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# Kinetics, Thermodynamics and Isotherm studies on the Removal of Chromium by Typha latifolia bioremediator Stem Carbon

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# Abstract

The removal of hexavalent chromium is a well-known poisonous metal and considered a priority pollutant from industrial wastewater include leather industry, electroplating, anodizing baths etc. To remove toxic chromium from waste water a low-cost abundant adsorbents was investigated. Typha latifolia, a variety of broad leaf cattail type bioremediator, stem and leaves are used to prepare the activated carbon which was used as a novel adsorbent. The influence of pH, adsorbent dose and contact time, metal concentration, adsorbent nature and concentration on the selectivity and sensitivity of the removal process was investigated. The kinetics of adsorption process was studied by Lagergren's pseudo-first order and pseudosecond order kinetics and the adsorption process depends on both time and concentration. The feasibility of the sorption was studied using Freundlich and Langmuir isotherms including linear regression methods. The mechanism of the adsorption process was evaluated with intra particle diffusion model. Various thermodynamic parameters such as the standard Gibbs free energy ( $\Delta G^{\circ}$ ), standard entropy ( $\Delta S^{\circ}$ ), and standard enthalpy ( $\Delta H^{\circ}$ ) were calculated. The Typha latifolia activated carbon (TLAC) adsorbent material was characterized by using Fourier Transform Infrared Spectroscopy (FTIR). In this study, Langmuir isotherm was the most favorable method for the adsorption of chromium. The kinetic result shows that the adsorption process follows pseudo-second order kinetics, which implies that the adsorption process depends on both time and concentration. This readily available low-cost adsorbent is efficient in the uptake of Cr (VI) ion in aqueous solution, thus, it could be an excellent alternative for the removal of heavy metals and organic matter from water and wastewater.

Key Words: Typha latifolia, chromium, adsorption, kinetics, thermodynamics

# **1. Introduction**

The ground water contamination due to the chromium compounds used in electroplating and tannery industries [1] requires the development of sustainable remediation technologies, With the Environmental Protection Agency (EPA) setting a limit of 0.1 mg L<sup>-1</sup> total chromium [2,3] in water, newer adsorbents having high performance efficiency are required for the removal of hexavalent chromium [4]. Amongst the low cost carbon based adsorbents, sawdust [5], agricultural bio-waste [6] and activated carbon [7] have good adsorption capacity for chromium. Chromium effluent is generated by the following industrial uses like mining of chrome ore, production of steel and alloys, metal finishing industries, pigments manufacturing units, photographic industry, glass industry, wood preservation, chromium salts being used as corrosion inhibitor in the cooling water treatment in the industry, textile industry and many other industrial applications [8].

Heavy metals like chromium ions enter especially into fresh water or soil and thereby into plants, animals and humans. Considering process in biosphere, the geochemical cycle is connected via metabolic processes by microorganisms in the ocean floor, in sediments or sludge, or in water. Microorganism plants and small animals serve as food source for fish. By means of plants and other animals, levels of heavy metals from water and soil find their way into our food, however when accumulated to high levels, more than the threshold limits of the organisms, it can generate serious problems and diseases. Chromium is highly reactive element. It exists in six oxidation states and the two most stable states are Cr (III) and Cr (VI). Chromium forms stable complexes as  $Cr_2O_7^{2-}$ ,  $HCrO_4^{-}$ ,  $CrO_4^{-2-}$ ,  $HCr_2O_7^{-1}$  and fraction of these complexes. Chromium is non-biodegradable and toxic beyond a given concentration. Chromium threshold concentration on inhibitory effect on heterotrophic organisms is 10 mg L<sup>-1</sup> for Cr (III) and 1 mg L<sup>-1</sup> for Cr (VI). All living organisms require varying amount of Cr (III) in micro amounts for proper growth. The same metal becomes toxic when present in elevated concentration. As per studies carried out Cr (VI) is 500 times more toxic to Cr (III) [9]. Cr (VI) is considered by International Agency for Research on Cancer (IARC) 1982 as a powerful carcinogenic agent that modifies the DNA transcription process causing important chromosomic aberration [10, 11]. The current BIS (Bureau of Indian Standards) recommended guideline value for chromium (as total Cr) in drinking water as 0.05 mg/L (maximum).

