

Biosorptive Removal of Cu(II), Cd(II) and Pb(II) Ions from Synthetic Wastewater Using Low Cost Biosorbent (*Pyras pashia*): Thermodynamic and Equilibrium Studies

HARISH SHARMA^{1,*}, RAJESH KUMAR^{1,*}, MAHESH CHANDRA VISHWAKARMA², SUSHIL KUMAR JOSHI¹ and NARENDER SINGH BHANDARI¹

¹Department of Chemistry, Kumaun University, S.S.J. Campus, Almora-263601, India

²Department of Chemistry, Laxman Singh Mahar P.G. College, Pithoragarh-262501, India

*Corresponding authors: E-mail: sharmaharish887@gmail.com; rathourrajesh22july@gmail.com

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In present study, *Pyras pashia* leaves were used as low cost biosorbent to study biosorption of Cu(II), Pb(II) and Cd(II) ions from contaminated wastewater. In the employed batch methods pH, contact time, metal ion concentration, temperature, biosorbent doses were taken as study parameters. The pH was varied from pH 1-9 to study the influence of pH on biosorption of metal ions by *Pyras pashia*. The optimum pH for the removal of Cu(II), Pb(II) and Cd(II) is observed at pH 5. The biosorption equilibrium time was varied between 15-75 min. Langmuir, Freundlich and Temkin isotherms were employed to study the biosorption. The biosorption parameter fits well with Langmuir isotherm. The biosorption of metal ions was increased with increasing biosorbent dose and contact time while increase in pH, metal ion concentration and temperature decrease the biosorption. Thermodynamic data suggest that the biosorption process was spontaneous, feasible and endothermic.

Keywords: *Pyras pashia*, Thermodynamics, Equilibrium, Isotherms, biosorption.

INTRODUCTION

Heavy metal ions contamination by industrial effluents is one of the critical environmental problems. Heavy metals are toxic and tend to accumulate in the food chains [1]. Thus contamination of these metals by industrial wastewaters is a serious threat to various life forms [2]. Among heavy metals, Cu(II) and Zn(II) are the essential traces elements, however, if taken beyond the prescribed limit, they cause serious health effects which may be fatal e.g., failure of gastrointestinal tract [3], kidney [4], prostate cancer [5], bone anomalies [6], etc. Although there are the several methods for removing heavy metals from wastewaters i.e. chemical precipitation, filtration, ion exchange, chromatography and carbon adsorption [7-9]. These methods have their own disadvantages such as secondary pollution, high cost, high energy consumption and many more [10].

Biosorption is an ecofriendly process used for the removal of heavy metal ions from wastewaters. In recent years, large number of biosorbents are used to remove heavy metal ions from wastewaters such as mango peel water [11], rice husk [12], sawdust [13], *Cedrus deodara* [14], *Citrus aurentifolia*

[15], coconut shell [16], patti [10], cocoa pod husk [17], etc. *Pyras pashia* plants are abundantly found in Shivalik hills of Mandi district of India. *Pyras pashia* is a deciduous tree, often armed with spines and can grow upto 12-15 m tall. The plant often produces suckers and use as a food, medicine and source of materials. The main objective of this study is to investigate the possibility of use of *Pyras pashia* as an alternative low-cost biosorbents for removal of Cu(II), Cd(II) and Pb(II) metal ions from synthetic wastewaters.

EXPERIMENTAL

Preparation of biosorbent: *Pyras pashia* leaves were collected from Mandi district, India. These leaves were washed with tap water. Again the washed leaves were cleaned with ethanol water thrice to remove dust and soluble materials. The dried leaves were then dried in hot air oven at 333 K for 24 h. The dried biomass was grinded to fine powder and then treated with 0.1 N HNO₃ at room temperature for 24 h, 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 μ sieves (170 BSS sieve). The sieved bio-

mass then stored in air tight bottle which is used as biosorbent in present studies.

