Utilization of *Erythrina variegata orientalis* leaf powder for the removal of cadmium

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Received 21 August 2008; revised 30 March 2009

Removal of cadmium, a priority pollutant, is carried out by abundantly and freely available *Erythrina variegata orientalis* (Indian coral tree) leaf powder. The extent of removal depends on initial concentration of cadmium in the solution, pH of the solution, temperature, etc. A significant increase in percentage removal of cadmium is observed as pH is increased from 2 to 4. The percentage removal of cadmium increases marginally for pH of 4 to 7. As the initial concentration of cadmium is increased from 23 to 188 mg/L, the % removal is decreased from 98.8 to 86.1%. Freundlich and Langmuir isotherm models well describe the data indicating favourable biosorption. The biosorption is endothermic, irreversible and follows pseudo-second-order kinetics, and rate constant is 0.23 g/(mg-min) for a dosage of 40 g/L. The equilibrium agitation time is 50 min.

**Keywords:** Biosorption, Cadmium, *Erythrina variegata orientalis*, Thermodynamics

The removal of pollutants has to keep pace with the increasing quantities of waste materials being injected into the environment. The discharge of heavy metals into water is a major concern because they accumulate in living organisms resulting in various disorders. In view of these problems, strict environmental regulations on the discharge of heavy metals are specified. These regulations make it necessary to develop efficient technologies for removal of heavy metals. Toxic heavy metals include cadmium, mercury, silver, lead, tin and chromium. Among these heavy metals, cadmium represents a major hazardous waste in the environment. The major resources of consumption of cadmium are: Ni-Cd batteries (79%), cadmium pigments (11%), cadmium stabilizers (2%), cadmium coatings (7%) and cadmium alloys and others (1%).

Prolonged exposure to bivalent cadmium plating baths causes serious toxicity problems. The presence of cadmium in the body causes hypertension, emphysema, renal cancer, prostate cancer, kidney disease, bones problem and human carcinogen. The allowable cadmium concentrations specified for different purposes are: < 2 mg/L for inland surface water and < 0.01 mg/L for drinking water¹. It is Herculean task to purify the effluent before discharging it into the environment. Several methods such as precipitation, filtration through lime stone beds, ion exchange, reverse osmosis, evaporation, electro-dialysis and chelating polymers are available for the removal of cadmium from industrial effluents. The capital and operating costs for the removal of metals using these methods is very high. Adsorption also plays an important role in the removal of metals from the effluents. Again the effective adsorbents like activated carbon are prohibitively costly at least in developing countries. The treatment costs should be minimized while technical objectives are met. Recently, biosorption has been gaining importance due to its cost effectiveness, performance enhancement and abundant availability. The details of some plant based biomass, which have been tried for the removal of cadmium are given in Table 1. The literature review indicates that *Erythrina variegata orientalis* leaf powder has not been tested for removal of cadmium from water/wastewater. This biomass is freely and abundantly available and can be disposed off without regeneration. The present investigation deals with the effectiveness of *Erythrina variegata orientalis* leaf powder to remove toxic cadmium from aqueous solutions.

**Experimental Procedure**

**Preparation of adsorbent**

Mature *Erythrina variegata orientalis* leaves are washed with water to remove dust and soluble
impurities. The dried leaves are powdered and washed two times with distilled water to free them of colour and turbidity. The leaf powder is dried, sieved and the size fractions - 53, 106 and 212 μm - are preserved in glass bottles for use as an adsorbent. The powder analysis indicates the presence of hydroxyl and carboxy moieties as major functional groups. The IR spectrum of *Erythrina variegata orientalis* leaf powder is recorded using Thermo Nicolet Nexus 670 FT-IR spectrophotometer (Fig. 1). The space lattices are measured with D-5000 Siemens XRD (Fig. 2). The BET surface area of the adsorbent is 22.08 m²/g with a cumulative volume of 7.05 mL/g at STP and monolayer of 5.07 cm³/g.

