II), Zn(II), and Cd(II) stock solutions 1000 mg/L were prepared by dissolving lead nitrate Pb(NO3)2, zinc nitrate Zn(NO3)2, and cadmium nitrate Cd(NO3)2 (Sigma Aldrich chemicals) in 1000 mL of double distilled water. The working solutions for the experiments with different concentrations of Pb(II), Zn(II), and Cd(II) ions were prepared by appropriate dilutions of the stock solution immediately prior to their use. Standard acid 0.1M HNO3 and a base solution 0.1M NaOH were used for pH adjustment. All of the reagents were of analytical grade and used without further purification.

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 60oC for 24 h to get rid of the moisture and volatile impurities. The dried LB pieces were ground using a grinding mill (Retsch RM100) to obtain particles with dimensions between (0.044-0.074 mm) and the resulting powder was dried at 60oC for 24 h. The dried LB sample was passed through 0.044 mm sieve to ensure the material uniformity. The LB sample was examined by Fourier Transform Infrared Spectroscopy (FTIR) (Fig. 1).

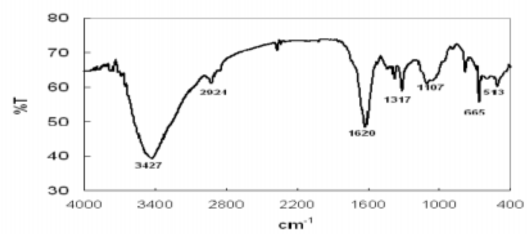

Fig. 1 FT-IR spectra of loquat bark before biosorption

B. Batch and Bisorption

Biosorption studies were performed by shaking 1 g of dried LB in a series of 250 mL flasks containing 20 mL of initial concentration of Pb(II), Zn(II), and Cd(II) ranging from 10 to 80 mgL^{-1} for 120 min. The initial pH value of Pb(II), Zn(II), and Cd(II) solutions was adjusted from 1.0 to 6.0 with either 0.1 M HNO3 or 0.1 M NaOH at 20oC, 30oC and 40oC). Flasks were agitated on a shaker at 350 rpm constant shaking rate for 120 min to ensure equilibrium was reached and centrifuged and then filtered through filter paper (Schleicher and Schưll 589), and the supernatant was analyzed for heavy metals by a sequential plasma emission spectrometer (ICPS-7510, Shimadizu). Each experiment was run in triplicate and mean values were reported.

The percentage metal removal (%Removal) was calculated for each run by Equation (1).

$$\%\,\mathrm{Re}moval = \frac{(C_i - C_{eq})}{C_i}\times 100 \qquad (1)$$

where Ci and Ceq are the initial and the equilibrium concentrations of metal ions in the solution (mg/L). The biosorption capacity qe (mg/g) of the biosorbent for each concentration of Pb(II), Zn(II), and Cd(II) at equilibrium was calculated using Equation (2).

$$q_e = \frac{(C_i - C_{eq})V}{m} \qquad (2)$$

where Ci and Ceq are the same as above. V is the volume of the solution (L) and m is the mass of biosorbent (g) used.

III. RESULTS AND DISCUSSION

A. Characterization 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, Fig. 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. 2924-2854 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 1327 and 1383 cm-1 are attributed to the N-H stretching of the primary and secondary amides. The band at 1317 cm-1 indicates the C-O of carboxylic acids. 1000-500 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 Pb(II), Zn(II), and Cd(II) ions.