Chromium ions are removed from the effluent using precipitation technique. This technique is widely practiced by the industry. The common problem associated with this process is generation of large volume toxic sludge. Safe disposal of this toxic sludge is another problem. Further this method depends on the addition of chemicals to the effluent. Ion exchange [12], adsorption [13,14], electro dialysis, membrane process, solvent extraction, freeze separation, bio-separation are some of the other methods for removal. Amongst these methods adsorption process can be a substantial method for the removal of chromium from waste water shown by various researches. For these purpose, a variety of natural and synthetic materials have been tested as chromium adsorbents [15]. The various adsorbents tested include activated carbon and char [16-24], the modified clay [25], rice husk ash, activated alumina, coal fly ash [26] and modified corn stalk [27], etc. Therefore, there is a need for the development of low cost, easily available materials that could allow removing Cr(VI) economically.

The present study aimed at development of suitable method using low cost bio adsorbent for selective removal of chromium by adsorption from industrial effluent. We report the synthesis of activated carbon prepared from Typha latifolia, a variety of broad leaf cattail type bioremediator, stem and leaves (TLAC) by chemical activation with acid and the removal of Cr(VI) from aqueous solution by adsorption onto TLAC. The influence of several important operating parameters, such as TLAC dosage, initial pH and temperature, were studied by batch experiments. Furthermore, the adsorption kinetics, isotherms and thermodynamics of Cr(VI) on TLAC were also investigated. The surface functional group characterization of the adsorbent material was done using Fourier Transform Infrared Spectroscopy (FTIR).

### 2. Materials and methods

### 2.1. Preparation of activated carbon

Typha latifolia activated Carbon (TLAC) was prepared from Typha latifolia stem and leaves. It was collected in Dr.Ambedkar Government Arts College, Chennai, premises and the stem was dried without sunlight for 10 days and carbonized with 1:1 sulfuric acid. Carbon was washed with distilled water to attain neutral pH and dried in hot air oven at 423 K for 24 h then kept in a muffle furnace at 773 K for complete carbonization. Carbon was powdered in a ball mill to get the desired size of an activated carbon [28-32].

### 2.2. Preparation of metal solution

Stock solution of 1000 (mg  $L^{-1}$ ) of potassium chromate (Merck, India limited, analytical grade (assay 99.8%)) solution was prepared in 1 L using distilled water. Fresh dilutions of desired metal solution concentrations were made at each experiment.

### 2.3. Sorption studies

Batch adsorption studies of Cr onto TLAC were determined by various parameters such as pH, metal concentration, adsorbent dose, contact time and temperature. The optimum concentration of metal solution was evaluated using 10 to 80 mg L<sup>-1</sup> with 10 mg L<sup>-1</sup> variation using 40 mL of metal solution. For the determination of the effect of pH of the sorption process, the pH values were adjusted from 2 to 10 using 0.1 M NaOH and 0.1 M HCl with a Elico pH meter. The adsorbent dosage was varied from 0.1 g to 1 g with 0.1 g variation. The effect of temperature of sorption process was estimated by using various temperatures as 303 K, 313 K, 323 K, 333 K and 343 K. The contact time of the process was predicted by varying the contact time as 10–80 min with 10 min variation. The metal solution concentration of supernatant liquids was

determined by using UV–Vis Spectrophotometer ( $\lambda$  max: 360 nm) model Elico Double Beam SL191. UV-Spectrophotometer.

#### 2.4. Isotherm and kinetic studies

The isotherm equations used in this study are Freundlich and Langmuir isotherm equations of linear regression methods. In Langmuir isotherm various forms of linearized equations were examined. The amount of sorption at equilibrium  $q_e$  (mg g<sup>-1</sup>), calculated by the following equation,

 $q_e = (C_o-C_e) \ge V/W$  ------- [1] where,  $C_o$  and  $C_e$  (mg L<sup>-1</sup>) are the liquid phase concentration of chromium at initial and equilibrium respectively. Kinetic study helps to predict the mechanisms involved during the sorption process. In order to obtain kinetic data of the adsorption process Lagegren's pseudo-first order and pseudo-second order kinetic equations were used.

#### 2.5. Characterization of the adsorbent

The Typha latifolia stem carbon was characterized by using FTIR Spectroscopy. The FTIR provides the information about the type of functional groups present on the surface of the adsorbent material. FTIR shows that changes occur on the surface of the adsorbent before and after adsorption of the adsorbate molecule.