Preparation of biosorbate: To prepare 1000 mg/L stock solution of Cu(II), Pb(II) and Cd(II) ions $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, CdCl_2 and $\text{Pb}(\text{NO}_3)_2$ were used. The working solution was prepared by diluting the stock solution with double distilled water. The working solution range of all metal ions were from 10 mg/L to 50 mg/L. Optimum pH for Cu(II), Cd(II) and Pb(II) ions were kept at pH 5.

Batch operation: The biosorption experiments were carried out with 100 mL of standard solution in 250 mL conical flask. The solution was shaken at 170 rpm for 45 min and then filtered by using Whatman No. 42 filter paper. The filtrate was digested with conc. HNO_3 . The digested solution was analyzed by atomic absorption spectrophotometer (Optima 4300DV ICP, Perkin-Elmer). The effect of pH on Cu(II), Cd(II) and Pb(II) ions biosorption was studied over pH range from 1.0 to 9.0 and the biosorbent dose varied from 1.0 g to 5.0 g. The effect of removal efficiency of the adsorbent was calculated using the equation:

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

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: Various functional groups present in *Pyrus pasia* which bind the metal ions in biosorption process are shown in Fig. 1. The broad band at 3276 cm^{-1} indicates the presence of hydroxyl (-OH). Peaks around 2920 and 2851 cm^{-1} indicates the C-H stretching and C-H bending of (-CHO) group in biomass. A strong absorption at 1731 and 1618 cm^{-1} indicate the presence of -C=O group. Another strong peak at 2360 cm^{-1} indicates the strong carbonate stretching. Vibrations at $1300\text{-}1000 \text{ cm}^{-1}$ shows presence of (C-O) stretching. And medium weak multiple bending between $1600\text{-}1400 \text{ cm}^{-1}$ shows the (C=C) aromatic stretching. The band at 776 cm^{-1} revealed the presence of 1,3-disubstituted aromatic ring.

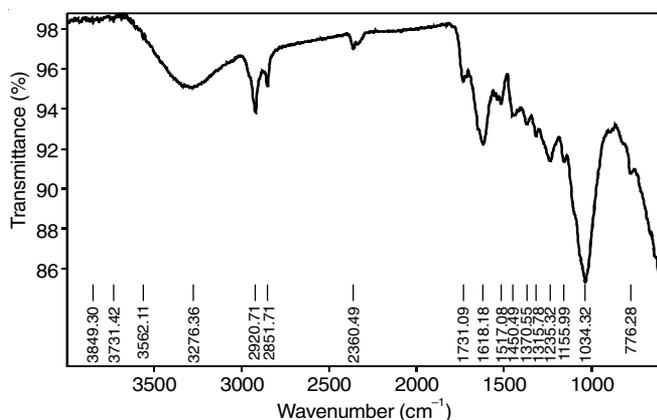


Fig. 1. FTIR spectrum of *Pyrus pasia* leaves

Effect of pH: The effect of pH on the biosorption of Cu(II), Pb(II) and Cd(II) ions by *Pyrus pasia* leave is shown in Fig. 2. The maximum removal efficiency for Cu(II) is 79.8 % for Pb(II) 85 % and for Cd(II) is 89.1 % at pH 5. At low pH, the

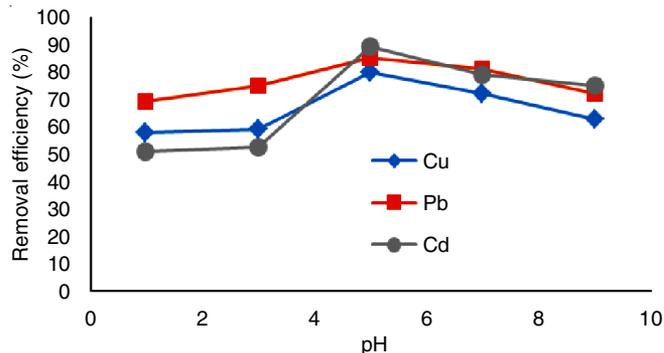


Fig. 2. Effect of pH on Cu(II), Pb(II) and Cd(II) ions adsorption capacity [Experimental condition initial metal ion concentration = 10 mg/L, contact time 45 min, temperature = 25 °C, pH = 5.0, agitation speed = 170 rpm]

hydrogen ions concentration was high and therefore, protons can compete with the metal ions for surface sites. When pH increased, there was a decrease in positive surface charges due to the deprotonation of the sorbent functional group which resulted to a lower electrostatic repulsion between the positively charged metal ions and the surface of biosorbent [18]. As pH value was higher, more exchangeable cations contained in the biosorbent can be exchanged with metal ions due to weak competitive adsorption of hydrogen ions and also could not performed due to the precipitation of Cu(II), Pb(II) and Cd(II) ions [19].