B. Effect of the Initial pH

The pH is one of the most important parameters that are effective on metal biosorption. It is directly related with competitions ability of hydrogen ions with metal ions to active sites on the biosorbent surface. The effect of pH on biosorbtion of Pb(II),Zn(II), and Cd(II) ions onto LB was studied in the pH range of 1.0-5.0, keeping concentration of metal ions constant at 40 mg/L and at 30oC. Percentage removal of the metal ions as a function of pH is shown in Fig. 2. It can be seen from Fig. 2 that the percent removal of metal ions increases sharply with increasing pH of metal ions from 1.0 to 4.0 and then decreases to reach pH 5.0. The maximum adsorption was observed around pH 4.0. The biosorption of metal ions onto LB surface reflects the nature of physiochemical interactions of the solution. At highly acidic pH (pH < 2.0), the overall surface charge on the active sites of LB became positive and Pb(II), Zn(II), and Cd(II) ions and protons compete for binding active sites on LB surface, which results in lower uptake of metal ions. The LB biosorbent surface become more negatively charged as the pH solution increased from 2.0 to 4.0. The functional groups became more deprotonated and thus available for the Pb(II), Zn(II), and Cd(II) ions.

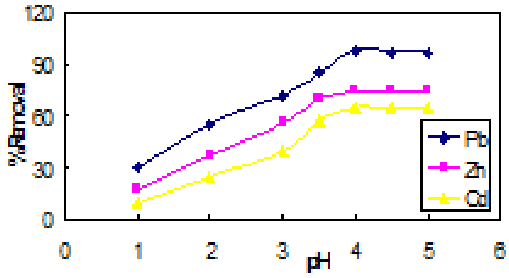

Fig. 2 Effect of pH on the bisorption of Pb(II), Zn(II), and Cd(II) onto loquat bark. Initial metal concentration 40 mg L-1; at temperature 30 oC

C. Effect of Biosorbent Dose on Biosorption

Biosorbent dosage is an important parameter because this determines the capacity of biosorbent for a given initial metal concentration. The biosorption efficiency for Pb(II), Zn(II), and Cd(II) ions as a function of LB biosorbent dosage was investigated (Fig. 3). The biosorption efficiency of metal ions with changing the biosorbent dose from 0.1 to 0.9 g increased with the biosorbent loading up to 0.9 g. This result can be explained by the fact that the increasing the bioasorbent (LB) dose provided greater surface area and availability of more active sites, thus leading to the enhancement of Pb(II), Zn(II), and Cd(II) ions uptake.

D. Effect of Contact Time

The effects of contact time of Pb(II), Zn(II), and Cd(II) on the biosorption process were studied in the time range from 10 to 120 min at pH 4.0 and at 30oC with a fixed LB biosorbent dose. Effect of the concentration of Pb(II), Zn(II), and Cd(II) was investigated by using different initial concentration 10, 20, and 40 mg/L of metal ions. It can be seen from Fig. 4 that the percent removal of metal ions increases with contact time until equilibrium is attained between the amount of metal ion on LB and the remaining metal in solution. Fig. 4 shows that the percentage removal of Pb(II) increases with contact time from 0 min to 60 min and then becomes almost constant up to the end of the experiment. It can be concluded that the binding of Pb(II), Zn(II), and Cd(II) with LB is high at initial stages and becomes almost constant after an optimum contact time of 60 min.

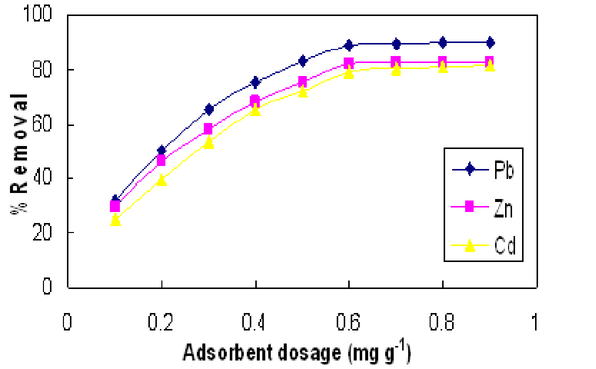

Fig. 3 Effect of biosorbent dosage on the biosorption of Pb(II), Zn(II), and Cd(II) onto loquat bark. Initial metal concentration 40 mg L-1; pH 4; at temperature 30 oC

