USE OF LITCHI (*Litchi Chinensis*) SEED POWDER AS AN EFFECTIVE ADSORBENT TOWARDS CHROMIUM (VI) REMOVAL FROM AQUEOUS SOLUTION: EQUILIBRIUM AND THERMODYNAMIC STUDY

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Abstract

The main objective of the study is to investigate the adsorption of chromium (VI) from aqueous solution by Litchi Seed Powder (LSP) by equilibrium and thermodynamic studies. The effect of initial chromium (VI) concentration, pH, bio adsorbent dose and contact time have been studied. Maximum chromium (VI) removal occurred at pH: 2, LSP dose: 1.5 g/50 mL, contact time: 60 minutes and initial concentration of 10 mg/L. Maximum adsorption capacity was found to be 1.053 mg/g. Freundlich isotherm model fitted well than the other models. The adsorption was physical. Chromium (VI) removal by LSP was spontaneous and endothermic. $\triangle S^o$ was found to be 65.1002 KJ/mol.

Key words: **Equilibrium, Thermodynamic, Freundlich, spontaneous**

I. INTRODUCTION

Heavy metals in water have been a major preoccupation for researchers for many years because they are considered as the most toxic environmental pollutants. Chromium is considered as one of the major toxic and hazardous metal for humans as well as other forms of life. Chromium is distributed widely in rocks but only in a few concentrated ores. Virtually all ores of chromium are composed of the mineral chromite ($FeCr_2O_4$). The demand of chromium has been increasing globally due to its extensive use in electroplating, leather tanning, dye, cement and photography industries due to its various physico–chemical properties. The effluents from these industries usually contain considerable amount of toxic chromium, which ultimately spreads into the environment through soils and water streams and finally accumulates along the food chain which causes human health hazards. Chromium has several oxidation states ranging from chromium (II) to chromium (VI), but the trivalent and the hexavalent states are the most stable (Yadav et al., 2005). The waste and effluent stream of chromite mines and processing units contain chromium in two oxidation states, i.e., chromium (VI) and chromium (III) in aqueous solution. Out of these, hexavalent form of chromium is highly toxic in nature (Baral and Engelken, 2002). The relationship between trivalent and a hexavalent form of chromium is given by:

$$Cr_2O_7{}^{2-} + 14H^+ + 6e \leftrightarrow 2Cr^{3+} + 7H_2O \qquad E^0 = 1.33 \text{ V}$$
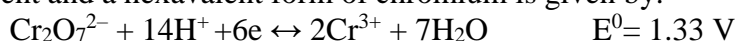
The high positive standard reduction potential value shows strong oxidizing power of the chromium (VI) species. In aqueous solution chromium (VI) mainly exists as five species: H_2CrO_4, $HCrO_4{}^-$, $CrO_4{}^{2-}$, $HCr_2O_7{}^-$ and $Cr_2O_7{}^{2-}$ (Cainelli and Cardillo, 1994). The distribution of these species is highly dependent on solution pH and total chromium (VI) concentration. In the pH range 2–4, most chromium (VI) exist as $HCrO_4{}^-$ and $Cr_2O_7{}^{2-}$. These anionic species are generally poorly adsorbed by the negatively charged soil particles due to their repulsive electrostatic interaction. So chromium (VI) is mobile and present in aqueous solution only. On the contrary, chromium (III), which generally exists in the form of Cr^{3+},