Effect of contact time: Biosorption experiments were carried out at different time intervals *viz.* 15, 30, 45, 60 and 75 min for the individual metal ions. It was observed (Fig. 3) that the biosorption of the resulting metal ions was optimum within a short period of 30-45 min. Removal efficiency of metal ions increases with increase in contact time and gradually decrease after 45 min hence optimum contact time was selected as 45 min for further experiments. Agitation speed for the experiments were 170 rpm.

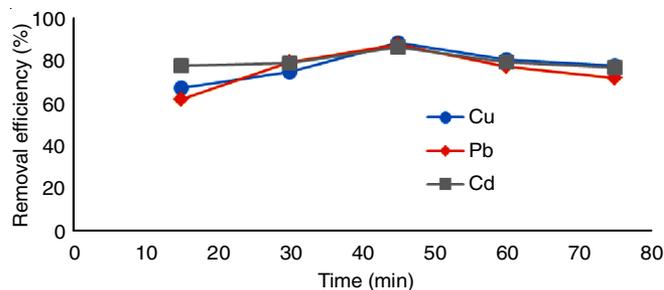


Fig. 3. Effect of contact time of Cu(II), Pb(II) and Cd(II) ions biosorption [experimental condition: initial metal ion concentration = 10 mg/L, biosorbent dose = 1 g/100 mL, temperature = 25 °C, pH = 5.0 and agitation speed = 170 rpm]

Effect of biosorbent dose: Biosorbent dose were studied between 1-5 g. In this study, it was observed that on increasing the biosorbent doses, the removal efficiency (Fig. 4) of Cu(II), Pb(II) and Cd(II) ions increases due to the availability more active site [20,21]. On further increasing the biosorbent dose, there is no further remarkable change due to absence of active sites. All the active sites are occupied by the metals ions. However, biosorption capacity (Q_e) decreases with increase in dose due to increased metal biosorbent ratio which in turn decrease with increase biosorbent dose [22] (Fig. 5).

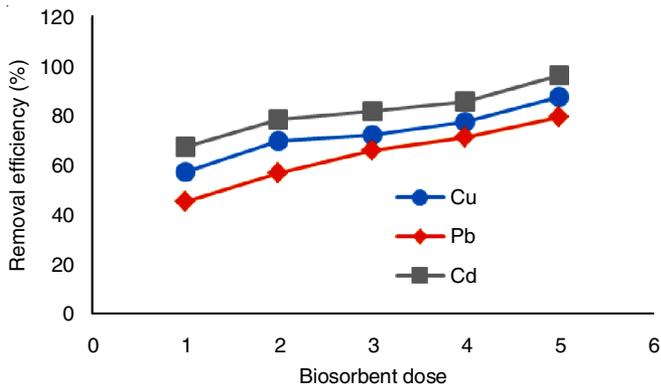


Fig. 4. Effect of biosorbent dose on Cu(II), Pb(II) and Cd(II) ions adsorption (experimental condition: Initial metal ions concentration 10 mg/L, contact time 45 min, room temperature, 5 pH, agitation speed 170 rpm)

