

Biosorption of chromium onto *Erythrina Variegata Orientalis* leaf powder

Gannavarapu Venkata Vamsi Aditya*, Bhagavatula Padma Pujitha*,
Nalluri Chitti Babu*, and Paladugu Venkateswarlu**†

*Department of Chemical Engineering, Andhra University, Visakhapatnam 530003, India

**Principal, PVP Siddhartha Institute of Technology, Vijayawada 520007, India

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Abstract—The biosorption of chromium from an aqueous solution onto *Erythrina Variegata Orientalis* leaf powder was investigated in batch operations. The equilibrium agitation time was 180 min. The extent of chromium biosorption increased from 74.2% to 86.4% with decrease in biosorbent size from 150 to 45 μm for a dosage of 30 g/L. The biosorption decreased from 99.1 (0.45 mg/g) to 45.5% (1.64 mg/g) with an increase in chromium initial concentration (C_0) from 22.5 to 180 mg/L. The extent of biosorption was maximum at pH=3. The experimental data were well explained by Langmuir and Redlich-Peterson isotherm models. The biosorption data followed second-order kinetics with a rate constant of 0.078 g/mg-min for 50 g/L of 45 μm size biosorbent. The biosorption was exothermic and feasible. The biosorption was tending towards irreversibility with increasing temperature.

Key words: Chromium, Biosorption, *Erythrina*, Thermodynamics

INTRODUCTION

Industrial wastewater requires the removal of many heavy metals, like lead [1], cadmium [2], mercury [1] etc., to meet the water quality standards consistent with environmental protection laws. Another heavy metal, hexavalent chromium is also a toxic pollutant generated from industries such as metal plating units, alkali producing units, polyvinyl chloride, coke ovens, chloro-alkali, petroleum refineries, fertilizers, paints and dyes, motor vehicles, mining and metallurgical. Breathing-in high levels (>2 mg/L) of chromium causes irritation to the nose such as runny nose, sneezing, itching, nose-bleeds, ulcers and holes in the nasal septum. Long-term exposure to chromium causes lung cancer, and high levels of chromium in the workplace cause asthma attacks. Accidental swallowing of larger amounts of chromium leads to stomach upset, convulsions, kidney and liver damage. The allowable chromium concentrations in effluent discharges, specified by the Central Pollution Control Board [3], are 0.05 mg/L for drinking water, 2 mg/L for public sewers, 1 mg/L for marine coastal areas and 0.1 mg/L for inland surface water and various industries.

Several methods are available for the removal of chromium from industrial effluents, including adsorption, precipitation, ion exchange, reverse osmosis, evaporation and electro dialysis. Adsorption is one of the efficient methods for the removal of chromium. Increasingly stringent water quality requirement and fiscal constraints are prompting chemists and environmentalists to find efficient, easily available and inexpensive adsorbents. The interesting features of the newly developed adsorbents are their high versatility, metal selectivity, high uptake and high tolerance. A number of studies have been reported using different kinds of adsorbents. They include rice bran [4], chitin and chitosan [5], Purolite-I and Purolite II [5], protonated thermally treated ectodermis of opuntia [6], staphylococcus saprophyt-

icus [7], salt bush biomass [8], pantoea sp. TEM18 [9], coir pith [10], fagus orientalis L [11], Dunaliella [12], tamarind seeds [13], and aeromonas caviae [14]. In the present investigation, Cr(VI) biosorption capacity of *Erythrina Variegata Orientalis* leaf powder is studied.

MATERIALS AND METHODS

1. Preparation of the Adsorbent

The matured *Erythrina Variegata Orientalis* leaves were obtained from Andhra University Engineering College campus. These are deciduous type light/dark green pinnate leaves of 5-15 cm length. The shape of the leaves is deltoid and broadly ovate with pointed tip and broad base. These leaves were freed from dust and soluble impurities by repeated washings with hydrochloric acid and followed by deionized water. They were dried at room temperature in the shade and sun-dried for crispness. The dried leaves were powdered and washed twice with distilled water to free them of color and turbidity. The resulting powder was dried and sieved. The size fractions (45 μm , 75 μm and 150 μm) were stored in glass bottles and subsequently used as a biosorbent.

The analyses of the leaves indicate the presence of scoulerine, saponin, hydrocyanic acid. Erythrinine (an alkaloid) has properties identical to those of hypaphorine ($\text{C}_{14}\text{H}_{18}\text{N}_2\text{O}_2$), (+) coreximine, l-Reticuline, erybidine [28]. The IR spectrum of *Erythrina Variegata Orientalis* leaf powder was recorded [15] using Thermo Nicolet Nexus 670 FT-IR spectrophotometer (Fig. 1) and by using D-5000 Siemens XRD the space lattices are measured (Fig. 2). The BET (Brunauer, Emmet & Teller) surface area of 45 μm powder is 25.29 m^2/g .

2. Preparation of Chromium Synthetic Solution

A synthetic solution of 1000 mg/L of chromium was prepared by dissolving 2.8284 g of 99.9% $\text{K}_2\text{Cr}_2\text{O}_7$ (analytical grade) in 1 L of distilled water. 90 mg/L of chromium solution was prepared by taking 90 mL of 1,000 mg/L synthetic solution in a 1,000 mL volu-