$Cr(OH)^{2+}$ or $Cr(OH)_2{}^+$, are adsorbed on the negatively charged surface of soil particles and thus are less mobile (Shrivastava and Nair, 2001). Chromium is considered as carcinogenic, mutagenic and teratogenic agent. It also causes epigastric pain nausea, vomiting, severe diarrhoea, producing lung tumors (Dupont and Guillon, (2003); Granados–Correa and Serrano–Gomez, (2009); Singh et al., (2009)). The recommended limit of Cr(VI) in waste water according to Bureau of Indian Standards is only 0.05 mg/L (BIS, 1991) . But the industrial and mining effluents contain much higher concentrations compared to the permissible limit. Therefore, the concentrations of Cr (VI) must be reduced to safe limits that satisfy environmental regulations for various bodies of water. Conventional treatment processes such as chemical precipitation, reverse osmosis, ultrafiltration, coagulation–flocculation, electrodialysis, flotation, ion exchange and adsorption have been applied for heavy metal ion removal. However, these processes have their inherent advantages and limitations in application. Among these methods adsorption is economically feasible and technically simple (Ahamad et al., 2009). Previously various adsorbents like neem bark powder (Kumar and Phanikumar, 2013), peanut shell (AL-Othman et al., 2013), rice straw (Wei et al., 2013), bio-chars (Huseyin and Yakup, 2013), almond shell, activated saw dust (Aliabadi et al., 2012), chitosan-coated fly ash (Wen et al., 2011), modified coconut husk (Olayinka et al., 2009) have been used for chromium (VI) removal.

In the present study Litchi (*Litchi Chinensis*) seed powder (LSP) was used as an effective adsorbent to chromium (VI) adsorption. The main objective of the study was whether Litchi seed powder was able to remove chromium (VI) from aqueous solution by equilibrium study. Different isotherm model has been tested in this study.

II. MATERIALS AND METHODS

II.1. *Preparation of the synthetic metal solution*

A 100 mg/L stock solution of chromium (VI) was prepared by dissolving analytical grade $K_2Cr_2O_7$ (purchased from E. Merck Ltd., India) in double distilled water. From the mother solution different solution having different concentrations range has been prepared by proper dilution of mother stock solution with double distilled water. Before mixing the adsorbent, the pH of each chromium solution was adjusted to the required value by 0.1 M NaOH or 0.1 M HCl solution.

II.2. *Preparation of biosorbent*

Litchi (*Litchi Chinensis*) was collected from the local fruit market of Purbasthali, Purba Bardhaman, west Bengal, India. From Litchi fruit seed was collected. It was initially washed with deionized water and then sun dried for 7 days followed by drying in hot air oven at 313 K for 5 hrs. It was then cooled at room temperature in desiccator. The dried material was then crushed with mixer machine and sieved to give a fraction of 150 mesh size with standard testing sieve. At last, powder form of seed was thoroughly washed with cold water followed by hot water to remove any water-soluble substances. Finally, it was dried in an oven at 318 K temperature and again cooled in desiccator and directly used as biosorbent for adsorption experiment.

II.3. *Batch experiments*

The effect of initial chromium (VI) concentrations (10-40 mg/lit), LSP dosage (0.5-1.5 g/50 ml), pH (2.0-8.0), contact time (10-60 min) and stirring rate (300 rpm) on the removal of chromium (VI) from aqueous solution was investigated using 50 mL of Cr(VI) solution in 250 mL Erlenmeyer flask at 303 K. At the end of each experiment, samples were collected from the flasks and filtered for analyzing the residual Cr (VI) concentration in the solutions. By using the following mass balance equation the amount of Cr(VI) ions adsorbed in milligram per gram was determined

$$q_e = \frac{(C_i - C_e)V}{m}$$ ………. (1)

Where q_e is the metal uptake (mg/g), C_i and C_e are the initial and equilibrium concentrations of chromium (VI) (mg/L). V is the volume of working solution in liter and m is the mass of bio adsorbent (g). The percentage of removal of chromium (VI) ions was calculated from the following equation:

$$Removal\,(\%) = \frac{(C_i - C_e)}{C_i} \times 100$$ …………… (2)

All the experiments were performed in triplicate and the average values were reported in this paper.

II.4. *Estimation of chromium (VI)*

An aliquot amount of chromate sample was taken in a 50 mL volumetric flask. To it, 1 mL of 6 (N) concentrated H_2SO_4 solution and 2.0 mL of 1,5–Diphenyl Carbazide solution were added successively and the solution was then diluted upto the mark volume and mixed well. Then absorbance of the developed red–violet color solution was measured against blank at 540 nm using UV–Visible Spectrometer (Systronics, Vis double beam Spectrophotometer 1203) (Sekhar et al., 2012).

