

## Adsorptive Removal of Pb(II), Cu(II) and Cd(II) Ions onto *Rubus ellipticus* as Low-Cost Biosorbent

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In the present study, removal efficiency (%) of *Rubus ellipticus* leaves (REL) as an adsorbent for the removal of Pb(II), Cu(II) and Cd(II) ions was investigated. Different parameters *i.e.*, pH, contact time, temperature, adsorbent dose and initial metal ion concentration were investigated to obtain the optimum adsorption efficiency. At pH 4, a maximum adsorption was 84.6, 80.2 and 74.5 % for Pb(II), Cu(II) and Cd(II) ions, respectively. The maximum adsorption of all the three metal ions obtained at contact time (75 min), initial metal ion concentration (10 mg/L), temperature (25 °C) and adsorbent dose (5.0 g). The equilibrium adsorption of Pb(II), Cu(II) and Cd(II) ions at different temperature was described by Langmuir, Freundlich and Temkin isotherms. The equilibrium data fitted well the Langmuir adsorption isotherm. Thermodynamic parameters like Gibb's free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) were also calculated. The calculated parameters indicated that adsorption of Pb(II), Cu(II) and Cd(II) ions onto *Rubus ellipticus* leaves (REL) was spontaneous ( $\Delta G^\circ < 0$ ), endothermic ( $\Delta G^\circ > 0$ ). The feasibility of the process was evident from the positive value of  $\Delta S^\circ$ .

**Keywords:** Biosorption, Isotherm models, Kinetics, *Rubus ellipticus*.

### INTRODUCTION

The presence of heavy metal ions contaminates aqueous streams which arise from the discharge of untreated metal ions containing effluent into water bodies. These heavy metal ions are non-degradable in the environment and are harmful to a variety of living species. Besides the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings [1]. For example, accumulation of copper causes liver damage and chronic poisoning, *etc.* The higher concentration of lead causes severe damage to the nervous system and affects the functioning of brain cells [2,3]. Owing to the toxic effects, industries are advised that the waste water be treated systematically to remove/minimize the metal contents in their wastes. Chemical precipitation [4], membrane filtration [5] ion exchange [6] and carbon adsorption [7] are few of the methods indicated in the literature for the removal of heavy metals from water and wastewaters. However, these methods have their own disadvantages such as secondary pollution, high cost and high energy input. Most of these methods suffer some drawback, some have high capital and operational cost, some faces problem

of the disposal of the residual metal sludge and some are not suitable for low concentration (10 mg/L) of metal ions [8].

Among these methods biosorption is economically feasible method for removal of heavy metals from the aqueous solution. Biosorption is a phenomenon where certain biomolecules can bind and concentrate selected ions or other molecules from aqueous solution [9]. Biosorption could be such an alternative method of treatment of effluents and wastewaters. It employs a wide variety of biomasses, such as algae, fungi, bacteria and plant leaves for removal of metal ions [10-12].

*Rubus ellipticus* is locally known as Hisalu. The plant grows in many parts of the country but found abundantly in Kumaun hills of Indian region. The objective of the present work is to investigate the possibility of the use of activated *Rubus ellipticus* leaves (REL) as an alternative low-cost adsorbent for the removal of Pb(II), Cu(II) and Cd(II) ions from synthetic wastewater.

### EXPERIMENTAL

**Preparation of adsorbent:** *Rubus ellipticus* leaves were collected from Bageshwar District, India. These leaves were thoroughly rinsed with double distilled water to remove dust

and soluble materials. The leaves were then dried in hot air oven at 333 K for 24 h. The dried biomass was grinded to fine powder in an electric grinder. The powdered mass was treated with 0.1N HNO<sub>3</sub> at room temperature for 24 h and then filtered and washed with double distilled water. The obtained biomass was dried in hot air oven at 333 K for 2 days and then subjected to pass through the 63 microns sieves (170 BSS sieve). The sieved biomass was then stored in air tight bottle.