†To whom correspondence should be addressed.
E-mail: pvl9@rediffmail.com

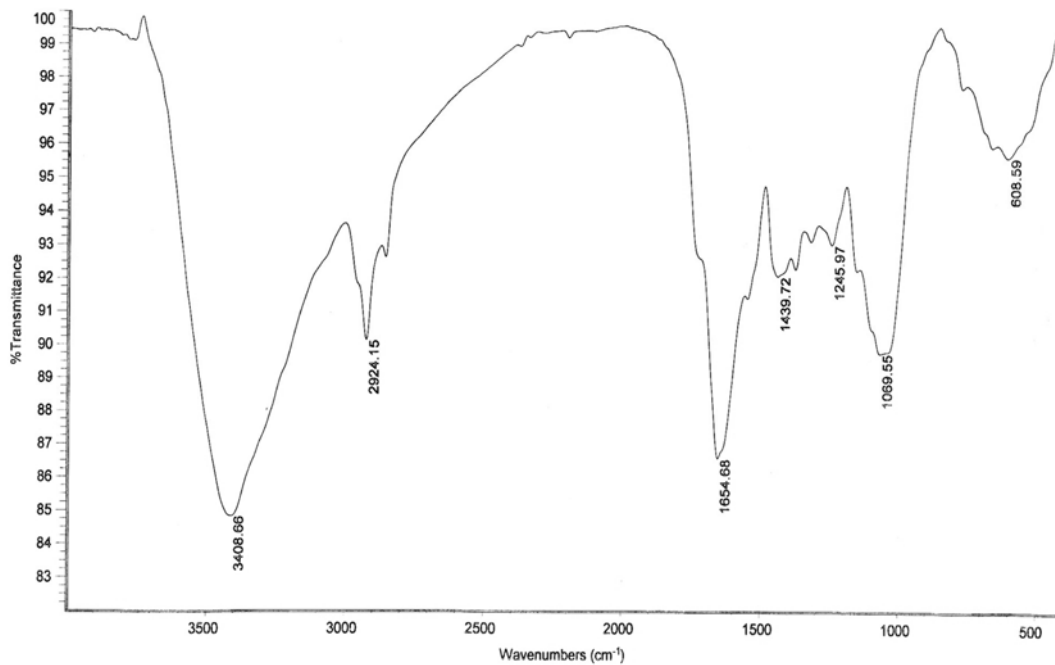


Fig. 1. FTIR for *Erythrina Variiegata Orientalis* leaf powder.

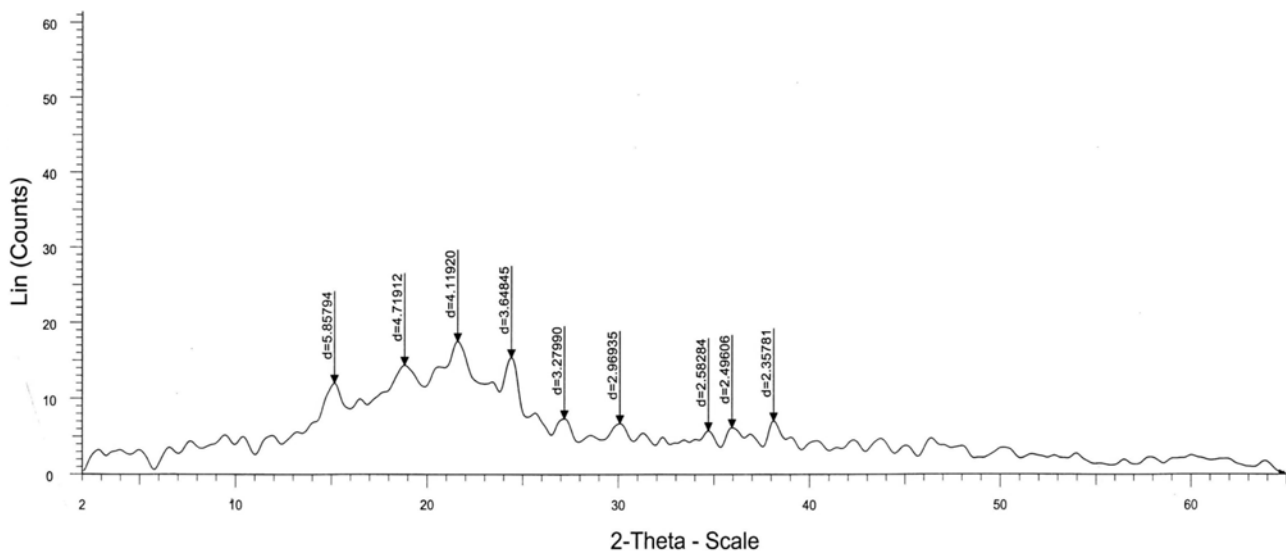


Fig. 2. XRD for *Erythrina Variiegata Orientalis* leaf powder.

metric flask and adding distilled water up to the mark. Similarly, chromium solutions of varying concentrations were prepared. Solutions of 0.1 N H_2SO_4 or 0.1 N NaOH were added for pH adjustment.

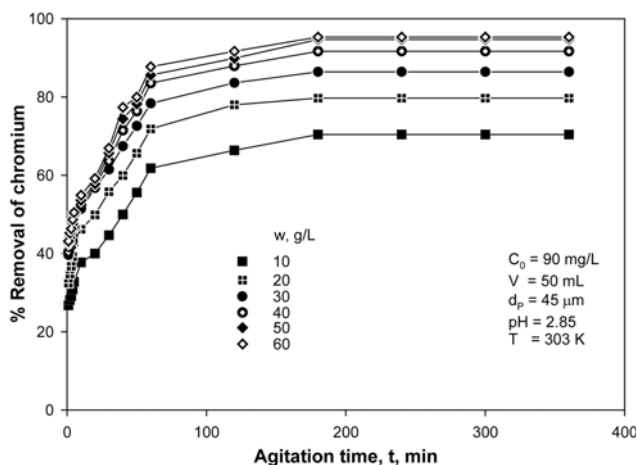
3. Studies on Equilibrium, Kinetics and Thermodynamics of Biosorption

The initial concentration of chromium in the aqueous solution was determined by atomic absorption spectroscopy (AAS, Perkin Almer, model-200, 357.87 nm wave length) and found to be 90 mg/L. 50 mL of aqueous solution was taken in a 250 mL conical flask, and 0.5 g (10 g/L) of 45 μm size biomass was added. This sample was shaken on an orbital shaker at 160 rpm at room temperature (303 K) for 1 min. Similarly, 15 more samples were prepared in

conical flasks adding 10 g/L of 45 μm size biomass and exposed to varying agitation times. These samples were filtered separately with 40 no. Whatman filter papers and the filtrates were analyzed in AAS to obtain final concentrations of chromium. The same experimental procedure was repeated with other biosorbent sizes (75 and 150 μm) for various agitation times and for other dosages (20, 30, 40, 50 and 60 g/L). The percentage removal (biosorption) of chromium is calculated as $(C_0 - C_t) \times 100 / C_0$. The amount of chromium adsorbed per unit mass of the biosorbent, q_t in mg/g is computed by using the expression: $q_t = (C_0 - C_t) / m$. From these data, the equilibrium agitation time, optimum biosorbent size and dosage were identified. The experiments were repeated at these optimum values by varying the initial concentration of chromium in the aqueous