Thus, obtained absorbance value was referred to a standard graph (drawn between absorbance and concentration) prepared with known amounts of chromium by adopting the method of least squares to find the concentration of chromium in unknown solutions.

III. RESULTS AND DISCUSSIONS

III.1. Adsorption isotherms

Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherm models were tested to explain the equilibrium data. The results are shown in Table 1.

III.1.1. The Langmuir isotherm model

Linear form of Langmuir isotherm equation can be written as:

$$\frac{1}{q_{eq}} = \frac{1}{q_{max} \, k_L \, C_e} + \frac{1}{q_{max}} \qquad \ldots\ldots\ldots\ldots (3)$$

Where C_e (mg/L) is the equilibrium concentration of Cr(VI) in solution, q_{eq} (mg/g) is the amount of chromium (VI) ions adsorbed per specific amount of adsorbent, q_{max} (mg/g) is the maximum adsorption capacity, and k_L (L/mg) is an equilibrium constant related to energy of adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate. q_{max} and k_L can be obtained from the linear plot of $1/q_{eq}$ vs $1/C_e$ (Fig.1). In Langmuir model a dimensionless constant called separation factor (R_L) is used which predict whether the adsorption is favourable or not. Separation factor (R_L) that can be defined by the following relationship (Das, 2019).

$$R_L = \frac{1}{1 + K_L \, C_i} \qquad \ldots\ldots\ldots\ldots\ldots (4)$$

Where C_i (mg/L) is the initial concentration and k_L (L/mg) is the equilibrium constant. The parameter R_L provides valuable information about the nature of adsorption. Langmuir isotherm is irreversible for $R_L = 0$, favourable when $0 < R_L < 1$ and linear if $R_L = 1$ or unfavourable when $R_L > 1$. It was reported that when $k_L > 0$, sorption system is favourable (Das, 2019). The evaluated constants are given in Table 1.
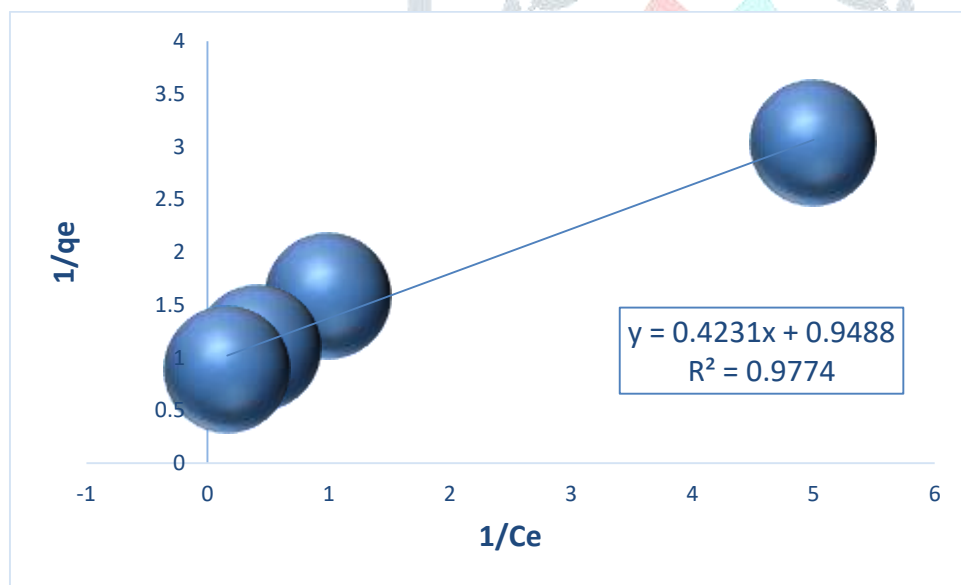

Fig. 1. Langmuir adsorption isotherm plot for chromium (VI) adsorption onto LSP.