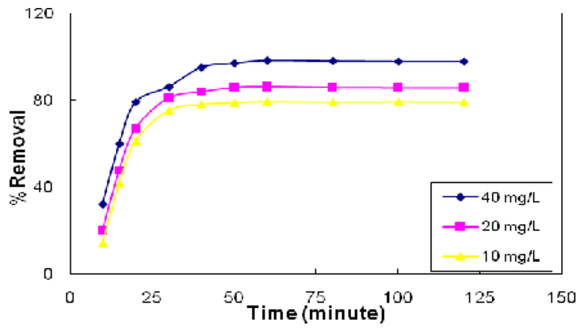

Fig. 4 Effect of initial concentration on the biosorption of Pb(II) onto loquat bark; pH = 4.0; at temperature 30 oC

E. Bisorption Kinetics

In order to analyze the rate of adsorption and possible adsorption mechanism of Pb(II), Zn(II), and Cd(II) onto LB, the pseudo-first order and pseudo-second order models were applied to adsorption data. The pseudo-first order model is given as [14]:

$$\ln(q_e - q_t) = \ln q_e k_1 t \tag{3}$$

Where qt is the amount of metal ions adsorbed at time, t (mg/g), qe is the amount of metal ions adsorbed at equilibrium (mg/g) and k1 is the pseudo-first-order rate constant (min-1) for the first order adsorption. The pseudo-first-order plots are shown in Fig. 5 and their constants are given in Table 1.

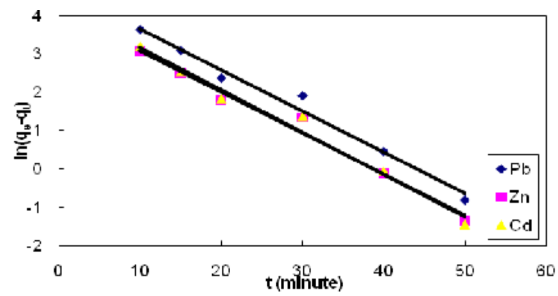

Fig. 5 Pseudo-first-order kinetics of biosorption of Pb(II), Zn(II), and Cd(II) onto loquat bark. Initial metal concentration 40 mg L-1; pH 4; at temperature 30 ^{o}C

TABLE I PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER ADSORPTION RATE CONSTANTS AND CALCULATED $Q_{E.CALCD.}$ VALUES FOR ADSORPTION OF PB(II), ZN(II) AND CD(II) IONS ONTO LOQUAT BARK AT 30 ^{o}C AND PH = 4.0

	Pseudo-First Order			Pseudo-Second Order		
$Q_{e.Exper.}$ mg/g	K_1 min^{-1}	$q_{e.Calcd.}$ mg/g	R^2	K_2 G/Mg.Min	$q_{e.Calcd}$ mg/g	R^2
			Pb(II)			
55.770	0.107	111.742	0.9831	0.018	57.471	0.9987
			Zn(II)			
29.447	0.105	62.847	0.9833	0.015	30.030	0.9978
			Cd(II)			
28.802	0.111	72.494	0.9811	0.011	29.314	0.9993

The pseudo second-order model can be expressed as [15]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Where k2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg. min). Values of qe and k2 were calculated from the slopes and intercepts of the linear plot of t/qt against t (Fig. 6). The rate constants k1, k, qe, and the correlation coefficient R2 of the bisorption of Pb(II), Zn(II), and Cd(II) onto LB were calculated from the relevant plots are given in Table I. The plots were found to be linear. Based on Table 1, the correlation coefficient R2 of pseudo-first order were found to be low and the values of calculated adsorption capacities were far higher than experimental ones suggesting that adsorption process did not fit the pseudo-first order model. On the other hand, the correlation coefficients R2 of the pseudo-second order were found to be high and the calculated value of adsorption capacity (qe.Calcd.) agreed well with the experimental ones (qe.Exper.), thus suggesting that the adsorption of these three metal ions follows the pseudo-second-order kinetic model.