**Preparation of cadmium stock solution**

Cadmium stock solution (1000 mg/L) is prepared by dissolving 2.132 g of 99% 3CdSO₄.8H₂O (analytical grade) in 1 L of distilled water. The cadmium solutions with different metal concentrations are prepared by appropriate dilutions of stock solution. The pH of the aqueous solution is varied by adding required amounts of 1 N H₂SO₄ or 1 N NaOH.

**Studies on equilibrium, kinetics and thermodynamics of biosorption**

The initial concentration of cadmium in the aqueous solution is analyzed by Atomic Absorption Spectroscopy (AAS, Perkin Elmer, model - 3100, 326.1 nm wave length) and found to be 81 mg/L. 50 mL of aqueous solution (cadmium, 81 mg/mL) is taken in each of sixteen 250 mL conical flasks and 0.5 g of 53 μm size adsorbent is added in each flask. These samples are shaken on an orbital shaker at 160 rpm at room temperature (303 K) for varying agitation times. These samples are filtered separately with Whatman no. 40 filter papers. The filtrates are analyzed in AAS to determine final concentrations of cadmium. The same experimental procedure is repeated with other adsorbent sizes (106 and 212 μm).

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**Table 1—Investigations reported on removal of cadmium**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Metal removed</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Juniper fiber²</td>
<td>Cd</td>
<td>Second order</td>
</tr>
<tr>
<td>Olive cake³</td>
<td>Cd, Pd</td>
<td>Maximum removal at pH= 6, second order, endothermic and first order</td>
</tr>
<tr>
<td>Corncob particles⁴</td>
<td>Cd, Cr</td>
<td>Maximum removal at pH= 7</td>
</tr>
<tr>
<td>Apricot stones⁵</td>
<td>Cd, Co, Cu &amp; Ni</td>
<td>Maximum removal at pH= 6</td>
</tr>
<tr>
<td>Rice polish⁶</td>
<td>Cd</td>
<td>Maximum removal at pH=8.6 and exothermic reaction</td>
</tr>
<tr>
<td>Carbonised jackfruit peel⁷</td>
<td>Cd</td>
<td>Maximum removal at pH= 7</td>
</tr>
<tr>
<td>Grape bagasse⁸</td>
<td>Cd, Pd</td>
<td>Maximum removal at pH= 7 for Cd, pH=3 for Pd</td>
</tr>
<tr>
<td>Sugar cane bagasse⁹</td>
<td>Cd</td>
<td>First order</td>
</tr>
<tr>
<td>Rice husk¹⁰</td>
<td>Cd</td>
<td>Maximum removal at pH= 7, second order &amp; endothermic</td>
</tr>
<tr>
<td>Seaweed waste¹¹</td>
<td>Cd</td>
<td>Second order</td>
</tr>
</tbody>
</table>

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![Fig.1—FTIR for Erythrina variegata orientalis leaf powder](image-url)
for various agitation times and with different dosages of adsorbent (1, 1.5, 2 and 2.5 g). The percentage removal of cadmium is calculated as \((C_o - C_t) \times 100/C_o\), where \(C_o\) and \(C_t\) are the initial and final concentrations of cadmium in the aqueous solution. The amount of solute adsorbed \((q, \text{mg/g})\) is calculated from the relation \(q = (C_o - C_t)/m\). From these data, the equilibrium agitation time, optimum adsorbent size and dosage are identified. The above experimental procedure is repeated at these optimum values by varying \(pH\) of the aqueous solution, the initial concentrations of cadmium in the aqueous solution and volume of the aqueous solution \((V)\) to assess the effects of these parameters on % removal. The order of biosorption is determined by conducting the experiments for agitation times of 1 to 50 min. The thermodynamic data of biosorption are obtained by varying the temperature of the aqueous solution for different \(C_o\) values. The experimental conditions investigated are shown in Table 2.