III.1.2. The Freundlich isotherm model

The linearized form of the Freundlich isotherm can be represented as:

$$\log q_{eq} = \log K_F + \frac{1}{n} \log C_e \qquad \ldots\ldots\ldots\ldots (5)$$

Where, K_F is a constant related to adsorption capacity (mg/g) $(L/g)^{1/n}$ and adsorption intensity of the adsorbent is represented by n. Plot of log q_{eq} versus log C_e (Fig.2) provides the constants K_F and n. The evaluated constants are given in Table 1.
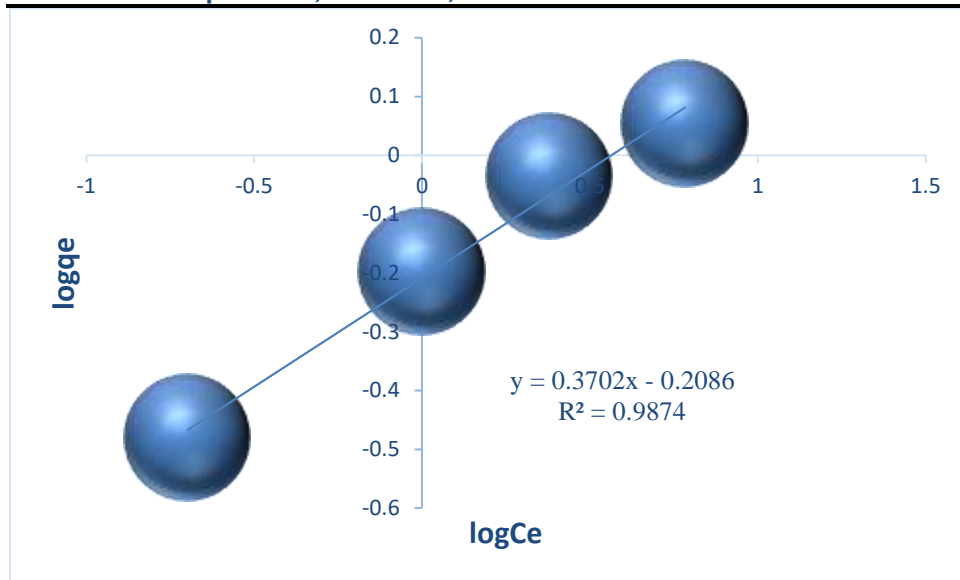
Fig. 2. Freundlich adsorption isotherm plot for chromium (VI) adsorption onto LSP.

III.1.3. The Temkin isotherm model

Temkin isotherm equation is expressed as:
$$q_e = BlnA + BlnC_e \qquad \text{...................... (6)}$$
Where C_e (mg/L) is the adsorbate concentration at equilibrium, q_e (mg/g) is the amount of chromium (VI) ions adsorbed at equilibrium, $RT/b_T = B$ where T is the temperature (K), and R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and A and b_T are constants. Temkin constants A and B are obtained from the plot of q_e versus lnC_e (Fig.3). The constant B is related to the heat of adsorption and A is the equilibrium binding constant (L/min) corresponding to the maximum binding energy. The values of A and B are given in Table 1.
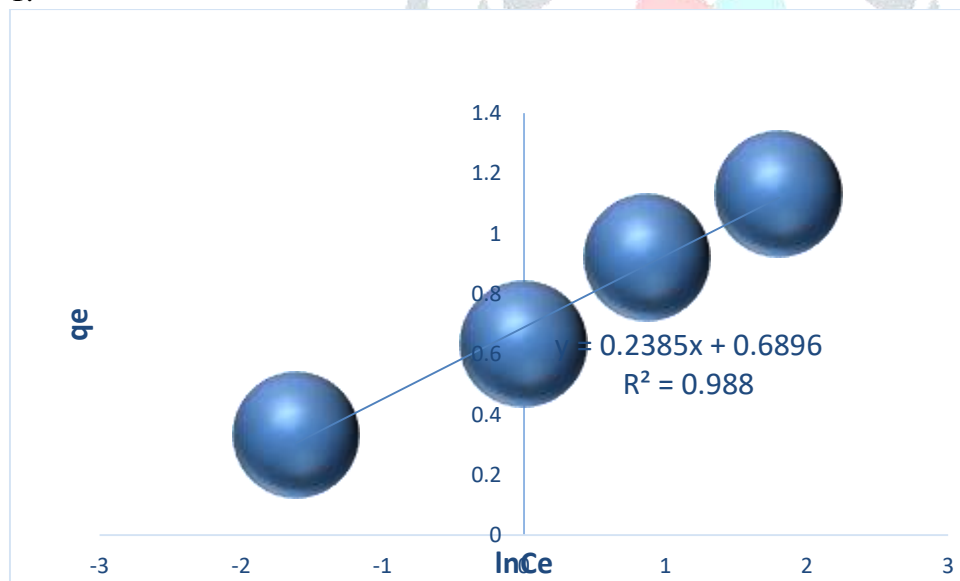