#### 2.6. Desorption studies

The desorption study of the adsorbed chromium(VI) was carried out with 40 ml of 120 mg L<sup>-1</sup> of chromium solution taken in a series, 100 mg of adsorbent material used for adsorption was then separated from the solution by centrifugation. The adsorbent was filtered using a Whatman filter paper and washed gently with water to remove the unadsorbed chromium (VI). A series of 25 ml of distilled water were taken and their pH values were adjusted in the range 2–12 by addition of 0.5 M HCl or 0.5 M NaOH solution using a pH meter. The spent adsorbent was mixed with pH adjusted distilled water using the estimated time intervals of longer than the equilibrium time. The desorbed chromium (VI) was estimated as before.

### 3. Results and discussion

#### 3.1.1. FTIR studies

FTIR studies are used for prediction of different types of functional groups present in the adsorbent material. The FTIR spectrum of carbon and Cr loaded carbon is presented in Fig.1a and 1 b.



The carbon spectrum shows the peaks in the positions of 3732 cm<sup>-1</sup>, 3452 cm<sup>-1</sup>, 2534 cm<sup>-1</sup>, 2018 cm<sup>-1</sup>, 1707cm<sup>-1</sup>, 1618cm<sup>-1</sup>, 1359 cm<sup>-1</sup> and 1146 cm<sup>-1</sup>. The peak position of 3452 cm<sup>-1</sup> indicates that the presence of stretching vibration of the OH group involves in the intermolecular or intra-molecular hydrogen bonding or moisture present either in carbon or KBr. The peak positions at 2018 cm<sup>-1</sup>, 1618cm<sup>-1</sup>, 1193 cm<sup>-1</sup> and 1035 cm<sup>-1</sup> shows that the presence of alkyl group or due to the presence of tannin, C-C bond in aromatic conjugation, C–N peptide bond and S, O interaction respectively. The Cr loaded spectrum of FTIR shows that there is no change in their position of the peaks but there is a reduction in peak heights and intensity of the peaks. This confirms that Cr was strongly adsorbed onto the Typha latifolia Carbon (TLAC).

### **3.2. Sorption studies**

Initial metal concentration is an important factor that affects the adsorption process. The increase of initial concentration of chromium results in the increased uptake capacity, further enhancement leads to a decreased percent removal since number of moles of chromium available on surface area of the adsorbent is high at higher concentrations [33]. Adsorption of chromium was studied at different metal concentrations from 10 mg L<sup>-1</sup> to 80 mg L<sup>-1</sup> with 10 mg L<sup>-1</sup> variation. Among all concentrations 60mg L<sup>-1</sup> shows the maximum adsorption rate for the removal of Cr at 30 min contact time.

Percentage Removal =  $(C_i - C_f) \times 100/C_i$  ------[2] Where,  $C_i$  and  $C_f$  are initial and final concentration of metal, before and after sorption process.

# 3.2.1 Effect of pH

Solution pH is an important factor that affects the rate of adsorption process. Chromium exists mostly in two oxidation states which are Cr (VI) and Cr (III) and the stability of these forms is dependent on the pH of the system [34, 35]. It was postulated that at low pH Cr (VI) could be reduced to Cr (III) in the presence of activated carbon under acidic conditions. Cr (VI) in H<sub>2</sub>O system, at low pH, acid chromate ions (HCrO<sub>4</sub><sup>-</sup>) are the dominant species [36] than chromate ions. In this study at low pH values such as 2 to 5 there was a slow enhancement of the adsorption capacity of Cr. When the pH is further increased, a sharp decrease in uptake capacity of adsorption was observed. This might be due to the weakening of electrostatic force of attraction between the oppositely charged adsorbate and adsorbent and ultimately lead to the reduction in sorption capacity. Fig. 2, the pH value 5 shows a higher adsorption rate of chromium. Hence, the optimum pH for the adsorption of chromium onto TLAC has been chosen as pH value of 5.0. It is clear that pH determines the extent of Cr (VI) removal and provides a favorable adsorption onto TLAC.

# **3.2.2. Effect of dosage**

The effect of adsorption capacity of chromium was found with the variation of dosage of adsorbent material. The dose of adsorbent varied from 0.05 g to 1.0 g  $L^{-1}$ . From Fig. 3, the effect of adsorbent dose on percent adsorption of chromium was found with a dose of 0.1 g adsorbent showing higher Cr removal when compared with other dosages. As the adsorbent dose increased, the percent removal of chromium slightly increased due to the availability of more surface area of the adsorbent. Increase in adsorbent dose also increased the reduction of Cr (VI) to Cr (III) [37].