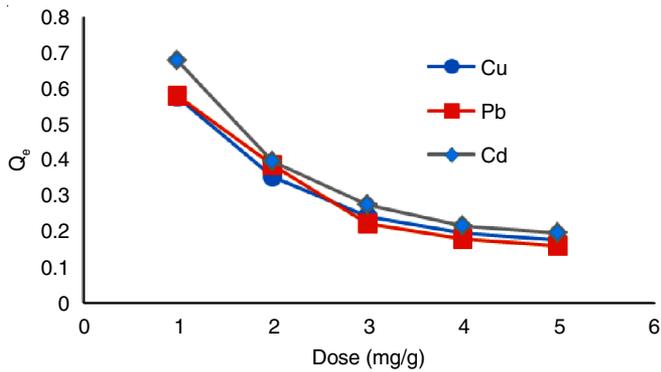


Fig. 5. Effect of adsorbent dose on Cu(II), Pb(II) and Cd(II) ions adsorption capacity [Experimental condition: initial metal ion concentration = 10 mg/L, contact time 45 min, temperature = 25 °C, pH = 5.0, agitation speed = 170 rpm]

Effect of initial metal(II) ions concentration: Fig. 6 manifest the percentage removal of Cu(II), Pb(II) and Cd(II) ions decrease with increase in metal ions concentrations with 1 g of biosorbent dose. The total number of available adsorption sites was fixed thereby adsorbing almost the same amount of adsorbate, thus resulting in a decrease in the removal of adsorbate corresponding to an increase in initial adsorbate concentration *i.e.* saturation of the adsorbent [23,24]. While the equilibrium uptake Q_e has been increased with increasing the initial metal ion concentration from 10 to 50 mg/L (Fig. 7).

Adsorption isotherms: The equilibrium relationships between biosorbent and adsorbate are best explained by sorption isotherms [25]. In the present study, Langmuir, Freundlich and Temkin models were used to illustrate the adsorption process of Cu(II), Pb(II) and Cd(II) ions onto *Pyras pashia* leaves.

Langmuir isotherm: Langmuir isotherm [26] presumed that biosorption occurs at specific homogeneous site on the biosorbent and is used successfully in many monolayer biosorption processes. This model can be written as follows:

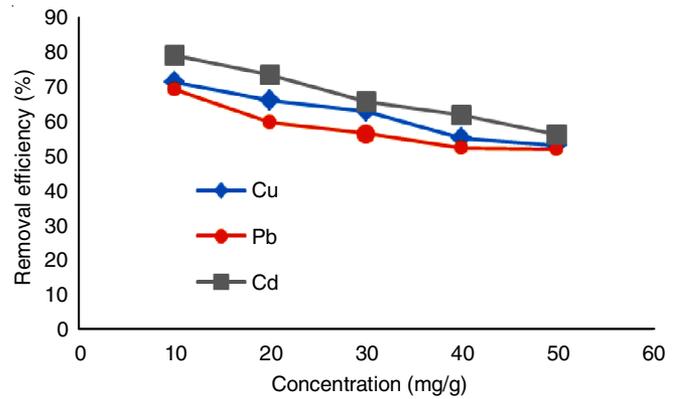


Fig. 6. Effect of initial Cu(II), Pb(II) and Cd(II) ions concentration on adsorption

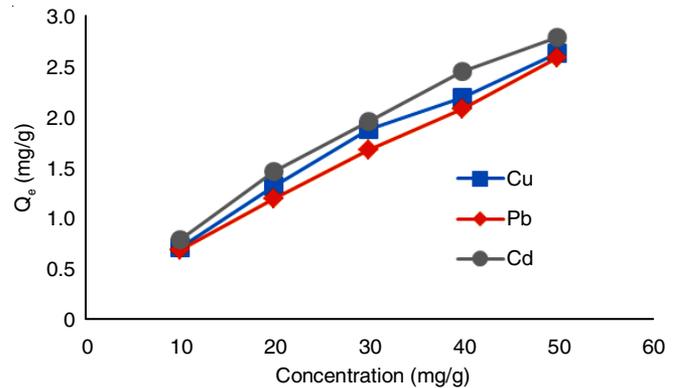


Fig. 7. Effect of initial Cu(II), Pb(II) and Cd(II) ions concentration on adsorption capacity [Experimental condition: Adsorbent dose = 1 g/100 mL, contact time 45 min, temperature = 25 °C, pH = 5.0 for Pb(II) and Cu(II) and 5.0 for Cd(II), agitation speed = 170 rpm]

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

where C_e and Q_e correspond to the mg of metal adsorbed per g of adsorbent and residual metal concentration in the solution when in equilibrium. The K_L (L/mg) and Q_{\max} are the Langmuir constant and maximum capacity of adsorption (mg/g), respectively. The 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 the Langmuir isotherm model can be expressed in terms of R_L , a dimensionless constant, separation factor or equilibrium parameter, which is defined by the following equation [27].