Fig. 3. Temkin isotherm plot for chromium (VI) adsorption onto LSP.

III.1.4. The Dubinin-Radushkevich isotherm model

The linear form of D-R isotherm equation is represented as:
$$lnq_e = lnq_m - \beta\epsilon^2 \qquad \text{.................. (7)}$$
$$\text{Where} \quad \epsilon = RT \ln(1 + \frac{1}{C_e}) \qquad \text{..................... (8)}$$
Where q_m (mol/g), β (mol^2/J^2) and ϵ represents the theoretical saturation capacity, mean free energy of adsorption per mole of the adsorbate and polanyi potential. C_e (mg/L) is the equilibrium concentration of adsorbate in solution, R (J mol^{-1} K^{-1}) is the gas constant and T(K) is the absolute temperature. D-R constants q_m and β were evaluated from the linear plots of lnq_e versus ϵ^2 (Fig. 4) and are shown in Table 1. The constant β gives an information about the mean free energy E (kJ/mol) of adsorption per molecule of the adsorbate when it is transferred from infinity in the solution to the solid surface and can be calculated from the relationship (Das, 2019)

$$E = \frac{1}{\sqrt{2\beta}} \qquad \ldots\ldots\ldots\ldots\ldots\ldots. \ (9)$$

The adsorption process is supposed to proceed via chemisorption if the magnitude of E is between 8 and 16 kJ mol^{-1}, while for values of E ⟨ 8 kJ mol^{-1}, the sorption process is of physical nature.
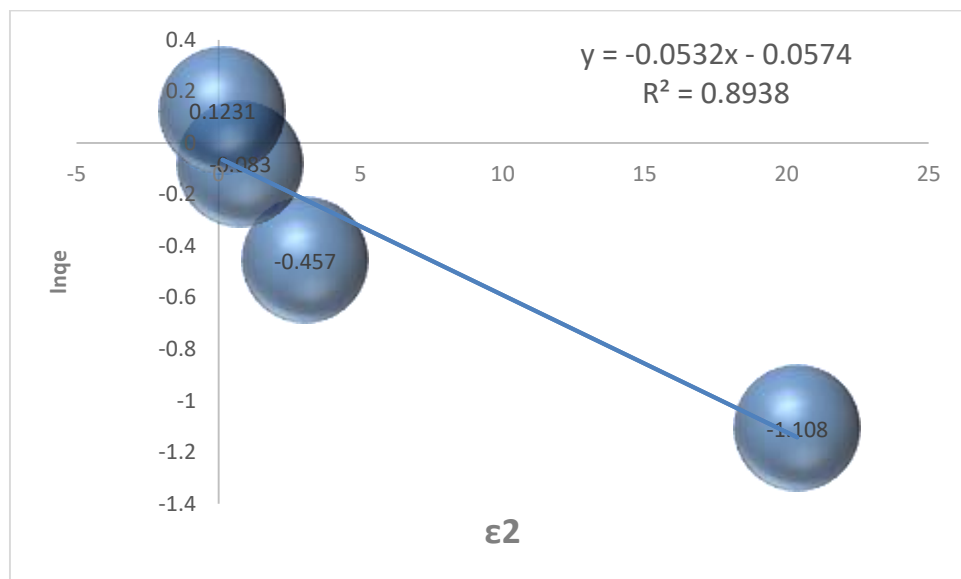