# **3.2.3 Effect of Temperature**

Temperature plays a vital role in any kind of adsorption processes. The adsorption test was carried out with five different temperatures 303 K, 313 K, 323 K, 333 K and 343 K to study the effect of temperature on adsorption. These experiments were carried out in the pH 4.5-5 with 120 mg L<sup>-1</sup> of metal solution on TLAC. At low concentration (10 ppm) the effect of temperature showed a remarkable change, with increase in temperature given in Fig 4. Percentage removal decreases whenever temperature increases the adsorption process slightly decreases. The decrease in percentage removal could be due to the reduction of the physical forces of attraction between chromium metal and TLAC. The experimental results showed that the removal of chromium is reduced with increase in temperature onto the adsorbent TLAC which is a kinetically controlled exothermic process [38]. The adsorption process does not favor the change of temperature and it shows only a slight increases and attain constant.



#### **3.3. Isotherm studies**

The adsorption data were analyzed with two adsorption isotherm models, namely Freundlich and Langmuir. Various forms of Langmuir and Freundlich were tested in their linear and non-linear forms [39] (Langmuir, 1916). The Langmuir adsorption model was based on the assumption that the adsorption process was monolayer of the solute molecules on the adsorbent surface. The Langmuir isotherm is expressed as :

$$q_{e} = q_{m} K_{a} C_{e} / 1 + K_{a} C_{e} -----[3]$$

The term  $q_e (mg g^{-1})$  and Ce  $(mg L^{-1})$  are the amount of chromium adsorbed per unit mass of sorbent and unabsorbed chromium concentration in solution. Where  $q_m$  is the maximum amount of chromium adsorbed per unit mass of sorbent at complete monolayer on surface bound, and  $K_a (L mg^{-1})$  is a constant related to the affinity of the binding sites. The formula of Langmuir and Freundlich isotherms of linear and non-linear are presented in Table 1.

The Freundlich isotherm equation is expressed as

$$q_e = K C_e^{1/n}$$
 ------ [4]  
Where K (mg g<sup>-1</sup>) (L g<sup>-1</sup>) is an indicator of the adsorption capacity, 1/n is the adsorption intensity.

The magnitude of the exponent 1/n, shows the favorability of adsorption, 1/n value when n < 1 represents favorable adsorption condition [40]. The best suited isotherm model of Freundlich and Langmuir isotherms is used to calculate  $q_m$ ,  $K_a$  and coefficient of determination  $r^2$  are presented in Table 2. The  $q_m$  and  $K_a$  values predicted using the parameters of  $1/q_e$  vs.  $1/C_e$ ,  $q_e$  vs.  $q_e/C_e$  and  $q_e/C_e$  vs.  $q_e$  by plotting graphs .various forms of Langmuir constants are varied with different forms of linear equations and that depends on the way isotherm equations has linearized [41].



Isotherms	Non-Linear	Linear	Plot	Reference
Freundlich	$q_e = K \ C_e^{1/n}$	$\log q_e = \log K + \frac{1}{n} \log C_e$	$\log q_e Vs. \log C_e$	Freundlich (1906)
Langmuir	$q_e = \frac{q_m K_a \ C_e}{1 + K_a \ C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$\frac{C_e}{q_e}$ vs. $C_e$	Langmuir (1916)



Table 2: Isomerni Parameters obtained from Linear Method							
Inothoma	Donomotoro	Temperature (K)					
Isotherin	Parameters	303	313	323	333		
	1/n	0.8358	1.9983	1.0756	1.5009		
Freundlich	$K (mg g^{-1}) (Lg^{-1})$	4.930	1.580	1.7955	1.557		
	r <sup>2</sup>	0.9598	0.993	0.9888	0.9919		
Langmuir	$q_m(mg g^{-1})$	5.146	5.803	8.0775	12.987		
	$K_a(L mg^{-1})$	3.736	3.380	3.278	4.166		
	$r^2$	0.9955	0.9967	0.9991	0.9902		