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

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

TABLE-1
BIOSORPTION ISOTHERM CONSTANT OF Cu(II), Pb(II) AND Cd(II) ONTO *Pyras pashia* LEAVES

Metal ions	Langmuir			Freundlich			Temkin		
	K_L (L/mg)	Q_{\max} (mg/g)	R^2	K_F (mg/g)	$1/n$	R^2	B (mg/g)	A	R^2
Cu(II)	0.06	4.73	0.9910	0.37	0.6738	0.9933	1.0228	0.64	0.9855
Pb(II)	0.04	5.73	0.9907	0.31	0.7242	0.9942	1.0816	0.55	0.9802
Cd(II)	0.13	3.83	0.9942	0.55	0.5390	0.9904	0.8551	1.11	0.9888

more reliable indicator of the adsorption. There are four probabilities for R_L value: For favourable adsorption $0 < R_L < 1$. For unfavourable adsorption, $R_L > 1$ for linear adsorption $R_L = 1$ for irreversible adsorption $R_L = 0$. The values of R_L are given in Table-2. In all cases, R_L is less than one, which confirmed that Langmuir isotherm model is favourable for adsorption of Cu(II), Pb(II) and Cd(II) ions onto *Pyras pashia* leaves.

TABLE-2
 R_L VALUE BASED ON LANGMUIR ISOTHERM

C_i (mg/L)	Cu(II)	Pb(II)	Cd(II)
10	0.625	0.714	0.434
20	0.384	0.555	0.277
30	0.294	0.454	0.204
40	0.238	0.384	0.161
50	0.250	0.333	0.133

Freundlich isotherm: The Freundlich isotherm model is authentic for multilayer biosorption on a heterogeneous biosorbent surface with sites that have different energies of adsorption. The Freundlich [28] equation is represented as follows:

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

Eqn. 4 can also be represent in the following form:

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

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

Temkin isotherm: Temkin isotherm is based on the assumption that the adsorption energy decreases linearly with surface coverage due to adsorbent-adsorbate interactions. The linear form of the Temkin isotherm [29] is given as:

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

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 the values are given in Table-1.

The equilibrium data obtained from the adsorption of Pb(II), Cu(II) and Cd(II) ions onto *Pyras pashia* leaves were fitted both Langmuir and Freundlich isotherm models. The K_L values for Pb(II) Cu(II) and Cd(II) is 0.06, 0.04 and 0.13, respectively having correlation coefficient (R^2) value of 0.9907, 0.9910 and 0.9942. The separation factor (R_L) value (Table-2) was found to be less than one in all cases and approached zero with increase in C_o value, indicated that the *Pyras pashia* leaves is a suitable biosorbent.

The values of Freundlich constant K_F were found to be 0.37, 0.31 and 0.55 for Cu(II), Pb(II) and Cd(II), respectively. The Freundlich constant $1/n$ was smaller than unity indicated that the biosorption process was favourable under studied condition. From these results, adsorption process of Cu(II), Pb(II) and Cd(II) onto *Pyras pashia* leaves was well fitted with the Langmuir and Freundlich isotherm models.

In order to check the performance of *Pyras pashia* leaves as biosorbent for Cu(II), Pb(II) and Cd(II) metal ions, a comparison was made with other reported biosorbents [30-42] that were used for removal of Cu(II), Pb(II) and Cd(II) metal ions. From Table-3, it is precisely indicated that the biosorptive capacity of *Pyras pashia* leaves is much superior to the other biosorbents. The difference in metal uptake by various biosorbents is due to the properties of each biosorbent such as structure, functional groups and surface area.