Fig.4. D-R isotherm plot for chromium (VI) adsorption onto LSP.

III.1.5. Error analysis

Sum of the square of the errors (SSE), sum of the absolute errors (SAE) and chi-square (χ^2)] were tested in this study to find out which isotherm is best fitted to the experimental equilibrium data. The error equation is given in below.

Error equation name	Error equation
Sum of square error (SSE)	$\text{SSE} = \sum_{i=1}^{n}(q_{e,estm} - q_{e,\exp})^2_i \qquad \ldots\ldots (10)$
Sum of absolute error (SAE)	$\text{SAE} = \sum_{i=1}^{n}\left|q_{e,estm} - q_{e,\exp}\right|_i \qquad \ldots\ldots.. (11)$
Chi-square (χ^2)	$\chi^2 = \sum_{i=1}^{n}\left[\frac{(q_{e,\exp} - q_{e,estm})^2}{q_{e,estm}}\right]_i \qquad \ldots\ldots\ldots.. (12)$

Where, q$_{e,estm}$ (mg/g) and q$_{e,exp}$ (mg/g) are the calculated and the experimental value of the adsorbate in the solid phase and n is the number of the data point.

Table 1: Adsorption isotherm constants for adsorption of chromium (VI) onto LSP

Adsorption isotherms	Parameters		R^2	χ^2	SSE	SAE
Langmuir isotherm	q$_{max}$(mg/g)	1.053	0.9774	0.74	0.686	2.65
	K$_L$ (L/mg)	2.24				
Freundlich isotherm	K$_F$ (mg/g)(L mg^{-1})$^{1/n}$	0.618	0.9874	0.078	0.436	2.043
	n	2.688				
Temkin isotherm	B (mg/g)	0.2385	0.988	0.1205	0.867	2.432
	A	17.993				
D-R isotherm	q$_m$ (mg/g)	0.9442	0.8938	0.178	1.865	2.56
	β (mol^{2}kJ^{-2})	0.0532				
	E(kJ mol^{-1})	3.06				

Both Temkin and Freundlich adsorption isotherm model fitted well to the experimental equilibrium adsorption data than the Langmuir and Dubinin-Radishkevich isotherm equation for Cr (VI) adsorption in terms of high value of regression coefficient (R^2). But with respect to the magnitude of different error functions (SSE, SAE and chi-square) Freundlich model better fitted than the Temkin model. The Langmuir maximum adsorption capacity q_{max} (mg/g) and the equilibrium constant K_L (L/ mg) were found to be   is 1.053 and 2.24 respectively. The separation factor (R_L) was 0.04, 0.021, 0.014 and 0.011 for 10, 20, 30 and 40 mg/L chromium (VI) concentration solutions. All the R_L values were found to be less than one but greater than zero indicating the favorable adsorption of Cr (VI) onto LSP. It was established that adsorption is favourable if the value of n lies in between 1 and 10 then (Slejko, 1985). In our study the value of 'n' at equilibrium is 2.688, indicates favourable adsorption. Adsorption energy (E) from D-R isotherm was found to be 3.06 kJ/mol. The estimated value of E for the present investigation was found in the range expected for physical adsorption. Thus the adsorption of Cr(VI) onto LSP was physical in nature.