Table 1. Experimental conditions investigated

Parameter	Values investigated
Agitation time, t , min	1, 2, 3, 4, 5, 10, 20, 30, 40, 50, 60, 120, 180, 240, 300 and 360
Biosorbent size, d_p , μm	45, 75 and 150
Biosorbent dosage, w , g/L	10, 20, 30, 40, 50 and 60
Initial chromium concentration, C_o , mg/L	22.5, 45, 67.5, 90, 112.5, 135 and 180
pH of the aqueous solution	1, 2, 3, 4, 5, 6, 7, 8, 9 and 10
Temperature, K	283, 293, 303, 313, 323 and 333

**Fig. 3. Effect of agitation time on % removal of chromium.**

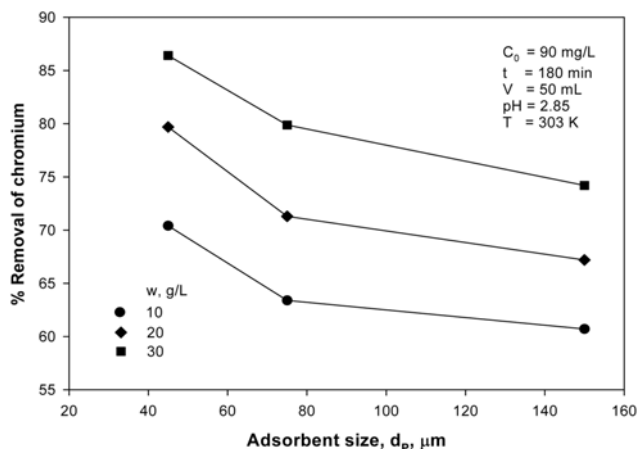
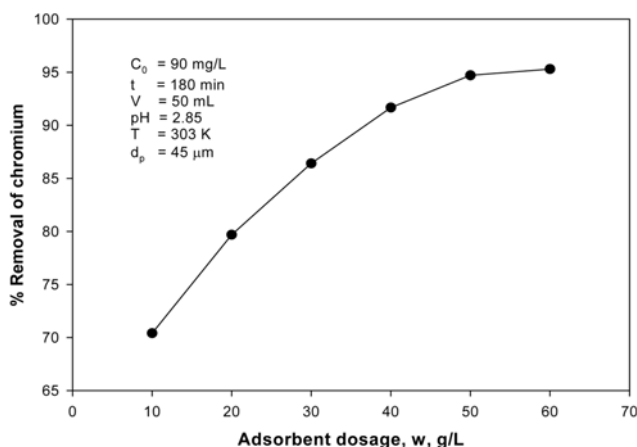
solution, pH of the aqueous solution and temperature. The experimental conditions investigated are shown in Table 1.

RESULTS AND DISCUSSION

1. Equilibrium Studies on Biosorption of Chromium

1-1. Effect of Agitation Time

Biosorption equilibrium agitation time is the time required for heavy metal concentration to reach a constant value during biosorption. The equilibrium agitation time is determined by plotting the percentage removal of chromium against agitation time in Fig. 3 for various 'w' values in the interaction time intervals of 1 to 360 min. For 45 μm size of 50 g/L adsorbent, 49.8% (0.9 mg/g) of chromium is adsorbed in the first 5 min. The biosorption is increased briskly up to 60 min reaching 85.6% (1.54 mg/g). From 60 to 180 min, the biosorption is marginally and gradually increased to 94.7% (1.7 mg/g) from 85.6%. Beyond 180 min, the percentage biosorption is constant, indicating the attainment of equilibrium conditions. The maximum biosorption of 94.7% is attained for 180 min of agitation time with 50 g/L of 45 μm size adsorbent mixed in 50 ml of aqueous solution ($C_o=90$ mg/L). The biosorption rate was rapid in the initial stages because adequate surface area of the biosorbent was available for the biosorption. As agitation time increased, more amount of chromium was adsorbed onto the surface of the biosorbent due to van der Waals' forces of attraction and resulted in decreased available surface area. The adsorbate normally forms a thin one molecule thick layer over the surface. When this monomolecu-

**Fig. 4. Variation of % removal of chromium with adsorbent size.****Fig. 5. % Removal of chromium as a function of adsorbent dosage.**

lar layer covers the surface, the capacity of the adsorbent is exhausted. 180 min equilibrium agitation time was reported earlier with treated sawdust [16].

1-2. Effect of Adsorbent Size and Dosage

The biosorption data were presented in Fig. 4 with percentage removal of chromium as a function of biosorbent size. The biosorption of chromium increased from 74.2% (2.22 mg/g) to 86.4% (2.59 mg/g) as the biosorbent size decreased from 150 to 45 μm with 30 g/L dosage, at 303 K for $C_o=90$ mg/L. With a decrease in biosorbent size, surface area of the biosorbent increases and the number of active sites on the biosorbent are better exposed to the adsorbate. The percentage removal of chromium is drawn against biosorbent dosage for 45 μm biosorbent size in Fig. 5. The removal of chromium increases from 70.4% (6.32 mg/g) to 95.2% (1.43 mg/g), with an increase in dosage from 10 to 60 g/L. Such behavior is obvious because with an increase in dosage, the number of active sites available for chromium removal would be more. The change in percentage removal of chromium is marginal [from 94.7 (1.7 mg/g) to 95.2% (1.43 mg/g)] when 'w' is increased from 50 to 60 g/L. So, all other experiments are conducted at 50 g/L dosage. Barala et al. [19] reported an optimum adsorbent dosage of 40 g/L with 88.67% (3.04 mg/g) removal of chromium from 100 mg/L chromium aqueous solution with the adsorbent calcined bauxite.