**Preparation of adsorbate:** The stock solution (1000 mg/L) of Pb(II), Cu(II) and Cd(II) ions were prepared. The working solution was prepared by diluting the stock solution with double distilled water. The working solution range of all metal ions were kept in 10-50 mg/L. The higher pH then desired was adjusted by using 0.1 N HCl and the lower pH then desired was adjusted by using 0.1 N NaOH.

**Procedure:** The adsorption experiments were carried out with 100 mL of standard solution in a 250 mL conical flask. The solution was shaken at 170 rpm for 45 min and then filtered with Whatman No. 42 filter paper. The filtrate was digested with conc. HNO<sub>3</sub>. The digested solution was analyzed by atomic absorption spectrophotometer (Optima 4300DV ICP, Perkin-Elmer, Boston, MA). The effect of pH on Pb(II), Cu(II) and Cd(II) ions adsorption was studied [13] over pH range from 1.0 to 7.0. The adsorbent doses were varied from 1.0 to 5.0 g. The effect of removal efficiency of the adsorbent was calculated as follows:

$$\text{Removal efficiency (\%)} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where  $C_i$  is the initial metal ion concentration (mg/L) and  $C_e$  is the equilibrium metal ion concentration (mg/L).

## RESULTS AND DISCUSSION

**FT-IR analysis:** The FT-IR spectra of functional groups present in unloaded *Rubus ellipticus* leaves is shown in Fig. 1. The spectrum gives information about the functional groups

at which complexation occurs. The absorption bands at 3749, 3673, 3613 and 3443 cm<sup>-1</sup> of REL were due to stretching vibration of (N-H) and (O-H) groups. The absorption bands at 2945 and 2886 cm<sup>-1</sup> indicate the presence of aldehydic (-CHO) functional group. A band at 2361 cm<sup>-1</sup> assigned to carbonate group. The absorption bands at 1773 and 1754 cm<sup>-1</sup> indicate the C=O group present in REL. Similarly, bands at 1619, 1556 and 1515 cm<sup>-1</sup> strongly indicates the presence of aromatic ring, while the bands at 813 and 728 cm<sup>-1</sup> indicates *ortho*- and *para*-substituents in the benzene moiety, respectively. The above results gave an idea about the presence of functional groups on biosorbent surface which are able to participate in the adsorption process. The results also suggested that the adsorption process of biosorbent was affected by ion-exchange and the process was governed by chemical adsorption [14].

**Effect of contact time:** Time of contact of adsorbate and adsorbent is of importance in adsorption process which depends on the nature of system used [15]. The effect of contact time on the biosorption of Cu(II), Pb(II) and Cd(II) ions performed on REL is shown in Fig. 2. The biosorption yield of Cu(II), Pb(II) and Cd(II) ions increased considerably with increase in reaction time from 15-75 min with stirring speed at 170 rpm.

**Effect of adsorbent dose:** One of the parameters that strongly affects the biosorption capacity is the amount of the biosorbent. The dependence of Cu(II), Pb(II) and Cd(II) sorption on REL was studied by varying amount of the adsorbent from 1 to 5 g while keeping the other parameters constant. Biomass provides binding sites for the sorption of metal ions; its concentration strongly affects the adsorption of metal ions from the solution. In all cases, removal percentage increases with increasing adsorbent dose as shown in Fig. 3. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption increased by increasing the biosorbent dose [16-18]. The maximum biosorption, 93.5 % for Pb(II), 89.9 % for Cu(II) and 87.1 % for Cd(II) was attained at adsorbent