IV. *Thermodynamic parameters*

Thermodynamic parameters such as free energy, enthalpy and entropy changes can be estimated from the following equations to ascertain whether adsorption process was spontaneous or not. (Sujana *et al.,* 2009):

$$K_C = \frac{C_{Ae}}{C_e} \qquad\qquad \dots\dots\dots\dots\dots\dots (13)$$

$$\Delta G^0 = -RT\ln K_C \qquad\qquad \dots\dots\dots\dots\dots\dots.. (14)$$

$$\log K_C = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303RT} \qquad \dots\dots\dots\dots\dots\dots\dots (15)$$

where C_e, C_{Ae} and K_c are the equilibrium concentration of solute in solution in mg/L, equilibrium concentration of solute on the adsorbent surface in mg/L, the equilibrium constant respectively. The Gibbs free energy (ΔG^o) for the adsorption of chromium (VI) onto LSP at all temperatures was obtained from Eq. 20 and are presented in Table 2. The values of ΔH^o and ΔS^o were calculated from the slope and intercept of the plot $\log K_c$ against 1/T (Fig. 5) and are also listed in Table 2.
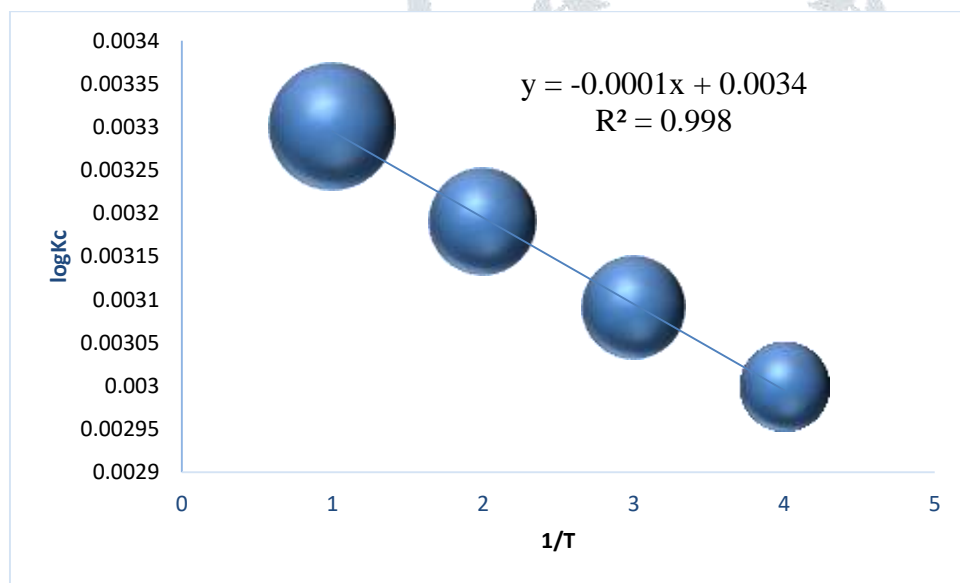

Fig. 5. Plot of 1/T vs logKc for chromium (VI) adsorption onto LSP.

Table 2. Thermodynamic parameters for adsorption of chromium (VI) onto LSP

Temperature (K)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o(kJ/mol)
		1.915	65.1002
303	–9.804		
313	–7.2538		
323	–6.987		
333	-5.3122		

Adsorption of chromium (VI) by LSP is very much spontaneous as indicated by the negative value of Gibbs free energy change (ΔG^o) at all the studied temperature (Table 2). Again positive $\triangle H^o$ value confirms that the adsorption is endothermic in nature. The positive value of $\triangle S^o$ reflects the affinity of the adsorbents for the chromium (VI) ions.

V. *Conclusions*

My present study mainly focused on the removal of chromium (VI) from aqueous solution by LSP under batch mode. Freundlich adsorption model nicely explained the adsorption process. Adsorption was highly favourable as evident from the negative value of Gibbs free energy change.   With the increase of temperature % removal of chromium (VI) gradually decreased. The adsorption was physical and endothermic. High positive value of $\triangle S^o$ suggested that chromium (VI) has high affinity towards LSP.

VI. *Acknowledgement*

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