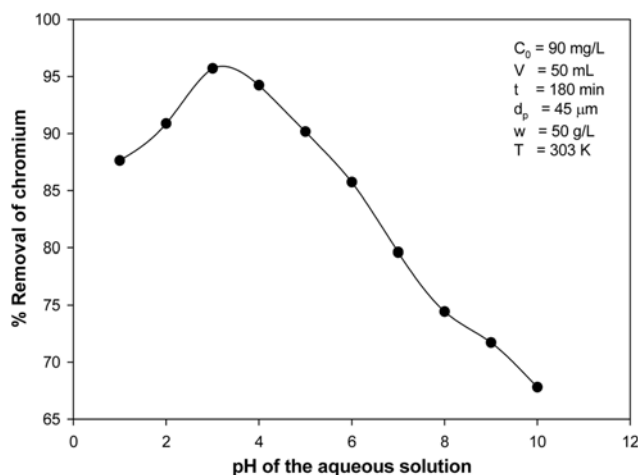


Fig. 6. Effect of pH of aqueous solution on % removal of chromium.

1-3. Effect of pH of the Aqueous Solution

The pH influences the surface charge of the adsorbent, the degree of ionization and the species of adsorbate in adsorption/biosorption. The effect of pH of aqueous solution ($C_0=90 \text{ mg/L}$) on percentage removal of chromium is presented in Fig. 6 by agitating 50 g/L of 45 μm size adsorbent for 180 min. The biosorption is increased from 87.6% (1.58 mg/g) to 95.7% (1.72 mg/g) as pH is increased from 1 to 3 and then decreased beyond pH value of 3 reaching 67.8% (1.22 mg/g) for pH value of 10. The presence of hydroxyl and carbonyl groups on the adsorbent surface imparts considerable cationic exchange capacity to the powder to adsorb the chromium metal. The XRD and FTIR of the leaf powder indicate the presence of hydroxyl and carbonyl as major functional groups [15]. The BET surface area of the leaf powder is 25.287 m^2/g for 45 μm diameter biosorbent. Low pH depresses biosorption of Cr(VI), which may be due to competition with H^+ ions for appropriate sites on the adsorbent surface. However, with increasing pH, this competition weakens and Cr(VI) ions replace H^+ ions bound to the adsorbent or forming part of the surface functional groups such as OH, COOH, etc. [21]. A maximum chromium removal of 86.6% (10 mg/g) was reported at pH=3 onto treated sawdust [16] as pH was varied from 2 to 10.

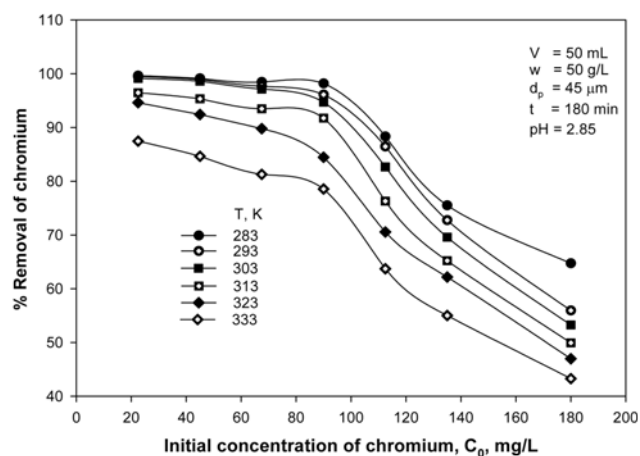


Fig. 7. Variation of % removal of chromium with initial concentration of chromium - Effect of temperature.

Table 2. Metal uptake capacities reported for various adsorbents

Adsorbent	Uptake capacity, mg/g	pH	Initial conc., mg/L
Tamarind seeds [13]	11.08	1-3	102
Treated sawdust [16]	10	3	100
Neurospora crassa [20]	9.15	1	250
Leaf mould [33]	43.1	2	1000
Coconut shell carbon [33]	10.88	4	25
Beech saw dust [33]	16.1	1	200
Sugarcane bagasse [33]	13.4	2	500
Coconut tree saw dust [33]	3.6	3	20
Treated saw dust of sal wood [34]	9.55	3.5	40
Present investigation	6.32	3	90

1-4. Effect of Initial Concentration of Chromium in the Aqueous Solution

The effect of initial concentration of chromium in the aqueous solution on the percentage removal of chromium is shown in Fig. 7. The removal of chromium decreased from 99.1% to 45.5% with an increase in C_0 from 22.5 mg/L to 180 mg/L at 303 K, while the uptake capacity increased from 0.45 to 1.64 mg/g. Such behavior can be attributed to the increase in the amount of adsorbate to the unchanging number of available active sites on the adsorbent (since the amount of adsorbent is kept constant). These plots also confirm that the % removal decreases with an increase in temperature. The metal uptake capacities obtained for various adsorbents are shown in Table 2. The removal of chromium decreased from 61% to 30.4% using waste pomace of olive oil factory in the range of initial concentration from 50 to 200 mg/L, whereas the uptake capacity increased from 6.1 to 12.15 mg/g [18]. Tunali et al. [20] conducted experiments for adsorption of chromium onto neurospora crassa in the C_0 range of 25 to 250 mg/L and reported 1 to 9.15 mg/g increase in the uptake capacity. The saturation curve is presented as Fig. 8.