Table 2:	Isotherm	Parameters	obtained	from	Linear Me	thod
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Langmuir isotherm shows a better correlation coefficient  $(r^2)$  value compared to Freundlich isotherm. The higher q<sub>m</sub> value of Langmuir confirms that the maximum quantity of adsorption at 303 K. The equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set of experimental data, by plotting log (q<sub>e</sub>) vs. log (C<sub>e</sub>). It was observed that at all solution temperatures, the  $r^2$  values were found to be relatively suggest that the Langmuir isotherm is the most appropriate isotherm than Freundlich isotherm for the present system. Fig. 6 and Fig.7 shows experimental data and the predicted equilibrium curve using linear method given in Table 2, for the two-equilibrium isotherms Freundlich and Langmuir at 303 K, 313 K, 323 K, 333 K and 343 K, respectively. It was observed that at different temperatures, 303 K was found to be more suitable condition. But in the case of other temperatures there was a deviation.

Table 3: Pseudo - first order and second order rate equations and their formulae

Туре	Non-Linear	Linear	Plot
Pseudo – first order	$q = q_e \left(1 - e^{-K_1 t}\right)$	$\log(q_e - q) = \log q_e - \frac{K_1 t}{2.303}$	$\log(q_e - q)vs.t$
Pseudo – second order	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t}$	$t/q = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	<sup>t</sup> / <sub>q</sub> vs.t

Table 4:	Pseudo – first	order and second	nd order rate	constant for the	sorption of	f Chromium	onto TLAC
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	Pseudo – First order kinetics		Pseudo – s				
C <sub>o</sub>	<b>K</b> <sub>1</sub>	$q_e$	$r^2$	q <sub>e</sub> (Experimental)	$K_2$	q <sub>e</sub> (Calculated)	$r^2$
30	0.00368	8.600	0.8247	1.23	0.1964	0.76	0.9969
50	0.00230	6.571	0.9687	3.51	0.088	2.36	0.9841
70	0.00138	9.996	0.4091	2.23	0.0896	1.45	0.9963

# 3.4. Kinetic studies

The equilibrium kinetic profiles were characterized to determine the rate limiting steps involved in the process of sorption of Cr onto TLAC. Lagergren's Pseudo first order (Eq. 5) and Pseudo second order (Eq. 6) kinetic models were applied [42, 43]. The linearized form of the pseudo-first order equation is

Log  $(q_e -q) = \log (q_e) - K_1 t / 2.303$  ------(5) Where,  $K_1$  is the pseudo first order adsorption rate constant,  $q_e$  is the amount of chromium adsorbed onto TLAC at equilibrium (mg g<sup>-1</sup>),  $q_t$  amount of chromium adsorbed onto TLAC at any time t (mg g<sup>-1</sup>). The linearized form of the pseudo-second order form is

$$T/q = 1 / K_2 q_e^2 + (1/q_e) t$$

----- (6)

Where,  $K_2$  is the pseudo second order adsorption rate constant,  $q_e$  is the amount of dye adsorbed onto TLAC at equilibrium (mg g<sup>-1</sup>);  $q_e^2$  is the pseudo second order adsorption rate Constant (g mg <sup>-1</sup> min <sup>-1</sup>). Various forms of pseudo-first order and pseudo-second order kinetic equations are presented in the Table 3. From the experiments (Fig. 8 and Fig.9), the calculated value of pseudo-first order rate constant ( $K_1$ ), pseudo-second order table value of pseudo-first order rate constant ( $K_1$ ), pseudo-second order kinetic equations are presented in the obtained  $q_e$  values are very high when compared with pseudo-second order kinetic values. On the other hand the obtained values of pseudo-second order kinetics have shown the correlation coefficient value 0.9924 while pseudo-first order shows 0.7341. Hence, the results intimate that sorption process follows second order rate equation throughout the process and the rate determining step governed by the chemical force of attraction. Moreover, the rate of the reaction process does not depend on the concentration factor (Pseudo-first order) but depends on both concentration as well as time (Pseudo-second order).