F. Adsorption Isotherm Study

Biosorption data for a wide range of biosorbent concentration are most conveniently described by adsorption isotherms. The experimental data for the removal of Pb(II), Zn(II), Cd(II) by LB were processed using the

Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models.

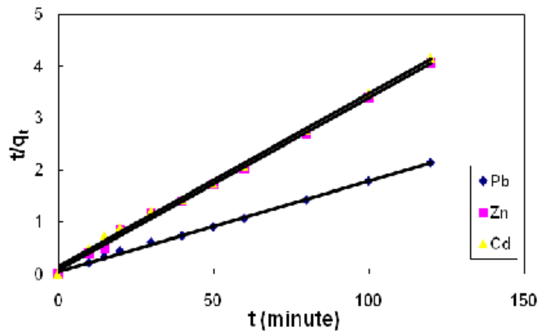

Fig. 6 Pseudo-second-order kinetics of biosorption of Pb(II), Zn(II), and Cd(II) onto loquat bark. Initial metal concentration 40 mg L-1; pH 4; at temperature 30 oC

The Langmuir isotherm model is given by the following equation [16]:

$$\frac{C_{eq}}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_{eq}}{q_{\max}} \tag{5}$$

Where q_e is the milligrams of metal ions adsorbed per gram of the adsorbent, C_{eq} is the concentration of the solution at the equilibrium (mg/L), q_{max} (mg/g) and K_L (L/g) are Langmuir constants related to sorption capacity and sorption energy, respectively. Maximum bioadsorption capacity denoted by q_{max} represents monolayer coverage of Pb(II), Zn(II), and Cd(II) with adsorbent and K_L implies the enthalpy of adsorption which should vary with temperature. A linear plot, Fig. 7, is obtained by plotting C_{eq}/q_e against C_{eq} over the entire range of metal cations concentration investigated.

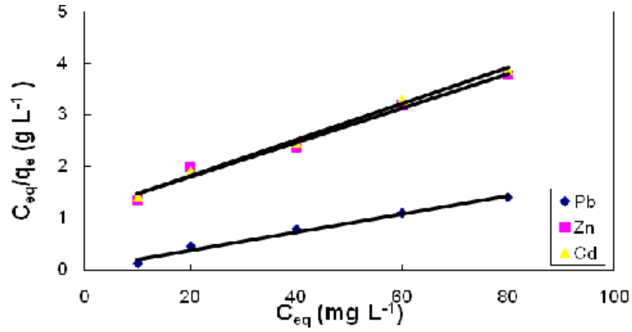

Fig. 7 The Langmuir isotherm plot of biosorption of Pb(II), Zn(II), and Cd(II) onto loquat bark; pH 4; at temperature 30 oC

Langmuir parameters qmax and KL, together with the regression coefficients R2 determined from the plot given in Table 2 confirm a good agreement between the theoretical model and experimental results obtained, qmax values are computed from slope while KL values from the intercept.

TABLE II PARAMETERS OBTAINED FROM LANGMUIR, FREUNDLICH AND D-R EQUATIONS AT DIFFERENT TEMPERATURES

Adsorbent	Langmuir Isotherm Constants				Freundlich Isotherm Constants			D-R Isotherm Constants		
	q_{max} mg/g	K_L	R_L	R^2	K_F	n	R^2	q_{max} mg/g	E kJ/mol	R^2
T = 293.15 K										
Pb(II)	57.803	0.911	0.014	0.9997	51.274	43.006	0.9664	57.397	9.542	0.9788
Zn(II)	31.546	0.124	0.092	0.9975	16.634	8.418	0.9405	29.964	3.450	0.8976
Cd(II)	30.864	0.118	0.096	0.9991	16.596	8.026	0.9912	34.532	1.474	0.9178
T = 298.15 K										
Pb(II)	58.823	0.783	0.016	0.9995	50.559	33.331	0.9273	58.148	9.962	0.9628
Zn(II)	31.447	0.129	0.088	0.9957	16.865	8.636	0.9269	29.500	3.454	0.9688
Cd(II)	30.960	0.119	0.095	0.9976	15.985	8.084	0.9888	34.581	1.3887	0.9275
T = 308.15 K										
Pb(II)	59.113	0.813	0.015	0.9995	51.286	34.014	0.9282	57.743	9.717	0.8891
Zn(II)	31.847	0.131	0.089	0.9958	16.982	8.673	0.9088	30.120	3.492	0.8799
Cd(II)	31.056	0.120	0.094	0.9987	16.147	8.117	0.9846	29.122	1.256	0.9145