1-5. Isothermal Studies

The Freundlich isotherm is the equilibrium relationship between the concentration of the metal in the fluid phase and its concentration in the adsorbent at a given temperature. Freundlich [24] pre-

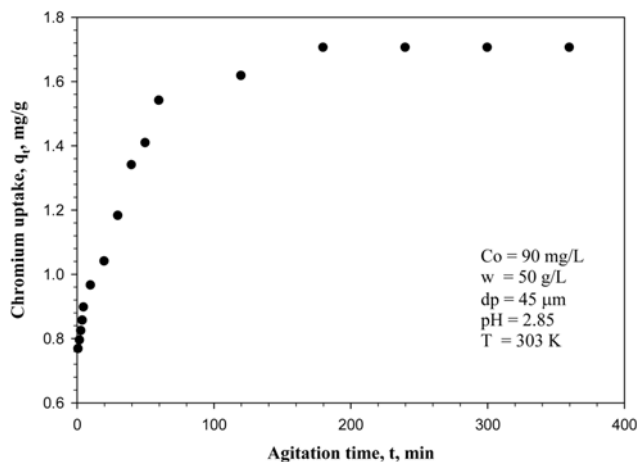


Fig. 8. Saturation curve for biosorption of chromium.

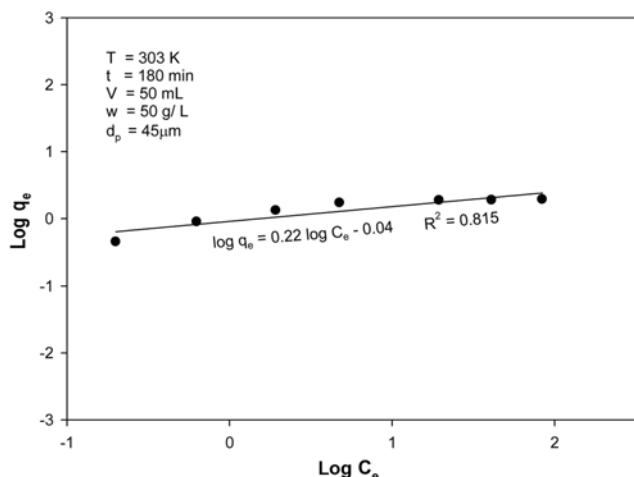


Fig. 9. Freundlich isotherm for biosorption of chromium.

sented an empirical adsorption isotherm equation that can be applied in case of low and intermediate concentration ranges:

$$\log q_e = \log K_f + n \log C_e \quad (1)$$

The Freundlich isotherm is obtained by plotting the relation between $\log C_e$ and $\log q_e$ (Fig. 9). The resulting equation is $\log q_e = 0.22 \log C_e - 0.0437$ with a correlation coefficient of 0.815. The 'n' value satisfies the condition of $0 < n < 1$ indicating favorable biosorption. K_f is varied between 0.341 and 1.1 with an increase in temperature from 283 to 333 K. Malkoc et al. [18] reported a slope (n) of 0.33 and K_f of 2.45 L/g drawing the Freundlich isotherm for adsorption of chromium onto waste pomace of an olive oil factory. Lazaridis and Charalambous [23] investigated adsorption of chromium onto composite alginate goethite beads. The Freundlich isotherm yielded a slope (n) of 0.133 and K_f of 17.24 L/g.

The Langmuir isotherm [25] is the most widely used simple two-parameter equation and is based on the assumptions that adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one adsorbed atom and the ability of a molecule to adsorb at a given site is indepen-

dent of the occupation of neighboring sites. The relationship is hyperbolic and the equation is:

$$(C_e/q_e) = 1/bq_m + C_e/q_m \quad (2)$$

From the plots between (C_e/q_e) and C_e , the slope ($1/q_m$) and the intercept ($1/bq_m$) are calculated. Further analysis of the Langmuir equation is made on the basis of separation factor (R_L), defined as

$$R_L = 1/(1 + bC_e) \quad (3)$$

The Langmuir isotherm, drawn in Fig. 10, is represented by the equation $(C_e/q_e) = 0.52 C_e + 0.4043$ and has good linearity (correlation coefficient = 0.999), indicating strong binding of chromium ions to the surface of *Erythrina Variegata Orientalis* leaf powder. The separation factor value of 0.14 indicates favorable adsorption ($0 < R_L < 1$).

Redlich and Peterson [26] proposed a three-parameter isotherm to incorporate features of both the Langmuir and Freundlich equations. It is described as:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (4)$$

or

$$\ln\left(\frac{AC_e}{q_e} - 1\right) = g \ln(C_e) + \ln B \quad (5)$$

Although a linear analysis is not possible for a three-parameter isotherm, three isotherm constants, A, B, and g are evaluated from the pseudo-linear plot represented by Eq. (5) using trial and error optimization method. A general trial and error procedure is used to determine the correlation coefficient, (R), for a series of assumed values of 'A' for the linear regression of $\ln(C_e)$ on $\ln[A(C_e/q_e) - 1]$, and the best fit is the best 'A' value that yields a maximum optimized value for R. The biosorption isotherm is characterized by certain constants, the values of which express the surface properties and affinity of the sorbent, and is used to compare biosorptive capacity of biomass for different metal ions. Fig. 11 is drawn between $\ln[(C_e/q_e) - 1]$ and $\ln C_e$ at $A = 1$ L/mg (assumed), $d_p = 45 \mu\text{m}$ and $C_0 = 90$ mg/L for $w = 50$ g/L. The higher correlation coefficient of 0.999 suggests that Redlich - Peterson isotherm model is better suited to de-

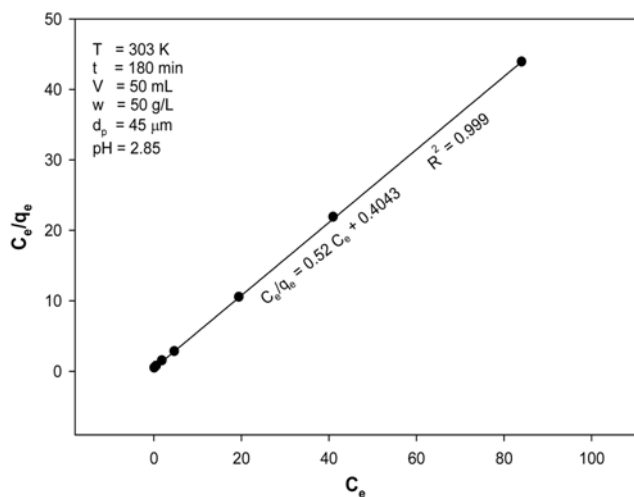


Fig. 10. Langmuir isotherm for biosorption of chromium.