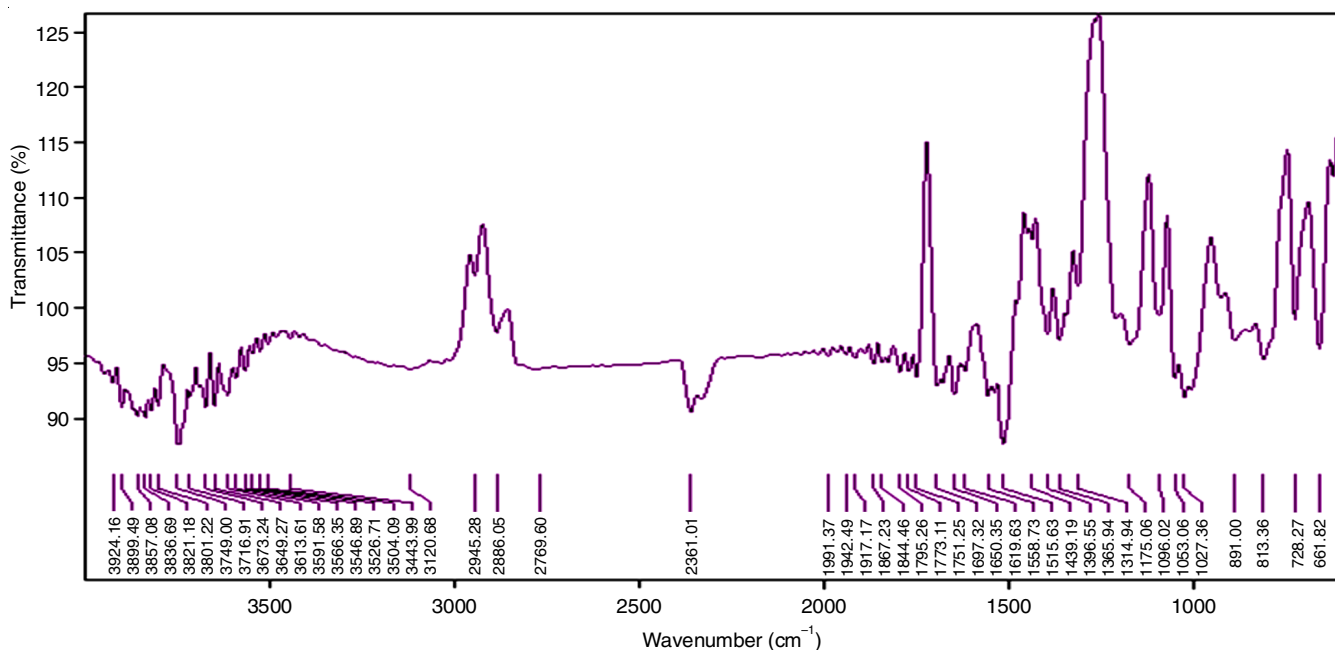


Fig. 1. FT-IR spectrum of unloaded REL biosorbent

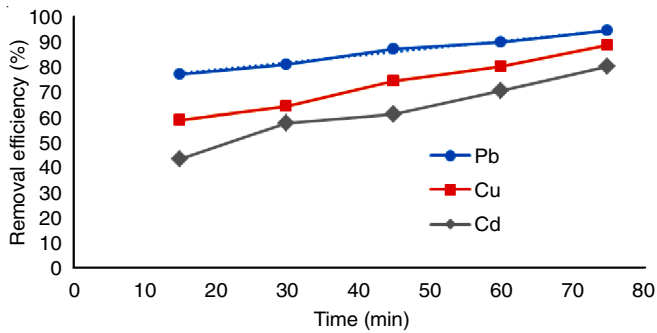


Fig. 2. Effect of contact time of Cu(II), Pb(II) and Cd(II) adsorption [experimental condition: initial metal ion concentration = 10 mg/L, adsorbent dose = 1 g/100 mL, temperature = 25 °C, pH = 5.0 and agitating speed = 170 rpm]

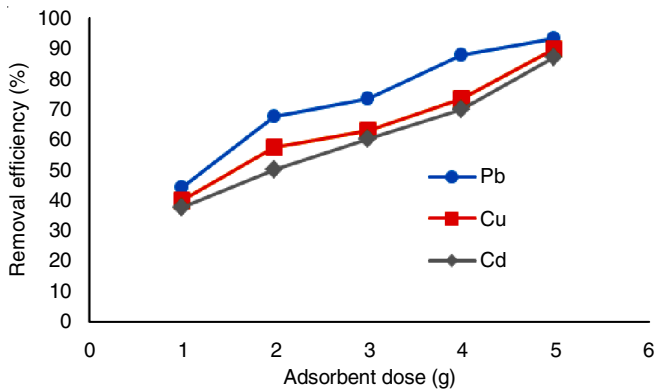


Fig. 3. Effect of adsorbent dose on Cu(II), Pb(II) and Cd(II) adsorption [Experimental condition: initial metal ion concentration = 10 mg/L, contact time 45 min, temperature = 25 °C, pH = 5.0, agitating speed = 170 rpm]