According to Vasanth and Kumara [17], the essential features of the Langmuir isotherm can be expressed in term of separation factor or equilibrium parameter RL that can be calculated from the relationship:

$$R_L = \frac{1}{1 + K_L C_o} \tag{6}$$

where Co is the highest initial concentration (mg/L). The value of RL indicates the type of isotherm to be irreversible adsorption (RL = 0), favourable adsorption (0 < RL > 1), unfavourable adsorption (RL > 1) and linear adsorption (RL = 1). In this study RL for Pb(II), Zn(II), and Cd(II) have the values less than 1 and indicating favorable adsorption.

The Freundlich isotherm model could be applied to the sorption process which describes the physical adsorption of Pb(II), Zn(II), and Cd(II) only. In contrast to the Langmuir monolayer model, the Freundlich isotherm is a consecutive layer model which does not predict any saturation of the adsorbent by metal ions. The linearized form of the Freundlich isotherm [18] used to evaluate the different sorption parameters is:

$$\log q_e = \log K_F + \frac{1}{n}\log C_{eq} \tag{7}$$

Where KF and n are the isotherm constants calculated from the intercepts and slopes of the Freundlich plot of logqe versus logCeq (Fig. 8). Freundlich parameters KF and n together with the regression coefficients R^2 determined from the plot are given in Table 2, and confirmed a good agreement between the theoretical model and experimental results obtained.

The D-R equation is given by Dubinin et al. [19]:

$$\ln q_e = \ln q_m - \beta\varepsilon^2 \quad (8)$$

In this equation, qe is the amount of heavy metal cations taken up by the material at equilibrium (mg/g), qm is the D-R monolayer capacity (mg/g), β is a constant related to the sorption energy (mol2/ kJ2), and ε is the Polanyi potential which is related to the equilibrium concentration as Eq. (9):

$$\varepsilon = RT\ln(1+\frac{1}{C_{eq}}) \quad (9)$$

where R is the gas constant (J/K.mol) and T is the temperature in K.

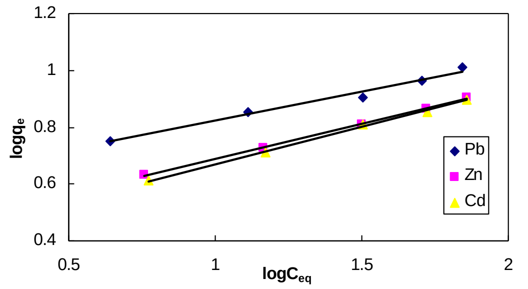

Fig. 8 The Freundlich isotherm plot for Pb(II), Zn(II), and Cd(II) adsorption on loquat bark; pH 4; at temperature 30^{o}C

The main energy of sorption (E) is calculated by using the following expression [20]:

$$E = (-2\beta)^{-0.5} \quad (10)$$

In Eq. (10) E provides information regarding the physical and the chemical features of the sorption process.

Thus the D-R isotherm is applied to the experimental data. A plot of lnqe versus ε^2 is given in Fig. 9. Sorption capacities qm and the main sorption energies E are calculated for the three metal cations removed from the aqueous phase by the LB and are listed in Table 2.

The Langmuir model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface and no interaction between adsorbate in the plane of the surface, whereas Freundlich model is applicable to highly heterogeneous surface with interaction between adsorbate molecules. The D-R model is useful for identifying the type of adsorption mechanism based on the mean adsorption energy (E).