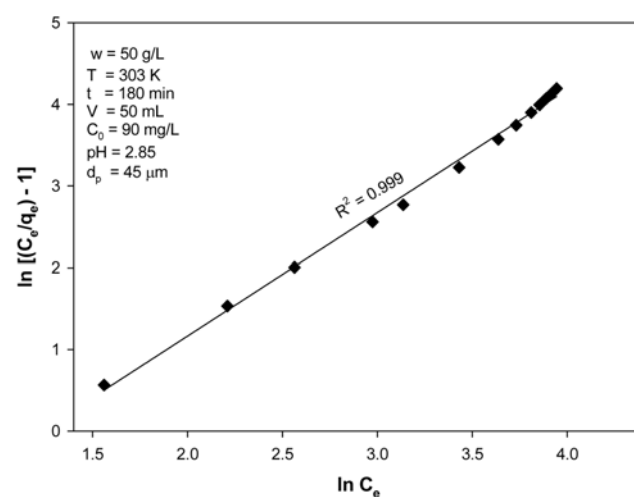


Fig. 11. Redlich - Peterson isotherm for biosorption of chromium.

Table 3. Freundlich, Langmuir and Redlich-peterson constants

Freundlich isotherm			Langmuir isotherm				Redlich-Peterson isotherm	
K_f , L/g	n	R^2	q_m , mg/g	B, L/mg	R_L	R^2	B, L/mg	R^2
0.9	0.22	0.815	1.923	1.286	0.14	0.999	0.1573	0.999

scribe the biosorption of chromium along with Langmuir isotherm model ($R^2=0.999$). The isotherm constants for chromium - *Erythrina Variegata Orientalis* leaf powder interactions at 303 K, $t=180$ min, $C_0=90$ mg/L, $d_p=45$ μ m and $w=50$ g/L are shown in Table 3. 1-6. Kinetics of Biosorption

The kinetics of biosorption describes the order of the reaction. Most of the adsorption/biosorption systems using different adsorbents for metal removal preceded by diffusion through a boundary are found to satisfy Lagergren's first order model [27].

$$(dq/dt)=K_{ad}(q_e-q) \quad (6)$$

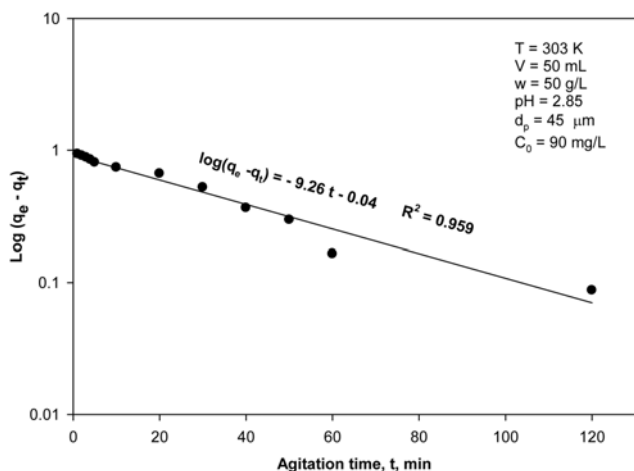
After applying the initial condition $q=0$ at $t=0$, we get

$$\log(q_e - q) = \log q_e - (K_{ad}/2.303) t \quad (7)$$

If the plot of $\log(q_e - q)$ vs 't' gives a straight line, it indicates that the first order kinetics better describes the biosorption. Then the biosorption rate constant (slope), K_{ad} can be calculated from Eq. (7). If the experimental results do not follow Eq. (7), the pseudo-second order kinetics is applied to describe these interactions in certain specific cases. The pseudo-second order kinetics considers the rate-limiting step as the formation of physisorption bond involving sharing or exchange of electrons between the adsorbate and adsorbent. The second order rate equation is given by:

$$(t/q) = (1/K q_e^2) + (1/q_e) t \quad (8)$$

If the plot yields a straight line, the biosorption is described by the second-order kinetics and q_e and K are calculated. In the present study, the kinetics are investigated with 50 mL of aqueous solution ($C_0=90$ mg/L) with adsorbent dosage of 50 g/L, using adsorbent size of 45 μ m, in the interaction time intervals of 1 to 180 min. The Lagergren plot of $\log(q_e - q)$ versus agitation time (t) for biosorption of chromium by *Erythrina Variegata Orientalis* leaf powder is

**Fig. 12. First order kinetics for biosorption of chromium.**

drawn in Fig. 12. The plot is linear with k_{ad} value of 21.325 min^{-1} and correlation coefficient of 0.959 for $d_p=45$ μ m. The pseudo-second order rate equation is also applied for the present data to identify the better rate equation. The plots of (t/q) versus 't' are indicated in Fig. 13. The 'K' value is 0.078 g/mg min with $R^2=0.993$. The results show that the data are well fitted both with a second-order equation with high correlation coefficient ($R^2=0.993$) and the first-order rate equation of Lagergren ($R^2=0.959$).

1-7. Thermodynamics of Chromium Biosorption

Biosorption is associated with the three thermodynamic parameters, namely, change in enthalpy of biosorption (ΔH), change in entropy of biosorption (ΔS) and change in Gibbs free energy (ΔG). van't Hoff expressed an equation that relates the change in biosorption affinity with change in temperature. The van't Hoff equation is

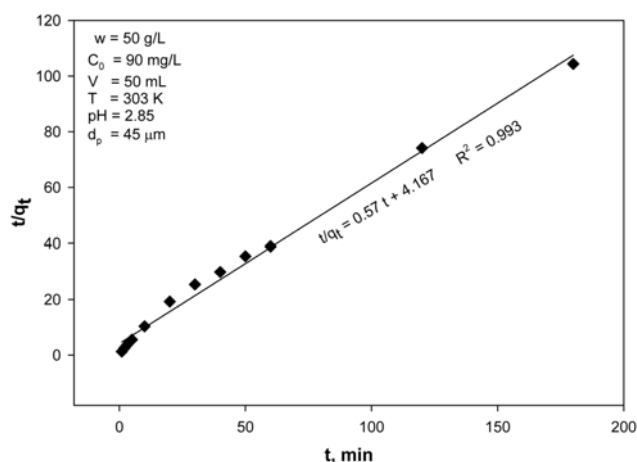
$$\log(q_e/C_e) = -\Delta H/(2.303RT) + \Delta S/(2.303 R) \quad (9)$$

where (q_e/C_e) is called the adsorption affinity.