Tuble ever Thermoughamme parameters for the sorption of emonitant onto Thire								
T (K)	$\Delta G^{o} (KJmol^{-1})$	$\Delta H^{o} (KJmol^{-1})$	$\Delta S^{o} (KJmol^{-1}K^{-1})$					
303	-2.83							
313	-1.77	0.18						
323	-2.00	0.18	66.53					
333	-1.08							
343	-1.58							

Table 5: Thermodynamic parameters for the sorption of Chromium onto TLAC



### 3.5. Thermodynamic studies

The effect of heat of adsorption of the adsorbate onto the adsorbent material was determined using the thermodynamic parameters like free energy change ( $\Delta G^0$ ), enthalpy change ( $\Delta H^0$ ), and entropy change ( $\Delta S^0$ ), were calculated from the Van Hoff's equation using the following equations [44,45]

$K_d = q_e / C_e$	(7)
$\Delta G = -RT \ln K_d$	(8)
$\ln K_{d} = \Delta S^{o} / R - \Delta H^{o} / RT$	(9)

Where, K<sub>d</sub> is the distribution coefficient, T is the temperature and R is a gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). From Figure 10, the thermodynamic parameters  $\Delta S^0$  and  $\Delta H^0$  are calculated using the linear regression analysis of Van't Hoff plot using the parameters ln K<sub>d</sub> vs. 1/T. The negative value of the enthalpy change of  $\Delta H^0$  value shows that the exothermic nature of the reaction involved during the adsorption process. The entropy ( $\Delta S^0$ ) shows negative value, this indicates that there was a decreased randomness between the solid-solution interfaces during the adsorption process (Table 5). The Gibbs free energy change ( $\Delta G^0$ ) shows a negative value which reveals that the adsorption process is spontaneous in nature for the adsorption of chromium onto TLAC.

The kinetic models do not provide enough information of an exact diffusion mechanism that is involved during the process and the rate controlling steps, which affect the nature of the adsorption process. The new method to provide the diffusion mechanism is intra particle diffusion model developed by the theory of Weber and Morris [46]. This method shows all the adsorption process with the chromium uptake capacity varying almost proportional with t <sup>1/2</sup> rather than with the contact time t. The intra particle diffusion equation is given by

$$q_{t} = K_{d} t^{\frac{1}{2}} + C$$

Where  $K_d$  is intra particle diffusion rate constant and C is intercept.

The plot between  $q_{t vs.} t^{\frac{1}{2}}$  shows a straight line and the parameters of  $K_d$  and C are calculated from the linear regression analysis of the slope and intercept. The experimental values are depicted in the Figure 11 which shows the quantity of chromium adsorbed vs t  $\frac{1}{2}$  for various chromium concentrations. The predicted plot does

not show linearity at different time intervals, which denotes that adsorption involves several modes of sorption rather than a single mode. The results suggest that an intra particle diffusion process is not only at a rate controlled step but also some unpredicted mechanism involved during the process of diffusion.



### **3.6. Desorption studies**

The presence of chromium (VI) in the environment may create a serious environmental issue because the chromium (VI) ions are highly hazardous to living organisms. So it is essential to remove the chromium (VI) from the adsorbent after adsorption using the desorption method. The percentage of Cr (VI) desorbed for distilled water using NaOH and HCl shows various desorption percentages as follows 14.32%, 26.44% and 38.61%, 57.16% and 34.16% and 21.42%, respectively. The remaining chromium ions bound to the adsorbent sites may lead to the minimum recovery percentage as compared to the initial desorption on TLAC. The undesorbed chromium (VI) ions present in the aqueous solution after desorption process mainly due to the strong electrostatic interaction [47] may be involved in the adsorption of chromium (VI) onto TLAC.

### Conclusion

From the experimental results, the linear regression analysis shows better result for both Langmuir and Freundlich equations. Langmuir isotherm was the most favorable method for the adsorption of chromium. So the adsorption process was favorable for the adsorption of chromium onto TLAC. The kinetic result shows that the adsorption process follows pseudo-second order kinetics, which implies that the adsorption process depends on both time and concentration. The thermodynamic parameter change in enthalpy ( $\Delta H^0$ ) shows negative value intimating that the adsorption process was exothermic in nature. The change in entropy ( $\Delta S^0$ ) shows a negative value indicating a decreased randomness between the solid-solution interfaces. The Gibbs free energy change ( $\Delta G^0$ ) shows a negative value revealing that the adsorption process is spontaneous in nature. The FTIR spectrum shows a well characterized variation before and after adsorption with reduction in peak height and intensity. The optimum condition maintained to remove Cr (VI) by TLAC were pH 5, dose rate 0.1g and temperature at 303 K of 30 ppm of Cr(VI). The desorption studies showed that the chromium ions were strongly adsorbed onto the TLAC due to the involvement of a strong electrostatic force. All the studies clearly indicate that TLAC is a low cost best alternative adsorbent for the removal of toxic chromium metal from industrial waste water.

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