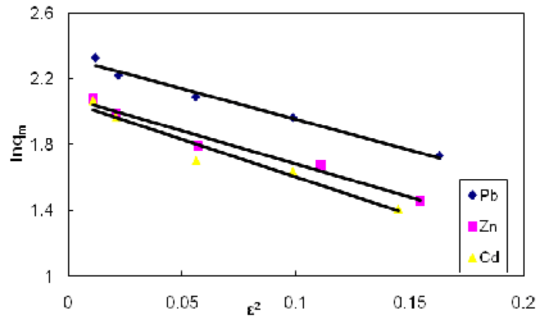

Fig. 9 The D-R isotherm plot for Pb(II), Zn(II), and Cd(II) adsorption on loquat bark; pH 4; at temperature 30 oC

The results obtained for the three isotherm equations are listed in Table 2. All isotherm models gave good correlation coefficients with R2 > 0.8799. Based on Langmuir isotherm, the highest value of maximum adsorption capacity of Pb(II), Zn(II), and Cd(II) ions onto LB was calculated 55.770, 29.447 and 28.802 mg/g respectively. The n value as indicated by Freundlich model was greater than unity, suggesting a favorable adsorption process. The maximum E values determined for D-R isotherm are 5.596, 3.748 and 3.549 kJ/mol for Pb(II), Zn(II), and Cd(II)ions, respectively. They are the orders of physisorption mechanism, in which the sorption energy < 16 kJ/mol [21]. Hence, the results obtained in this study indicating that the adsorption has low potential barrier and assigned to physisorption.

Table 3 shows the biosorption capacity values of various barks biosorbents for Pb(II). The comparison between our results and those of literature shows that the loquat bark (LB) without any treatment exhibit good sorption efficiency. It can be seen the capacity in this work 55.77 mg/g at pH 4.0 is relatively better than the most of results shown in the works listed in Table 3.

TABLE III COMPARISON OF BIOSORPTION CAPACITY OF LOQUAT BARK FORTHE REMOVAL OF LEAD WITH THOSE OF LITERATURE

Biosorbent Bark	q_{max}/ mg/g	References
Pine	76.80	[1]
Pine	6.71	[11]
Moringa oleifera	34.60	[12]
Juniper	15.75	[7]
Acacia leucocephala	185.2	[13]
Loquat	55.77	This work

G. *Effect of Temperature and Bisorption Thermodynamics*

To study the effect of temperature on the uptake of Pb(II), Zn(II), and Cd(II) by LB, the process was carried out at three different temperatures (20oC, 30oC, and 40oC) with 40 mg/L of initial metal concentration at pH 4.0. The biosorption capacity was found to be varied with temperature. When increase in temperature from 20oC to 40oC, the biosorption capacity increased (Fig. 10). Higher uptake at higher temperature may be attributed to the availability of more active sites on the surface of LB.

The mechanism of Biosorption of Pb(II), Zn(II), and Cd(II) ions onto LB may be determined through thermodynamic quantities such as change in Gibbs free energy, ΔG, change in enthalpy of adsorption, ΔH and change in entropy, ΔS. The thermodynamic equilibrium constant Kd for adsorption was determined by Gunay et al. [22] by plotting lnqe/Ci versus qe, and extrapolating qe, to zero. The decrease in Kd with increase in temperature indicates the exothermic nature of the process. The ΔH, ΔG and ΔS were calculated using the equations:

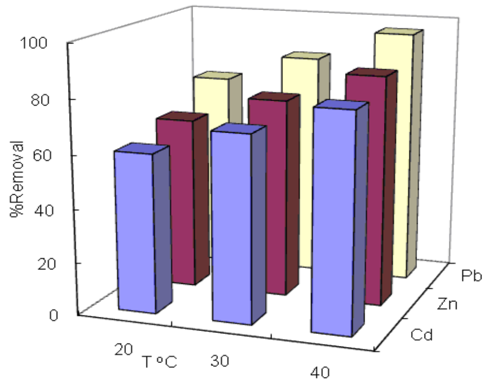

Fig. 10 Effect of temperature on the biosorption of Pb(II), Zn(II), and Cd(II) onto loquat bark; pH 4