### Results and Discussion

#### Equilibrium studies on biosorption of cadmium

**Effect of agitation time**

The equilibrium agitation time is determined by plotting the % removal of cadmium against agitation time for different dosages (Fig. 3). The % removal increased up to 50 min and attained 92.6% (1.875 mg/g) with 40 g/L concentration of 53 μm size adsorbent. Thereafter, negligible increase in % biosorption is noticed in the agitation time period of 50 to 360 min. It is also observed that the rate of biosorption is fast up to 20 min. The % removal increased from 64.2% (1.3 mg/g) to 84% (1.7 mg/g) in 1 - 20 min time interval because of the availability of adequate surface area of the adsorbent for biosorption. In the agitation time period of 20 to 50 min, % removal is increased from 84% (1.7 mg/g) to 92.6% (1.875 mg/g). As agitation time increases beyond 20 min, further amount of cadmium is adsorbed onto the surface of the adsorbent and the available surface area decreases. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers

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**Table 2—Experimental conditions investigated**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values investigated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adsorbent dosage, w, g/L</td>
<td>10, 20, 30, 40 &amp; 50</td>
</tr>
<tr>
<td>Initial concentration of cadmium, (C_o), mg/L</td>
<td>23, 44, 65, 81, 117, 145 &amp; 188</td>
</tr>
<tr>
<td>Volume of the aqueous solution, (V), mL</td>
<td>10, 25, 50, 75, 100, 125 &amp; 150</td>
</tr>
<tr>
<td>pH of the aqueous solution</td>
<td>2, 3, 4, 5, 6, 7, 8 &amp; 9</td>
</tr>
<tr>
<td>Temperature, K</td>
<td>283, 293, 303, 313, 323 &amp; 333</td>
</tr>
</tbody>
</table>
KUMAR et al.: REMOVAL OF CADMIUM WITH ERYTHRINA VARIEGATA ORIENTALIS LEAF POWDER

...the surface, the capacity of the adsorbent is exhausted. So, the % removal of cadmium becomes more or less constant after 50 min. Different equilibrium agitation times have been reported in literature for the removal of cadmium. Bayat\textsuperscript{12} found an equilibrium agitation time of 2 h with Turkish fly ash as the adsorbent. An equilibrium agitation time of 4 h was reported by Mathialagan and Viraraghavan\textsuperscript{13} with vermiculate. Thus, the equilibrium time with the present adsorbent is less as compared to these previously investigated biomasses.

**Effect of adsorbent dosage and size**

The plots in Fig. 4 reveal that the percentage removal of cadmium from the aqueous phase increases with an increase in the adsorbent dosage. The % removal increases from 74.1 to 93.2\% for \( d_p = 53 \mu m \), as the dosage is increased from 10 to 50 g/L. Such behaviour is obvious because the number of active sites available for metal removal would be more as the amount of the adsorbent increases. The change in % removal of cadmium is marginal when dose of the adsorbent is increased from 2 to 2.5 g. Anoopkrishna and Anirudhan\textsuperscript{14} while investigating the removal of cadmium onto activated carbon observed an increase from 50 to 98.8\% as dosage was increased from 2 to 10 g. The percentage removal of cadmium is increased from 87 to 92.59\% when the adsorbent size decreases from 212 to 53 \( \mu m \). This is due to the fact that as the size of the adsorbent decreases, surface area of the adsorbent increases and thereby the number of active sites on the adsorbent are better exposed to the adsorbate.

**Effect of pH**

The \( pH \) of a solution is an important factor controlling the process of adsorption as \( pH \) influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate. The biosorption data were obtained in the initial \( pH \) range of 2 to 9 for \( C_0 = 81 \text{ mg/L} \) and 40 g/L of 53 \( \mu m \) size adsorbent. The effect of \( pH \) of aqueous solution on % removal of cadmium is shown in Fig. 5. The % removal of cadmium from the aqueous solution increases significantly with an increase in \( pH \) from 2 to 4 (74 to 92.6 \%). However, increase in percentage removal becomes marginal for \( pH \) varying from 4 to 7 (92.6 to 95.1\%). This is due to partial hydrolysis of metal ions resulting in the formation of \( M(OH)^+ \) and \( M(OH)_2 \). \( M(OH)_2 \) would have been adsorbed on the...
nonpolar surface than on M(OH)$^+$. The % removal decreases for pH value above 7. Maximum % removal of cadmium at pH = 7, similar to the present investigation, was reported for the adsorbents Turkish fly ash$^{12}$ and grape bagasse$^8$. Mathialagan and Viraraghavan$^{13}$ reported higher % removal at pH = 6 for vermiculate adsorbent. However, higher values of % removal have been reported at pH=8.3 with chitosan as the adsorbent$^{15}$.