dose of 5 g. However, uptake capacity of metal ion per unit mass of biosorbent (mg/g) decreases with increase in dose of biosorbent (Fig. 4), which may be due to lower utilization of adsorption capacity of the biosorbent at higher doses [19].

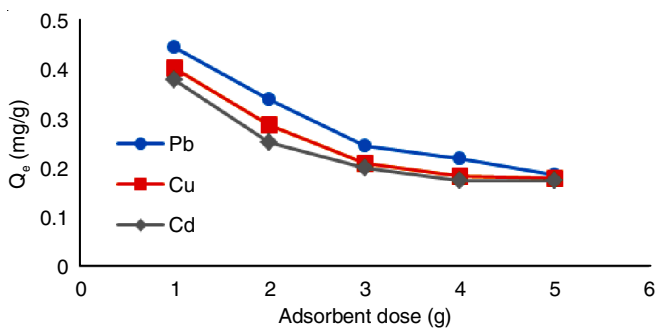


Fig. 4. Effect of adsorbent dose on Cu(II), Pb(II) and Cd(II) adsorption capacity [Experimental condition: initial metal ion concentration = 10 mg/L, contact time 45 min, temperature = 25 °C, pH = 4.0, agitating speed = 170 rpm]

**Effect of pH:** The effect of pH on Cu(II), Pb(II) and Cd(II) ions and uptake capacity of *Rubus ellipticus* leaves was investigated between pH 1.0-7.0 at 10 mg/L initial metal ion concentration at 25 °C. The percentage removal of Cu(II) and Pb(II) ions increases with increasing pH from 1.0-4.0. In case of cadmium, percentage removal increases from pH 1.0-5.0. At low pH, H<sup>+</sup> ions concentration is very high and these H<sup>+</sup> ions compete with Cu(II), Pb(II) and Cd(II) ions for being adsorbed

on the surface of adsorbent [20]. This results in a decrease of metal ion adsorption at low pH. At pH values higher than 6.0, biosorption studies could not be performed due to the precipitation of Cu(II), Pb(II) and Cd(II) ions [3]. Fig. 5 shows that the maximum biosorption of Cu(II) and Pb(II) ions on the biosorbent was observed at pH 4 whereas for Cd(II), the maximum adsorption was observed at 5.0.

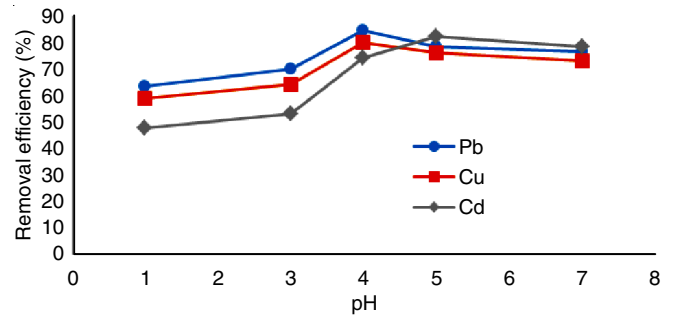


Fig. 5. Effect of pH on Cu(II), Pb(II) and Cd(II) adsorption capacity [Experimental condition: initial metal ion concentration = 10 mg/L, contact time 45 min, temperature = 25 °C, agitating speed = 170 rpm]

**Effect of initial metal ion concentration:** The initial metal ion concentration remarkably influenced the equilibrium metal uptake and adsorption yield as shown in Fig. 6. Cu(II), Pb(II) and Cd(II) ions biosorption onto REL was studied at different initial metal ion concentration ranging from 10-50 mg/L. The graph indicates that the removal percentage decreases on increasing the initial metal ion concentration. However, amount adsorbed per unit mass of adsorbent increases with the increase of initial metal ion concentration (Fig. 7). This was due to the concentration gradient which acted as increasing driving force to overcome the resistance to mass transfer of metal ions between the aqueous and solid phases [21].