TABLE-3
COMPARISON OF BIOSORPTION
CAPACITY WITH OTHER BIOSORBENTS

Biosorbents	Biosorption capacity (Q_{max} mg/g)			Ref.
	Cu(II)	Pb(II)	Cd(II)	
Kaolin	–	4.5	–	[30]
Periwinkle shell carbon	–	0.0558	–	[31]
Rolling mill scale	–	2.74	–	[32]
Tea leaf	–	2.096	–	[33]
<i>Artemisia vulgaris</i>	–	0.86	–	[10]
<i>Penicillium spiniulosum</i>	2.4	–	–	[34]
Pre treated <i>Aspergillus niger</i>	2.61	–	–	[35]
<i>Utrica dioica</i> leaves	1.490	–	–	[24]
<i>Acer oblongum</i>	3.338	–	–	[36]
Pomegranate peel	1.32	–	–	[37]
<i>Streptomyces noursei</i>	–	–	3.4	[38]
<i>Aspurgillus niger</i> (live)	–	–	1.31	[39]
Sugar beat pulp	–	0.37	0.13	[40]
Montmorillonite	–	–	0.72	[41]
Coconut copra meal	–	–	2.01	[42]
<i>Pyras pashia</i> leaves	4.73	5.73	3.83	Present study

Thermodynamic equilibrium: The expediency of the biosorption process was examined by the thermodynamic parameters along with free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The ΔG° was calculated from the following equation:

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

where R is the universal gas constant (8.314 J/Kmol), T is the temperature (K) and K_d is the distribution coefficient [43]. The K_d value was calculated using following equation:

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

where Q_e and C_e are the equilibrium concentration of Cu(II), Pb(II) and Cd(II) ions on biosorbent (mg/L) and in solution (mg/L), respectively. The enthalpy change (ΔH°) and entropy change (ΔS°) of biosorption 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 ΔH° and ΔS° were obtained from the slope and intercept of the plot between $\ln K_d$ versus $1/T$ (figure not shown). The values of ΔG° , ΔH° and ΔS° for the adsorption of Cu(II), Pb(II) and Cd(II) ions onto *Pyras pashia* leaves at different temperatures are given in Table-4. The negative value of ΔG° proved that the adsorption process was feasible and spontaneous. The positive value of

TABLE-4
THERMODYNAMIC PARAMETER FOR BIOSORPTION OF
Cu(II), Pb(II) AND Cd(II) ONTO *Pyras pashia* LEAVES

Metal ions	T (K)	ln K _c	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol)
Cu(II)	298	1.380056	-3.419	14.96	58.19
	308	1.45001	-3.713		
	318	1.734601	-4.586		
	328	2.175197	-5.931		
	338	2.586689	-7.268		
Pb(II)	298	1.938742	-1.6641	32.46	98.10
	308	2.016235	-1.8918		
	318	2.169054	-2.3133		
	328	2.230014	-2.5747		
	338	2.261763	-2.7775		
Cd(II)	298	2.173615	-5.385	9.97	56.55
	308	2.195000	-5.620		
	318	2.230014	-5.895		
	328	2.251292	-6.139		
	338	2.272126	-6.384		

ΔH° specify the endothermic nature of biosorption. And the positive ΔS° value indicates an increase in randomness at solid-solution interface [44,45].

Conclusion

In this work, *Pyras pashia* leaves were used as an adsorbent for the removal of heavy metal ions. The results of this study indicated that the highest biosorption efficiency was 79.8, 85 and 89.1 % for Cu(II), Pb(II) and Cd(II) ions that was conducted in optimum condition of pH 5, biosorbent dose 1 mg/g, contact time 45 min and initial metal ions concentration 10 mg/L. Langmuir, Freundlich, and Temkin adsorption models were used to represent the experimental data and data fitted well to the Langmuir isotherm model. Thermodynamic analysis suggested that the removal of Cu(II), Pb(II) and Cd(II) ions from synthetic wastewater onto *Pyras pashia* leaves was spontaneous and endothermic in nature. Since, *Pyras pashia* leaves are abundantly available and has considerable high biosorption capacity, it may be treated as an alternative biosorbent in the removal of heavy metal ions from wastewater.

CONFLICT OF INTEREST

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

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