In the present investigation, the maximum cadmium % removal of 98.75% is obtained for 40 g/L of 53 μm size adsorbent at 333 K. The principal driving force for metal ion biosorption is the electrostatic interaction between adsorbent and adsorbate. The greater the interaction, biosorption of cadmium will be more. With an increase in interaction, the cadmium ions replace H$^+$ ions bound to the adsorbent for forming part of the surface functional groups such as – OH, - COOH etc. As the electro-negativity of Erythrina variegata orientalis leaf powder is greater, more cadmium ions are adsorbed.

**Effect of initial concentration of cadmium**

The effect of $C_0$ on the percentage removal of cadmium is shown in Fig. 6 for different temperatures. The percentage removal decreases from 95.7% (0.55 mg/g) to 86.7% (4.1 mg/g) by increasing the $C_0$ from 23 to 188 mg/L at 303 K. Such behaviour can be attributed to the increased adsorbate amount to the constant adsorbent dosage. Similar observations have previously been recorded in case of % removal of cadmium by sugarcane bagasse when removal of metal ions is decreased from 95 to 82% by increasing the concentration of cadmium from 10 to 400 mg/L$^9$. In case of adsorption of cadmium onto activated carbon, Anoopkrishna and Anirudhan$^{14}$ reported 98.8 to 48.2% decrease in % removal when the initial concentration of cadmium is increased. Figure 6 also confirms that the % removal of cadmium is decreased from 98.8 to 86.1% with decrease in temperature. The metal uptake capacities obtained in this investigation are shown in Table 3.

**Sorption isotherms**

The adsorption isotherm is an equilibrium relationship between the concentration of the metal in the fluid phase and its concentration on the adsorbent at a given temperature. Freundlich$^{16}$ relationship: $q_e = K_f C_e^n$ is an empirical equation. It does not indicate a finite uptake capacity of the adsorbent and can be applied in case of low and intermediate concentration ranges. It can be anticipated as first pointed out by Langmuir$^{17}$ that chemisorbed adsorbate layers may be only one molecule thick. The relationship $q_e/q_m = b C_e / (1 + b C_e)$ can be rearranged as $C_e/q_e = 1/bq_m + C_e/q_m$. From the plots between $C_e/q_e$ and $C_e$, the slope $1/q_m$ and the intercept $1/bq_m$ can be calculated. Further analysis of the Langmuir equation is made on the basis of separation factor $R_L$ and according to Mckay et al.$^{18}$, $0 < R_L < 1$ indicates favourable biosorption.

<table>
<thead>
<tr>
<th>Table 3—Metal uptake capacities obtained in the present investigation for 53 μm adsorbent size</th>
</tr>
</thead>
<tbody>
<tr>
<td>$w$, g for $C_o = 81$ mg/L &amp; $V = 50$ mL</td>
</tr>
<tr>
<td>0.5</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>2.5</td>
</tr>
<tr>
<td>—</td>
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<tr>
<td>—</td>
</tr>
</tbody>
</table>