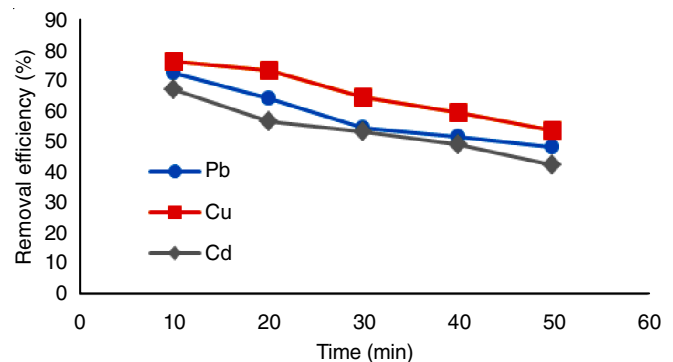


Fig. 6. Effect of initial Cu(II), Pb(II) and Cd(II) ions concentration on adsorption. [Experimental condition: contact time 45 min, temperature = 25 °C, agitating speed = 170 rpm, pH 4.0]

**Adsorption isotherms:** Adsorption isotherms were used to describe the amount of sorbate molecules that were distributed between liquid and solid phases at fixed temperature at equilibrium. The adsorption process of Pb(II), Cu(II) and Cd(II) ions onto REL was studied by using Langmuir, Freundlich and Temkin isotherms.

**Langmuir isotherm:** Langmuir isotherm [22,23] describes an adsorption process and suggests that the uptake occurs on a homogenous surface by monolayer adsorption without lateral

TABLE-1  
ADSORPTION ISOTHERM CONSTANT FOR ADSORPTION OF Pb(II), Cu(II) AND Cd(II) ONTO REL

Metal ion	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	$K_L$ (L/mg)	$Q_{max}$ (mg/g)	$R^2$	$K_F$ (mg/g)	$1/n$	$R^2$	$b_T$ (mg/g)	A	$R^2$
Pb(II)	0.08	3.38	0.9905	0.443	0.52	0.9952	0.76	0.84	0.9937
Cu(II)	0.07	4.48	0.9914	0.469	0.59	0.9985	0.93	0.92	0.9906
Cd(II)	0.12	2.80	0.9938	0.477	0.47	0.9959	0.62	1.13	0.9915

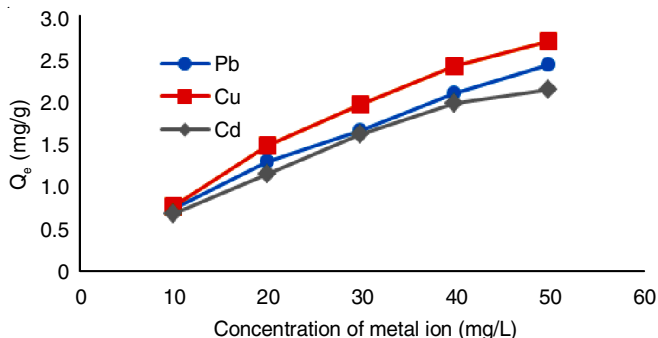


Fig. 7. Effect of initial Cu(II), Pb(II) and Cd(II) ions concentration on adsorption. [Experimental condition: Adsorbent dose = 1g/100 mL, contact time 45 min, temperature = 25 °C, pH = 4.0 for Pb(II) and Cu(II) and 5.0 for Cd(II), agitating speed = 170 rpm]

interaction between adsorbed molecules, which can be represented as:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{max}} + \frac{1}{K_L Q_{max}} \quad (2)$$

where  $C_e$  and  $Q_e$  correspond to the mg of metal adsorbed per g of adsorbent and residual metal concentration in solution when in equilibrium.  $K_L$  (L/mg) and  $Q_{max}$  are the Langmuir constant and maximum capacity of adsorption (mg/g), respectively. Values of Langmuir parameters  $Q_{max}$  and  $K_L$  were calculated from the slope and intercept of linear plot of  $C_e/Q_e$  versus  $C_e$  (figure not shown). The calculated values of constants are given in Table-1.