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

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

$$\ln K_d = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (12)$$

A plot of lnKd versus 1/T was found to be linear (Fig. 11), ΔH and ΔS determined from the slope and intercept of the plot, respectively. The values of ΔG and ΔS for biosorption of Pb(II), Zn(II), and Cd(II) ions onto LBare given in Table 4. Negative values of, ΔH suggest the exothermic nature of adsorption and the negative values of Gibbs free energy changes ΔG confirms that the adsorption process has a natural tendency to proceed spontaneously. Generally, the change of free energy for physisorption is between –20 kJ/mol and 0 kJ/mol, but chemisorption is a range of – 80 kJ/mol to – 400 kJ/mol [23]. The overall free energy change during the adsorption process was negative for the experimental range of temperature (see Table 4), corresponding to a spontaneous physical process of Pb(II), Zn(II), and Cd(II) adsorption and that the system does not gain energy from an external source. The positive values of ΔS indicate increased randomness at the solid solution interface during the adsorption of these metal ions on LB (Table 4).

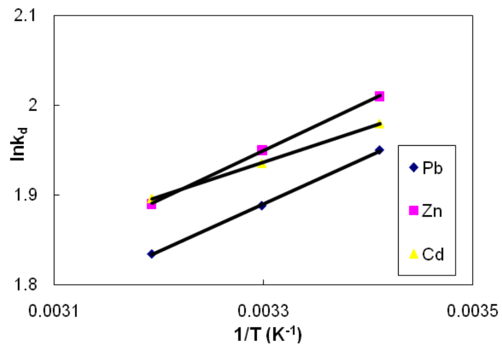

Fig. 11 Plot of lnKd vs. 1/T for the estimation of thermodynamic parameters for biosorption of Pb(II), Zn(II), and Cd(II) onto loquat bark; pH 4

TABLE IV THERMODYNAMIC PARAMETERS CALCULATED FOR THE ADSORPTION OF PB(II), ZN(II) AND CD(II) IONS ON LOQUAT BARK

Metal Cations	ΔG **/kJ/mol**			ΔH **(kJ/mol)**	ΔS **(kJ/K.mol)**
	293.15 K	***303.15 K***	***313.15 K***		
Pb(II)	-10.865	-11.031	-11.206	-5.728	17.459
Zn(II)	-8.713	-8.846	-8.979	-4.816	13.302
Cd(II)	-7.838	-7.969	-8.154	-3.209	15.819

IV. CONCLUSIONS

The results in this paper demonstrate that raw loquat bark (LB) is an effective adsorbent and can be successfully used as an biosorbing agent for the removal of Pb(II), Zn(II), and Cd(II) ions from aqueous solutions. Biosorption of Pb(II), Zn(II), and Cd(II) ions onto loquat bark was found to be dependent on experimental conditions, initial metal ion concentration, contact time, and pH. The percentage removal of metal ions by loquat bark decreased in the order of Pb(II) > Zn(II), and Cd(II). Loquat bark shows a preference for Pb(II) biosorption over Zn(II), and Cd(II). Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were found applicable. The kinetic of adsorption of Pb(II) > Zn(II), and Cd(II) on LB follow the pseudo-second-order kinetics. The adsorption capacity of adsorption of Pb(II) > Zn(II), and Cd(II) decreased with increasing temperature, this means that the adsorption process was exothermic in nature. For Pb(II) > Zn(II), and Cd(II) adsorption, the thermodynamic values of ΔG are negative for all systems indicating a spontaneous process.

Positive value of ΔS in all systems indicates increase of order, (decrease of disorder) of the process. The thermodynamic parameters are very useful if the present results are to be utilized on large scale industrial processes.

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