Fig. 6— Variation of % removal of Cd with initial concentration of cadmium
Freundlich isotherm for the present data is drawn between log $C_e$ and log $q_e$ (Fig. 7). The data are well represented by log $q_e = 0.627 \log C_e - 0.258$ and has a correlation coefficient of 0.995. ‘$n$’ and $K_f$ values obtained in the present study are 0.627 and 0.55 L/g respectively at 303 K. The ‘$n$’ value satisfies the condition $0 < n < 1$ indicating favourable biosorption. The values of ‘$n$’ and $K_f$ obtained for removal of cadmium with juniper fiber$^2$ are 0.41 and 0.68 L/g respectively whereas $K_f = 0.37$ L/g and n= 0.135 with the adsorbent corncob$^4$. Langmuir isotherm is shown in Fig. 8 and the data are represented by the equation $C_e/q_e = 0.1785 C_e - 2.04$. The linearity of 0.965 indicates the applicability of isotherm for biosorption of cadmium ions. The $q_m$ value is 5.6 mg/g at 303 K. The separation factor ($R_L$) value of 0.625 conforms favourable biosorption ($0 < R_L < 1$). Hence, the present data can be well explained by Freundlich isotherm as well as by Langmuir isotherm. The $q_m$ and $R_L$ values are 9.2 mg/g and 0.23 for the removal of cadmium by juniper fiber$^2$ where as as $q_m = 5.12$ mg/g and $R_L = 0.47$ with the adsorbent, corncob$^4$.

**Kinetics**

The kinetics of sorption describes the solute uptake, which in turn governs the residence time or sorption reaction. It is one of the important characteristics in defining the sorption. In the present study, the kinetics of the cadmium removal has been carried out to understand the behaviour of the low cost *Erythrina* biomass. The pseudo first order model derived by Lagergren$^{19}$ traditionally finds wide application to describe the order of adsorbate–adsorbent interaction. In the case of adsorption preceded by diffusion through a boundary, the kinetics in most cases follows the pseudo first order rate equation of Lagergren: $\frac{dq}{dt} = K_1 (q_e - q_t)$. This can be written as: $\log (q_e - q_t) = \log q_e - (K_1/2.303) t$. On the other hand, several authors have shown that pseudo second order kinetics can describe these interactions very well in certain specific cases. The adsorbent used in the present investigation, *Erythrina variegata orientalis* leaf powder, contains polar functional groups that can be involved in chemical bonding and are responsible for the cation exchange capacity of the adsorbent. Thus, for the adsorbent-divalent cadmium, the reaction may be represented in two ways:

$$2P^- + Cd^{2+} \rightarrow CdP_2$$

and

$$2HP + Cd^{2+} \rightarrow CdP_2 + 2H^+$$

where $P^-$ and $HP$ are polar sites on the adsorbent surface. The rate of sorption to the surface should be proportional to a driving force times an area. The pseudo second order kinetics considers the rate limiting step as the formation of chemisorption bond involving sharing or exchange of electrons between the adsorbate and adsorbent. The rate of the pseudo-second order reaction may be dependent on the amount of solute sorbed on the surface of the adsorbent at any time and the amount sorbed at equilibrium.

The rate expression for the sorption can be described as:

$$\frac{d(P)}{dt} = K[(P)_0 - (P)]^2$$

and
\[
\frac{d(HP)}{dt} = K[(HP) - (HP)_e]^2
\]

where \((P)\) and \((HP)\) are the number of active sites occupied on the adsorbent at time, \(t\), and \((P)_0\) and \((HP)_0\) are the number of equilibrium sites available on the adsorbent.

The driving force, \((q_e - q_t)\), is proportional to the available fraction of active sites. The kinetic rate equations can be rewritten as follows:

\[
\frac{dq_t}{dt} = K (q_e - q_t)^2
\]

i.e. \[
\frac{dq_t}{(q_e - q_t)^2} = K dt
\]

Integration of the above relation for the boundary conditions \(t=0\) to \(t\) and \(q_t = q_e\), results as:

\[
q_t = \frac{K t q_e^2}{1 + K t q_e}
\]

The above equation is the integrated rate law for a second order reaction. The above equation can be rearranged as \(1/q_t - 1/q_e = 1/(K q_e^2) + (1/q_e) t\). If the pseudo second order kinetics is applicable, the plot of \(t/q_t\) versus \(t\) gives a linear relationship that allows computation of \(q_e\) and \(K\).