The essential features of Langmuir isotherm model can be expressed in terms of  $R_L$  a dimensionless constant, separation factor or equilibrium parameter [24], which is defined by the following equation:

$$R_L = \frac{1}{1 + K_L C_i} \quad (3)$$

where  $C_o$  (mg/L) is the initial amount of adsorbate and  $b$  (L/mg) is the Langmuir constant. The  $R_L$  parameter is considered as more reliable indicator of adsorption. The values of  $R_L$  given in Table-2 and noted that in all cases  $R_L$  was found to be less than one. This confirmed that Langmuir isotherm model was favourable for adsorption of Cu(II), Pb(II) and Cd(II) onto REL.

**Freundlich isotherm:** The Freundlich isotherm model is valid for multilayer adsorption on a heterogeneous adsorbent surface with sites that have different energies of adsorption. The Freundlich equation [25] has the following form:

$$Q_e = K_F C_e^{1/n} \quad (4)$$

Eqn 4 can be modified as follows:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

TABLE-2 $R_L$ VALUES BASED ON THE LANGMUIR ISOTHERM			
$C_i$ (mg/L)	Pb(II)	Cu(II)	Cd(II)
10	0.555	0.588	0.454
20	0.384	0.416	0.294
30	0.294	0.322	0.217
40	0.238	0.263	0.172
50	0.200	0.222	0.142

where  $K_F$  is a constant to the adsorption capacity and  $n$  is related to the adsorption intensity of adsorbent.  $K_F$  and  $1/n$  can be determined from the slope and intercept of line plot,  $\log Q_e$  versus  $\log C_e$  (figure not shown). The values of constants are given in Table-1.

**Temkin isotherm:** Temkin isotherm is based on the assumption that adsorption energy decreases linearly with surface coverage due to adsorbent-adsorbate interactions. The linear form of Temkin equation [26] is given as follows:

$$Q_e = b_T \ln A + b_T \ln C_e \quad (6)$$

where  $b_T$  is the Temkin constant related to heat of sorption (J/mol) and  $A$  is the Temkin isotherm constant (L/g). Values of  $b_T$  and  $A$  were calculated from the slope and intercept of the plot of  $Q_e$  versus  $\ln C_e$  (figure not shown) and are given in Table-1.

The separation factor ( $R_L$ ) value is less than one in all cases and approached zero with increase in  $C_i$  value indicated that *Rubus ellipticus* leaves (REL) is a suitable adsorbent (Table-2). The Freundlich constant  $1/n$  was smaller than unity indicated that the adsorption process was favourable under studied condition. From the results, the adsorption process of Pb(II), Cu(II) and Cd(II) onto REL was well fitted with Langmuir and Freundlich isotherm models.

**Comparison with other biosorbents:** Table-3 represents the comparison of biosorption capacity ( $Q_{max}$ ) of *Rubus ellipticus* leaves for Pb(II), Cu(II) and Cd(II) ions with that of various biosorbents reported in literature. The biosorption capacity of metal uptake is due to properties of each adsorbent such as adsorbent structure, functional groups and surface area [35]. It is seen from Table-3 that *Rubus ellipticus* leaves has good adsorbent capacity with  $Q_{max}$  (mg/g) 3.38, 4.48 and 2.80 for Pb(II), Cu(II) and Cd(II) ions, respectively compared with other untreated biosorbents. Therefore, it can be noteworthy that *Rubus ellipticus* leaves as biosorbent has important potential for the removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution.