From the plots between $\log(q_e/C_e)$ and $(1/T)$, slope $-\Delta H/(2.303R)$ and intercept $\Delta S/(2.303R)$ are determined and ΔH and ΔS values are calculated. Change in Gibbs free energy (ΔG) is related to change in enthalpy (ΔH) and change in entropy (ΔS) as

$$\Delta G = \Delta H - T(\Delta S) \quad (10)$$

The positive value of ΔH indicates endothermic nature, and a negative value of ΔH indicates exothermic nature. If the value of ΔS is less than zero, the process is highly reversible. If ΔS is more than or equal to zero, it indicates the irreversibility of the process. The negative value for (ΔG) indicates the spontaneity of biosorption [17, 22]. The experiments are conducted to understand the biosorption behavior varying the temperature from 283 to 333 K. The plots in Fig. 7 indicate that there is a decrease in % removal of chromium with an increase in temperature for different C_0 values. The van't Hoff plots for the biosorption data obtained for various initial con-

**Fig. 13. Second order kinetics for biosorption of chromium.**

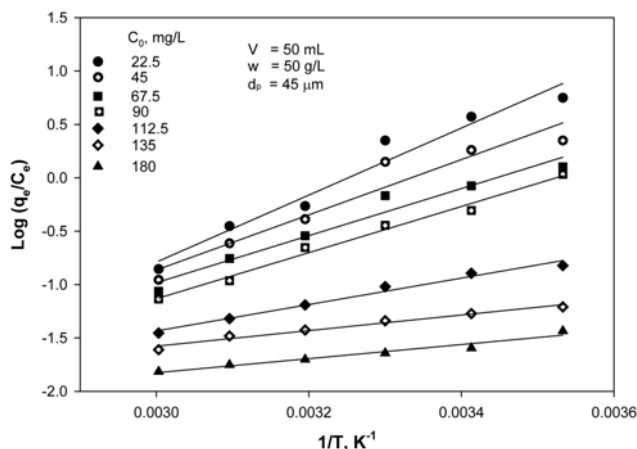


Fig. 14. Effect of temperature on biosorption of chromium (Van't Hoff plot).

centrations of the chromium are shown in Fig. 14.

In the present study, the change in enthalpy (ΔH) is negative, indicating the exothermic nature of biosorption. The increase in ΔH confirms the spontaneous nature of biosorption [21]. The negative value of ΔS [29] confirms the reversibility of the biosorption, and the gradual increase in ΔS value with the concentration indicates that the process is tending towards irreversibility. It also suggests a decrease in biosorption energy with no structural changes in adsorbate and adsorbent [30]. The increase in ΔG value with an increase in temperature indicates that the biosorption is less favorable at high temperatures [22] and also shows the physical nature of the biosorption [31,32]. The spontaneity of the biosorption is demonstrated further by the increase in ΔG with temperature [21]. The increase in positive value of ΔG shows the reaction as spontaneous and feasible at lower temperatures [22]. The values of ΔS , ΔH and ΔG obtained in the present investigation for different C_0 values are shown in Table 4. The exothermic nature and spontaneity of biosorption are reported in the literature [17,22] with the biosorbents treated eucalyptus bark and cross linked cationic starch.

CONCLUSIONS

The equilibrium agitation time for chromium biosorption is 180 min. Biosorption of chromium from the aqueous solution increases significantly from 87.6% (1.58 mg/g) to 95.7% (1.72 mg/g) with an increase in pH from 1 to 3. Thereafter percentage biosorption decreases for further increase in pH. The biosorption is increased

from 45.5 (1.64 mg/g) to 99.1% (0.45 mg/g) as chromium initial concentration is decreased from 180 to 22.5 mg/L. The biosorption of chromium is increased from 70.4% (6.32 mg/g) to 94.7% (1.71 mg/g) with an increase in dosage from 10 to 50 g/L. The experimental data have shown good fits with Langmuir and Redlich-Peterson isotherms, indicating favorable biosorption. The biosorption of chromium is better described by pseudo-second order kinetics ($K=0.078$ g/mg-min). The percentage biosorption decreases with an increase in temperature. The biosorption is exothermic and spontaneous. The biosorption is reversible initially and is tending towards irreversibility with increase in temperature.

NOMENCLATURE

- A : Redlich-Peterson isotherm constant [L/mg]
- B : Redlich-Peterson isotherm constant [L/mg]
- b : Langmuir equilibrium constant [L/mg]
- C_0 : initial concentration of chromium in aqueous solution [mg/L]
- C_t : concentration of chromium in aqueous solution after 't' min [mg/L]
- C_e : equilibrium biosorption concentration of chromium [mg/L]
- d_p : adsorbent size [μm]
- g : Redlich-Peterson isotherm exponent
- ΔG : change in Gibbs free energy [kJ/mol]
- ΔH : heat of reaction [J/mol]
- K_{ad} : first order rate constant [min^{-1}]
- K : second order rate constant [g/mg-min]
- K_f : Freundlich coefficient for chromium in aqueous solution [L/g]
- m : amount of adsorbent consumed per 1 L aqueous solution [mg/L]
- n : Freundlich constant for chromium in the aqueous solution
- q_e : mass of solute adsorbed per mass of adsorbent at equilibrium, $(C_0 - C_e)/m$ [mg/g]
- q_t : mass of solute adsorbed per mass of adsorbent at 't' min, $(C_0 - C_t)/m$ [mg/g]
- q_m : Langmuir monolayer adsorption capacity [mg/g]
- R : gas constant [8.314 J/mole-K]
- R^2 : correlation coefficient
- R_L : separation factor, $1/(1 + bC_0)$
- ΔS : entropy change [J/mol-K]
- t : agitation time [min]
- T : absolute temperature [K]
- V : volume of aqueous solution [mL]
- w : adsorbent dosage in 1 L of aqueous solution [mg/L or g]