Lagergren plot of \(\log (q_e - q_t)\) versus agitation time \(t\) is shown in Fig. 9 for the present data. The adsorption rate constant \((K_{ad})\) obtained in the present investigation is 1.74 min\(^{-1}\) and correlation coefficient is 0.9. For manganese nodule residue adsorbent, Agarwal and Sahu\(^2\) obtained \(K_{ad}\) of 1.34 min\(^{-1}\) and correlation coefficient of 0.99 for removing 400 mg/L cadmium. Inbaraj and Sulochana\(^7\) reported correlation coefficient of 0.57 for adsorption of 40 mg/L concentration cadmium onto carbonised jackfruit peel.

To assess the applicability of pseudo second order model, \(t/q_t\) versus 't' plots for the present data are drawn in Fig. 10. The linearity of the plots (correlation coefficient > 0.995) confirms the suitability of pseudo second order rate equation. The deviations between experimental \(q_e\) and \(q_{emodel}\) are less than 3.66%. The smaller deviations prove the suitability of second order equation to explain the kinetics. Also, based on Chi-square analysis, the value of \(\sum[(q_e-q_{emodel})^2]/q_{emodel}\) is less than 0.00778 indicating the validity of second order kinetic equation. The linearity of the second order kinetics is higher \((R>0.995)\) compared to the first order kinetics \((R=0.9)\). So, the second order kinetics better explains the biosorption of cadmium. The following second order rate equations are obtained from the graph for \(w = 10, 20, 30, 40\) and 50 g/L of \(d_p = 53 \mu m\) respectively.

\[
\begin{align*}
t/q_t &= 0.1608 t + 0.505 & q_e &= 6.22, & K &= 0.051 \text{ g/mg-min}, & R &= 0.995 \\
/t/q_t &= 0.311 t + 0.3656 & q_e &= 3.22, & K &= 0.26 \text{ g/mg-min}, & R &= 0.999 \\
/t/q_t &= 0.4449 t + 0.5608 & q_e &= 2.25, & K &= 0.35 \text{ g/mg-min}, & R &= 0.999 \\
/t/q_t &= 0.5176 t + 1.165 & q_e &= 1.93, & K &= 0.23 \text{ g/mg-min}, & R &= 0.999 \\
/t/q_t &= 0.6433 t + 1.28 & q_e &= 1.55, & K &= 0.325 \text{ g/mg-min}, & R &= 0.999
\end{align*}
\]

Anoopkrishna and Anirudhan\(^14\) obtained an adsorption rate constant of 0.474 L/(mol-min) and correlation coefficient of 0.99 for activated carbon. For carbonised jackfruit peel adsorbent, Inbaraj and Sulochana\(^7\) obtained a rate constant of 0.43 L/(mol-min) and correlation coefficient of 0.99 for 40 mg/L of cadmium.
cadmium. The rate constant obtained in this investigation [0.646 L/(mol-min)] is higher than those reported with other adsorbents indicating it is temperature dependent.

**Thermodynamics**

The changes occurring during biosorption can be explained by the three main important thermodynamic parameters i.e., enthalpy change ($\Delta H$), entropy change ($\Delta S$) and Gibbs free energy change ($\Delta G$). The Van’t Hoff's equation relates $\Delta H$ and $\Delta S$ as

$$\log \left( \frac{q_e}{C_e} \right) = \frac{-\Delta H}{(2.303 RT)} + \frac{\Delta S}{(2.303 R)}$$

$\Delta H$ and $\Delta S$ are calculated from the plots between $\log \left( \frac{q_e}{C_e} \right)$ and $(1/T)$ as Slope = $\Delta H / (2.303 R)$ and Intercept = $\Delta S / (2.303 R)$

$\Delta G$ is related to $\Delta H$ and $\Delta S$ as $\Delta G = \Delta H - T(\Delta S)$.

The present data are obtained with 40 g/L of 53 μm size adsorbent at different initial concentrations of the cadmium, and temperatures of the aqueous solutions. These data are shown in Fig. 11. The values of $\Delta H$, $\Delta S$ and $\Delta G$ obtained in the present investigation for different initial concentrations of cadmium are shown in Table 4. $\Delta H > 0$ indicates that the biosorption is endothermic. The negative value of Gibbs free energy change shows the biosorption as spontaneous. The change in entropy above zero confirms the irreversibility of the biosorption. The cadmium biosorption by rice husk indicates $\Delta H = 69.32$ J/mol, $\Delta S = 82.45$ J/(mol-K) and $\Delta G = -8.41$ kJ/mol. Based on the results obtained, *Erythrina variegata orientalis* leaf powder can be effective for cadmium removal and can be appreciably considered as versatile, economical and feasible adsorbent for reclamation of cadmium from aqueous solutions.