**Thermodynamic equilibrium:** The feasibility of adsorption process was evaluated by thermodynamic parameters including Gibb's free energy change ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ).  $\Delta G^\circ$  was calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_d \quad (7)$$

TABLE-3  
COMPARISON IN ASPECT OF ADSORPTION CAPACITIES ( $Q_{max}$ , mg/g) BETWEEN LOW-COST ADSORBENTS AND *Rubus ellipticus* BIOSORBENT

Adsorbent	$Q_{max}$ (mg/g)			Ref.
	Pb(II)	Cu(II)	Cd(II)	
<i>Artemisia vulgarise</i> leaves	0.86	0.88	–	[3]
Sugar beet pulp	0.37	–	0.13	[27]
Clinoptilolite	1.64	–	2.40	[28]
Montmorillonite	0.68	–	0.72	[29]
<i>Urtica dioica</i> leaves	1.493	1.490	–	[18]
Bagasse fly ash	–	2.26	–	[30]
Low rank Turkish coals	–	1.62	–	[31]
Sawdust	–	1.79	–	[32]
Coconut copra meal	–	–	2.01	[33]
<i>Chlorella vulgaris</i>	–	–	0.02	[34]
<i>Rubus ellipticus</i> (REL)	3.38	4.48	2.80	This study

where R is the universal gas constant (8.314 J/K mol), T is the temperature (K) and  $K_d$  is the distribution coefficient. The  $K_d$  value was calculated as follows:

$$K_d = \frac{Q_e}{C_e} \quad (8)$$

where  $Q_e$  and  $C_e$  are the equilibrium concentration of Pb(II), Cu(II) and Cd(II) ions on adsorbent (mg/L) and in solution (mg/L), respectively. The enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) of adsorption were calculated from the following equation:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

The thermodynamic parameters of  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the slope and intercept of the plot between  $\ln K_d$  versus  $1/T$  (figures not shown). The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the adsorption of Pb(II), Cu(II) and Cd(II) ions onto *Rubus ellipticus* leaves at different temperatures are given in Table-4. The negative value of  $\Delta G^\circ$  indicated that the adsorption process was feasible and spontaneous. The positive value of  $\Delta H^\circ$  indicated the endothermic nature of biosorption. The adsorption process in the solid-liquid system is a combination of two processes: (a) adsorption of solvent (water) molecules

TABLE-4  
THERMODYNAMIC PARAMETERS VALUE FOR ADSORPTION OF Pb(II), Cu(II) AND Cd(II) IONS ONTO REL

Metal ion	T (K)	$\ln K_c$	$\Delta G^\circ$ (KJ/mol)	$\Delta H^\circ$ (KJ/mol)	$\Delta S^\circ$ (KJ/mol)
Pb(II)	298	1.025281	-2.540	14.12	56.00
	308	1.231036	-3.152		
	318	1.398841	-3.698		
	328	1.529956	-4.172		
	338	1.719000	-4.830		
Cu(II)	298	1.259848	-3.121	14.89	60.21
	308	1.398841	-3.582		
	318	1.578556	-4.173		
	328	1.774367	-4.838		
	338	1.964322	-5.520		
Cd(II)	298	0.355703	-0.881	19.96	70.07
	308	0.658841	-1.687		
	318	0.856839	-2.265		
	328	1.125459	-3.069		
	338	1.312911	-3.689		

previously adsorbed and (b) adsorption of adsorbate species [36].

## Conclusion

The batch experiments conducted in present study provide significant information regarding the biosorption of Pb(II), Cu(II) and Cd(II) ions onto *Rubus ellipticus* leaves (REL). The maximum percentage removal of Pb(II), Cu(II) and Cd(II) was obtained at pH 4.0 for Pb(II) and Cu(II), and 5.0 for Cd(II). The monolayer adsorption capacity was found to be 3.38, 4.48 and 2.80 mg/g for Pb(II), Cu(II) and Cd(II), respectively. The adsorption process results showed that Langmuir and Freundlich isotherm models were best fitted for the adsorption of Pb(II), Cu(II) and Cd(II) ions onto *Rubus ellipticus* leaves. The negative  $\Delta G^\circ$  value indicated that adsorption of Pb(II), Cu(II) and Cd(II) ions onto REL was spontaneous and feasible in nature.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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