Table 4. Thermodynamic parameters

C_0 , mg/L	$-\Delta S$, J/(mol K)	$-\Delta H$, kJ/mol	ΔG , kJ/mol at different temperatures, K					
Temp.	\rightarrow		283	293	303	313	323	333
22.5	195.51	60.13	-4.80	-2.84	-0.89	1.07	3.02	4.98
45	165.06	49.51	-2.79	-1.14	0.51	2.16	3.80	5.46
67.5	145.46	42.21	-1.05	0.41	1.86	3.32	4.77	6.23
90	145.88	41.39	-0.11	1.35	2.81	4.27	5.73	7.19
112.5	98.52	23.68	4.20	5.18	6.17	7.16	8.14	9.12
135	72.14	13.98	6.44	7.16	7.88	8.60	9.32	10.04

REFERENCES

1. B. C. Son, K. M. Park, S. H. Song and Y. J. Yoo, *Korean J. Chem. Eng.*, **21**(6), 1168 (2004).
2. K. Srinivasa Rao, Shashi Anand and P. Venkateswarlu, *Korean J. Chem. Eng.*, **27**(5), 1547 (2010).
3. Web site of Central Pollution Control Board: www.cpcb.nic.in.
4. E. A. Oliveira, S. F. Montanher, A. D. Andrade, J. A. Nobrega and M. C. Rollemberg, *Process Biochem.*, **40**, 3485 (2005).
5. A. Baran, E. Bıcak, S. H. Baysal and S. Onal, *Bioresour. Technol.*, **98**, 661 (2006).
6. H. Barrera, F. Urena-Nunez, B. Bilyeu and C. Barrera-Diaz, *J. Hazard. Mater.*, **B136**, 846 (2006).
7. S. Ilhan, M. Nurbas, S. Nourbakhsh, Kilicarslan and H. Ozdag, *Turkish Electron. J. Biotechnol.*, **2**, 50 (2004).
8. M. F. Sawalha, J. L. Gardea-Torredey, J. G. Parsons, G. Saupe and J. R. Peralta-Videa, *Microchem. J.*, **81**, 122 (2005).
9. G. Ozdemir, N. Ceyhan, T. Ozturk, F. Akirmak and T. Cosar, *Chem. Eng. J.*, **102**, 249 (2004).
10. P. Suksabye, P. Thiravetyan, W. Nakbanpote and S. Chayabutra, *J. Hazard. Mater.*, **141**(3), 637 (2007).
11. F. N. Acar and E. Malkoc, *Bioresour. Technol.*, **94**, 13 (2004).
12. G. Donmez and Z. Aksu, *Process Biochem.*, **38**, 751 (2002).
13. S. Gupta and B. V. Babu, *Adsorption of chromium (VI) by a low-cost adsorbent prepared from tamarind seeds*, Paper presented at CHEMCON-2006, India.
14. M. X. Loukidou, A. I. Zouboulis, T. D. Karapantsios and K. A. Matis, *Colloids and Surfaces, A: Physicochem. Eng. Aspects*, **242**, 93 (2004).
15. P. Rohinikumar, M. Venkateswara Rao, N. Chittibabu, P. V. Ravikumar and P. Venkateswarlu, *Ind. J. Chem. Technol.*, **16**, 308 (2009).
16. V. K. Garg, R. K. Gupta and R. K. Gupta, *Bioresour. Technol.*, **92**, 79 (2004).
17. V. Sarin and K. K. Pant, *Bioresour. Technol.*, **97**, 5 (2006).
18. E. Malkoc, Y. Nuhoglu and M. Dunder, *J. Hazard. Mater.*, **B138**, 142 (2006).
19. S. S. Barala, S. N. Das, P. Rath and G. R. Choudary, *Biochem. Eng. J.*, **34**, 69 (2007).
20. S. Tunali, I. Kiran and T. Akar, *Miner. Eng.*, **18**, 681 (2005).
21. K. G. Bhattacharya and A. Sharma, *J. Hazard. Mater.*, **B113**, 97 (2004).
22. G. Xing, S. Zhang, B. Ju and J. Yang, *Carbohydr. Polym.*, **66**, 246 (2006).
23. N. K. Lazaridis and Ch. Charalambous, *Water Res.*, **39**, 4385 (2005).
24. H. Freundlich, *Z. Phys. Chem.*, **57**, 387 (1906).
25. L. Langmuir, *J. Am. Chem. Soc.*, **40**, 1361 (1918).
26. O. Redlich and D. L. Peterson, *J. Phys. Chem.*, **63**, 1024 (1959).
27. S. Lagergren, *K. Sven. Vetenskapsakad. Handl.*, **24**, 1 (1898).
28. B. Kiran, A. Kaushik and C. P. Kaushik, *J. Hazard. Mater.*, **141**(3), 662 (2006).
29. A. Sharma and G. Bhattacharya, *J. Hazard. Mater.*, **B125**, 102 (2005).
30. M. Erdem, H. S. Altundogan and F. Taumen, *Miner. Eng.*, **17**, 1045 (2004).
31. E. Sabah, M. Turan and M. S. Celik, *Sep. Sci. Technol.*, **37**, 3081 (2005).
32. M. Kara, H. Yuzer, E. Sabah and M. S. Celik, *Water Res.*, **37**, 224 (2003).
33. T. Karthikeyan, S. Rajagopal and L. R. Mireanda, *J. Hazard. Mater.*, **124**(1-3), 192 (2005).
34. S. S. Baral, S. N. Das and P. Rath, *Biochem. Eng. J.*, **34**, 69 (2007).