**Conclusions**

The *Erythrina variegata orientalis* leaf powder can be used as an effective adsorbent for the removal of cadmium from its aqueous solutions. The equilibrium agitation time for the cadmium biosorption onto *Erythrina variegata orientalis* leaf powder is 50 min. The percentage removal increases with a decrease in the size of the adsorbent from 212 to 53 μm. The percentage removal is increased with an increase in the adsorbent dosage from 10 to 50 g/L. Percentage removal is increased significantly with increase in pH from 2 to 4. The percentage removal decreases as pH is increased beyond 7. The data are well represented by Freundlich ($R=0.9951$) and Langmuir isotherms ($R=0.965$) indicating favourable biosorption. The percentage removal increases with an increase in temperature indicating biosorption as endothermic. Also, the biosorption is endothermic as $\Delta H$ is positive. The biosorption follows pseudo-second order kinetics with a rate constant of 0.23 g/(mg-min) for a dosage of 40 g/L. The biosorption is irreversible as $\Delta S$ is varied from 17.68 to 96.04 J/(mol-K).

### Nomenclature

- **B** = Langmuir equilibrium constant
- **$C_o$** = Initial concentration of cadmium in aqueous solution, mg/L
- **$C_t$** = Concentration of cadmium in aqueous solution after 't' min, mg/L

### Table 4—Thermodynamic parameters for biosorption of cadmium for various initial concentrations of cadmium

<table>
<thead>
<tr>
<th>S.No.</th>
<th>$C_o$ (mg/L)</th>
<th>$\Delta S$ (J/mol-K)</th>
<th>$\Delta H$ (J/mol)</th>
<th>$-\Delta G$ (kJ/mol) at different temperatures</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
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<td>283K</td>
</tr>
<tr>
<td>1</td>
<td>23</td>
<td>96.04</td>
<td>30.52</td>
<td>27.14</td>
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<td>2</td>
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<td>145</td>
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<td>10.84</td>
<td>6.51</td>
</tr>
<tr>
<td>6</td>
<td>188</td>
<td>17.68</td>
<td>9.61</td>
<td>4.99</td>
</tr>
</tbody>
</table>
\( C_e = \) Equilibrium biosorption concentration of cadmium, mg/L
\( d_p = \) Adsorbent size, \( \mu m \)
\( \Delta G = \) Change in Gibbs free energy, kJ/mol
\( \Delta H = \) Enthalpy change, J/mol
\( K = \) Second order rate constant, g/(mg-min)
\( K_f = \) Freundlich coefficient for cadmium in aqueous solution, L/g
\( K_{ad} = \) First order rate constant, min \(^{-1}\)
\( m = \) Amount of adsorbent taken per 1L of aqueous solution, mg/L
\( n = \) Freundlich constant for cadmium in the aqueous solution
\( q_e = \) Mass of solute adsorbed per unit mass of adsorbent at equilibrium, \( (C_o - C_e)/m, \) mg/g
\( q_t = \) Mass of solute adsorbed per unit mass of adsorbent at ‘t’ min, \( (C_o - C_t)/m, \) mg/g
\( q_m = \) Langmuir monolayer capacity, mg/g
\( R_l = \) Separation factor, \( 1/(1+bC_e) \)
\( R = \) Correlation coefficient
\( \Delta S = \) Entropy change, J/(mol-K)
\( t = \) Agitation time, min
\( T = \) Absolute temperature, K
\( V = \) Volume of the aqueous solution, mL
\( w = \) Adsorbent dosage, g or g/L

**References**

1. ISI, Drinking water specifications, IS 10500, 1991